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for the IB Diploma

COURSEBOOK

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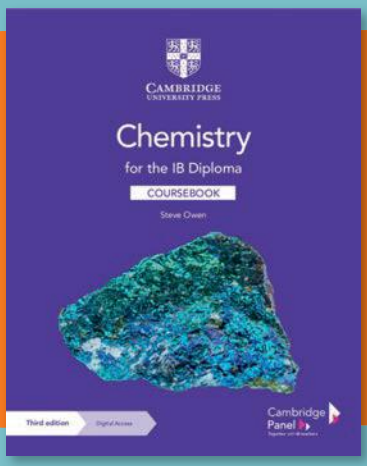
This suite of resources supports students and teachers of the IB Chemistry Diploma course. All of the books in the series work together to help students develop the necessary knowledge and scientific skills required for this subject.



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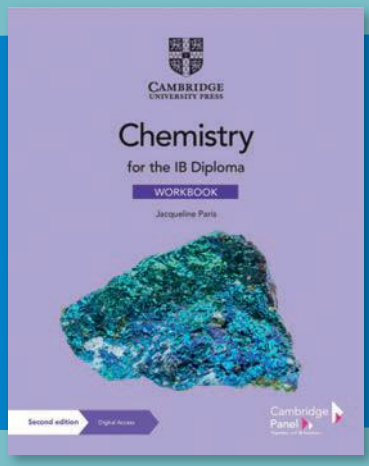

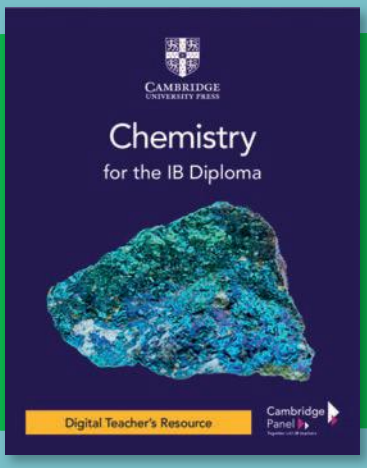

The teacher's resource supports and enhances the coursebook with digital access and the workbook with digital access. This resource includes teaching plans, overviews of required background knowledge, learning objectives and success criteria, common misconceptions, and a wealth of ideas to support lesson planning and delivery, assessment and differentiation. It also includes editable worksheets for vocabulary support and exam practice (with answers) and exemplar PowerPoint presentations, to help plan and deliver the best teaching.

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How to use this book

Throughout this book, you will find lots of different features that will help your learning. These are explained below.

UNIT INTRODUCTION

A unit is made up of a number of chapters. The key concepts for all the chapters covered in a unit are summarised in the Unit opening chapter as the introduction.

LEARNING OBJECTIVES

Each chapter in the book begins with a list of learning objectives. These set the scene for each chapter, help with navigation through the coursebook and indicate the important concepts in each topic. A bulleted list at the beginning of each section clearly shows the learning objectives for the section.

GUIDING QUESTIONS

These are questions on subject knowledge you will need before starting each chapter.

EXAM TIPS

These short hints provide useful information that will help tackle the tasks in the exam.

Link

These are a mix of questions and explanation that refer to other Chapters or sections of the book.

The content in this book is divided into Standard and Higher Level material. Either a chevron or a vertical line running down the margin of all Higher Level material, allows you to easily identify Higher Level from Standard material.

Key terms are highlighted in **orange bold** font at their first appearance in the book so you can immediately recognise them. At the end of the book, there is a glossary that defines all the key terms.

KEY POINTS

This feature contains important key learning points (facts) and/or equations to reinforce your understanding and engagement.

SCIENCE IN CONTEXT

This feature presents real-world examples and applications of the content in a chapter, encouraging you to look further into topics. You will note that some of these features end with questions intended to stimulate further thinking, prompting you to look at some of the benefits and problems of these applications.

NATURE OF SCIENCE

Nature of Science is an overarching theme of the IB Chemistry Diploma course. The theme examines the processes and concepts that are central to scientific endeavour, and how science serves and connects with the wider community. Throughout the book, there are 'Nature of Science' paragraphs that discuss particular concepts or discoveries from the point of view of one or more aspects of Nature of Science.

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THEORY OF KNOWLEDGE

This section stimulates thought about critical thinking and how we can say we know what we claim to know. You will note that some of these features end with questions intended to get you thinking and discussing these important Theory of Knowledge issues.

INTERNATIONAL MINDEDNESS

Throughout this Chemistry for the IB Diploma course, the international mindedness feature highlights international concerns. Chemistry is a truly international endeavour, being practised across all continents, frequently in international or even global partnerships. Many problems that chemistry aims to solve are international and will require globally implemented solutions.

TEST YOUR UNDERSTANDING

These questions appear within each chapter, to help you develop your understanding. The questions can be used as the basis for class discussions or homework assignments. If you can answer these questions, it means you have understood the important points of a section.

WORKED EXAMPLE

Many worked examples appear throughout the text to help you understand how to tackle different types of questions.

REFLECTION

The questions appear at the end of each chapter. The purpose is for you as a learner to reflect on the development of your skills proficiency and your progress against the objectives. The reflection questions are intended to encourage your critical thinking and inquiry-based learning.

EXAM-STYLE QUESTIONS

Exam-style questions at the end of each topic provide essential practice and self-assessment. These are signposted in the print coursebook and can be found in the digital version of the coursebook.

SELF-ASSESSMENT CHECKLIST

These appear at the end of each chapter as a series of statements. You might find it helpful to rate how confident you are for each of these statements when you are revising. You should re-visit any topics that you rated 'Needs more work' or 'Almost there'.

I can	Section	Needs more work	Almost there	Confident to move on

Free online material

Additional material to support the Chemistry for the IB Diploma course is available online.

This includes Assessment guidance – a dedicated chapter in the digital coursebook helps teachers and students unpack the new assessment and model exam specimen papers. Additionally, answers to the Test your understanding and Exam-style questions are also available.

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Unit 1

The nature of matter

INTRODUCTION

We have all heard of atoms: the particles from which everything is made. Democritus and his teacher, Leucippus, fifth-century BCE Greek philosophers, are usually credited with first suggesting the idea of the atom as the smallest indivisible particle from which all matter is made, but the modern understanding of science in terms of atoms only really began in the 19th century with the work of John Dalton (1766–1844). An understanding of atoms and atomic structure is now regarded as fundamental to chemistry, but we usually talk about atomic *theory*, so does that mean that atoms may not really exist? We will not look specifically at the evidence for the existence of atoms, but does the fact that everything in this book and other scientific literature is explained by assuming the existence of atoms provide that evidence?

So, assuming that atomic theory is the best way of explaining the world around us, what do we know about atoms? Atoms are most definitely small – there are many more atoms in a drop of water than there are stars in the Milky Way, and there are probably more atoms in a glass of water than there are stars in the universe (although no one is sure how many stars there are in the universe). We know that there are different types of atoms, but how many are there? A simple answer would be as many as there are elements, but there are also isotopes, and which isotope we are talking about can make a big difference to the properties of the element and to the world – a country with a storage vault full of uranium-235 (which can be used for making nuclear weapons) will be viewed very differently by other governments from one with uranium-238!

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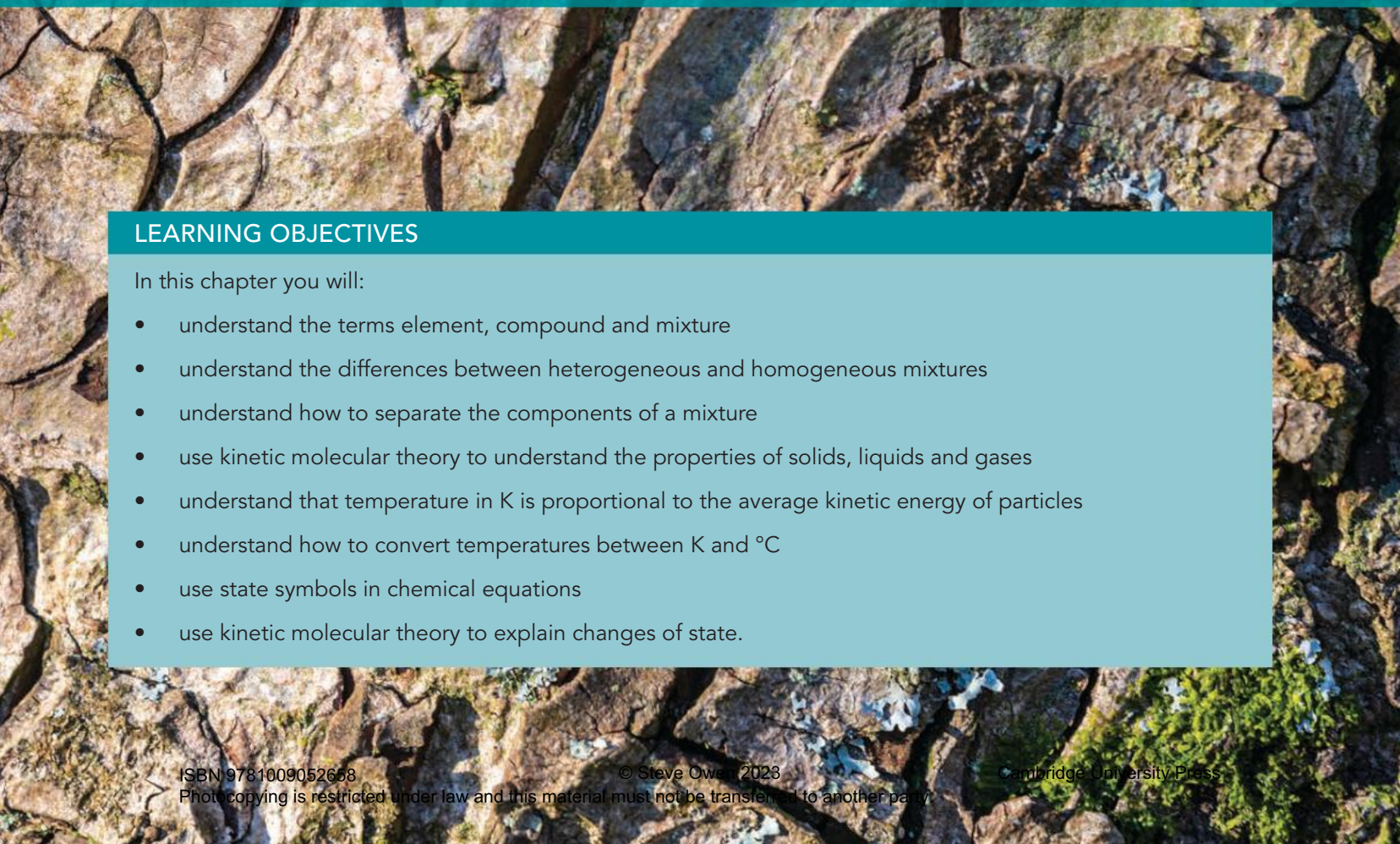
Chapter 1
The particulate nature of matter



LEARNING OBJECTIVES

In this chapter you will:

- understand the terms element, compound and mixture
- understand the differences between heterogeneous and homogeneous mixtures
- understand how to separate the components of a mixture
- use kinetic molecular theory to understand the properties of solids, liquids and gases
- understand that temperature in K is proportional to the average kinetic energy of particles
- understand how to convert temperatures between K and °C
- use state symbols in chemical equations
- use kinetic molecular theory to explain changes of state.

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GUIDING QUESTIONS

- What are the differences between elements, compounds and mixtures?
- How can the components of a mixture be separated?
- How can kinetic molecular theory be used to explain the properties of solids, liquids and gases?

Introduction

The song 'Woodstock', released in 1970, includes the words 'we are stardust' and, strangely enough, this is pretty much true. The lightest elements (mostly hydrogen and helium with some lithium) were formed in the immediate aftermath of the Big Bang, but the other elements that we, and everything around us, are made of were formed in stars. In this chapter, we will look at the distinction between **elements**, **compounds** and **mixtures**, explain their properties in terms of kinetic molecular theory and look at how to separate the components of mixtures. The distinction between elements, compounds and mixtures is fundamental to an understanding of chemistry and, although in subsequent chapters we will mention very little about mixtures, it is important to remember that most substances in everyday life are actually mixtures.

1.1 Elements, compounds and mixtures

Elements

Elements are the primary constituents of matter. There are 118 elements that have been discovered so far, and these are shown in the periodic table. Of these, about 90 occur naturally in reasonable amounts, and the rest are present in only trace amounts or are artificially made. By far the most abundant element in the universe is hydrogen, followed by helium, but in the Earth's crust oxygen is the most abundant and astatine is the least abundant. Astatine has no stable isotopes and scientists estimate that, at any one time, there is probably less than 30 g present in the whole of the Earth's crust.

An element can be defined in different ways and, for the moment, we will define it in terms of its properties:

KEY POINT

An **element** is a chemical substance that cannot be broken down into a simpler substance by chemical means.

Gold only contains gold **atoms** and sulfur only contains sulfur atoms, and because of this, these cannot be broken down into anything simpler than gold atoms or sulfur atoms using chemical reactions.

In Chapter 2, we will look at the structure of atoms, and this will allow us to define an element in terms of the particles that make up the atom:

KEY POINT

An element is a pure substance in which each atom has the same number of protons in the nucleus (see Chapter 2).

So, for example, gold is an element and all samples of pure gold contain only atoms that have 79 protons in the nucleus.

The symbols for elements are shown in the periodic table (Chapter 10, section 10.1). In a sample of an element, the atoms may be present as individual atoms (e.g. helium, He), be chemically bonded as individual **molecules** (e.g. oxygen, O_2, or ozone, O_3) or be chemically bonded as part of a giant structure (e.g. gold, Au, or carbon, C). Some representations of elements are shown in Figure 1.1. The key thing to notice is that, in each part of Figure 1.1, all the atoms are the same.

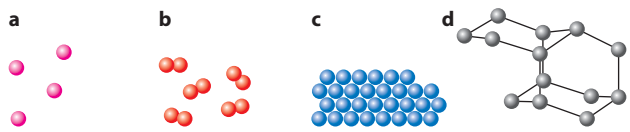

Figure 1.1: Some elements. **a** This could be a noble gas, such as helium, which consists of just individual atoms. **b** This could be gaseous oxygen, consisting of O_2 molecules, in which the oxygen atoms are chemically bonded to each other. **c** This could be a metal, such as gold. **d** This could be carbon – the lines represent bonds between atoms.

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THEORY OF KNOWLEDGE

What is an element?

The concept of an element is fundamental to the study of chemistry, but, strangely enough, chemists do not necessarily agree on the definition of an element. If we say that oxygen is an element, that is fine, but do we mean an O atom, a sample of oxygen gas, which contains O_2 molecules, or even ozone, which contains O_3 molecules?

Chemistry is partly a study of how chemical elements combine to make the world and the universe around us. When different elements combine chemically, they form compounds.

Compounds

In water (H_2O), a compound, there are always exactly twice as many hydrogen atoms as oxygen atoms – this ratio never varies for a particular compound. If the ratio is different, it is a different compound; for example, if the ratio is 1:1, the compound is hydrogen peroxide (H_2O_2) and not water.

KEY POINT

A **compound** is a pure substance formed when two or more elements combine chemically in a fixed ratio.

The atoms (or ions) in a compound are chemically bonded to each other – this may be covalent bonding (see Chapter 7, section 7.1) or ionic bonding (see Chapter 6, section 6.1). Some representations of the structures of compounds are shown in Figure 1.2.

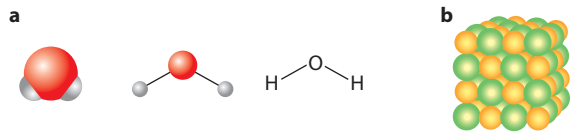

Figure 1.2: Some representations of compounds. The key thing to notice here is that more than one type of atom is present in each structure. Sometimes the chemical bonds (lines) will be shown and sometimes not. **a** Three different ways of showing the structure of water. **b** An ionic compound, such as sodium chloride.

KEY POINT

The elements in a compound are chemically combined, and therefore, compounds can only be converted into their elements again by chemical reactions.

For example, hydrogen can be obtained from water by reacting it with sodium, or hydrogen and oxygen could both be produced by electrolysis (passing electricity through) of water.

The **physical properties** and **chemical properties** of a compound are different from those of the elements from which it is formed.

KEY POINTS

Chemical properties how a substance behaves in a chemical reaction.

Physical properties all the other properties of a substance, such as melting point, density, hardness and electrical conductivity.

For example, hydrogen, an explosive gas, combines with oxygen, a highly reactive gas, to form water, which is a liquid at room **temperature**. Water reacts in very different ways to hydrogen and oxygen (it has different chemical properties) – you would not try to put a fire out with hydrogen or oxygen!

Similarly, when sodium (a highly reactive metal) is heated with chlorine (a toxic gas), a white, crystalline substance, sodium chloride (common salt), is formed, which reacts in very different ways to sodium and chlorine.

Mixtures

Elements and compounds are pure substances, but most things around us are not pure, they are mixtures. We breathe in air, which is a mixture; all the foods we eat are mixtures; oxygen is carried around our body by blood, another mixture.

The components of a mixture can be elements or compounds – or even mixtures! Air is a mixture of mostly elements (nitrogen, oxygen, argon) with smaller amounts of compounds (carbon dioxide, water vapour etc.). Representations of mixtures are shown in Figure 1.3.

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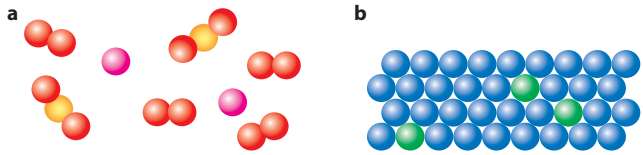

Figure 1.3: Some mixtures. **a** A mixture of gases. **b** An alloy.

KEY POINT

The components of a mixture are not chemically bonded together, so they retain their individual properties.

In a mixture of iron and sulfur, the two elements retain their individual chemical and physical properties, so iron is magnetic and will react with dilute acids to form hydrogen gas, and sulfur is yellow and burns in air to form sulfur dioxide. When the mixture is heated and forms the compound iron sulfide, this has a different appearance, is not magnetic (Figure 1.4) and, for example, reacts with acids to form the extremely smelly and toxic gas hydrogen sulfide – the compound has different properties to its elements.

Figure 1.4: The iron in a mixture of iron and sulfur (left) retains its magnetic properties, but iron sulfide (right) is not magnetic.

KEY POINT

The components of a mixture can be mixed together in any proportion.

When atoms combine to form compounds, they do so in fixed ratios (according to the formula of the compound), but there are no such limitations on making a mixture, and iron and sulfur can be mixed together in absolutely any proportions. **Solutions** are mixtures, and a solution of sodium chloride could be made by dissolving 1 g of sodium chloride in 100 cm^3 of water, 2 g of sodium chloride in 100 cm^3 water, 10 g of sodium chloride in 100 cm^3 of water etc., up to the limit of solubility (how much dissolves at a certain temperature).

Link

Alloys are mixtures of metals with other metals (or non-metals). In alloys, there is **metallic bonding** throughout the structure (see Chapter 8, section 8.1), so the components of the mixture are actually chemically bonded to each other. An alloy is, however, still regarded as a mixture because it will not have a fixed composition – the metals can be mixed together in various proportions.

Mixtures can be homogeneous or heterogeneous

KEY POINTS

A **homogeneous mixture** has the same (uniform) composition throughout the mixture – it consists of only one phase.

Solutions and mixtures of gases are homogeneous mixtures.

A **heterogeneous mixture** does not have uniform composition – it consists of separate phases.

The term *phase* can be used in different ways in chemistry; here, it refers to a region that is the same throughout, in terms of chemical composition and physical properties. In a **heterogeneous mixture**, there will be distinct boundaries between different phases.

An example of a **homogeneous mixture** is a solution. The concentration is the same throughout: if several 1 cm^3 samples of a solution of sodium chloride are taken from a beaker and evaporated separately to dryness, the same mass of solid sodium chloride will be recovered from each sample.

One example of a heterogeneous mixture is sand in a sample of water. Sand and water can be distinguished from each other – they are separate phases. Other examples include milk and orange juice. Orange juice is a complex mixture, containing an aqueous phase with various substances dissolved or suspended in it. Suspended material in orange juice includes cellulose, proteins, lipids and pectins. If you leave some freshly squeezed orange juice to stand, some parts will settle out (but will it become completely clear?). Milk, as a colloid, is discussed in detail in the Science in Context section next.

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Mixtures of solids are always heterogeneous mixtures. For example, a mixture of iron and sulfur is a heterogeneous mixture. Even though the mixture may have been made very carefully, so that there are the same masses of iron and sulfur in each cubic centimetre, the composition is not uniform because there are distinct particles of iron and sulfur (you may need to use a magnifying glass to see them), and each particle of iron and sulfur represents a different phase.

When looking at mixtures that are liquids or gases, if the mixture is clear, so that you can see through it, it is a homogeneous mixture; if it is cloudy/opaque, so that some/all of the light is scattered as it passes through it, then the mixture is heterogeneous.

SCIENCE IN CONTEXT

Solutions and mixtures

Figure 1.5: White coffee and doughnuts are heterogeneous mixtures.

Tea or coffee without milk are solutions. This is usually easier to see with tea, but, if you dilute your black coffee in a glass cup with some water, you will be able to see that, although it is coloured, it is clear, so that light passes through it without being scattered, and therefore, it is a solution and a homogeneous mixture (although, if you used a cafetiere or a not-very-good filter, you may still have a few coffee grounds in it, which would make it a heterogeneous mixture!). If you add sugar and stir it well, the sugar dissolves, and so, you still have a homogeneous mixture; however, if you add milk (Figure 1.5), your coffee goes cloudy – this is now a heterogeneous mixture. Milk is a type of mixture called a colloid (or colloidal system) and contains very small droplets of fat and solid protein particles dispersed throughout an aqueous phase. These particles scatter light (the Tyndall effect) and, therefore, white coffee is not clear but opaque. Other heterogeneous mixtures you will come across in a coffee shop include whipped cream, hot chocolate, doughnuts and muffins.

TEST YOUR UNDERSTANDING

1 Classify each of the following as an element, a compound or a mixture:

a water

b oxygen

c potassium iodide

d vanadium

e ammonia

f air

g hydrogen chloride

h magnesium oxide.

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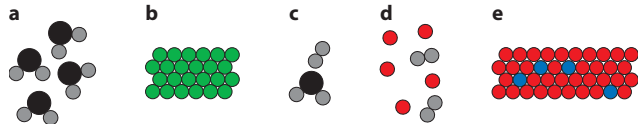
CONTINUED

2 Classify each of the diagrams shown as an element, compound or mixture:



3 Classify each of the following as a heterogeneous or a homogeneous mixture:

a a mixture of carbon dioxide gas and helium gas

b a mixture of solid copper(II) oxide and solid calcium carbonate

c potassium hydroxide solution

d mayonnaise.

Separating the components of a mixture

The components of a mixture can be separated from each other by physical processes – physical processes are things like filtration and distillation, which do not involve chemical reactions.

Filtration

In a chemistry laboratory, filtration is usually used to separate an insoluble solid from a liquid, but it can also be used to separate a solid from a gas. The apparatus most often used for filtration is shown in Figure 1.6. The solid left in the filter paper is called the *residue*, and the liquid that passes through the filter paper is called the *filtrate*. The filter paper acts as a physical barrier to the pieces of solid but allows the liquid to pass through gaps between fibres.

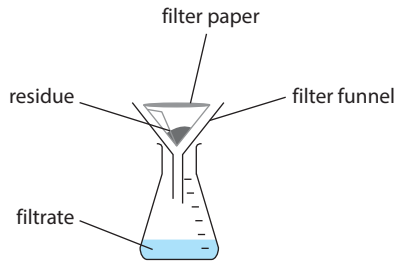


Figure 1.6: Filtration can be used to separate a solid from a liquid.

Filtration is used as part of the process in the preparation of copper(II) sulfate. Copper(II) sulfate solution can be made by the reaction between copper(II) oxide (a black solid that is insoluble in water) and dilute sulfuric acid. Excess (more than enough to react with all the sulfuric acid) copper(II) oxide is added to hot sulfuric acid. The excess copper(II) oxide is then filtered off. In this case, copper(II) oxide is the residue and copper(II) sulfate solution is the filtrate.

The equation for the reaction is

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

Link

Copper(II) oxide is a base and reacts with sulfuric acid in a neutralisation reaction (Chapter 19).

INTERNATIONAL MINDEDNESS

Diesel engines

Diesel engines are used extensively in heavy-duty commercial vehicles, such as lorries and buses, as well as cars. One of the major environmental concerns with the use of vehicles with diesel engines is that they emit significantly more particulate matter (soot) than gasoline (petrol) engines, and this can be damaging to health. Diesel engines are, therefore, fitted with particulate filters, to filter out as much of the particulate matter as possible. Different countries have different regulations on emissions from diesel vehicles.

Evaporation

Evaporation can be used to remove a **solvent** from a solution to leave the **solute**. If a solution of sodium chloride is heated, water will evaporate/boil off to leave solid sodium chloride (Figure 1.7).

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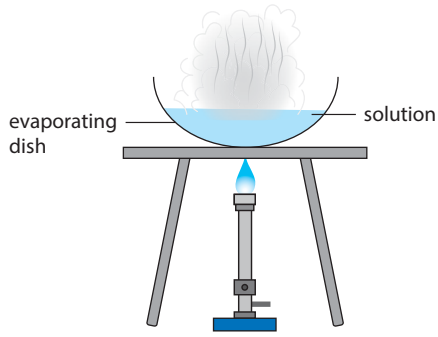

Figure 1.7: Evaporation of the solvent can be used to obtain a solute from a solution. If larger crystals are required, only some of the water should be boiled off and then the solution should be left to crystallise.

Solvation

Solvation can be used to separate a mixture of two or more substances, due to differences in solubility.

For example, a mixture of solid copper(II) oxide (insoluble in water) and sodium chloride (soluble in water) can be separated by putting the mixture into a beaker of warm distilled/deionised water and stirring to make sure that all the sodium chloride has dissolved. The mixture is filtered: copper(II) oxide is the residue and sodium chloride solution is the filtrate. Copper(II) oxide is washed with distilled water to remove any traces of sodium chloride solution and then dried in a warm oven (distilled water will evaporate). Solid sodium chloride can be obtained from the solution by heating it in an evaporating dish until all the water evaporates.

Note that distilled/deionised water must be used because tap water contains dissolved solids and, when heated, will leave a residue of these solids, so that the copper(II) oxide and sodium chloride obtained will not be pure.

Application of solvation to the extraction of caffeine

A common laboratory experiment is the extraction of caffeine from tea. The basic principles of the technique are that tea leaves are boiled with water to make an aqueous solution, which is shaken with dichloromethane (an organic liquid with the formula CH_2Cl_2) in a separatory funnel (Figure 1.8). Dichloromethane is not soluble in water and remains as a separate phase in the separatory funnel. Caffeine is more soluble in dichloromethane than in water and distributes itself between the water layer and the dichloromethane layer, with much more in the dichloromethane layer. The dichloromethane layer can then be run off and the solvent evaporated to leave caffeine (a white solid).

This technique is called solvent extraction, and we talk about a solute *partitioning* itself between two solvents.

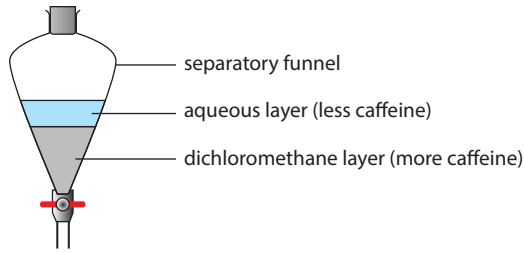

Figure 1.8: A separatory funnel is used in the extraction of caffeine from tea.

Link

Dichloromethane and water form a heterogeneous mixture rather than a homogeneous one (a solution). A general rule for solubility is 'like dissolves like'. The intermolecular forces between dichloromethane molecules (dipole–dipole interactions) are very different to those between water molecules (hydrogen bonds). Caffeine is more soluble in dichloromethane than in water. The intermolecular forces are more similar between caffeine (dipole–dipole interactions) and dichloromethane (dipole–dipole interactions) than between caffeine (dipole–dipole interactions) and water (hydrogen bonds). Intermolecular forces will be discussed in Chapter 7.

EXAM TIP

The word solvation is used here because it is used on the IB syllabus, but it is not actually the correct word. Solvation will be discussed further in Chapter 7. The process here is probably best described as *dissolving*.

Distillation

Distillation could be used, for example, to separate water from a sodium chloride solution. The sodium chloride solution is heated, water evaporates and condenses again in the condenser, so that it can be collected in the collection vessel (water here is called the distillate).

Suitable apparatus for distillation is shown in Figure 1.9.

If heating is continued for a long enough time, only solid sodium chloride will be left in the round-bottomed flask, and all the water will be in the collection vessel.

The difference between distillation and evaporation is that, in distillation, the solvent is boiled off, but

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then condensed again, so that it can be collected. So, evaporation would generally be used when it is the solute that is the desired product and distillation when it is the solvent (or solvent and solute) that is required.

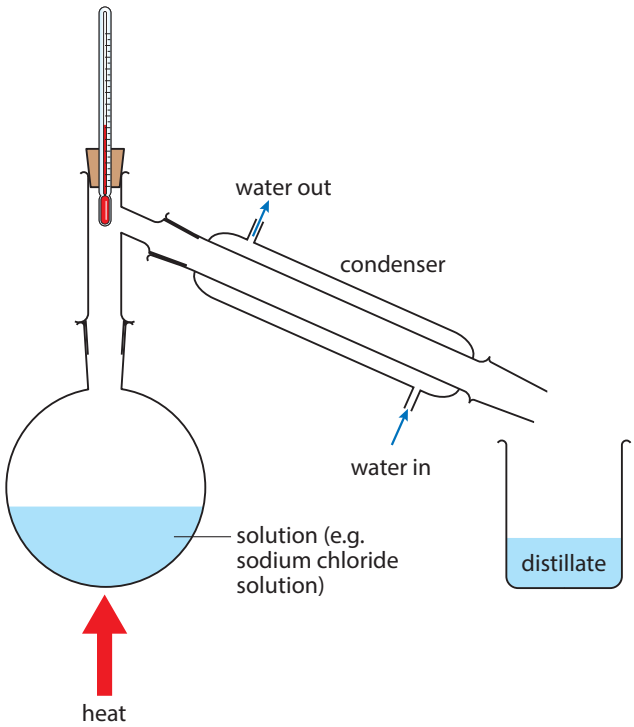

Figure 1.9: The experimental set-up for distillation.

KEY POINT

Distillation (simple distillation) can be used to separate the solute and solvent from a solution (where the solute was a solid) or to separate a mixture of two liquids with sufficiently different boiling points.

INTERNATIONAL MINDEDNESS

Fresh water

Seawater is a mixture, and distillation can be used to obtain water without salt from seawater. The process of removing salt from seawater is called desalination. Desalination is very important in some parts of the world, where sufficient freshwater is not available, for example, in parts of Southwest Asia and North Africa. Water obtained by desalination can be used for human consumption, agriculture or in industry.

Distillation can also be used to separate a mixture of two liquids, as long as there is a large enough difference between their **boiling points** (about 70 °C).

The liquid with the lower boiling point (more volatile) will go into the vapour phase more easily and will be collected in the collection vessel (Figure 1.9), whereas the liquid with the higher boiling point will be left in the round-bottomed flask. If the boiling points of the two liquids are too close, then complete separation will not be obtained, and a mixture will distil over.

This technique is used extensively in organic chemistry for extracting the more volatile liquid product of a reaction from the reaction mixture and for purifying a liquid product of a reaction. When used for purification, the pure liquid is collected in the collection vessel, and any non-volatile impurities will be left in the round-bottomed flask. The purity of the liquid could be tested by using chromatography (see the Paper chromatography section next).

Recrystallisation

Recrystallisation is a technique used to purify solids which contain relatively small amounts of impurities.

The solid is dissolved in the minimum volume of hot solvent to produce a (close to) **saturated solution**. The solution is then filtered hot (usually under vacuum for speed) to remove any insoluble impurities. The solution is then allowed to cool, and crystals form because solids are less soluble in cold solvent. The impurities are present in much smaller quantities and so remain dissolved in the solvent. The mixture is then filtered to remove the crystals, which are then washed with a small amount of ice-cold, pure solvent (to remove any residual impure solvent) and dried (Figure 1.10).

Drying can either be carried out at room temperature (under vacuum) or in a warm oven, depending on the crystals (could they decompose if heated?). Drying means allowing any residual solvent on the crystals to evaporate off. We can check that the crystals are dry by weighing them, allowing them to dry for a further period of time, and then weighing them again; if the masses are the same the crystals are dry. If the mass is lower when the crystals are weighed again, they must be left to dry for longer – at the end of this further period, they are weighed again – this is repeated until consecutive masses are the same. This technique is called *drying to constant mass*.

The purity of the crystals can be tested by measuring the melting point. If the substance is pure, it should have a well-defined melting point. If the crystals are impure, they will melt at a lower temperature and over a range

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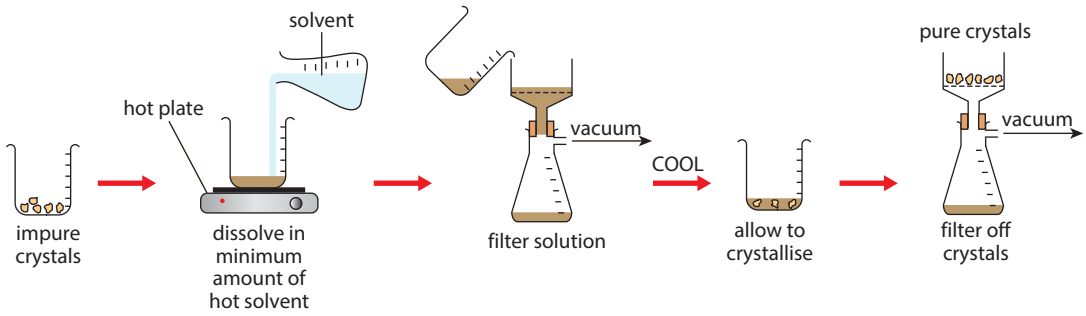

Figure 1.10: Recrystallisation

of temperatures. Recrystallisation could then be carried out again to further purify the crystals.

Paper chromatography

Paper chromatography may be used, for example, to separate the various dyes in coloured inks, to separate a mixture of sugars or amino acids or to test the purity of a substance. The experimental set-up for paper chromatography is shown in Figure 1.11.

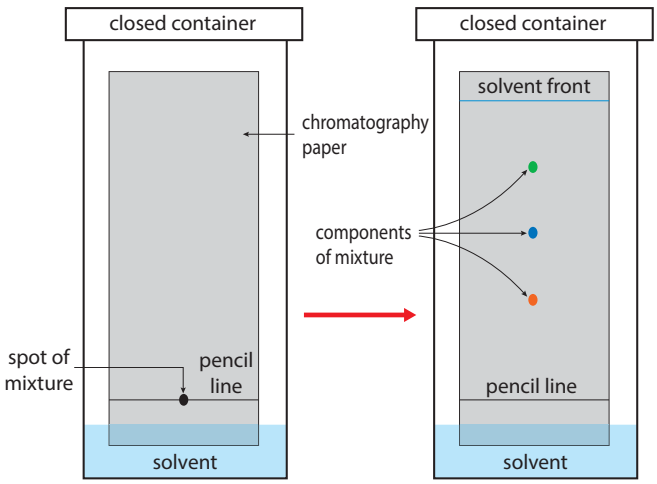

Figure 1.11: A paper chromatography experiment. The process of the solvent travelling up the paper to produce a chromatogram is called development.

To carry out a paper chromatography experiment:

- A line is drawn with a pencil (not a pen, as the inks may move with the solvent) across a piece of chromatography paper about 1 cm from the bottom.
- A sample of the mixture is placed on the pencil line and allowed to dry.
- The paper is suspended in a container with a small amount of solvent at the bottom, so that the end of the paper dips into the solvent (the original sample spot must be above the top of the solvent; otherwise it will just dissolve into the solvent).
- The container is closed, so that the atmosphere becomes saturated with the solvent – this prevents evaporation of the solvent from the surface of the paper.
- The solvent is drawn up the paper by capillary action.
- The process is stopped when the solvent front is about 1 cm from the top of the paper. A pencil line is drawn to record the position of the solvent front and the paper is dried.

At the simplest level, the number of spots present on a chromatogram indicates the number of components of the mixture (although other tests might need to be done, to check whether a particular spot is indeed a pure substance).

KEY POINT

Chromatography can be used to test the purity of the product of a reaction. The presence of more than one spot indicates that the substance is impure.

It can take quite a bit of research and trial and error to find a suitable solvent for chromatography that provides good separation of the components of the mixture. The polarity (see Chapter 7) of the substances influences the choice of solvent, but there are also other factors involved. The solvent does not have to be a pure liquid, and very often mixtures are used.

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All chromatography techniques involve a **stationary phase** and a **mobile phase**. The components in a mixture are separated because of their differences in affinity for the stationary and mobile phases. This is explained in Chapter 7.

Location of spots

If the substances to be separated are colourless (e.g. amino acids or sugars), then some method must be used to locate the spots on the paper. The spots may be located using a locating agent. Amino acids, which are colourless, may be located by spraying with ninhydrin, which makes them show up as pink or purple spots. For organic solutes exposing the paper to iodine vapour (the spots become brown) or spraying the plate with concentrated sulfuric acid then heating it (the spots appear as brown–black). The spots may also be located by exposing the paper to iodine vapour (the spots become brown) or by the use of an ultraviolet lamp, as some substances fluoresce under ultraviolet light.

TEST YOUR UNDERSTANDING

4 Select a technique that could be used to separate the components of the following mixtures:

- **a** sand from water
- **b** potassium chloride from a potassium chloride solution
- **c** different indicators in universal indicator solution
- **d** a mixture of ethoxyethane ($CH_3CH_2OCH_2CH_3$, boiling point 34 °C) and 1-(hexyloxy)hexane ($CH_3(CH_2)_5O(CH_2)_5CH_3$, boiling point 220 °C).

5 Explain how you would separate a mixture of potassium bromide (soluble in water) and calcium carbonate (insoluble in water).

6 Explain how you would separate iodine from an aqueous iodine solution, given that iodine is much more soluble in hexane than in water, and hexane is immiscible with water. *Immiscible* means that hexane and water do not mix – they form separate layers.

1.2 Kinetic molecular theory

Kinetic molecular theory (often just called kinetic theory) is a model that was developed originally to explain the properties of gases, but it is usually also extended to describe liquids and solids. Within this model, we describe all matter as being made up of individual particles that are in constant motion (hence, the word 'kinetic').

NATURE OF SCIENCE

Models are used throughout science. A model is a way of making sense of the world around us. Models may either be qualitative, as here, or quantitative (involving numbers and equations). The validity of a particular model can be tested by looking at how closely predictions made using the model agree with experimental observations.

The three states of matter most commonly encountered are solid, liquid and gas, and these differ in terms of the arrangement and movement of particles. The particles making up a substance may be individual atoms or molecules or ions. Simple diagrams of the three states of matter are shown in Figure 1.12, in which the individual particles are represented by spheres.

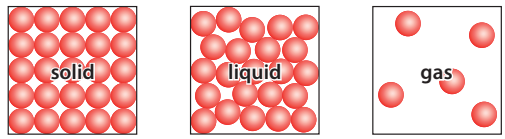

Figure 1.12: The three states of matter.

EXAM TIP

In diagrams showing the states of matter, remember the following:

- Solid: the particles should be arranged regularly and touching.
- Liquid: the particles are arranged randomly but still mostly touching.
- Gas: the particles are arranged randomly and are shown far apart.

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	Solids	Liquids	Gases
Distance between particles	close together	close but further apart than in solids	far apart
Arrangement	regular	random	random
Shape	fixed shape	no fixed shape; take the shape of the container	no fixed shape; fill the container
Volume	fixed	fixed	not fixed
Movement	vibrate	move around each other	move around in all directions
Speed of movement	slowest	faster	fastest
Energy	lowest	higher	highest
Forces of attraction	strongest	weaker	weakest

Table 1.1: Properties of the three states of matter.

Solid: the particles are generally regularly arranged and, due to relatively strong forces of attraction between them, are only able to vibrate about mean positions. As the forces between the particles are relatively strong, solids have fixed shapes.

Liquid: the particles have weaker forces between them, and so are able to move around each other. As the forces between the particles are weaker than those in solids, liquids flow (are fluid) and take the shape of the container they are in. There are, however, still forces between the particles, so they stay together and do not fill the container.

Gas: the particles are assumed to have no forces between them (see Chapter 5) and move around randomly in all directions. There are no forces between the particles, so they are free to move around anywhere in a container, and thus, 'fill' the container. To give you some idea of how quickly the particles in a gas are moving: the average speed of molecules in air (mostly nitrogen and oxygen) at 25 °C and atmospheric pressure is almost 500 ms^{-1}; the particles collide, on average, every 150 ps (1.5×10^{-10} s) and only travel about 7×10^{-8} m between collisions.

The properties of the three states of matter are summarised in Table 1.1.

Temperature

There are two temperature scales that are used commonly in everyday life: the Fahrenheit scale (melting point of ice = 32 °F and boiling point of water = 212 °F), which is used predominantly in the USA and a few other countries, and the Celsius or centigrade scale (melting point of ice = 0 °C and boiling point of water = 100 °C), which is used in the rest of the world. In science, however, we much more commonly use the absolute, or Kelvin, scale of temperature. For calculations involving temperatures in science, it is usually essential to use temperatures in kelvin.

KEY POINT

The kelvin is the SI unit of temperature.

SI stands for Système International and is the internationally accepted system of units used in science. Within the SI, seven base units are defined by reference to seven fundamental constants (such as the speed of light in a vacuum and the Planck constant), which have agreed specific values. Other SI base units include the second, the metre and the mole.

The absolute, or Kelvin, scale of temperature starts at **absolute zero**, which is the lowest temperature possible. All molecular motion does not actually stop at absolute zero (this would contravene the Heisenberg uncertainty principle), but it is the temperature at which everything would be in its lowest energy state. It is not possible to actually reach absolute zero, but scientists have managed to get very close – below one nanokelvin!

KEY POINTS

Absolute zero the lowest temperature possible, corresponds to 0 K or –273.15 °C (often taken as –273 °C).

A change of 1 °C is the same as a change of 1 K.

EXAM TIP

A temperature *change* in °C is the same as one in K.

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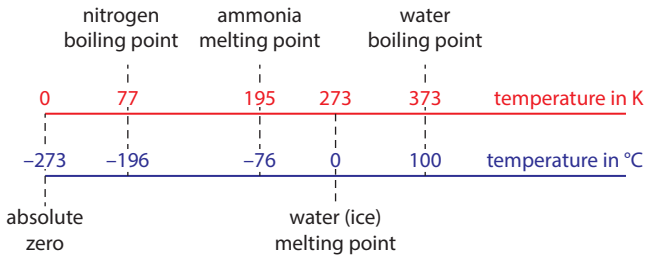

Figure 1.13: Some temperatures in K and °C.

Figure 1.13 compares some temperatures in K and °C. The fact that a change of 1 °C is the same as a change of 1 K makes it quite straightforward to convert temperatures between the two scales.

KEY POINTS

To convert °C into K, add 273.15.

To convert K into °C, subtract 273.15.

WORKED EXAMPLE 1.1

Convert a temperature of 25.00 °C into kelvin.

Answer

To do this, we add 273.15 to the temperature in °C:
25.00 + 273.15 = 298.15 K

WORKED EXAMPLE 1.2

Convert a temperature of 350.50 K into °C.

Answer

To do this, subtract 273.15 from the temperature in K:
350.50 – 273.15 = 77.35 °C

1.3 Temperature and kinetic energy

KEY POINTS

Temperature is a measure of the average (mean) kinetic energy (E_k) of the particles in a substance.

The higher the temperature, the higher the average kinetic energy of the particles.

The particles in gases and liquids are constantly colliding and, therefore, the particles will not all be moving at the same speed, and there will be a spread of kinetic energies for the particles, which is why we use the term *average* **kinetic energy**. The distribution of kinetic energies in a sample of gas at two different temperatures is shown in Figure 1.14. At higher temperature, there are fewer particles with lower kinetic energy and more particles with higher kinetic energy, and so, the average kinetic energy of the particles is greater. This will be explored more in Chapter 17.

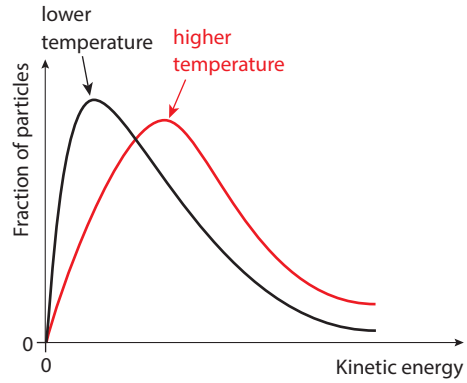

Figure 1.14: The distribution of kinetic energies in a sample of gas is called the Maxwell–Boltzmann distribution.

If two gases are at the same temperature, their particles will have the same average kinetic energy. This does not mean that the average speed of the particles is the same. Kinetic energy is calculated using the following equation:

$$E_k = \frac{1}{2}mv^2$$

where m is the mass of the particle and v is the speed.

This means that, the lighter the particles, the higher the average speed at a particular temperature. The average speed of carbon dioxide molecules (relative mass 44.01) at 25 °C is about 380 m s^{-1}, whereas the average speed of hydrogen molecules (relative mass 2.02) is about 1770 m s^{-1}.

TEST YOUR UNDERSTANDING

7 Convert each of the following temperatures in °C to temperatures in K.

a 35.00 °C **b** 500.00 °C

c –100.00 °C **d** –145.00 °C

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CONTINUED

8 Convert each of the following temperatures in K to temperatures in °C.

a 323.15 K **b** 100.85 K

c 50.00 K **d** 500.20 K

9 What is wrong with the temperatures –50 K and –300 °C?

1.4 Changes of state

When one state of matter becomes another state of matter, we describe this as a *change of state*. Changes of state are summarised in Figure 1.15. Converting one state of matter into another usually involves heating (the change of state is an endothermic process) or cooling the substance (the change of state is an exothermic process) but can also be achieved by changing pressure. Endothermic and exothermic processes will be considered in Chapter 12.

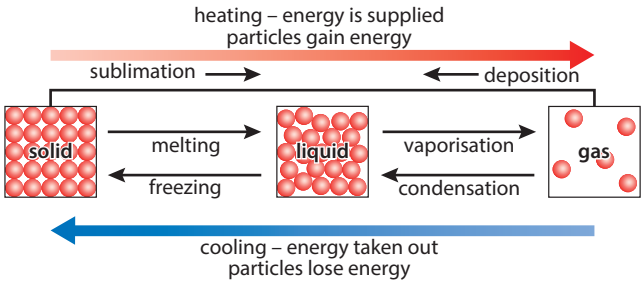

Figure 1.15: Changes of state.

Sublimation is the change of state when a substance goes directly from the solid state to the gaseous state, without going through the liquid state. Both iodine and solid carbon dioxide (dry ice) sublime at atmospheric pressure. The reverse process is called deposition.

The temperatures at which a substance changes state are called its melting point (change from solid to liquid) and boiling point (change from liquid to gas).

KEY POINT

A substance will be:

- a solid if the temperature is below its melting point
- a liquid if the temperature is between its melting point and its boiling point
- a gas if the temperature is above its boiling point

So, for example, bromine melts at –7.2 °C and boils at 58.8 °C; therefore, below –7.2 °C bromine will be a solid, between –7.2 °C and 58.8 °C it will be a liquid, and above 58.8 °C it will be a gas. There is no universally accepted definition of 'room temperature', but it is often taken as 25 °C, and so bromine is one of only two elements that is a liquid at room temperature.

The change of state from liquid to gas is called vaporisation and can happen in two ways – boiling and evaporation. Boiling and evaporation are not the same thing – boiling only occurs at a certain temperature (the boiling point), but evaporation of the liquid can occur at any temperature between the melting and boiling points.

Using state symbols in equations

State symbols are used in chemical equations to indicate the physical state that the substances are in.

KEY POINT

The state symbols are:

(s) = solid

(l) = liquid

(g) = gas

(aq) = aqueous (dissolved in water)

We saw the following chemical equation in the previous section on Filtration:

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

This indicates that solid copper(II) oxide (CuO) reacts with sulfuric acid, which is an aqueous solution (dissolved in water) to form an aqueous solution of copper(II) sulfate and liquid water.

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Changes of state may be described using equations including state symbols, for example:

Melting of ice to form water: $H_2O(s) \rightarrow H_2O(l)$

Boiling/evaporation of liquid bromine: $Br_2(l) \rightarrow Br_2(g)$

Sublimation of iodine: $I_2(s) \rightarrow I_2(g)$

How to write balanced chemical equations will be discussed in Chapter 16.

Temperature and changes of state

If a pure substance is heated slowly, from below its melting point to above its boiling point, a graph of temperature against time can be obtained (Figure 1.16).

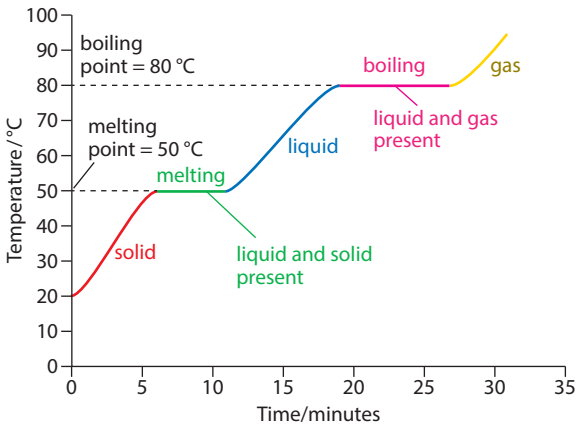

Figure 1.16: A heating curve showing changes of state.

As a solid is heated, its particles vibrate more vigorously. The particles gain kinetic energy and the temperature of the solid rises. At 50 °C, the solid in Figure 1.15 begins to melt – at this stage, there is solid and liquid present together, and the temperature remains constant until all the solid has melted. All the heat energy being supplied is used to partially overcome the forces of attraction between particles, so that they can move around each other. Another way of saying this is that, at the melting point, all the heat energy being supplied goes into increasing the potential energy of the substance (overcoming forces between particles) and not to increasing the kinetic energy, so the temperature does not change.

When all the solid has melted, the continued supply of heat energy causes the kinetic energy of the particles to increase, so that the particles in the liquid move around each other more quickly and the temperature increases.

The average kinetic energy of the particles increases, until the boiling point of the liquid is reached. At this point (80 °C), the continued supply of heat energy is used to overcome the forces of attraction between the particles completely and the temperature of the substance remains constant, until all the liquid has been converted into gas. Once all the liquid has been converted to a gas, the continued supply of heat energy increases the average kinetic energy of the particles and, therefore, the temperature of the gas. The particles move around faster, as the temperature of the gas increases.

KEY POINT

Changes of state which involve overcoming (breaking) forces of attraction between particles are endothermic – heat energy is required to overcome these forces. Changes of state which involve forming forces of attraction between particles are exothermic – heat energy is released when these forces are formed.

TEST YOUR UNDERSTANDING

10 State the names of the following changes of state:

- **a** from solid to liquid
- **b** from solid to gas
- **c** from gas to liquid
- **d** from gas to solid.

11 Use data in the table to determine whether each of the elements will be a solid, liquid or gas at the specified temperature:

Substance	Melting point / °C	Boiling point / °C
Magnesium	650	1090
Fluorine	–220	–188
Polonium	254	962
Mercury	–39	357

- **a** magnesium at 100 °C
- **b** fluorine at –200 °C
- **c** polonium at 1000 °C
- **d** mercury at 25 °C.

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the terms element, compound and mixture, and distinguish between them	1.1			
explain the difference between heterogeneous and homogeneous mixtures and give examples of each	1.1			
explain the different methods for separating the components of a mixture and suggest a suitable method for separating a particular mixture	1.1			
explain the properties of solids, liquids and gases in terms of kinetic molecular theory	1.2			
state the relationship between temperature in K and the average kinetic energy of particles	1.3			
convert temperatures between K and °C	1.3			
use state symbols in chemical equations	1.4			
explain changes of state in terms of kinetic molecular theory.	1.4			

REFLECTION

To what extent do you feel that you have met many of the ideas in this chapter before? Can you highlight specific areas that are new to you? Are you confident with these areas? Can you use your knowledge to identify heterogeneous and homogeneous mixtures around your home or school? Do you think that you could explain the difference between elements, compounds and mixtures to another student?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 2
The nuclear atom

LEARNING OBJECTIVES

In this chapter you will:

- describe the structure of an atom
- understand the terms *atomic number* (*Z*) and *mass number* (*A*)
- calculate the numbers of protons, neutrons and electrons in atoms and ions
- understand the term *isotope*
- understand that isotopes of an element have the same chemical properties but different physical properties
- calculate the *relative atomic mass* (A_r) from the relative abundances of isotopes
- calculate the relative abundance of an isotope from the relative atomic mass

- Understand that the abundance of isotopes in a sample can be determined from a mass spectrum
- Understand how to calculate relative atomic mass from a mass spectrum.

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GUIDING QUESTIONS

- What is the structure of the atom?
- What makes an atom of one element different from an atom of another element?
- Are all atoms identical in a sample of an element?
- How do we compare the masses of atoms?

Introduction

The smallest part of an element that can still be recognised as that element is an atom. There are currently, therefore, 118 different atoms (ignoring isotopes), and the world around us is made from different combinations of these atoms chemically bonded to each other. Actually, only a few of these different types of atoms make up most of the things around us; for instance, over 98% of the mass of the human body comes from just six different types of atom (O, C, H, N, Ca, P). Things get even stranger when you realise that these atoms are only different because they are made up of different combinations of three subatomic ('smaller than an atom') particles, and so the whole world around us is made up of combinations of just three things: protons, neutrons and electrons.

KEY POINTS

Atoms consist of a central positively charged nucleus made up of protons and neutrons, where most of the mass is concentrated. The negatively charged electrons occupy the space outside the nucleus.

Protons and neutrons, the particles that make up the nucleus, are sometimes called *nucleons*.

2.1 The structure of atoms

Figure 2.1 shows a simple representation of an atom. The electrons are often shown in shells orbiting the nucleus. The arrangement of electrons in atoms will be discussed in Chapter 3.

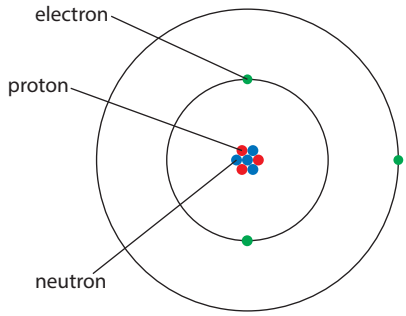

Figure 2.1: A simple representation of a lithium atom (not to scale).

The actual mass of a proton is 1.67×10^{-27} kg and the charge on a proton is $+1.6 \times 10^{-19}$ C (coulomb, C, is the unit of charge); however, it is not very often that we need these actual values, and most of the time we are much more interested in the mass and charge of these particles relative to each other. Relative masses and charges are shown in Table 2.1; because the values are relative, there are no units.

Particle	Relative mass	Relative charge
proton	1	+1
neutron	1	0
electron	5×10^{-4}	–1

Table 2.1: The properties of protons, neutrons and electrons.

From these values, it can be seen that virtually all the mass of the atom is concentrated in the nucleus. If we consider a uranium-238 atom, which has 92 protons, 146 neutrons and 92 electrons, we can calculate that

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approximately 0.02% of the mass is due to the electrons. When a sodium atom loses an electron to form a 1+ ion (Na^+), its mass changes by 0.002%. In most discussions about the masses of atoms, we can, therefore, regard the mass of an electron as negligible (essentially zero) compared to the mass of the atom.

Most of the volume of the atom is due to the electrons – the nucleus is very small compared with the total size of the atom. The diameter of an atom is approximately 1×10^{-10} m and that of a nucleus between about 1×10^{-14} m and 1×10^{-15} m, meaning that a nucleus is about 10 000 to 100 000 times smaller than an atom. So, if the nucleus were the size of the full stop at the end of this sentence, the atom would be between 3 and 30 m across.

THEORY OF KNOWLEDGE

None of these particles can be observed directly. These particles were originally 'discovered' by the interpretation of experimental data. Do we know or believe in the existence of these particles?

If we looked at a science textbook of 200 years ago, there would be no mention of protons, electrons and neutrons. If we could look at a chemistry textbook of 200 years in the future, would there be any mention of them? Are these particles a true representation of reality, or a device invented by scientists to make sense of experimental data and provide an explanation of the world around us?

Atomic number

KEY POINTS

Atomic number (*Z*) is the number of protons in the nucleus of an atom.

number of electrons in an atom = number of protons = the atomic number

The **atomic number (*Z*)** defines an element – it is unique to that particular element. For example, the element with atomic number 6 is carbon and that with atomic number 79 is gold (Figure 2.2). This means that we could use the atomic number of an element instead of its name. However, the name is usually simpler and more commonly used in everyday speech.

Figure 2.2: Bars of the element with atomic number 79.

The number of electrons in an atom

The overall charge on an atom is zero and, therefore, since the charge on an electron (–1) is equal but opposite to the charge on a proton (+1), an atom must contain equal numbers of these. So, if we consider a carbon atom, which has atomic number six, we can work out that it contains six protons in the nucleus and, therefore, there must also be six electrons in the atom.

Atomic number is defined in terms of protons rather than electrons because electrons are lost or gained when ions are formed in chemical reactions.

Link

The elements are arranged in order of atomic number in the periodic table, see Chapter 10.

Mass number

KEY POINT

Mass number (*A*) is the total number of protons plus neutrons in the nucleus of an atom; therefore: number of neutrons in an atom = mass number – atomic number

If a titanium atom has a mass number of 48 and an atomic number of 22, we can work out that there must be 48 – 22 = 26 neutrons in the nucleus.

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The nuclear symbol for an atom

The nuclear symbol of an element shows the atomic number, the mass number and the symbol of the element (Figure 2.3).

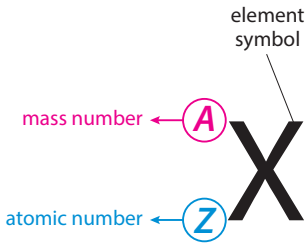

Figure 2.3: The nuclear symbol for an atom.

For example, the nuclear symbol for sodium is $^{23}_{11}Na$, so we can see that sodium has an atomic number of 11 and a mass number of 23.

From the atomic number, we can deduce that a sodium atom must contain 11 protons. Because the atom is neutral, there must also be 11 electrons surrounding the nucleus.

From the mass number, we can deduce the number of neutrons in the nucleus: number of neutrons = 23 – 11 = 12 (Figure 2.4).

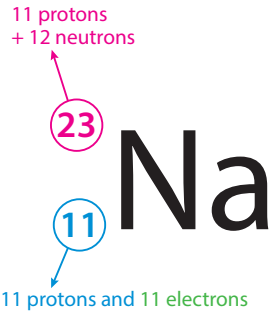

Figure 2.4: The number of subatomic particles in the Na atom.

EXAM TIP

The mass number is always the larger number (except $^{1}_{1}H$, where the numbers are the same). Hydrogen-1 is the only atom that does not contain a neutron.

Working out the numbers of protons, neutrons and electrons in ions

KEY POINTS

Ions are charged particles that are formed when an atom loses or gains (an) electron(s):

cation a positive ion

anion a negative ion

A positive **ion** (**cation**) is formed when an atom loses (an) electron(s), so that the ion has more protons (+) than electrons (–). A negative ion (**anion**) is formed when an atom gains (an) electron(s), so that the ion has more electrons (–) than protons (+). It is important to remember that protons are never lost/gained from the nucleus in chemical reactions – charges arise when the number of electrons changes.

An Na^+ ion has a positive charge because it has one more proton than electrons. Sodium has an atomic number of 11, so the nucleus must contain 11 protons and the charge on the nucleus (nuclear charge) must be 11+. Because the overall charge is 1+, there must only be 10 electrons (total charge 10–) in the atom: 11+ + 10– = 1+ (Figure 2.5).

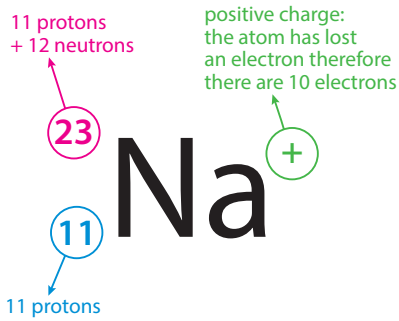

Figure 2.5: The number of subatomic particles in the Na^+ ion.

An O^{2-} ion has two more electrons than protons. Because the element is oxygen, the atomic number is 8 and there are 8 protons in the nucleus – the nuclear charge is 8+. To give an overall charge of 2–, there must be 10 electrons, with a total charge of 10–: 8+ + 10– = 2– (Figure 2.6).

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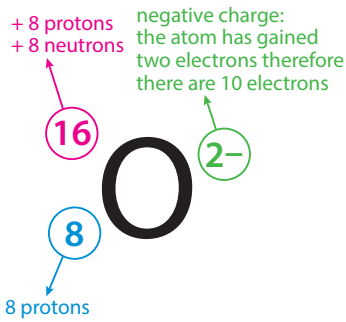

Figure 2.6: The number of subatomic particles in the O^{2-} ion.

A $_{12}Mg^{2+}$ ion contains two more protons than electrons. Therefore, there are 12 protons and 10 electrons.

$^{31}_{15}P^{3-}$ contains 15 protons, 18 electrons and 16 neutrons.

2.2 Isotopes

Not all atoms of an element are identical. For instance, there are two different chlorine atoms in a naturally occurring sample of chlorine. The symbols for these are $^{35}_{17}Cl$ and $^{37}_{17}Cl$. They must have the same atomic number (number of protons) – otherwise they would not be chlorine – but they have different masses due to different numbers of neutrons in the nucleus.

^{35}Cl: 17 protons 18 neutrons

^{37}Cl: 17 protons 20 neutrons

These different forms of chlorine are called **isotopes**.

TEST YOUR UNDERSTANDING

1 Complete the following sentence:

Atoms contain a ..... charged nucleus composed of ..... and .....

2 Complete the following sentences (you may need to use more than one word in each gap):

Electrons have a ..... charge and are found .....
Virtually all the mass of an atom is due to the .....

3 State whether each of the following statements is TRUE or FALSE:

a The atomic number has the symbol *A*, and the mass number has the symbol *Z*.

b Mass number − atomic number = number of neutrons in the nucleus.

c Protons and neutrons together are called nucleons.

d The charge on a neutron is equal in size but opposite in sign to the charge of a proton.

e All atoms have no overall charge.

f If an atom has an atomic number of 20, it must be a calcium atom.

4 State the number of protons, neutrons and electrons in the following atoms:

a $^{23}_{11}Na$ **b** $^{15}_{7}N$

c $^{35}_{17}Cl$ **d** $^{239}_{92}U$

e $^{75}_{33}As$ **f** $^{81}_{35}Br$

5 State the number of protons, neutrons and electrons in the following ions:

a $^{7}_{3}Li^{+}$ **b** $^{2}_{1}H^{+}$

c $^{31}_{15}P^{3-}$ **d** $^{33}_{16}S^{2-}$

e $^{1}_{1}H^{-}$ **f** $^{40}_{20}Ca^{2+}$

g $^{127}_{53}I^{-}$ **h** $^{140}_{58}Ce^{3+}$

6 Sort the following atoms/ions into three categories:

A more electrons than neutrons

B same number of electrons and neutrons

C more neutrons than electrons.

$^{24}_{11}Na^{+}$ $^{18}_{8}O^{2-}$ $^{29}_{14}Si^{+}$ $^{18}_{9}F^{-}$ $^{52}_{24}Cr$ $^{59}_{27}Co^{3+}$

$^{3}_{1}H^{-}$ $^{32}_{16}S^{2-}$ $^{76}_{35}Br^{-}$ $^{26}_{13}Al^{3+}$ $^{71}_{33}As^{5+}$

7 What is the nuclear charge of a $^{37}_{17}Cl$ atom?

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KEY POINT

Isotopes are different atoms of the same element (same atomic number/number of protons in the nucleus) with different mass numbers, i.e., different numbers of neutrons in the nucleus.

All elements have isotopes, but only some isotopes are stable and occur in a natural sample of that element. Usually, one isotope is far more abundant than the others, and the mass number of the most common isotope is quoted.

The numbers of protons, neutrons and electrons in some isotopes are shown in Table 2.2.

Isotope	Protons	Neutrons	Electrons
$^{1}_{1}H$	1	0	1
$^{2}_{1}H$	1	1	1
$^{3}_{1}H$	1	2	1
$^{12}_{6}C$	6	6	6
$^{13}_{6}C$	6	7	6
$^{14}_{6}C$	6	8	6
$^{35}_{17}Cl$	17	18	17
$^{37}_{17}Cl$	17	20	17

Table 2.2: The numbers of subatomic particles in some isotopes.

When talking about isotopes, we distinguish between them by including the mass number, so, for instance, we might talk about chlorine-37 or uranium-235. The isotopes of hydrogen are sometimes given different names and symbols: hydrogen-1 is called protium, hydrogen-2 is deuterium (D), and hydrogen-3 is tritium (T).

KEY POINT

Isotopes have the same chemical properties (they react in exactly the same way) but different physical properties (e.g. different melting points and boiling points).

Physical and chemical properties of isotopes

Isotopes react in the same way because they have the same numbers of electrons, and chemical reactions depend on the number and arrangement of electrons and not on the composition of the nucleus. For example, both protium (^{1}H) and deuterium (^{2}H or D) would react in the same way with nitrogen:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad N_2 + 3D_2 \rightleftharpoons 2ND_3$$

But because isotopes have different masses, they have different physical properties, such as melting point, boiling point and density.
For example, the boiling point of $^{1}H_2$ is –253 °C, whereas that of $^{2}H_2$ (D_2) is –250 °C. Heavy water (D_2O) has a melting point of 3.8 °C and a boiling point of 101.4 °C, whereas ordinary water (H_2O) has a melting point of 0 °C and a boiling point of 100 °C. Because of differences in densities, ice made from heavy water will sink when put into normal water, but ice cubes made from normal water will float when put into normal water or heavy water.

It is not straightforward to explain why isotopes should have different boiling points but, at this level, it should be sufficient to state that the different mass of an isotope affects how much energy is required to convert it from a liquid into a gas.

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TEST YOUR UNDERSTANDING

8 What is the definition of *isotopes*?

9 The following table shows the number of protons, electrons and neutrons in a series of atoms and ions.

Symbol	Protons	Neutrons	Electrons
D	27	30	25
X	43	54	42
Q	35	44	35
L	27	32	26
M	35	46	36
Z	54	78	54

a Which symbols represent isotopes?

b Which symbols represent positive ions?

10 State the number of protons, neutrons and electrons in each of the following:

a $^{11}_{5}B$ $^{10}_{5}B$

b $^{28}_{14}Si$ $^{29}_{14}Si$ $^{30}_{14}Si$

c $^{32}_{16}S$ $^{33}_{16}S$ $^{36}_{16}S$

11 A television program made reference to 'palladium-46'. Why does this show a lack of understanding of the science?

12 Complete the following sentence (you may need more than one word in some gaps):
Isotopes have the same ..... properties because they have ..... but different ..... properties because they have .....

SCIENCE IN CONTEXT

Radioisotopes are radioactive isotopes and have lots of uses in medicine and other fields. For example, carbon-14 is used to date objects that were once alive, cobalt-60 is used in radiotherapy to kill cancer cells and technetium-99m is used widely as a radioactive tracer in medical imaging to diagnose illnesses.

Probably the most well-known radioisotopes are those of uranium. There are two main naturally occurring isotopes of uranium: uranium-235 and uranium-238. The isotope that undergoes fission (when a nucleus breaks apart into smaller nuclei) in a reactor in a nuclear power station is uranium-235, but the problem is that the natural abundance of this isotope is only 0.7%. The proportion of uranium-235 present in a sample, therefore, generally has to be increased before it can be used in a nuclear reactor. The process by which this is done is called *enrichment*. Different reactors require uranium that has been enriched to different extents, but most require the fuel to be enriched to contain at least 3% uranium-235. Nuclear weapons require uranium that has been enriched to contain at least 90% uranium-235.

The different physical properties of isotopes are exploited in the enrichment of uranium. Before enrichment can occur, uranium must be converted into a volatile form: uranium hexafluoride, UF_6. UF_6 has a fairly low boiling point, and one of the enrichment techniques relies on the fact that gaseous $^{235}UF_6$ molecules diffuse slightly faster (because of their lower mass) through a porous membrane than $^{238}UF_6$ molecules.

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Relative atomic masses

If you look at a periodic table, you will usually find that mass numbers are not quoted but rather **relative atomic masses**. Depending on which periodic table you look at, these can be stated to different numbers of decimal places – those in the IB data booklet are stated to two decimal places. These are not the masses of individual atoms but rather average masses, taking into account the proportion of each isotope in a naturally occurring sample. This type of average is called the *weighted average* or *weighted mean*.

It is inconvenient to work with the actual average mass of an atom, for instance, that of oxygen is 2.66×10^{-26} kg, so we use a scale of *relative* masses based on the mass of a carbon-12 atom, which is assigned a mass of exactly 12.00. This allows much easier comparison between the masses of atoms because the numbers are much simpler, for example, the relative atomic mass of oxygen is 16.00. Relative atomic mass is given the symbol A_r.

KEY POINT

The **relative atomic mass (A_r)** of an element is the weighted average of the masses of the atoms of the isotopes compared to $\frac{1}{12}$ of the mass of a carbon-12 atom.

The relative atomic mass of Mg is 24.31. A natural sample of magnesium is made up of a mixture of isotopes and, on average, an Mg atom is 24.31 times as heavy as $\frac{1}{12}$ of a carbon-12 atom.

One-twelfth of a carbon-12 atom has a relative mass of 1,00. This is basically the same as the mass of a ^{1}H atom (actually 1.008 on this scale), so we are essentially comparing everything to the mass of a hydrogen atom. A magnesium atom is approximately 24 times as heavy as a ^{1}H atom.

Although we assign ^{12}C a mass of 12.00, if you look at a periodic table, you will see that the relative atomic mass of carbon is 12.01. This is because a naturally occurring sample does not just contain ^{12}C but also contains about 1% ^{13}C.

How to calculate relative atomic mass given the percentages of the isotopes present in a sample

What we are doing here is finding the average mass of an atom by taking into account the proportion of each isotope in the sample – the weighted average. The proportion of an isotope in a naturally occurring sample is called the *natural abundance*. We will illustrate how to calculate the relative atomic mass with a worked example involving just two isotopes, but the method can be extended to any number of isotopes, for instance, tin has ten naturally occurring stable isotopes and the method would work in exactly the same way but would just take a bit longer!

WORKED EXAMPLE 2.1

Lithium has two naturally occurring isotopes:

^{6}Li: natural abundance 7%

^{7}Li: natural abundance 93%

Calculate the relative atomic mass of lithium.

Imagine we have 100 Li atoms: 7 will have mass 6 and 93 will have mass 7. The average mass of these atoms is:

$$\frac{(7 \times 6) + (93 \times 7)}{100} = 6.93$$

Therefore, the A_r of Li is 6.93.

EXAM TIP

Does the question specify to how many decimal places the answer should be given? You will lose a mark if you do not get this correct.

How to calculate the relative proportion of the isotopes in a sample given the relative atomic mass

The method for this is best understood with a worked example and uses basically the same ideas as above but working backwards from the relative atomic mass, with a little bit of extra algebra thrown in. It only works when there are two isotopes in the sample, unless you are given more information.

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WORKED EXAMPLE 2.2

Iridium has a relative atomic mass of 192.22 and consists of iridium-191 and iridium-193 isotopes. Calculate the percentage composition of a naturally occurring sample of iridium.

Answer

We will assume that we have 100 atoms and that x of these will have a mass of 191. This means that there will be $(100 - x)$ atoms with a mass of 193.

The total mass of these 100 atoms will be $191x + 193(100 - x)$.

The average mass of the 100 atoms will be $\frac{191x + 193(100 - x)}{100}$

Therefore, we can write the equation as follows: $\frac{191x + 193(100 - x)}{100} = 192.22$

Rearranging this we get, $x = 39$

This means that the naturally occurring sample of iridium contains 39% iridium-191 and 61% iridium-193.

Alternatively, this calculation can be summarised in an equation, which can be useful for multiple-choice questions:

$$\frac{A_r - \text{mass number of lighter isotope}}{\text{difference in mass number of two isotopes}} \times 100 = \% \text{ of heavier isotope}$$

In the example here: $\frac{192.22 - 191}{193 - 191} \times 100 = 61\%$

INTERNATIONAL MINDEDNESS

The relative abundances of the isotopes of particular elements are not the same everywhere on Earth, and both physical and chemical processes can cause variations to occur. This means that the relative atomic mass values for some elements can vary, depending on where a sample comes from. The uncertainties on the internationally accepted values for relative atomic masses for several elements (including hydrogen, carbon and oxygen) reflect the range of variations that occur and not just the limitations of the instruments used to determine the values. This can also mean that the orange juice you drink in the morning may have a very slightly different isotopic composition than your coffee. Variations in isotopic abundances within countries and between them have also been used to track the migratory routes of animals.

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TEST YOUR UNDERSTANDING

13 Bromine has two naturally occurring isotopes, and their masses and natural abundances are shown in the table.

Isotope	Natural abundance / %
^{79}Br	50.69
^{81}Br	49.31

Calculate the relative atomic mass of bromine to two decimal places.

14 Chromium has four naturally occurring isotopes, and their masses and natural abundances are shown in the table.

Isotope	Natural abundance / %
^{50}Cr	4.35
^{52}Cr	83.79
^{53}Cr	9.50
^{54}Cr	2.36

Calculate the relative atomic mass of chromium to two decimal places.

15 Silicon has three naturally occurring isotopes and their details are given in the table.

Isotope	Natural abundance / %
^{28}Si	92.2
^{29}Si	4.7
^{30}Si	3.1

Calculate the relative atomic mass of silicon to two decimal places.

16 Krypton has six naturally occurring isotopes, and their masses and natural abundances are shown in the table.

Isotope	Natural abundance / %
^{78}Kr	0.35
^{80}Kr	2.25
^{82}Kr	11.6
^{83}Kr	11.5
^{84}Kr	57.0
^{86}Kr	17.3

Calculate the relative atomic mass of krypton to two decimal places.

17 **a** Indium has two naturally occurring isotopes: indium-113 and indium-115. The relative atomic mass of indium is 114.82. Calculate the natural abundance of each isotope.

b Gallium has two naturally occurring isotopes: gallium-69 and gallium-71. The relative atomic mass of gallium is 69.723. Calculate the natural abundance of each isotope.

c Copper has two naturally occurring isotopes: copper-63 and copper-65. The relative atomic mass of copper is 63.546. Calculate the natural abundance of each isotope.

d The relative atomic mass of a sample of strontium is 87.71. There are four naturally occurring isotopes. The natural abundance of ^{84}Sr is 0.56% and that of ^{88}Sr is 82.58% Calculate the natural abundances of ^{86}Sr and ^{87}Sr.

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The mass spectrum of an element and relative atomic mass

The proportion of each isotope present in a sample of an element can be measured using an instrument called a *mass spectrometer* (Figure 2.7).

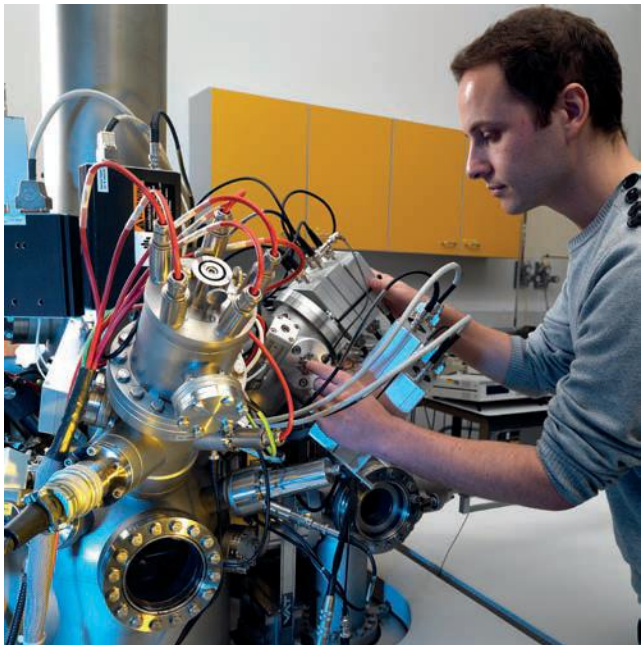

Figure 2.7: Setting up a mass spectrometer.

The readout from a mass spectrometer is called a mass spectrum (*plural: mass spectra*). In the mass spectrum of an element, we get one peak for each individual isotope. The height of each peak (more properly, the area under each peak) is proportional to the number of atoms of this isotope in the sample tested. The mass spectrum of magnesium is shown in Figure 2.8.

The scale on the *x*-axis in a mass spectrum is the mass:charge ratio (*m*/*z* or *m*/*e*).

To pass through a mass spectrometer, atoms are bombarded with high-energy electrons to produce positive ions (the mass of an electron is negligible, so it can be ignored when calculating the relative atomic mass). Sometimes more than one electron is knocked out of the atom, which means that the ions behave differently (as if they have smaller masses – a $^{24}Mg^{2+}$ ion would behave as if it had a mass of $\frac{24}{2} = 12$), hence, the use of mass:charge ratio. We can generally ignore this and assume that the horizontal scale refers to the mass of the isotope.

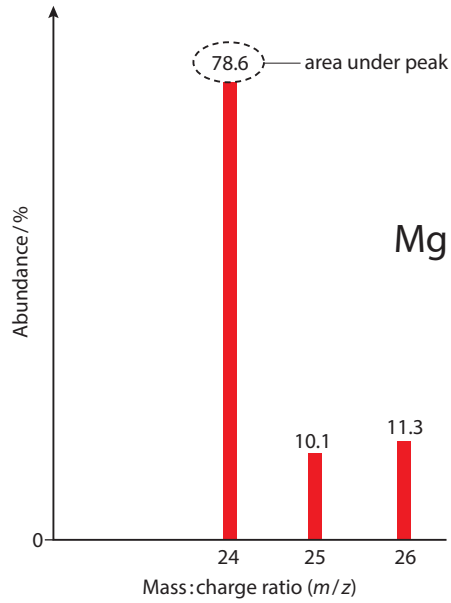

Figure 2.8: The mass spectrum of magnesium showing the amounts of the different isotopes present.

The relative atomic mass (A_r) can be calculated from a mass spectrum. For example, using data about the abundance of the isotopes in a sample of magnesium, as shown in Figure 2.8, we get

$$A_r = \frac{(78.6 \times 24) + (10.1 \times 25) + (11.3 \times 26)}{100} = 24.3$$

Link

Mass spectrometry can also be used to provide information about the structures of molecules. This is discussed in Chapter 11.

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TEST YOUR UNDERSTANDING

18 Determine the relative atomic mass of each element to two decimal places from the mass spectra in Figure 2.9.

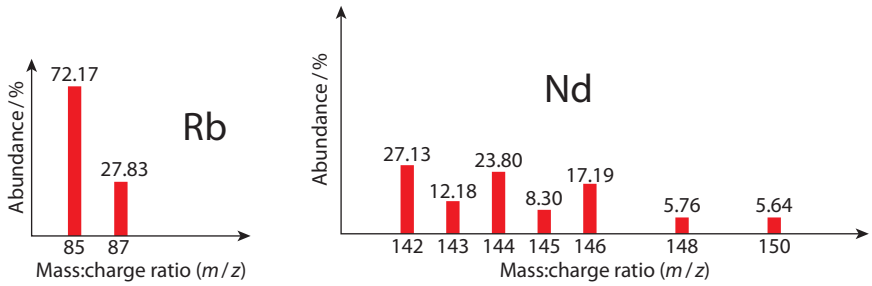

Figure 2.9: Mass spectra of two elements.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
state the relative masses and charges of protons, neutrons and electrons	2.1			
describe the structure of the atom in terms of the locations of protons, neutrons and electrons	2.1			
explain the terms mass number (A) and atomic number (Z)	2.1			
write the nuclear symbol for an atom given values of A and Z	2.1			
work out the number of protons, neutrons and electrons in atoms	2.1			
work out the number of protons, neutrons and electrons in ions	2.1			
explain the term isotope	2.2			
explain why isotopes have the same chemical properties	2.2			
give examples of physical properties that are different for isotopes	2.2			
determine the relative atomic mass of a sample of an element given the natural abundances	2.2			
determine the natural abundance of the isotopes in a sample given the relative atomic mass	2.2			

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CONTINUED

I can...	Section	Needs more work	Nearly there	Confident to move on
name the instrument used to find the isotopic composition of an element, so that its relative atomic mass can be determined	2.2			
use mass spectra to determine the relative atomic mass (A_r) of an element.	2.2			

REFLECTION

Would you feel more confident with the material by reading through the key points again?

Do you need more practice on the mathematical parts of the topic?

Try to explain the following to another student:

- the structure of an atom
- how a gold atom differs from a copper atom
- the difference between mass number and atomic number
- isotopes.

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 3
Electron configurations

LEARNING OBJECTIVES

In this chapter you will:

- describe the emission spectrum of hydrogen
- understand how the lines in the emission spectrum of hydrogen arise
- describe the relationship between wavelength, frequency, energy and colour in the electromagnetic spectrum
- write full and condensed electron configurations for atoms and ions up to $Z = 36$
- understand what orbitals are and draw diagrams of s and p orbitals
- draw orbital diagrams for atoms and ions up to $Z = 36$

- understand that the ionisation energy for hydrogen can be deduced from the emission spectrum
- calculate the first ionisation energy from the wavelength or frequency of the convergence limit
- understand what information about the electronic structure of atoms can be deduced from successive ionisation energy data

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GUIDING QUESTIONS

- How are electrons arranged in atoms and ions?
- How can atoms give out light?
- Why does it take different amounts of energy to remove electrons from different atoms?

Introduction

Chemistry is about the movement of electrons. In chemical reactions, electrons are either transferred between atoms or the electrons are rearranged so that they are shared between different atoms, therefore an understanding of the electronic structure of atoms is fundamental to an understanding of chemistry. The electron was discovered in 1897 by J. J. Thomson of Cambridge University, UK – this was the first of the subatomic particles revealed and was the beginning of a period of intense development in theories of atomic structure. Thomson proposed a model of the atom, which is often referred to as the plum-pudding model. This was followed by Rutherford's nuclear atom and then the Bohr model, which still has its uses today. Modern models of the structure of an atom describe it in terms of quantum theory.

3.1 The electromagnetic spectrum

Visible light, microwaves (cooking and Wi-Fi), ultraviolet (what you try to protect yourself from by putting on sun cream), etc. are familiar terms to everyone. These are all electromagnetic radiation, which is a form of energy. Electromagnetic radiation (Figure 3.1) is usually described as waves that travel at the speed of light in a vacuum (3.0×10^8 m s^{-1}). Although visible light, microwaves, etc. are given different names, they are all basically the same thing – they just vary in their frequency/energy/wavelength.

Frequency is the number of waves (passing a particular point) per second (measured in Hertz, Hz), whereas wavelength is the distance between corresponding points (e.g. peaks or troughs) of consecutive waves (measured in m, cm, etc.).

The frequency, wavelength and energy of electromagnetic radiation are related by the following equations:

$$\text{frequency} \propto \frac{1}{\text{wavelength}}$$

$$\text{frequency} \propto \text{energy}$$

$$\text{energy} \propto \frac{1}{\text{wavelength}}$$

So, the longer the wavelength, the lower the energy and frequency of the radiation; and the higher the frequency, the higher the energy.

Visible light is just one part of the electromagnetic spectrum. *White light* is the name given to the normal visible light that surrounds us every day. White light is made up of light of all the colours of the visible spectrum. In order of increasing energy, the colours of the spectrum are:

red < orange < yellow < green < blue < indigo < violet

Although electromagnetic radiation is usually described as a wave, it can also display the properties of a particle, and we sometimes talk about particles of electromagnetic

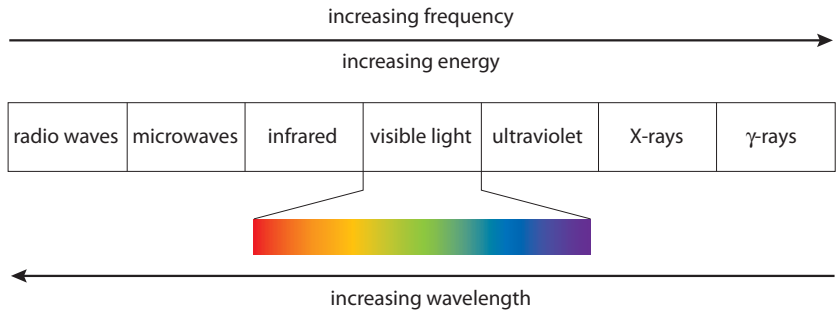

Figure 3.1: The electromagnetic spectrum.

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radiation called **photons**. A beam of light could, therefore, be regarded as a stream of photons. A higher energy photon corresponds to higher frequency or shorter wavelength electromagnetic radiation.

$$\text{Energy of photon} \propto \text{frequency}$$

$$\text{Energy of photon} \propto \frac{1}{\text{wavelength}}$$

3.2 The hydrogen atom spectrum

When hydrogen gas at low pressure is subjected to a very high voltage, the gas glows pink (Figure 3.2). The glowing gas can be looked at through a spectroscope, which contains a diffraction grating (or prism) which separates the various wavelengths of light emitted from the gas.

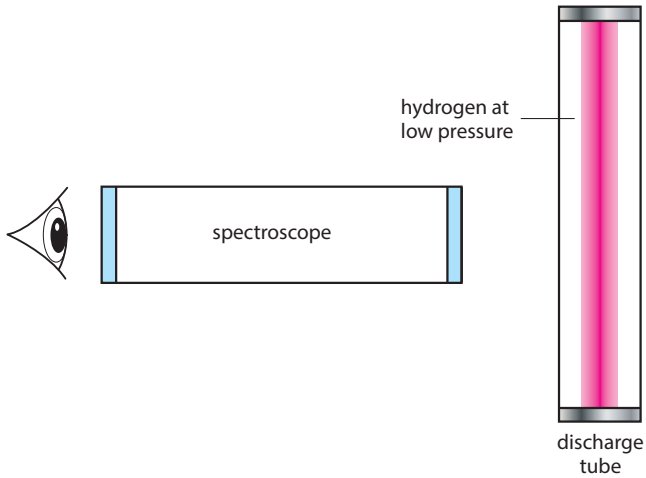

Figure 3.2: Observing the emission spectrum of hydrogen.

Because light is emitted by the gas, this is called an **emission spectrum**. Although hydrogen is usually present as H_2 molecules, collisions with high-energy electrons in the discharge tube cause the molecules to split up into H atoms. The spectrum we study here is due to the hydrogen *atoms* in the tube.

In the visible region, the spectrum consists of a series of sharp, bright lines on a dark background (Figure 3.3).

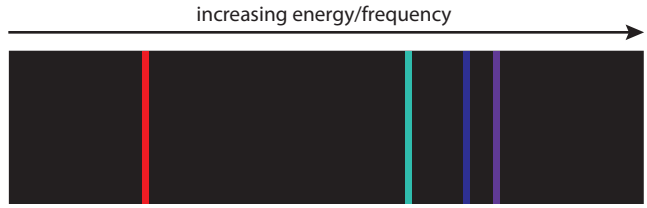

Figure 3.3: A representation of the atomic emission spectrum of hydrogen.

KEY POINT

The lines in an emission spectrum get closer together (converge) at higher frequency/energy.

This is a **line spectrum**, as opposed to a **continuous spectrum**, which consists of all the colours merging into each other (Figure 3.4).

Each element has its own unique emission spectrum, and this can be used to identify the element.

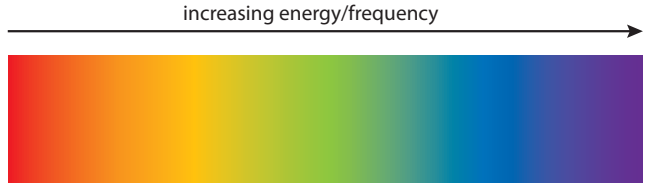

Figure 3.4: A continuous spectrum.

KEY POINT

- line spectrum – only certain frequencies/ wavelengths of light present
- continuous spectrum – all frequencies/ wavelengths of light present.

The Bohr model of the atom

The **Bohr model of the atom** (also called the Rutherford–Bohr model), which was developed towards the beginning of the 20th century, provides an explanation of the lines in the hydrogen atom emission spectrum.

In this model, atoms consist of a central nucleus with electrons moving around the nucleus in circular orbits (Figure 3.6).

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SCIENCE IN CONTEXT

You may have already encountered atomic emission spectra without realising it, if you have carried out a flame test. If you sprinkle some sodium chloride into a non-luminous Bunsen burner flame, you will see a bright yellow–orange colour – you are observing the emission spectrum of sodium atoms. With potassium salts, you get a lilac colour, and red with lithium salts. Each different atom has a unique emission spectrum, and elements such as rubidium, caesium and helium were discovered when lines were observed in a spectrum that could not be accounted for by any existing element. The names of these three elements reflect the nature of this discovery – rubidium and caesium come from Latin words for red and blue–grey, respectively, after the colours of lines in their spectra, and helium was named after the Greek god of the sun because it was discovered through observation of the spectrum of the sun.

Outside the laboratory, you may have also seen emission spectra in neon signs. Neon glows bright red when it is subjected to a high voltage in a discharge tube (Figure 3.5).

Figure 3.5: A true neon sign is red.

'Neon signs', however, come in a variety of colours and most of these do not actually contain neon – other colours are obtained generally by using argon and mercury and by coating the inside of the tubes with a phosphor that produces the required colour.

The emission spectrum of mercury is also exploited in the fluorescent tubes that are familiar from many offices and industrial buildings. Mercury is, however, extremely toxic, and the use of mercury in lighting is controversial and subject to legislation.

The energy of an electron in a particular orbit is constant, so these orbits can also be regarded as *energy levels* (sometimes referred to as *shells*). Only certain orbits (energy levels) can exist so that the electron within an atom can only have certain amounts of energy. These allowed energy levels are different for atoms of different elements. An electron in an orbit closer to the nucleus has lower energy than an electron in an orbit further from the nucleus.

The energy levels are labelled with a number, n (the principal quantum number). The level closest to the nucleus has $n = 1$ and the numbers increase as you go outwards from the nucleus.

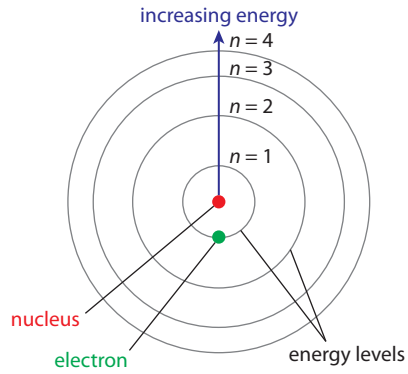

Figure 3.6: The Bohr model of a hydrogen atom (not to scale).

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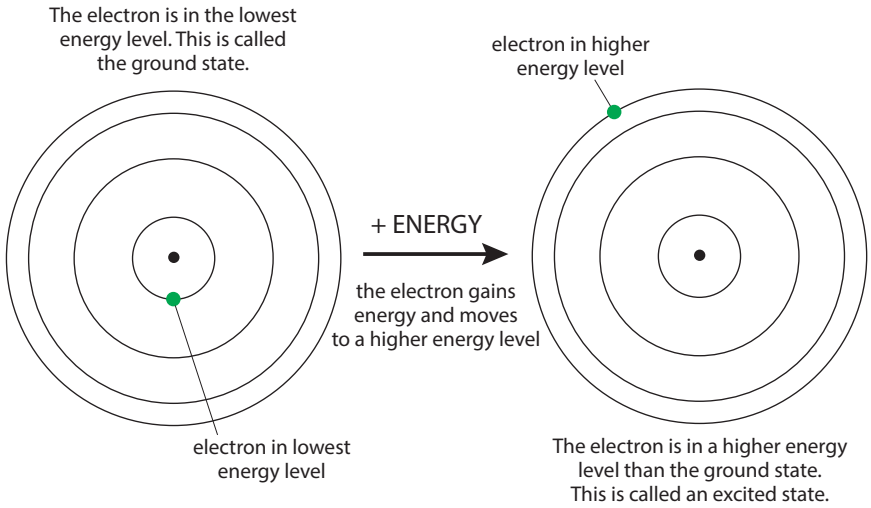

Figure 3.7: An electron can be promoted to a higher energy level in a discharge tube.

How an emission spectrum is formed

The electron in a hydrogen atom is usually in the lowest possible energy level ($n = 1$), closest to the nucleus – this is the **ground state**. Passing an electric discharge through hydrogen gas causes an electron to be promoted to a higher energy level – this is an **excited state** (Figure 3.7).

The electron is unstable in this higher level and will fall to a lower energy level (not necessarily the *lowest* level) (Figure 3.8).

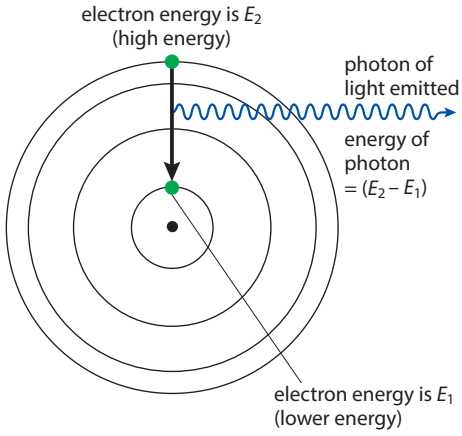

Figure 3.8: When an electron falls from a higher to a lower energy level on an atom, a photon of light is emitted.

As it moves from a level at energy E_2 (higher energy) to E_1 (lower energy), the extra energy $(E_2 - E_1)$ is given out in the form of a photon of light. This forms a line in the emission spectrum.

KEY POINTS

The ground state is the lowest possible energy state for an atom. For hydrogen, this occurs when the electron is in the lowest energy level ($n = 1$), closest to the nucleus.

The excited state is a higher energy state of an atom. For hydrogen, the electron gains energy – it is promoted to a higher energy level.

In reality, a great number of these transitions are required to produce a line that we can see.

The electron can have either energy E_1 or E_2 – it cannot have any amount of energy in between, and so, the amount of energy $(E_2 - E_1)$ must be given out in one go, as a photon of light.

KEY POINT

Each line in the emission spectrum comes from the transition of an electron from a higher energy level to a lower energy level.

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The transitions between energy levels can also be shown as in Figure 3.9.

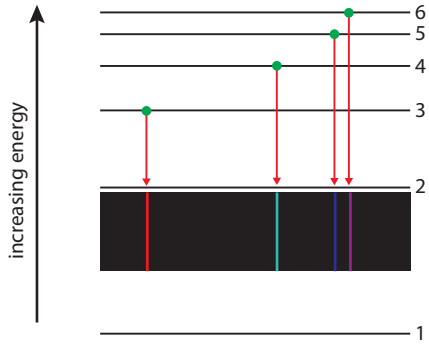

Figure 3.9: How the lines arise in the emission spectrum of hydrogen. The transitions down to level 2 are shown because these are the ones that produce lines in the visible region of the electromagnetic spectrum.

The line spectrum as evidence for energy levels for an electron in an atom

The fact that a line spectrum, rather than a continuous spectrum, is produced provides evidence for electrons being in discrete energy levels: i.e., electrons in an atom are only allowed to have certain amounts of energy. If an electron in an atom could have any amount of energy, it could gain any amount of energy in a discharge tube and give this energy out again, so that all frequencies of light would be emitted – a continuous spectrum (Figure 3.10).

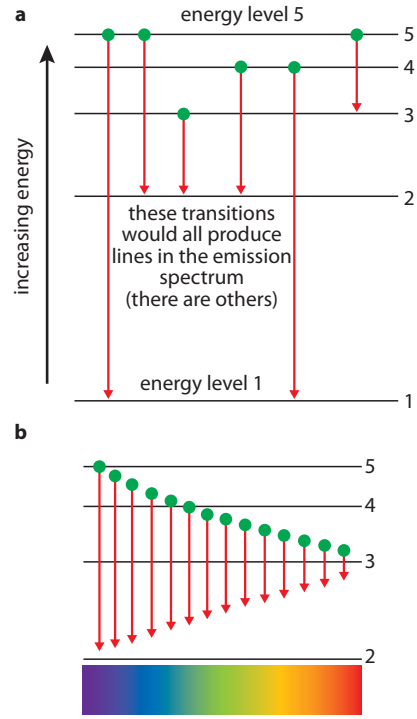

Figure 3.10: a Electrons in energy levels: only transitions between two discrete energy levels are possible, and a line spectrum is produced. **b** If the electrons in an atom could have any energy, all transitions would be possible. This would result in a continuous spectrum.

Different series of lines

Figure 3.11 shows a representation of the emission spectrum of hydrogen across the infrared, visible and ultraviolet regions. The series in each region consists of a set of lines that get closer together at higher frequency. Each series is named after its discoverer.

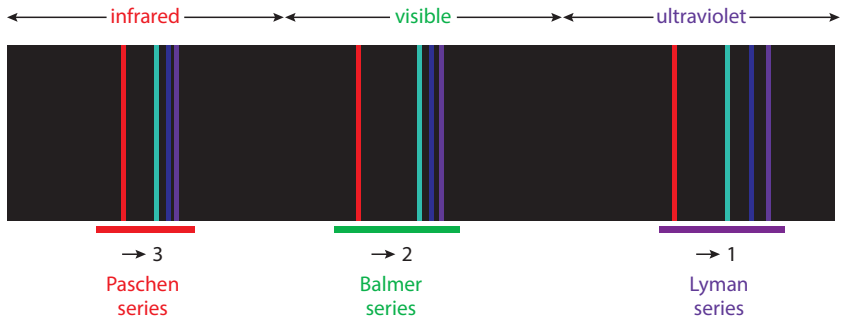

Figure 3.11: A representation of the emission spectrum of hydrogen. The colours and lines in the spectrum in the infrared and ultraviolet regions are just for illustrative purposes.

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EXAM TIP

The names of the series do not have to be learned for the examination.

Figure 3.12 shows how the different series arise.

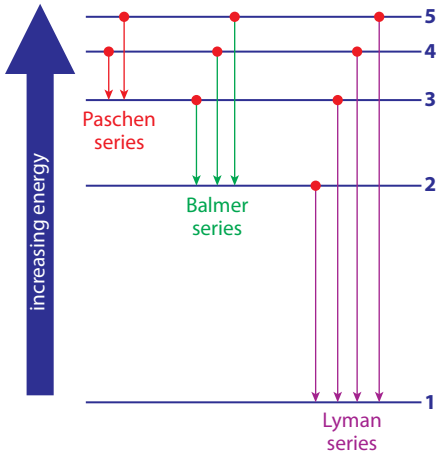

Figure 3.12: The different series of lines arise when electrons fall to different energy levels.

KEY POINT

The different series of lines in an emission spectrum occur when electrons fall back down to different energy levels.

So, for instance, the lines in the Balmer series arise when electrons fall from various higher energy levels to level 2, and the Lyman series arises when the electron falls to level 1.

All the transitions that occur in the visible region of the spectrum (those we can see) involve electrons falling down to energy level 2 (creating the Balmer series). All transitions down to energy level 1 occur in the ultraviolet region. So, for example, the transition $n = 5$ to $n = 2$ occurs in the visible region of the spectrum and the transition $n = 2$ to $n = 1$ occurs in the UV region. UV radiation has higher energy than visible light; therefore, we can deduce that the energy difference between energy level 1 and energy level 2 in a hydrogen atom is bigger than that between energy level 2 and any other higher energy level.

The atomic emission spectrum of hydrogen is relatively simple because hydrogen atoms contain only one electron. Ions such as He^+ and Li^{2+}, which also contain one electron, would have spectra similar to hydrogen, but not exactly the same because the number of protons in the nucleus influences the electron energy levels (energy of electrons). The simple model of energy levels presented here cannot be used to explain the spectra of atoms with more than one electron because repulsion between electrons affect electron energy levels in atoms.

Convergence

The lines in the emission spectrum get closer together at higher frequency/energy (Figure 3.13).

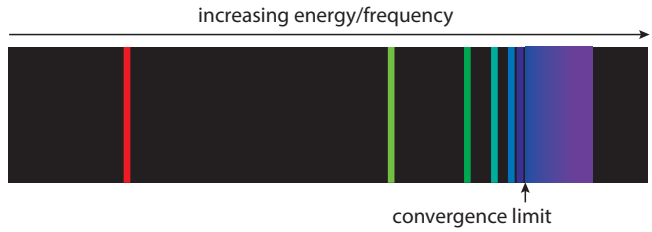

Figure 3.13: A representation of the Lyman series (electron falling to $n = 1$) of hydrogen in the ultraviolet region of the electromagnetic spectrum.

Eventually, the lines merge to form a continuum. The point at which this occurs is called the **convergence limit**. Beyond this point, the electron can have any energy, and so, must be free from the influence of the nucleus, i.e., the electron is no longer in the atom (Figure 3.14).

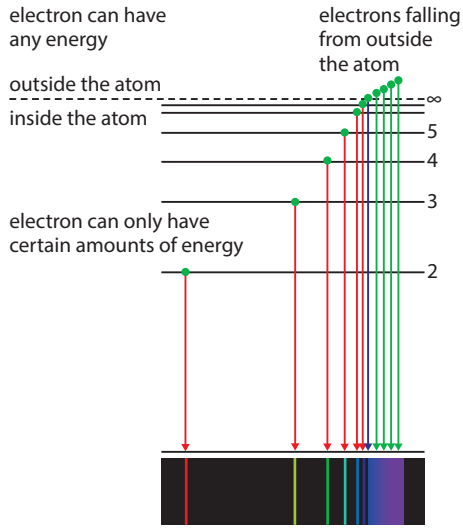

Figure 3.14: The blue arrow represents the transition giving rise to the convergence limit in the Lyman series (electron falling from the limit of outside the atom to $n = 1$) for hydrogen.

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TEST YOUR UNDERSTANDING

1 Arrange the following in order of

a increasing energy

b decreasing wavelength.

ultraviolet radiation, infrared radiation, microwaves, orange light, green light

2 Describe how a line in the Lyman series of the hydrogen atom spectrum arises.

3 Draw an energy level diagram showing the first four energy levels in a hydrogen atom, and mark with an arrow on this diagram one electron transition that would give rise to the following:

a a line in the ultraviolet region of the spectrum

b a line in the visible region of the spectrum

c a line in the infrared region of the spectrum.

NATURE OF SCIENCE

Advances in technology are often accompanied by advances in science – Bunsen's development of his burner with a high-temperature flame in the 1850s enabled spectroscopic analysis of substances.

Scientific theories often develop from a need to explain natural phenomena. For instance, Niels Bohr, building on the work of Rutherford, proposed the model for the atom in which electrons orbit the nucleus and only exist in certain allowed energy levels to try to explain the line spectra of hydrogen and other elements.

3.3 Electron configurations

Main energy levels

As we extend the Bohr model to atoms other than hydrogen, we will change the words we use slightly and talk about *main* energy levels (shells) rather than just *energy levels*. The word 'main' is being used here because we will see later that these energy levels are divided up into sub-levels.

As we saw previously, these main energy levels are labelled with a number, n. The level closest to the nucleus has $n = 1$, and the numbers increase as we go outwards from the nucleus. The maximum number of electrons in each main energy level is given by $2n^2$. The maximum number of electrons in each main energy level is shown in Table 3.1.

Main energy level number	1	2	3	4	5
Maximum number of electrons	2	8	18	32	50

Table 3.1: Distribution of electrons in the main energy levels.

KEY POINT

Electrons fill the main energy levels from the lowest energy to the highest (from the nucleus out).

So, the first main energy level must be completely full (two electrons) before an electron can be put into the second main energy level, and the second main energy level must be completely full (eight electrons) before an electron can be put into the third main energy level. Some electron configurations are shown in Figure 3.15.

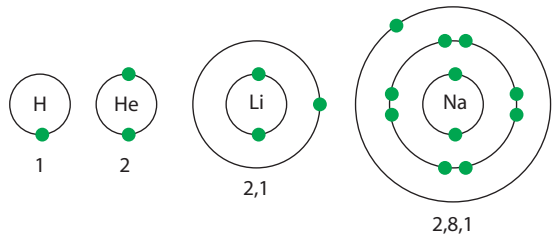

Figure 3.15: Electron configurations of some atoms, showing the number of electrons in each main energy level.

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This scheme for working out the number of electrons in each main energy level works for elements with atomic number up to 18, but breaks down after that as the electron configuration of potassium ($Z = 19$) is 2,8,8,1 (or 2.8.8.1) and not 2,8,9 (Figure 3.16). The third main energy level is only filled to eight before electrons are put into the fourth main energy level (we will see why below).

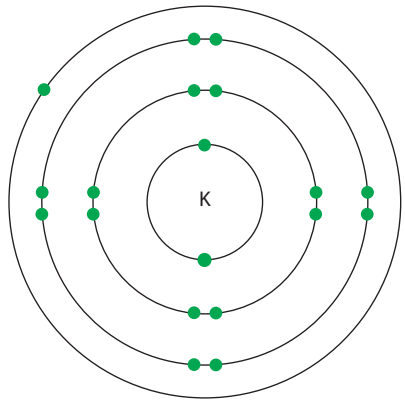

Figure 3.16: The electron configuration of potassium, showing electrons in main energy levels.

Full electron configurations

The Bohr model failed to explain experimental observations such as the emission spectra of atoms with more than one electron and the variation in ionisation energy across a period in the periodic table; therefore, a more sophisticated model had to be developed. This was based on treating the electron in the atom as a wave. This more sophisticated theory led to the concepts of sub-energy levels and orbitals.

Energy sub-levels and orbitals

Each main energy level in an atom is made up of **sub-levels** (subshells). The first main energy level consists solely of the 1s sub-level, the second main energy level is split into the 2s sub-level and the 2p sub-level. The sub-levels in each main energy level up to 4 are shown in Table 3.2.

Main energy level	Sub-levels				Maximum number of electrons in each sub-level			
					s	p	d	f
1	1s				2			
2	2s	2p			2	6		
3	3s	3p	3d		2	6	10	
4	4s	4p	4d	4f	2	6	10	14

Table 3.2: The sub-levels in each main energy level up to level 4.

Within any main energy level (shell), the ordering of the sub-levels (subshells) is always s < p < d < f. The relative energies of the sub-levels (subshells) are shown in Figure 3.17. It is important to notice that the 4s sub-level is lower in energy than the 3d sub-level.

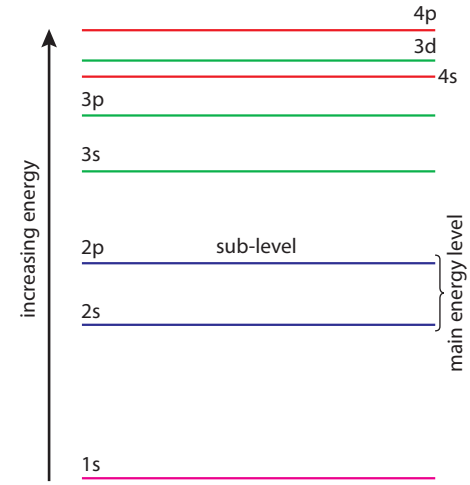

Figure 3.17: The ordering of the energy levels and sub-levels within an atom. The sub-levels within a main energy level are shown in the same colour.

The Aufbau (building-up) principle

The **Aufbau principle** is the name given to the process of working out the electron configuration of an atom.

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Electron configurations of atoms with 1–18 electrons

KEY POINT

Electrons fill sub-levels from the lowest energy level upwards – this gives the lowest possible energy overall.

So, the full electron configuration of sodium (11 electrons) can be built up as follows:

- The first two electrons go into the 1s sub-level → $1s^2$; this sub-level is now full.
- The next two electrons go into the 2s sub-level → $2s^2$; this sub-level is now full.
- The next six electrons go into the 2p sub-level → $2p^6$; this sub-level is now full.
- The last electron goes into the 3s sub level → $3s^1$.

The full electron configuration of sodium is, therefore, $1s^2\ 2s\ ^2 2p^6\ 3s^1$ (Figure 3.18).

EXAM TIP

The number of electrons in each sub-level must be written as a superscript.

Condensed electron configurations

The full electron configuration of sodium can be abbreviated to [Ne] $3s^1$, where the electron configuration of the previous **noble gas** atom is assumed and everything after that is given in full. This is known as a *condensed electron configuration*.

$[1s^2\ 2s^2\ 2p^6]\ 3s^1$
from neon

The full and condensed electron configurations for the first 18 elements are shown in Table 3.3.

Atom	Atomic number	Full electron configuration	Condensed electron configuration
H	1	$1s^1$	$1s^1$
He	2	$1s^2$	$1s^2$
Li	3	$1s^2\ 2s^1$	[He] $2s^1$
Be	4	$1s^2\ 2s^2$	[He] $2s^2$
B	5	$1s^2\ 2s^2\ 2p^1$	[He] $2s^2\ 2p^1$
C	6	$1s^2\ 2s^2\ 2p^2$	[He] $2s^2\ 2p^2$
N	7	$1s^2\ 2s^2\ 2p^3$	[He] $2s^2\ 2p^3$
O	8	$1s^2\ 2s^2\ 2p^4$	[He] $2s^2\ 2p^4$
F	9	$1s^2\ 2s^2\ 2p^5$	[He] $2s^2\ 2p^5$
Ne	10	$1s^2\ 2s^2\ 2p^6$	[He] $2s^2\ 2p^6$
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$	[Ne] $3s^1$
Mg	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$	[Ne] $3s^2$
Al	13	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	[Ne] $3s^2\ 3p^1$
Si	14	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	[Ne] $3s^2\ 3p^2$
P	15	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	[Ne] $3s^2\ 3p^3$
S	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	[Ne] $3s^2\ 3p^4$
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	[Ne] $3s^2\ 3p^5$
Ar	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	[Ne] $3s^2\ 3p^6$

Table 3.3: The electron configurations of the first 18 elements. Remember that the atomic number tells you the number of electrons in a neutral atom.

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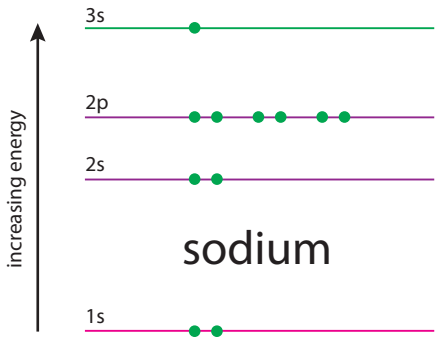

Figure 3.18: The arrangement of electrons in energy levels for a sodium atom.

Electron configurations of atoms with 19–36 electrons

Once the 3p sub-level has been filled, there are now 8 electrons (2 in the 3s and 6 in the 3p sub-levels) in the third main energy level, but the third main energy level can hold a total of $2 \times 3^2 = 18$ electrons, so there is room for another 10 electrons in this main energy level. However, if you look at Figure 3.17, you can see that the next lowest sub-level is 4s, so the next two electrons go into there. The electron configurations of potassium and calcium are shown in Table 3.4.

Atom	Atomic number	Full electron configuration	Condensed electron configuration
K	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	[Ar] $4s^1$
Ca	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	[Ar] $4s^2$

Table 3.4: The electron configurations of potassium and calcium atoms.

From Figure 3.17, we can see that the next lowest sub-level, once 4s has been filled, is 3d, and so, the electron configuration of scandium ($Z = 21$) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$.

The electron configuration of scandium is sometimes written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$ to keep the sub-levels in a main energy level together.

Once the 3d sub-level has been filled, the electrons then go into the 4p sub-level. The electron configurations of atoms with 21–36 electrons are shown in Table 3.5.

Atom	Atomic number	Full electron configuration	Condensed electron configuration
Sc	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	[Ar] $4s^2\ 3d^1$
Ti	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$	[Ar] $4s^2\ 3d^2$
V	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	[Ar] $4s^2\ 3d^3$
Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$	[Ar] $4s^1\ 3d^5$
Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$	[Ar] $4s^2\ 3d^5$
Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	[Ar] $4s^2\ 3d^6$
Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	[Ar] $4s^2\ 3d^7$
Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	[Ar] $4s^2\ 3d^8$
Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$	[Ar] $4s^1\ 3d^{10}$
Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$	[Ar] $4s^2\ 3d^{10}$
Ga	31	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^1$	[Ar] $4s^2\ 3d^{10}\ 4p^1$
Ge	32	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$	[Ar] $4s^2\ 3d^{10}\ 4p^2$
As	33	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^3$	[Ar] $4s^2\ 3d^{10}\ 4p^3$
Se	34	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$	[Ar] $4s^2\ 3d^{10}\ 4p^4$
Br	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$	[Ar] $4s^2\ 3d^{10}\ 4p^5$
Kr	36	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$	[Ar] $4s^2\ 3d^{10}\ 4p^6$

Table 3.5: The full and condensed electron configurations of atoms with between 21 and 36 electrons.

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Chromium and copper are exceptions

There are a small number of exceptions to the rules for filling sub-levels, i.e., electron configurations that are not quite as expected. Two of these exceptions are chromium and copper, which, instead of having electron configurations of the form [Ar] $4s^2$ $3d^n$, have only one electron in the 4s sub-level:

$_{24}$Cr: [Ar] $4s^1$ $3d^5$

$_{29}$Cu: [Ar] $4s^1$ $3d^{10}$

The reasons for this are complex and beyond the level of the syllabus, but, in general, having the maximum number of electron spins the same within a set of degenerate (same energy) orbitals gives a lower energy (more stable) situation. Orbitals and electron spin are discussed next.

Using the periodic table to work out electron configurations

The periodic table (Figure 3.20) is divided into blocks (s, p, d, f) according to the highest energy sub-level that contains electrons. For instance, Li and Ca are in the *s block* because they have electron configurations [He] $2s^1$ and [Ar] $4s^2$, so the s sub-level is the highest energy level occupied, but N is in the *p block* because it has the electron configuration [He] $2s^2$ $2p^3$, and so, a p sub-level is the highest energy level occupied.

All elements in the same group (vertical column) will have the same number of electrons in the highest occupied main energy level (we normally say *outer-shell electron configuration*). So, for instance, the electron configurations of the elements in Group 1 (Li → Cs) all end in ns^1 and those of elements in Group 14 all end in ns^2 np^2.

The period (horizontal row) number tells you the highest energy main energy level occupied.

WORKED EXAMPLE 3.1

Deduce the full electron configuration of selenium (Se).

Answer

This can be done most easily from the periodic table in Figure 3.19 – just follow the arrows from the beginning until you reach the element you are interested in. For selenium (Se), we have

H → He $1s^2$

Li → Be $2s^2$ B → Ne $2p^6$

Na → Mg $3s^2$ Al → Ar $3p^6$

K → Ca $4s^2$ Sc → Zn $3d^{10}$ Ga → Se $4p^4$

(remember to go down 1 for the main energy level in the d block – it is 3d, not 4d here).

Therefore, the electron configuration of selenium is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^4$.

A way to remember the order in which the sub-levels are filled

If you have not got a periodic table, you can remember the order in which the sub-levels are filled by using the following trick. Draw out the sub-levels in each main energy level with all the s sub-levels above each other and all the p sub-levels above each other, as in Figure 3.20. Starting at 1s, follow the diagonal arrows to give the ordering of the sub-levels.

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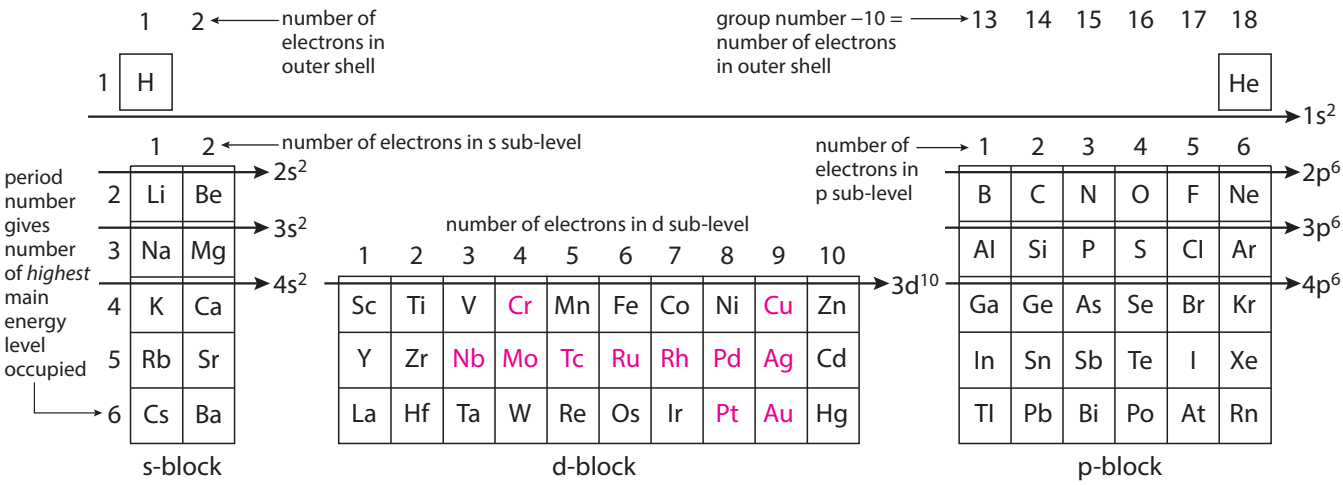

Figure 3.19: Electron configurations can be worked out from the periodic table. Some exceptions to the general rules for filling sub-levels are highlighted in pink. Helium has the electron configuration $1s^2$ and so has no p electrons – despite this, it is usually put in the p block to be in the same group as the other noble gases (Group 18).

TEST YOUR UNDERSTANDING

4 Give the full electron configurations of the following atoms:

a N **b** Si
c Ar **d** As
e V **f** Cr

5 Give the condensed electron configurations of the following atoms:

a O **b** Cl
c Mn **d** Ga
e Br **f** Cu

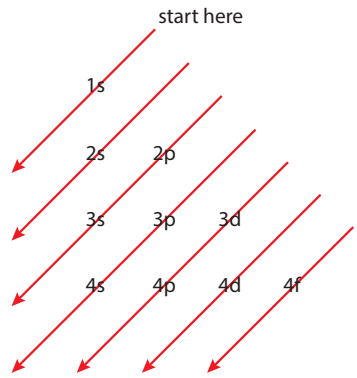

Figure 3.20: Follow the arrows to get the order in which sub-levels are filled.

Orbitals

A more advanced model of the behaviour of electrons in an atom regards the electrons as waves. Solutions of a complex equation, called the Schrödinger Equation, are mathematical functions that allow us to define the regions of space occupied by electrons within atoms.

An **orbital** is a region of space in which there is a high probability of finding an electron.

KEY POINTS

Electrons occupy atomic orbitals in atoms.

An orbital can contain a maximum of two electrons.

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There are four different types of atomic orbital: s, p, d and f.

The first main energy level (maximum number of electrons = 2) consists of a 1s orbital, and this makes up the entire 1s sub-level. This is spherical in shape (Figure 3.21a).

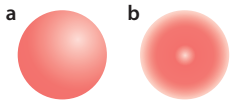

Figure 3.21: a The shape of a 1s orbital; **b** the electron density in a 1s orbital.

The 1s orbital, like all other atomic orbitals, is centred on the nucleus (Figure 3.21b). The electron is moving all the time, and the intensity of the colour here represents the probability of finding the electron at a certain distance from the nucleus. The darker the colour, the greater the probability of the electron being at that point. This represents the *electron density*. The electron can be found anywhere in this region of space (except the nucleus – at the centre of the orbital), but it is most likely to be found at a certain distance from the nucleus.

The second main energy level (maximum number of electrons = 8) is made up of the 2s sub-level and the 2p sub-level. The 2s sub-level just consists of a 2s orbital, whereas the 2p sub-level is made up of three 2p orbitals. The 2s orbital is spherical in shape (like all others orbitals) and bigger than the 1s orbital (Figure 3.22).

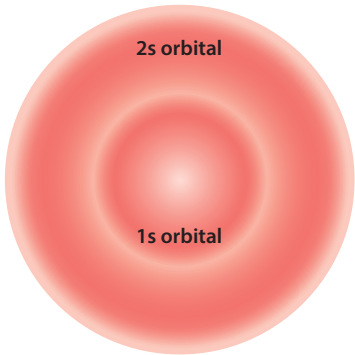

Figure 3.22: A cross-section of the electron density of the 1s and 2s orbitals together.

The p orbitals have a 'dumb-bell' shape (Figure 3.23).

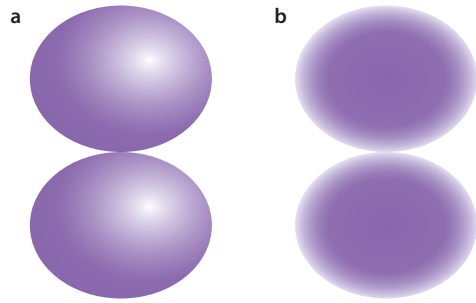

Figure 3.23: a The shape of a 2p orbital; **b** the electron density in a 2p orbital.

Three p orbitals make up the 2p sub-level. These lie at 90° to each other and are labelled p_x, p_y and p_z (Figure 3.24). The p_x orbital points along the *x*-axis, the p_y orbital points along the *y*-axis, etc. The three 2p orbitals all have the same energy – they are described as **degenerate**.

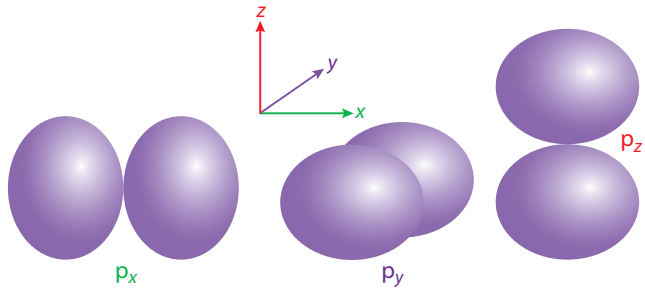

Figure 3.24: a The three p orbitals that make up a p sub-level pointing at 90° to each other.

Figure 3.25 shows the orbitals that make up the 2s and 2p sub-levels in the second main energy level.

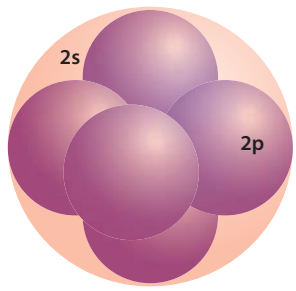

Figure 3.25: The 2s and 2p sub-levels in the second main energy level.

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The third main energy level (maximum 18 electrons) consists of the 3s, 3p and 3d sub-levels. The 3s sub-level is just the 3s orbital, the 3p sub-level consists of three 3p orbitals, and the 3d sub-level is made up of five 3d orbitals. One of the five 3d orbitals is shown in Figure 3.26a.

The fourth main energy level (maximum 32 electrons) consists of one 4s, three 4p, five 4d and seven 4f orbitals. The seven 4f orbitals make up the 4f sub-level. One of the f orbitals is shown in Figure 3.26b.

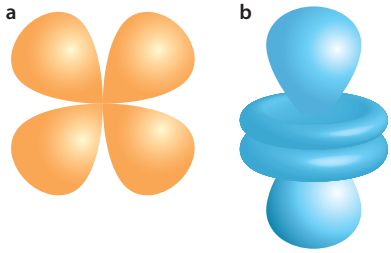

Figure 3.26: One of the five 3d orbitals (a) and one of the f orbitals in the 4f sub-level (b).

KEY POINT

Within any subshell, all the orbitals have the same energy (they are degenerate).

For example, the three 2p orbitals are degenerate and the five 3d orbitals are degenerate.

The number of orbitals in each main energy level is shown in Table 3.6.

Main energy level (shell)	s	p	d	f
1	1			
2	1	3		
3	1	3	5	
4	1	3	5	7

Table 3.6: The number of orbitals in each energy level.

EXAM TIP

We do not do much with elements containing f electrons at this level, but you should remember that the f subshell is made up of seven f orbitals and contains up to 14 electrons.

KEY POINT

Each orbital has a certain defined amount of energy.

The energy of an orbital depends on the following:

- The atom – both the number of protons in the nucleus and the number of other electrons influence the energy of orbitals. The energy of a 1s orbital in a hydrogen atom is, therefore, different from that of a 1s orbital in a helium atom.
- The electron configuration – different numbers of electrons cause different amounts of repulsion between electrons. The energy of, for example, a 2p orbital in a sodium atom (Na) is different from that of a 2p orbital in a sodium ion (Na^+).
- The chemical environment of the atom – the energy of the 1s orbital of C in CH_3Cl is not the same as the energy of the 1s orbital of C in CCl_4.

THEORY OF KNOWLEDGE

The diagrams of atomic orbitals that we have seen here are derived from mathematical functions that are solutions to the Schrödinger equation. Exact solutions of the Schrödinger equation are only possible for a system involving one electron, i.e., the hydrogen atom. It is not possible to derive exact mathematical solutions for more complex atoms. What implications does this have for the limit of scientific knowledge? When we describe more complex atoms in terms of orbitals, we are actually just extending the results from the hydrogen atom and gaining an approximate view of the properties of electrons in atoms.

3.4 Putting electrons into orbitals

As well as moving around in space within an orbital, electrons also have another property called *spin*.

We use a single-headed arrow to represent an electron having spin in one direction

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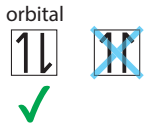
or in the opposite direction

Each box represents an orbital.

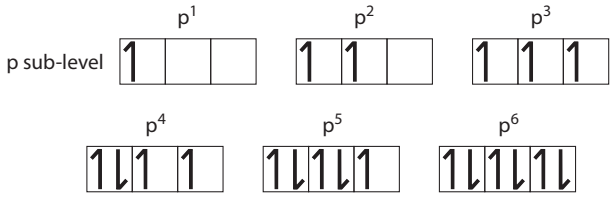
There are two rules that must be considered for understanding how electrons occupy orbitals:

1 The **Pauli exclusion principle**: Remember: the maximum number of electrons in an orbital is 2. There are two further rules that must be considered for understanding how electrons occupy orbitals: if there are two electrons in an orbital, they must have opposite spins:

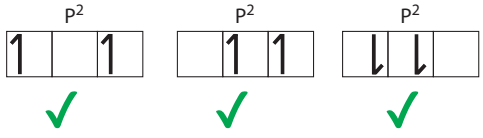


2 **Hund's rule**: electrons fill orbitals of the same energy (degenerate orbitals) to give the maximum number of electrons with the same spin.

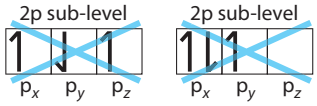
So, the electrons fill the orbitals of a p sub-level as shown:



The direction of electron spin (as long as the maximum number have the same spins – parallel spins) or which of the p orbitals an electron goes into (they are all the same energy) make no difference to the overall energy, so other arrangements for the p^2 electron configuration are also acceptable.



By contrast, these higher energy situations do not occur:



EXAM TIP

When an electron is alone in an orbital, it is called an unpaired electron.

Orbital diagrams

We are now in a position to use the Aufbau principle to draw **orbital diagrams** that show the full electron configurations of atoms. Figure 3.27**a** and **b** shows orbital diagrams for oxygen and silicon atoms, respectively.

EXAM TIP

In exam papers, the orbitals/sub-levels may sometimes be shown all on the same level.

Partial orbital diagrams for some transition metal atoms are shown in Figure 3.28.

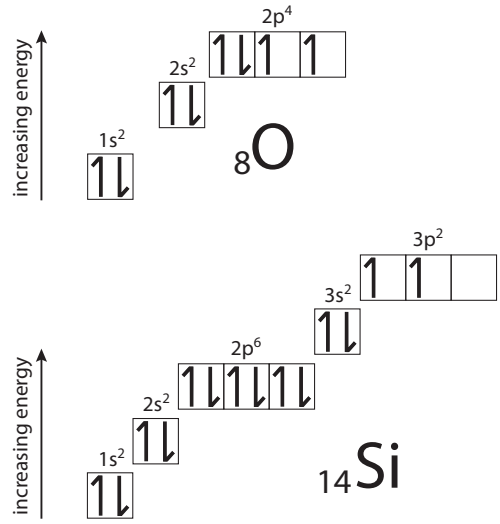


Figure 3.27: Electron configurations of **a** oxygen and **b** silicon.

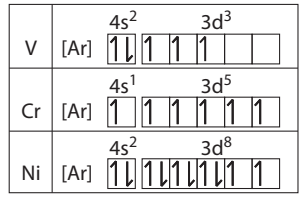


Figure 3.28: Orbital diagrams for three transition metal atoms, showing how the electrons occupy the 4s and 3d orbitals.

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The arrangement of electrons in a Cr atom cannot actually be predicted by this treatment, which would not give us information about whether the spin of the electron in the 4s orbital will be the same or different from those of the 3d electrons. But, in general, electrons with the same spin tend to stay further apart, and so there is less repulsion between them, giving a lower energy situation. It is unlikely that you would be required to know that at this level.

TEST YOUR UNDERSTANDING

6 Draw orbital diagrams for the following atoms, showing electrons in boxes:

a N **b** S

c Cr **d** Fe.

7 Deduce how many unpaired electrons are present in an atom of each of the following:

a B **b** P

c Ca **d** Mn

e As.

Electron configurations of ions

Ions are formed when atoms lose or gain electrons.

KEY POINTS

Positive ions (cations) are formed when atoms lose electrons.

Negative ions (anions) are formed when atoms gain electrons.

Link

A cation moves towards the cathode (negative electrode) in an electrolytic cell and an anion moves towards the anode (positive electrode) – see Chapter 20.

Formation of negative ions

When an electron is added to an atom to form a negative ion, we just follow the rules of the Aufbau principle. The electron configuration of some atoms and negative ions are shown in Table 3.7.

Atom	Full electron configuration	Ion	Full electron configuration
P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$	P^{3-}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	S^{2-}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	Cl^-	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Table 3.7: Full electron configurations of some negative ions.

Formation of positive ions

When an atom loses electrons, the highest energy electrons are easiest to remove and are, therefore, lost first. The general rule is that electrons are removed in the reverse order to which we have just learned to put them into orbitals; in other words, 'last in, first out'.

Figure 3.29 shows how electrons are removed from a magnesium atom to form positive ions.

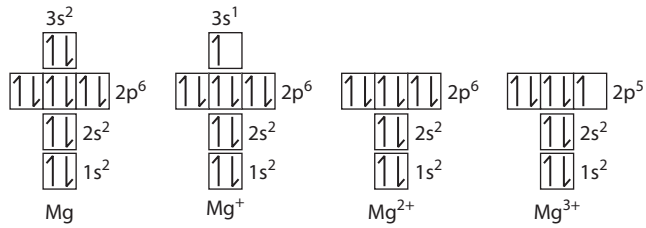

Figure 3.29: Orbital diagrams showing the removal of successive electrons from a Mg atom. In reality, the energies of all the orbitals would change as electrons were removed. Mg does not form a 1+ or a 3+ ion in chemical reactions/compounds.

Transition metal ions

The **transition metals** are the elements in the *d block,* in the middle of the periodic table, and represent a slight departure from the 'last in, first out' rule for ionisation energy.

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KEY POINT

The 4s electrons are removed before the 3d electrons.

Although the sub-levels are filled in order of 4s and then 3d, *the 4s electrons are always removed before the 3d electrons*.

Some condensed electron configurations of transition-metal atoms and ions are shown in Table 3.8.

Atom	Condensed electron configuration	Ion	Condensed electron configuration
V	[Ar] $4s^2\ 3d^3$	V^{2+}	[Ar] $3d^3$
Cr	[Ar] $4s^1\ 3d^5$	Cr^{3+}	[Ar] $3d^3$
Fe	[Ar] $4s^2\ 3d^6$	Fe^{3+}	[Ar] $3d^5$
Cu	[Ar] $4s^1\ 3d^{10}$	Cu^{2+}	[Ar] $3d^9$

Table 3.8: The condensed electron configurations of some transition metal atoms and ions.

From Ga to Kr

For these elements, the 4p electrons are lost before the 4s electrons, which are lost before the 3d electrons. Therefore, the electron configurations of Ga and Ga^{3+} are:

Ga: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$

Ga^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

TEST YOUR UNDERSTANDING

8 Write the full electron configurations of the following ions:

a F^- **b** O^{2-} **c** K^+

d Mn^{2+} **e** Co^{3+}

9 Write condensed electron configurations for each of the following ions:

a S^{2-} **b** Ge^{4+} **c** Zn^{2+}

d V^{3+} **e** Ni^{2+}

3.5 Ionisation energy

The relationship between the energy of a photon and the frequency or wavelength of electromagnetic radiation

Light, and other forms of electromagnetic radiation, exhibit the properties of both waves and particles – this is known as wave–particle duality.

The energy (E) of a photon is related to the frequency of the electromagnetic radiation:

$$E = hf$$

where

f is the frequency of the light (Hz or s^{-1})

h is the Planck constant (6.63×10^{-34} J s)

The wavelength of the light is related to the frequency using the equation:

$$c = f\lambda$$

where

λ is the wavelength of the light (m)

c is the speed of light (3.0×10^8 ms^{-1})

The two equations $E = hf$ and $c = f\lambda$ can be combined:

$$E = \frac{hc}{\lambda}$$

This relates the energy of a photon to its wavelength.

Ionisation energy and the convergence limit in the hydrogen emission spectrum

We saw earlier in the chapter that the lines got closer together in the hydrogen emission spectrum until they reached the convergence limit. The convergence limit in the Lyman series represents an electron falling from the limit of where it is in/outside the atom (level ∞ in Figure 3.30) to level 1.

Knowing the frequency of light emitted at the convergence limit of the Lyman series enables us to work out the **ionisation energy** of a hydrogen atom – the energy for the process:

$H(g) \rightarrow H^+(g) + e^-$

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The ionisation energy for hydrogen represents the minimum energy for the removal of an electron (from energy level 1 to ∞) (Figure 3.30), and the frequency (or wavelength) of the convergence limit in the Lyman series allows us to calculate the quantity of energy given out when an electron falls from the limit of in/outside the atom to energy level 1 (∞ to 1). These are the same quantities of energy.

The ionisation energy of hydrogen can be obtained only from a study of the series of lines when the electron falls back to its ground state (normal) energy level – in other words, only the Lyman series, where the electron falls back down to level 1.

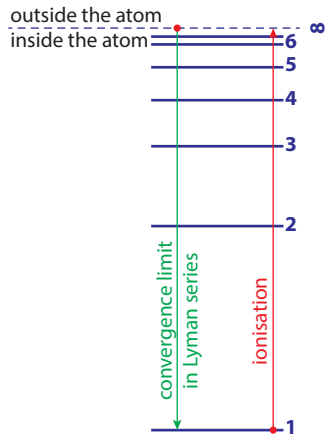

Figure 3.30: The convergence limit and ionisation in a hydrogen atom. Note: the arrows go in opposite directions.

WORKED EXAMPLE 3.2

If the wavelength of the convergence limit in the Lyman series for hydrogen is 91.46 nm calculate the ionisation energy of hydrogen in kJ mol^{-1}.

Answer

The wavelength is given in nanometres, but must be converted to metres (because the speed of light, c, is in ms^{-1}). The meaning of 'nano' is given in the data booklet: nano refers to 10^{-9}. Therefore, to convert nm to m, multiply by 10^{-9}.

Wavelength at the convergence limit is: 91.46×10^{-9}, that is 9.146×10^{-8} m

$c = f\lambda$, therefore $f = c/\lambda$

$$f = \frac{3.00 \times 10^{8}}{9.146 \times 10^{-8}} = 3.28 \times 10^{15} \text{ Hz}$$

$E = hf$

Therefore, $E = 6.63 \times 10^{-34} \times 3.28 \times 10^{15} = 2.17 \times 10^{-18}$ J

This represents the minimum amount of energy required to remove an electron from just one atom of hydrogen, but we are required to calculate the total energy required to remove one electron from each atom in 1 mole of hydrogen atoms – therefore we must multiply by the Avogadro constant (6.02×10^{23} mol^{-1} – see Chapter 4).

The energy required is $2.17 \times 10^{-18} \times 6.02 \times 10^{23} = 1.31 \times 10^{6}$ J mol^{-1}.

Dividing by 1000 gives the answer in kJ mol^{-1}, so the ionisation energy of hydrogen is 1.31×10^{3} kJ mol^{-1}.

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TEST YOUR UNDERSTANDING

10 In the emission spectrum of deuterium (^2H), the frequency of the convergence limit in the series of lines where the electron falls to $n = 1$ is 3.29×10^{15} Hz. Calculate the ionisation energy of deuterium in kJ mol^{-1}.

11 In the emission spectrum of a helium ion (He^+), the wavelength of the convergence limit in the series of lines where the electron falls to $n = 1$ would be 22.81 nm. Calculate the ionisation energy of a helium ion in kJ mol^{-1}.

Successive ionisation energies

The **first ionisation energy** for an element is the minimum amount of energy required to remove an electron from a gaseous atom – the energy for the following process:

$M(g) \rightarrow M^+(g) + e^-$

The full definition is the energy required to remove one electron from each atom in one mole of gaseous atoms under standard conditions (see Chapter 13).

EXAM TIP

You must remember to include the state symbols.

The second ionisation energy is $M^+(g) \rightarrow M^{2+}(g) + e^-$

The nth ionisation energy is $M^{(n-1)}(g) \rightarrow M^{n+}(g) + e^-$

The second ionisation energy for a particular element is always higher than the first, and this can be explained in two ways:

1. Once an electron has been removed from an atom, a positive ion is created. A positive ion attracts a negatively charged electron more strongly than a neutral atom does. More energy is, therefore, required to remove the second electron from a positive ion.
2. Once an electron has been removed from an atom, there is less repulsion between the remaining electrons. They are, therefore, pulled in closer to the nucleus (Figure 3.31). If they are closer to the nucleus, they are more strongly attracted and more difficult to remove.

Similarly, the third ionisation energy for a particular element is always higher than the second ionisation energy, etc.

Successive ionisation energies and main energy levels

The graph in Figure 3.32 shows the energy required to remove each electron in turn from a gaseous potassium atom.

From the graph, we can see that the first electron is relatively easy to remove, then there is a jump to a group of eight electrons, then another jump to a further group of eight electrons and then finally a jump to a group of two electrons. This pattern corresponds to the number of electrons in main energy levels (shells) in potassium – 2,8,8,1 – with the large jumps in the graph occurring

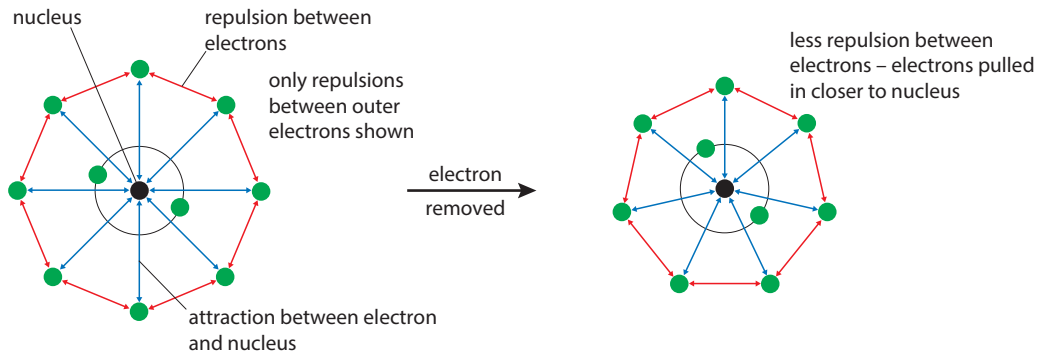

Figure 3.31: When an electron is removed from an atom, the remaining electrons are drawn closer to the nucleus due to reduced repulsion.

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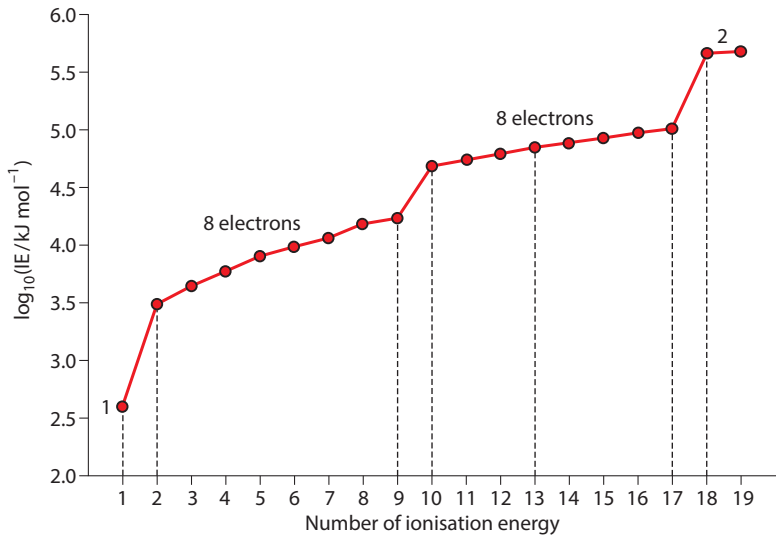

Figure 3.32: Successive ionisation energies (IEs) for potassium. Plotting $\log_{10}$ of these numbers reduces the range. The 1st ionisation energy of potassium is 418 kJ mol^{-1}, whereas the 19th is 475 000 kJ mol^{-1}. It would be very difficult to plot these values on a single graph with a linear scale.

when an electron is removed from a different main energy level (shell).

Remember that the electrons (negatively charged) are held in the atom by electrostatic attraction to the positively charged nucleus. The outermost electron in potassium is furthest from the nucleus and, therefore, least strongly attracted by the nucleus, so this electron is easiest (least energy is required) to remove. It is also shielded (screened) from the full attractive force of the nucleus by the other 18 electrons in the atom (Figure 3.33).

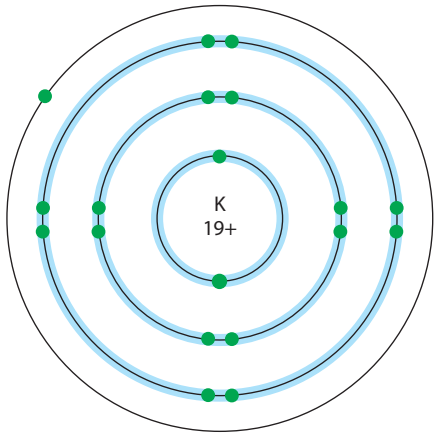

Figure 3.33: The outer electron in a potassium atom is shielded from the full attractive force of the nucleus by the inner shells of electrons (shaded in blue).

THEORY OF KNOWLEDGE

A log scale is used in Figure 3.34 to allow all the data to be plotted on one graph, but, although on one level, this has made the data easier to interpret and supports the explanations that have been given, it has also distorted the data. The difference between the 1st and 2nd ionisation energies of potassium is about 2600 kJ mol^{-1}, but the difference between the 18th and 19th ionisations energies is over 30 000 kJ mol^{-1} – the first one is regarded as a *large jump* but the second one is not!

- How can the way in which data are presented be used by scientists to support their theories?
- Is scientific knowledge objective or is it a matter of interpretation and presentation?

The arguments for and against human-made climate change are a classic example of where the interpretation and presentation of data are key in influencing public opinion.

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Shielding

Complete shells (main energy levels) of electrons between the nucleus and a particular electron reduce the attractive force of the nucleus for that electron. The outer electron is said to be *shielded* or *screened* by the inner electrons. If we look at a potassium atom, we can see that there are three full shells of electrons between the outermost electron and the nucleus which shield the outer electron from the full attractive force of the nucleus. The charge on the nucleus of a potassium atom is 19+, but because of the shielding by inner electrons the nuclear charge experienced by the outermost electron is effectively lower. If the **shielding** by the inner shells were perfect, the **effective nuclear charge** felt by the outer electron would be 1+ (19+ in the nucleus but 18 shielding electrons cancel out 18+). This shielding is not perfect, however, and the effective nuclear charge felt by the outermost electron is higher than 1+.

An alternative view of shielding is that the outer electron is attracted by the nucleus but repelled by the inner electrons.

Removing the remaining electrons from a potassium atom

Once the first electron has been removed from a potassium atom, the next electron is considerably more difficult to remove (there is a large jump between first and second ionisation energies). This is consistent with the electron being removed from a new main energy level (shell). This electron is closer to the nucleus and, therefore, more strongly attracted (Figure 3.34). It is also shielded by fewer electrons (the ten electrons in the inner main energy levels highlighted in blue), because electrons in the same shell do not shield each other very well (they do not get between the electron and the nucleus).

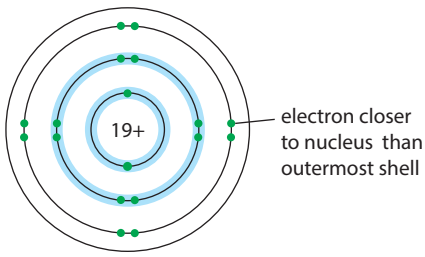

Figure 3.34: An electron in the third main energy level (shell) requires more energy to remove than one in the fourth (outermost) main energy level.

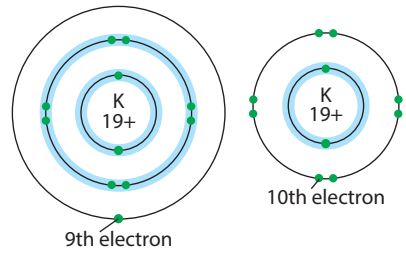

Figure 3.35: The tenth electron is substantially harder to remove because it is in a different main energy level, closer to the nucleus.

The ionisation energy now rises steadily as the electrons are removed successively from the same main energy level. There is no significant change in shielding, but, as the positive charge on the ion increases, it becomes more difficult to remove a negatively charged electron (less electron–electron repulsion, so the electrons are pulled in closer to the nucleus).

There is another large jump in ionisation energies between the ninth and tenth electrons (Figure 3.35) because the ninth electron is the last to be removed from the third main energy level, but the tenth is the first to be removed from the second level. The tenth electron is significantly closer to the nucleus and is less shielded than the ninth electron.

EXAM TIP

Many students use the term effective nuclear charge incorrectly and get it mixed up with 'nuclear charge'. It is, therefore, usually better to avoid mentioning *effective* nuclear charge in the exam and just talk about nuclear charge and shielding.

Graphs of successive ionisation energies

Graphs of successive ionisation energy give us information about how many electrons are in a particular energy level. Consider the graphs for silicon and phosphorus shown in Figure 3.36.

For silicon, there is a large jump in the ionisation energy between the fourth and fifth ionisation energies. The first four electrons are removed from the outermost shell (third main energy level), but the fifth electron is removed from the second main energy level (shell) – the electrons in the second main energy level are closer to the nucleus and less shielded so they are significantly more strongly attracted

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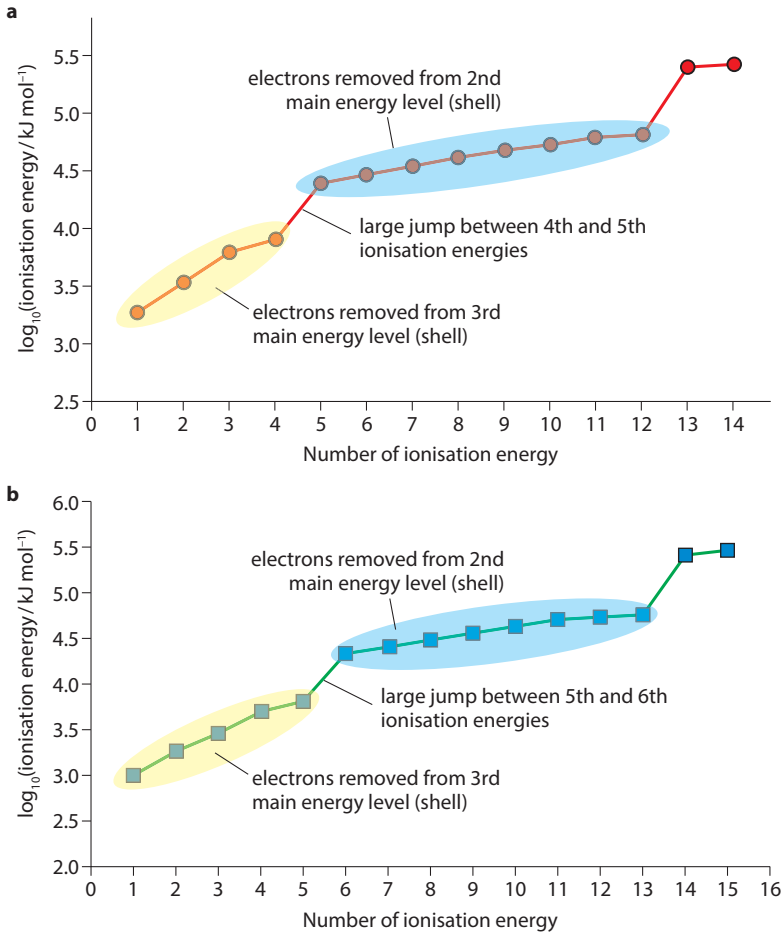

Figure 3.36: a The successive ionisation energies of silicon. **b** The successive ionisation energies of phosphorus.

to the nucleus and require significantly more energy to remove. It can, therefore, be deduced that silicon has four electrons in its highest main energy level (outer shell) and is in Group 14 of the periodic table. For phosphorus, it can be seen that the large jump comes after the fifth electron is removed, so it must have five electrons in its outer shell (highest main energy level) and be in Group 15. The connection between group number and the number of electrons in the outer shell of an atom is shown in Table 3.9.

Group number	1	2	13	14	15	16	17	18
Electrons in outer shell	1	2	3	4	5	6	7	8

Table 3.9: The number of electrons in the highest main energy level in the s and p blocks of the periodic table.

If a graph of ionisation energy (rather than $\log_{10}$ ionisation energy) is plotted for the removal of the first few electrons from a silicon atom, more features can be seen (Figure 3.37).

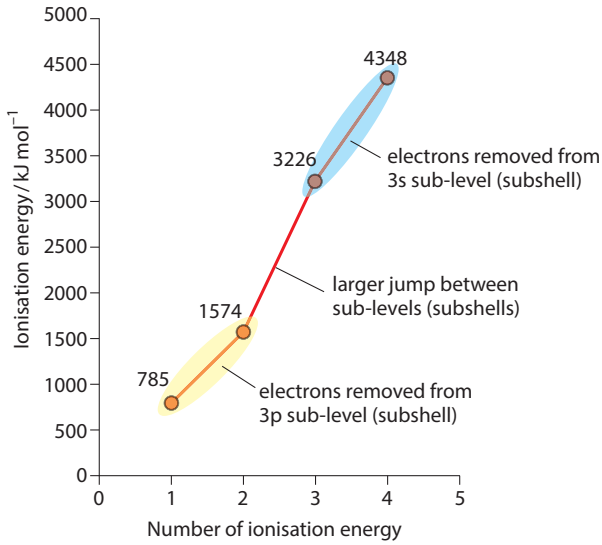

Figure 3.37: The first four ionisation energies of silicon.

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For example, there is a larger jump in the ionisation energy between the second and third ionisation energies.

The full electron configuration of silicon is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$. The first two electrons are removed from the 3p sub-level (subshell), whereas the third electron is removed from the 3s sub-level. The 3p sub-level is higher in energy than the 3s sub-level and, therefore, less energy is required to remove the electron (Figure 3.38).

This provides evidence for the existence of sub-energy levels (subshells) in an atom.

Another way of thinking about why it takes less energy to remove a 3p electron than a 3s electron is that the 3p electrons are shielded, to a certain extent, by the 3s electrons, which means the electrons in the 3p sub-level are not attracted as strongly by the nucleus and are, therefore, relatively easier to remove.

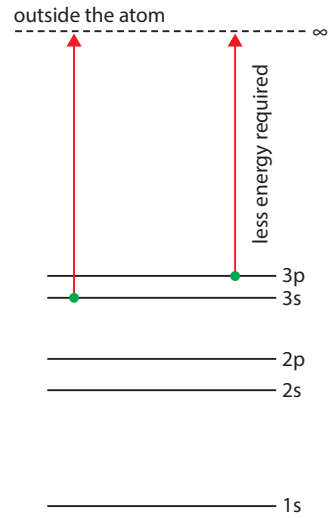

Figure 3.38: More energy is required to remove an electron from the 3s sub-level of silicon than from the 3p sub-level.

TEST YOUR UNDERSTANDING

12 **a** Write an equation for each of the following processes:

- **i** the first ionisation energy of calcium
- **ii** the second ionisation energy of chlorine
- **iii** the tenth ionisation energy of iron
- **iv** the 29th ionisation energy of copper.

b Which of the processes in question **10a** will require the most energy?

13 The table shows the successive ionisation of some elements. Deduce which group in the periodic table each element is in.

	Ionisation energy / kJ mol^{-1}		
Number of ionisation energy	Element X	Element Z	Element Q
1	1085	736	1400
2	2349	1448	2851
3	4612	7719	4570
4	6212	10 522	7462
5	37 765	13 606	9429
6	47 195	17 964	53 174

14 The 9th to 12th ionisation energies of two successive elements in the periodic table are shown in the table. Suggest possible identities for the elements.

Element	Ionisation energy / kJ mol^{-1}			
	9th	**10th**	**11th**	**12th**
A	32 000	35 000	170 000	190 000
T	32 000	38 000	43 000	200 000

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
describe the emission spectrum of hydrogen	3.2			
explain how the lines in the emission spectrum of hydrogen arise	3.2			
describe the relationship between wavelength, frequency, energy and colour in the electromagnetic spectrum	3.1			
write full and condensed electron configurations for atoms and ions up to $Z = 36$	3.3			
explain the term orbital and draw diagrams of s and p orbitals	3.3			
draw orbital diagrams for atoms and ions up to $Z = 36$	3.4			
understand that the ionisation energy for hydrogen can be deduced from the emission spectrum	3.5			
calculate the first ionisation energy from the wavelength or frequency of the convergence limit	3.5			
explain successive ionisation energy data and deduce from it the group an atom is in	3.5			

REFLECTION

What is the most difficult part of this topic? To what extent do you feel that you are able to do the questions but are unsure about the underlying theory? Try to explain to another student how the hydrogen emission spectrum arises. Does your attempt at an explanation highlight any gaps in your knowledge?

Do you think that you would be able to draw a graph of how second ionisation energy varies down a group or across a period?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 4

Counting particles by mass: The mole

LEARNING OBJECTIVES

In this chapter you will:

- understand the terms relative atomic mass and relative formula mass
- understand what a mole is
- calculate molar masses
- calculate amounts of a substance in mol from masses and vice versa
- carry out calculations involving amounts of a substance in mol, masses and number of particles
- understand what empirical and molecular formulas are
- deduce empirical and molecular formulas from experimental data
- understand what is meant by the concentration of a solution
- carry out calculations involving concentrations in mol dm^{-3} and g dm^{-3}
- understand Avogadro's law
- solve problems involving gases using Avogadro's law.

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GUIDING QUESTIONS

- How do we work out the numbers of particles in a sample of a substance?
- How do we work out the formula of a compound from experimental data?
- How do we work out concentrations of solutions?
- In what ratio do gases react together?

Introduction

You have been saving coins all year to buy a present for your chemistry teacher. Is it possible to find out how much money you have without counting each and every coin? If you do not have a specialist coin sorting/counting machine but are in a chemistry laboratory, what is the fastest way of doing this?

The first thing you are going to have to do is sort the coins into different denominations and weigh them. The mass of a £1 (GBP) coin is 8.75 g. If you weigh all the £1 coins and the total mass is 708.75 g, how many £1 coins do you have?

Twenty 5 pence coins have a total mass of 65 g and a value of £1. If the total mass of the 5 pence coins you have saved is 910 g, how many 5 pence coins do you have and what is the value in £?

What does this have to do with chemistry? It is actually the basis of the mole concept, which provides the connection between the mass of a substance you have and how many particles there are. If you can do the calculations with £1 and 5 pence coins, you have the mathematical skills to cope with all the calculations in this chapter.

4.1 Relative masses

The masses of individual atoms, ions or molecules are very small and not convenient to use in everyday life. For example, the mass of a hydrogen atom is approximately 1.67×10^{-24} g and that of an oxygen atom is 2.66×10^{-23} g. Looking at these masses, it is not immediately obvious that the mass of an oxygen atom is about 16 times the mass of a hydrogen atom. For this reason, chemists use a scale of relative masses in which the masses of atoms, molecules, etc. are compared to the mass of one atom of carbon-12, which is assigned a mass of exactly 12.00. On this scale, the mass of a hydrogen atom is 1.01 and that of an oxygen atom is 16.00, so we can immediately see the relationship between them. Because these masses are *relative*, they have no units.

Relative atomic mass (A_r)

KEY POINT

The relative atomic mass (A_r) of an element is the average mass of the naturally occurring isotopes of the element relative to the mass of 1/12 of an atom of carbon-12.

For example, the **relative atomic mass (A_r)** of silver is 107.87. A naturally occurring sample of silver contains the isotopes ^{107}Ag and ^{109}Ag. The 107 isotope is slightly more abundant than the 109 isotope. Taking into account the amount of each isotope present in a sample (the weighted mean), it is found that, on average, the mass of a silver atom is 107.87 times the mass of 1/12 of a carbon-12 atom. No silver atoms actually exist with a mass of 107.87; this is just the *average* relative mass of a silver atom.

Link

How to calculate relative atomic masses is explained in Chapter 2.

Although relative masses are defined in terms of carbon, sometimes it is easier to think of everything relative to hydrogen, the lightest atom. One-twelfth of a carbon-12 atom has a mass of 1, which is basically the same as the mass of a hydrogen atom (actually 1.008 on this scale). A silver atom is thus approximately 108 times as heavy as a hydrogen atom.

Relative molecular mass (M_r)

A **relative molecular mass (M_r)** is the sum of the relative atomic masses of the individual atoms making up a molecule. The relative molecular mass of methane (CH_4) is:

$12.01(A_r \text{ of C}) + 4 \times 1.01(A_r \text{ of H}) = 16.05.$

So, a methane molecule is roughly 16 times as heavy as a hydrogen atom.

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KEY POINT

The relative molecular mass (M_r) of a compound is the mass of a molecule of that compound relative to the mass of $\frac{1}{12}$ of an atom of carbon-12.

Note: A_r of carbon is not 12.00 because carbon contains isotopes other than carbon-12 (see Chapter 2, section 2.2).

The relative molecular mass of ethanoic acid (CH_3COOH) is

$12.01 + (3 \times 1.01) + 12.01 + (2 \times 16.00) + 1.01 = 60.06$

Relative formula mass (M_r)

If a compound is made up of ions and, therefore, does not contain discrete molecules, we should not really talk about a *molecular* mass and should, instead, use the more general term: **relative formula mass**.

KEY POINT

The relative formula mass is the mass of one formula unit relative to the mass of $\frac{1}{12}$ of an atom of carbon-12.

Relative formula mass is worked out in exactly the same way as the relative molecular mass, by adding up the relative atomic masses of the atoms/ions present in a formula unit. Relative formula mass is the more general term and can be used for all compounds, irrespective of the type of bonding and whether they contain molecules or not. However, the term relative molecular mass is still used more widely in everyday speech.

WORKED EXAMPLE 4.1

Calculate the relative formula mass of magnesium nitrate, $Mg(NO_3)_2$.

Answer

We must be careful with the brackets here – the two after the bracket multiplies everything inside the brackets by two, so we have one Mg, two N and six O.

The relative formula mass is, therefore,
$(1 \times 24.31) + (2 \times 14.01) + (6 \times 16.00) = 148.33$

EXAM TIP

You will be supplied with relative atomic masses to two decimal places in the exam, and you must use these values in your calculations.

TEST YOUR UNDERSTANDING

1 Work out the relative formula masses of the following compounds:

SO_2, NH_3, C_2H_5OH, $MgCl_2$, $Ca(NO_3)_2$, $CH_3(CH_2)_5CH_3$, PCl_5, $Mg_3(PO_4)_2$, $Na_2S_2O_3$, $CH_3CH_2CH_2COOCH_2CH_3$.

4.2 Moles

The mass of one ^{12}C atom is approximately 12 times the mass of 1 H atom, so if we had 10 C atoms, the total mass of these would be 12 times the mass of 10 H atoms, because each individual C atom is 12 times the mass of an H atom; if we had 20 C atoms… (Figure 4.1).

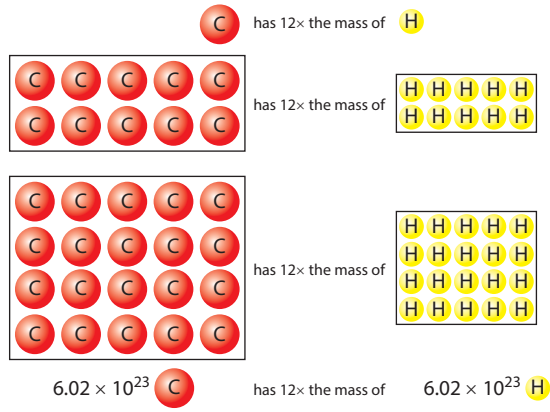

Figure 4.1: The mass of a certain number of C atoms is always 12 times the mass of the same number of H atoms.

If we have 12.0 g of ^{12}C, this contains a certain number of C atoms. The mass of a ^{12}C atom is 1.993×10^{-23} g; therefore, the number of C atoms in 12.0 g of carbon-12 is

$$\frac{12.0}{1.993 \times 10^{-23}} = 6.02 \times 10^{23} \text{ atoms}$$

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Because the mass of 6.02×10^{23} C atoms is 12 g, the mass of 6.02×10^{23} H must be 1 g, because the mass of each individual C atom is 12 times the mass of each H atom.

The mass of a hydrogen atom is 1.67×10^{-24} g, so we can check the mass of 6.02×10^{23} H atoms:

$6.02 \times 10^{23} \times 1.67 \times 10^{-24} = 1.01$ g

It does not come out to exactly 1.00 because the mass of an H atom is actually 1.01 times the mass of $\frac{1}{12}$ of a ^{12}C atom.

The A_r of oxygen is 16.00, which means that, on average, each oxygen atom is $\frac{16.00}{12.00}$ times as heavy as a carbon-12 atom:

$$\frac{O\ 16.00}{C\ 12.00} = 1.333$$

Therefore, the mass of 6.02×10^{23} O atoms must be 1.333 times the mass of 6.02×10^{23} C atoms:

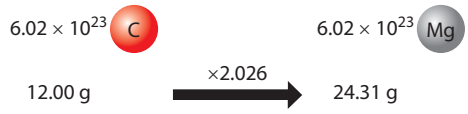
We can check this: the mass of an O atom is 2.658×10^{-23} g, so the number of O atoms in 16.00 g is

$16.00 \div 2.658 \times 10^{-23} = 6.02 \times 10^{23}$

Similarly, one magnesium atom ($A_r = 24.31$) is, on average, $\frac{24.31}{12.00}$ times as heavy as a carbon-12 atom:

$$\frac{Mg\ 24.31}{C\ 12.00} = 2.026$$

Therefore, the mass of 6.02×10^{23} Mg atoms must be 2.026 times the mass of 6.02×10^{23} C atoms:



We could repeat this process for all the atoms in the periodic table, but it will always come out the same: the relative atomic mass, in grams of an element, contains 6.02×10^{23} atoms of that element.

This number of particles (the number of carbon atoms in 12 g of ^{12}C), therefore gives us convenient masses to work with and is called the **Avogadro number**.

We can define a quantity called the **mole** in terms of the Avogadro number:

KEY POINT

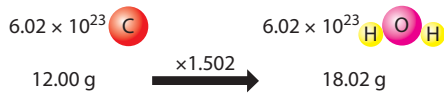
The mole is the unit of the amount of substance. One mole (1 mol) contains the Avogadro number of particles (atoms, ions, molecules, etc.).

So, we can see that 16.00 g of oxygen atoms is 1 mole since it contains 6.02×10^{23} oxygen atoms and that 24.31 g of magnesium atoms is 1 mole because it contains 6.02×10^{23} magnesium atoms.

The relative molecular mass of water (H_2O) is 18.02, which means that a water molecule is about one and a half times $\left(\frac{18.02}{12.00}\right)$ the mass of a ^{12}C atom:

$$\frac{H\ O\ H\ 18.02}{C\ 12.00} = 1.502$$

The mass of 6.02×10^{23} water *molecules* is 1.502 times the mass of 6.02×10^{23} C atoms:



Therefore, 18.02 g (the relative molecular mass in g) is 1 mole of water *molecules*.

We can see from this discussion that, to work out the amount of substance that is 1 mol, we just need the relative atomic mass in g for atoms or the relative formula mass in g for everything else.

KEY POINT

The molar mass (M) of a substance is the mass that contains 1 mol of particles (atoms, molecules, ions) and is its A_r or M_r in g.
The units of molar mass are g mol^{-1}.

Amount of substance

The amount of substance (symbol n) is how much of the specified entities (atoms, molecules, ions, etc.) of a substance we have in moles, so we can talk about 2 mol

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magnesium atoms, 0.4 mol water molecules or 0.1 mol Na^+ ions.

Although it is more correct to refer to the *amount of substance*, people often talk about the *number of moles* – this is like saying that we can talk about the mass or the number of grams.

The amount in moles of a certain mass of substance can be worked out using the following equation:

$$\text{amount of substance } (n) = \frac{\text{mass } (m)}{\text{molar mass } (M)}$$

The **molar mass** is the mass of 1 mol, and so we are essentially seeing how many times this goes into a given mass to calculate the number of moles. So, if the mass of 1 mol of a substance is 50 g and we have 500 g of it, we must have $500 \div 50 = 10$ mol.

EXAM TIP

The equation $n = \frac{m}{M}$ is given in the IB data booklet.

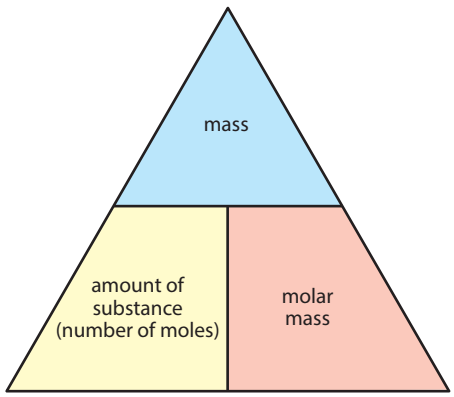

Figure 4.2: The relationship between the mass of a substance, the amount in mol and the molar mass.

The triangle in Figure 4.2 is a useful shortcut for working out all the quantities involved in the equation. If any one of the sections of the triangle is covered up, the relationship between the other two quantities to give the covered quantity is revealed. For example, if 'mass' is covered, we are left with amount of substance (number of moles) multiplied by molar mass:

$$\text{mass} = \text{amount of substance (mol)} \times \text{molar mass}$$

If 'molar mass' is covered, we are left with mass divided by amount of substance (number of moles):

$$\text{molar mass} = \frac{\text{mass}}{\text{amount of substance (mol)}}$$

EXAM TIP

When you encounter the word 'amount' with no further explanation in an exam, assume that it means the amount of substance in mol.

THEORY OF KNOWLEDGE

The Avogadro number is an enormous number and beyond the scope of our normal experience. How do we understand a number this large?

One way is to describe the number in terms of things we are familiar with from everyday life. For instance, the Avogadro number of ping-pong balls would cover the surface of the Earth to about 800 times the height of Mount Everest! Assuming we know what a ping-pong ball looks like and that we have a rough idea of the height of Mount Everest, perhaps this description gives us a context in which we can understand 6.02×10^{23}. Another description sometimes used is in terms of the Avogadro number of sheets of computer printer paper: the Avogadro number of these paper sheets, if stacked one on top of each other, would stretch over 6000 light years (one light year is the distance that light travels in one year) – this is over twice the thickness of our galaxy! Is this description better or worse than the previous one? It certainly sounds more impressive, but does it suffer from the fact that we have no real concept of the size of our galaxy? Can you think of any other ways of describing this number in terms of things you are familiar with from everyday life? This is an example of a wider idea that we tend to understand quantities that are beyond our normal experience by reference to things with which we are more familiar.

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WORKED EXAMPLE 4.2

Calculate the amount in mol of 10.0 g of magnesium.

Answer

$$\text{amount of substance } (n) = \frac{\text{mass } (m)}{\text{molar mass } (M)}$$

$$n = \frac{10.0}{24.31} = 0.411 \text{ mol}$$

10.0 g of magnesium is equivalent to 0.411 mol. Magnesium is an element, and so, what we are talking about here is 0.411 mol of Mg atoms.

The answer is given to three significant figures, because the mass of substance is given to three significant figures.

Note: the unit for moles is mol without the 'e'. Never put an 's' on a unit because 's' means seconds.

EXAM TIP

The answer to a calculation should be stated to the same number of significant figures as the least precise (fewest significant figures) piece of data in the question.

EXAM TIP

When calculating the amount of substance in mol, the mass of the substance must be in grams.

WORKED EXAMPLE 4.3

A student weighs out 9.00 kg of water. Calculate the amount of substance.

Answer

molar mass of water = $(2 \times 1.01) + 16.00 = 18.02 \text{ g mol}^{-1}$

The mass of water must be converted into g because the molar mass is in g mol^{-1}: $9.00 \times 1000 = 9000$ g

$$\text{amount of substance} = \frac{\text{mass}}{\text{molar mass}} = \frac{9000}{18.02} = 499 \text{ mol}$$

Here, we are talking about a compound; therefore, 9.00 kg of water is 499 mol of H_2O *molecules*.

WORKED EXAMPLE 4.4

Calculate the mass of 0.3800 mol of CH_3COOH.

Answer

mass = amount of substance × molar mass

molar mass of $CH_3COOH = 12.01 + (3 \times 1.01) + 12.01 + (2 \times 16.00) + 1.01 = 60.06 \text{ g mol}^{-1}$.

mass = $0.3800 \times 60.06 = 22.82$ g

The mass of 0.3800 mol of CH_3COOH is 22.82 g.

The answer is given to four significant figures because the amount of substance and the molar mass are given to four significant figures.

EXAM TIP

Be careful with gases…

With the exception of the noble gases (He, Ne, Ar, Kr, Xe, Rn), elements that are gases at room temperature and pressure exist as diatomic molecules, with the formula X_2, e.g., H_2, O_2, N_2, and Cl_2. You must remember this when working out the amount of substance or the mass. Other diatomic molecules you will come across, which are not gases, are Br_2 and I_2.

WORKED EXAMPLE 4.5

A student measures out 0.32 g of oxygen gas. Calculate the amount of substance.

Answer

Oxygen gas contains O_2 molecules, so the molar mass of oxygen is $2 \times 16.00 = 32.00 \text{ g mol}^{-1}$

$$\text{amount of substance} = \frac{\text{mass}}{\text{molar mass}} = \frac{0.32}{32.00} = 0.010 \text{ mol}$$

So, 0.32 g is 0.010 mol of O_2 molecules.

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WORKED EXAMPLE 4.6

Calculate the mass of 0.200 mol of nitrogen gas.

Answer

Nitrogen gas has the formula N_2 and, therefore, the molar mass is $2 \times 14.01 = 28.02$ g mol^{-1}

mass = amount of substance × molar mass = $0.200 \times 28.02 = 5.60$ g

TEST YOUR UNDERSTANDING

2 Copy and complete the table. The first row has been done for you.

Compound	Molar mass / g mol^{-1}	Mass / g	Amount of substance / mol
H_2O	18.02	9.01	0.500
CO_2		5.00	
H_2S			0.100
NH_3			3.50
Q		1.00	0.0350
Z		0.0578	1.12×10^{-3}
$Mg(NO_3)_2$		1.75	
C_3H_7OH		2500	
Fe_2O_3			5.68×10^{-5}
nitrogen gas		10.00	
chlorine gas			5.000×10^{-3}

3 Calculate the amount (in mol) of 10.0 g of each of the following:

a $CuCl_2$ **b** C_2H_4

c S **d** O_3

e $C_6H_5NO_2$.

4 Calculate the mass in g of each of the following:

a 0.155 mol $Ca(OH)_2$

b 1.78×10^{-3} mol Al_2O_3

c 2.50 mol NH_4NO_3

d 400 mol helium

e 0.245 mol hydrogen gas.

5 Calculate the amount (in mol) of each of the following:

a 10.0 kg CH_4

b 25.0 kg NaCl

c 10.0 t CO_2

d 50.0 t $CaCO_3$

e 1.20 kg $Na_2S_2O_3$.

1 t = 1 tonne

1 tonne is equivalent to 1000 kg

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4.3 The mass of a molecule

The mass of one mole of water is 18.02 g. This contains 6.02×10^{23} molecules of water. The mass of one molecule of water can be worked out by dividing the mass of one mole (18.02 g) by the number of molecules it contains (6.02×10^{23}):

$$\text{mass of one molecule} = \frac{18.02}{6.02 \times 10^{23}} = 2.99 \times 10^{-23} \text{ g}$$

EXAM TIP

Remember, the mass of a molecule is a very small number. Do not confuse the mass of a single molecule with the mass of one mole of a substance, which is a number greater than one.

The number of particles

We know that 1 mol of a substance contains the Avogadro number of particles, so 2 mol would contain $2 \times 6.02 \times 10^{23}$ particles and 10 mol would contain $10 \times 6.02 \times 10^{23}$ particles. Therefore, we can write the equation as follows:

$$N = N_A \times n$$

where N is the number of particles, N_A is the **Avogadro constant** and n is the amount of substance (number of moles).

The relationship is summarised in the triangle in Figure 4.3.

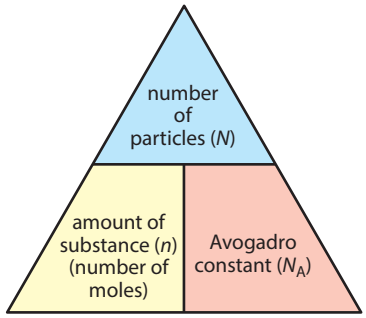

Figure 4.3: The relationship between the amount of substance and the number of particles.

The Avogadro constant has the same numerical value as the Avogadro number, but it has units of mol^{-1} (per mol), whereas the Avogadro number is a pure number and has no units. The units are required because the amount of substance has units of mol, but the number of particles has no units.

KEY POINT

The Avogadro constant has symbol N_A (or L) and has the value 6.02×10^{23} mol^{-1}.

WORKED EXAMPLE 4.7

Calculate the number of sulfur atoms in 10.0 g of sulfur.

Answer

We first need to work out the amount of substance, n, in mol:

$$n = \frac{\text{mass}}{\text{molar mass}} = \frac{10.0}{32.07} = 0.312 \text{ mol}$$

$$N = N_A \times n = 6.02 \times 10^{23} \times 0.312 = 1.88 \times 10^{23}$$

Therefore, 10.0 g of sulfur contains 1.88×10^{23} atoms.

WORKED EXAMPLE 4.8

Calculate the mass of a sample of copper that contains 4.00×10^{22} atoms.

Answer

If we work out the amount of substance, this can be converted into a mass:

$$n = \frac{N}{N_A} = \frac{4.00 \times 10^{22}}{6.02 \times 10^{23}} = 0.0664 \text{ mol}$$

$$\text{mass} = n \times \text{molar mass} = 0.0664 \times 63.55 = 4.22 \text{ g}$$

When we write '1 mol O_2', it means one mole of O_2 molecules, that is, 6.02×10^{23} O_2 molecules. Each O_2 molecule contains two oxygen atoms, so four oxygen molecules contain $2 \times 4 = 8$ atoms (Figure 4.4) and one mole of O_2 molecules contains $2 \times 6.02 \times 10^{23} = 1.204 \times 10^{24}$ atoms. In other words, one mole of O_2 *molecules* is made up of two moles of oxygen *atoms*.

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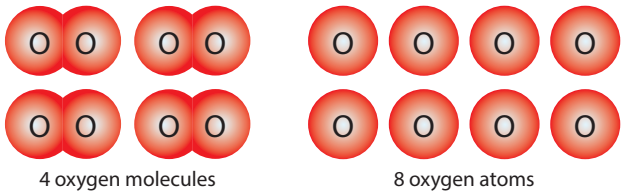

Figure 4.4: Each oxygen molecule is made up of two oxygen atoms, so the number of oxygen atoms in four O_2 molecules is $4 \times 2 = 8$.

When we talk about '0.1 mol H_2O', we mean 0.1 mol of H_2O molecules, that is, $0.1 \times 6.02 \times 10^{23} = 6.02 \times 10^{22}$ H_2O molecules.

Each H_2O molecule contains two hydrogen atoms and one oxygen atom. So, if we have four water molecules, the total number of H atoms is $4 \times 2 = 8$ (Figure 4.5). The total number of hydrogen atoms in 0.1 mol H_2O is, therefore, $6.02 \times 10^{22} \times 2 = 1.204 \times 10^{23}$ hydrogen atoms. This is 0.2 mol hydrogen atoms.

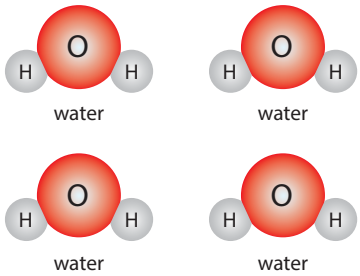

Figure 4.5: Four water molecules contain eight hydrogen atoms.

In general, if we multiply the number of moles of molecules by the number of a particular type of atom in a molecule (i.e. by the subscript of the atom), we get the number of moles of that type of atom. Thus, in 0.25 mol of H_2SO_4, there are $4 \times 0.25 = 1.0$ mol of oxygen atoms.

If we multiply the total number of atoms in a molecule by the number of moles of molecules, we get the total number of atoms.

Each H_2SO_4 molecule contains seven atoms. The total number of atoms in four molecules of H_2SO_4 is $4 \times 7 = 28$ atoms (Figure 4.6).

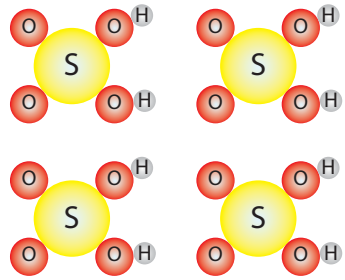

Figure 4.6: In four H_2SO_4 molecules, there are $4 \times 4 = 16$ O atoms and a total of $4 \times 7 = 28$ atoms.

The number of moles of atoms in 0.40 mol of H_2SO_4 is $0.40 \times 7 = 2.8$ mol or $2.8 \times 6.02 \times 10^{23} = 1.7 \times 10^{24}$ atoms.

If you look at Table 4.1, you can see the connection between the number of moles of molecules and the total number of atoms.

EXAM TIP

You must be clear which type of particle (elementary entity) you are considering. Do you have one mole of atoms, molecules or ions?

Molecule	Amount / mol	Total number of atoms
H_2O	1	$3 \times 1 \times 6.02 \times 10^{23} = 1.81 \times 10^{24}$
SO_2	0.1	$3 \times 0.1 \times 6.02 \times 10^{23} = 1.81 \times 10^{23}$
SO_3	0.1	$4 \times 0.1 \times 6.02 \times 10^{23} = 2.41 \times 10^{23}$
H_3PO_4	0.1	$8 \times 0.1 \times 6.02 \times 10^{23} = 4.82 \times 10^{23}$

Table 4.1: The relationship between the amount of substance and the number of atoms.

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TEST YOUR UNDERSTANDING

6 Calculate the mass of one molecule of each of the following:

- **a** H_2O
- **b** NH_3
- **c** CO_2.

7 Calculate the average mass of one atom of each of the following:

- **a** H
- **b** Cu
- **c** Ne.

8 Calculate the number of atoms in each of the following:

- **a** 0.100 mol of silicon
- **b** 2.00×10^{-3} mol rubidium
- **c** 0.280 mol manganese.

9 Calculate the number of atoms in 1.00 g of each of the following:

- **a** argon
- **b** zinc
- **c** gold.

10 Calculate the number of molecules in 10.00 g of each of the following:

- **a** water (H_2O)
- **b** oxygen (O_2)
- **c** carbon dioxide (CO_2).

11 Calculate the total number of atoms in each of the following:

- **a** 0.0100 mol NH_3
- **b** 0.200 mol C_2H_6
- **c** 0.0400 mol C_2H_5OH.

12 Calculate the number of moles of oxygen atoms in each of the following:

- **a** 0.2 mol H_2SO_4
- **b** 0.1 mol Cl_2O_7
- **c** 0.03 mol XeO_4.

13 Work out the total number of hydrogen atoms in each of the following:

- **a** 1.00 mol H_2
- **b** 0.200 mol CH_4
- **c** 0.0500 mol NH_3.

4.4 Empirical and molecular formulas

Percentage composition of a compound

The percentage by mass of each element present in a compound can be worked out using the following formula:

$$\%\text{ by mass of an element} = \frac{\text{number of atoms of the element} \times A_r}{M_r} \times 100$$

WORKED EXAMPLE 4.9

Find the percentage by mass of carbon and hydrogen present in $C_6H_5NO_2$.

Answer

The relative molecular mass of $C_6H_5NO_2$ is 123.12.

Percentage of carbon: the relative atomic mass of carbon is 12.01, and there are six carbon atoms present, so the total mass of carbon atoms is 6×12.01, i.e., 72.06.

$$\%\text{ carbon} = \frac{72.06}{123.12} \times 100 = 58.53\%$$

There are five hydrogen atoms present, so:

$$\%\text{ hydrogen} = \frac{5 \times 1.01}{123.12} \times 100 = 4.10\%$$

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WORKED EXAMPLE 4.10

Calculate the mass of oxygen present in 2.20 g of CO_2.

Answer

The relative molecular mass of CO_2 is 44.01. Of this, the mass contributed by the two oxygen atoms is $2 \times 16.00 = 32.00$

So, the fraction of the mass of this compound that is contributed by oxygen is $\frac{32.00}{44.01}$.

Therefore, in 2.20 g of CO_2, the mass of oxygen is $\frac{32.00}{44.01} \times 2.20 = 1.60$ g.

WORKED EXAMPLE 4.11

What mass of HNO_3 contains 2.00 g of oxygen?

Answer

The relative molecular mass of HNO_3 is 63.02. Each molecule contains three oxygen atoms with a total mass of 3×16.00, i.e., 48.00.

The masses of oxygen and HNO_3 are, therefore, in the ratio 48.00 : 63.02.

So the mass of HNO_3 containing 2.00 g of oxygen is $\frac{63.02}{48.00} \times 2.00 = 2.63$ g

Alternative method

The percentage of oxygen in HNO_3 is $\frac{3 \times 16.00}{63.02} \times 100 = 76.2\%$

So 76.2% of this sample is oxygen and has a mass of 2.00 g. We need, therefore, to find the mass of 100%, which is given by

$\frac{2.00}{76.2} \times 100 = 2.63$ g

Note: to obtain this answer, more figures were carried through on the calculator.

TEST YOUR UNDERSTANDING

14 Calculate the percentage by mass of oxygen in each of the following compounds:

- **a** C_2H_5OH
- **b** CH_3CH_2COOH
- **c** Cl_2O_7.

15 Calculate the percentage by mass of each element present in the following:

- **a** NaCl
- **b** KIO_3
- **c** $C_6H_3(NO_2)_3$.

16 Calculate the mass of oxygen in each of the following samples:

- **a** 6.00 g of C_3H_7OH
- **b** 5.00 g of SO_2
- **c** 10.0 g of P_4O_{10}.

17 For each of the following compounds, work out the mass of substance that will contain 1.00 g of oxygen:

- **a** CH_3OH
- **b** SO_3
- **c** P_4O_6.

Defining empirical and molecular formulas

KEY POINTS

The **empirical formula** is the simplest whole number ratio of the elements present in a compound.

The **molecular formula** is the total number of atoms of each element present in a molecule of the compound.

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A **molecular formula** is a whole number multiple of the **empirical formula**. Therefore, if the empirical formula of a compound is CH_2, the molecular formula is $(CH_2)_n$, i.e., C_2H_4 or C_3H_6 or C_4H_8, etc. Sometimes an empirical formula and molecular formula can be the same, for example, H_2O, where the molecular formula is also the simplest ratio of atoms present. We can understand a bit more about empirical and molecular formulas by looking at some worked examples.

WORKED EXAMPLE 4.12

If the molecular formulas of two compounds are

a $C_4H_{10}O_2$ **b** Re_3Cl_9

what are the empirical formulas?

Answer

We need to find the simplest ratio of the elements present and, therefore, the largest number that divides exactly into the subscript of each element.

a In this case, each subscript can be divided by two, and so the empirical formula is C_2H_5O.

b In this case, each subscript is divisible by three, and so the empirical formula is $ReCl_3$.

WORKED EXAMPLE 4.13

The empirical formula of benzene is CH. Given that the molar mass is 78.12 g mol^{-1}, work out its molecular formula.

Answer

The mass of the empirical formula unit (CH) is 12.01 + 1.01 = 13.02

The number of times that the empirical formula unit occurs in the actual molecule (n) is given by

$$n = \frac{\text{relative molecular mass}}{\text{empirical formula mass}} = \frac{78.12}{13.02} = 6$$

Therefore, the molecular formula is $(CH)_6$, which is more commonly written as C_6H_6.

Working out empirical and molecular formulas using information about substance composition

If we could analyse the composition of an unknown substance by counting the number of atoms present in it, then we would be able to work out the empirical formula from the ratio between the different types of atoms. For instance, if there are three times as many H atoms as C atoms in a sample of a compound, then the empirical formula is CH_3.

Chemical analysis of a substance can provide the composition by mass of the compound. If we know the mass of each element present in a sample, then we can work out the amount in mol (number of moles) of each element. The amount is proportional to the number of each atom present; therefore, we can use the amounts to find the formula. So, if we find that a compound contains 0.10 mol of C and 0.20 mol of H, we know that there are twice as many H atoms present as C atoms and, therefore, the empirical formula must be CH_2.

If we find that another compound contains 0.40 mol of H, 0.20 mol of S and 0.80 mol of O, then we can see that there are twice as many H atoms as S atoms but that the number of O atoms is four times the number of S atoms, and so, the formula is H_2SO_4.

The amounts (numbers of moles) are quite simple here, and it is fairly straightforward to see what the ratio is, but if the numbers are a bit more difficult, then we divide by the smallest amount (number of moles) to find the ratio; this is shown in the worked examples that follow.

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WORKED EXAMPLE 4.14

A compound has the following composition by mass: C, 0.681 g; H, 0.137 g; O, 0.181 g.

a Calculate the empirical formula of the compound.

b If the relative molecular mass of the compound is 88.17, calculate the molecular formula.

Answer

a This is most easily done by laying everything out in a table.

	C	H	O
mass / g	0.681	0.137	0.181
divide by relative atomic mass to give amount in mol	0.681 ÷ 12.01	0.137 ÷ 1.01	0.181 ÷ 16.00
amount / mol	0.0567	0.136	0.0113
divide by the smallest value to get the ratio	0.0567 ÷ 0.0113	0.136 ÷ 0.0113	0.0113 ÷ 0.0113
ratio	5	12	1

Therefore, the empirical formula is $C_5H_{12}O$.

b The empirical formula mass ($5 \times 12.00 + 12 \times 1.01 + 16.00$) is 88.17. This is the same as the relative molecular mass, and so, the molecular formula is the same as the empirical formula, $C_5H_{12}O$.

WORKED EXAMPLE 4.15

If a fluoride of uranium contains 67.62% uranium by mass, what is its empirical formula?

Answer

A uranium fluoride contains only uranium and fluorine; therefore, if we know the percentage of uranium, we can work out the percentage of fluorine:

% fluorine = 100.00 – 67.62 = 32.38%

It makes no difference here that the percentage composition is given instead of the mass of each element present, as the percentage is the same as the mass present in 100 g.

	U	F
percentage	67.62	32.38
mass in 100 g / g	67.62	32.38
divide by relative atomic mass to give amount in mol	67.62 ÷ 238.03	32.38 ÷ 19.00
amount / mol	0.2841	1.704
divide by the smallest value to get the ratio	0.2841 ÷ 0.2841	1.704 ÷ 0.2841
ratio	1	6

There are, therefore, six fluorine atoms for every uranium atom, and the empirical formula is UF_6.

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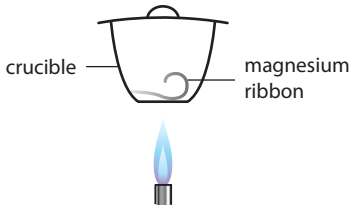
WORKED EXAMPLE 4.16

When magnesium ribbon is heated strongly in air, it burns to form magnesium oxide.
A piece of magnesium ribbon was heated in a crucible and the following measurements made.



Mass of empty crucible / g	27.32
Mass of crucible + magnesium / g	27.47
Mass of crucible + contents at end of experiment / g	27.57

Calculate the empirical formula of the magnesium oxide.

Answer

The mass of the empty crucible is subtracted from the masses in the table:

mass of magnesium at start = 27.47 – 27.32 = 0.15 g

mass of magnesium oxide at end = 27.57 – 27.32 = 0.25 g

The mass increases in this experiment because oxygen in the air combines with magnesium to form magnesium oxide (the lid is lifted periodically to let in more oxygen). The difference in mass between the start and end readings is, therefore, equal to the mass of oxygen that has reacted with magnesium:

mass of oxygen in magnesium oxide = 0.25 – 0.15 = 0.10 g

$$\text{amount of magnesium atoms} = \frac{0.15}{24.31} = 6.17 \times 10^{-3} \text{ mol}$$

$$\text{amount of oxygen atoms} = \frac{0.10}{16.00} = 6.25 \times 10^{-3} \text{ mol}$$

Divide each amount in mol by the smaller number (6.17×10^{-3}):

$$\text{Mg: } \frac{6.17 \times 10^{-3}}{6.17 \times 10^{-3}} = 1 \qquad \text{O: } \frac{6.25 \times 10^{-3}}{6.17 \times 10^{-3}} = 1.01$$

Therefore, the ratio of magnesium to oxygen is 1:1, and the empirical formula is MgO.

EXAM TIP

When working out empirical formulas, numbers such as 1.01 or 0.98 can be rounded to 1 but 1.25, 1.33, 1.5, etc. should not be – these values should be multiplied by appropriate numbers to generate whole numbers.

Heating to constant mass

How can we be sure in the experiment outlined in Worked example 4.16 that all the magnesium has reacted? One way of doing this is to *heat to constant mass*. If you suspect that the reaction has finished, allow the crucible to cool and weigh it, then heat it again for a few more minutes and weigh again. If the mass is the same as before, then you can be fairly confident that all the magnesium has reacted, but, if the mass goes up, the reaction is not complete, and the crucible and contents should be heated and weighed again until the mass remains constant for successive weighings.

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NATURE OF SCIENCE

The values obtained here actually give the formula of magnesium oxide as $Mg_{100}O_{101}$. When you do this sort of question in the exam, you will be expected to round this to 1:1, but, if you actually do this experiment, how do you know to do that? At what point does a scientist decide that they have made a mistake or a discovery? If there is a literature value for a particular quantity, as there is here (the formula of magnesium oxide is accepted as MgO), things are a lot easier, and you would probably just analyse the uncertainties for the experiment and decide that your value agrees with the literature value. But what if you are the first person to do an experiment? You would repeat the experiment to see whether you keep getting the same result, then you would look at sources of error (random and systematic), and the accepted theory – does your result 'make sense'? What if you really cannot find any sources of error, and your result does not agree with the accepted theory, at what point do you decide to publish your findings? This really depends on how brave you are and how much you have to lose or gain! If you want to find out more about the difficulties that scientists face when deciding to publish or not, try an internet search for 'neutrinos faster than light' or 'cold fusion'.

TEST YOUR UNDERSTANDING

18 Which of the following represent empirical formulas?

C_2H_4	CO_2	CH
HO	C_3H_8	C_4H_{10}
H_2O	H_2O_2	N_2H_4
PCl_5	CH_3COOH	$C_6H_5CH_3$

19 Deduce the molecular formula of each of the compounds in the table.

Empirical formula	Relative molecular mass
HO	34.02
ClO_3	166.90
CH_2	84.18
BNH_2	80.52

20 Analysis of a sample of an organic compound produced the following composition:

C: 0.399 g, H: 0.101 g.

a Calculate the empirical formula.

b Given that the relative molecular mass is 30.08, determine the molecular formula.

21 If an oxide of chlorine contains 81.6% chlorine, calculate its empirical formula.

22 A compound contains 76.0% iodine and 24.0% oxygen. Calculate the empirical formula of the compound.

23 Work out the empirical formula of each of the following iron oxides from the percentage iron:

a 77.7% Fe

b 72.4 % Fe.

24 Work out the empirical formulas of the following compounds containing sodium, chromium and oxygen:

	Na / %	Cr / %	O / %
a	28.4	32.1	39.5
b	17.55	39.70	42.75

25 Calculate the empirical formula of each of the following compounds containing C and H only:

Compound	C / %	H / %
A	74.83	25.17
B	79.85	20.15
C	85.60	14.40
D	81.68	18.32
E	83.21	16.79

26 When 5.60 g of an iron oxide is heated with carbon, 3.92 g of iron is produced. Calculate the empirical formula of the iron oxide.

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4.5 Solutions

In this section, we will be looking at solutions. Solutions are homogeneous mixtures formed when a solute is dissolved in a solvent. The solutions we will be dealing with here are all aqueous solutions – the solvent is water – but it is possible to extend everything to solutions made with different solvents.

When a sodium chloride (NaCl) *solution* is prepared, NaCl solid (the *solute*) is dissolved in water (the *solvent*). Solutions in water (aqueous solutions) are given the symbol (aq) in chemical equations. So, we can write sodium chloride solution as NaCl(aq) in a chemical equation.

KEY POINT

The concentration of a solution is defined as the quantity (in mol), or mass, of solute dissolved in a unit volume of solution.

Concentration is defined in terms of the volume of the solution rather than the volume of the solvent. This is because, when a solute is dissolved in a certain volume of water, say 100.0 cm^3, the total volume of the solution is not simply 100.0 cm^3 or the sum of the volumes occupied by the solute and the solvent. The total volume of solution produced depends on the forces of attraction between the solute particles and the solvent particles compared with the forces of attraction in the original solvent.

The volume that is usually taken when quoting concentrations is 1 dm^3. How much solute is dissolved may be expressed in g or mol; therefore, the units of concentration are g dm^{-3} or mol dm^{-3}.

1 dm^3 is equivalent to 1 litre or 1000 cm^3. Figure 4.7 shows how to convert between cm^3 and dm^3.

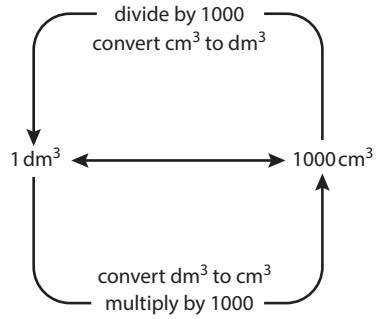

Figure 4.7: Converting between cm^3 and dm^3.

So, for example, to convert 25.0 cm^3 to dm^3, we divide 25.0 by 1000; therefore, 25.0 cm^3 is equivalent to 0.0250 dm^3.

To convert 0.46 dm^3 into cm^3, we multiply by 1000; therefore, 0.46 dm^3 is equivalent to 460 cm^3.

The relationship between concentration, amount of substance in mol and volume of solution is

$$\text{concentration (mol dm}^{-3}) = \frac{\text{amount of substance (mol)}}{\text{volume (dm}^3)}$$

This is summarised in Figure 4.8.

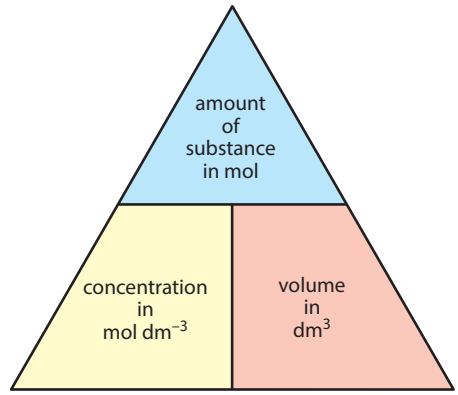

Figure 4.8: The relationship between concentration, amount of substance and volume of solution.

If the concentration is expressed in g dm^{-3}, the relationship is

$$\text{concentration (g dm}^{-3}) = \frac{\text{mass (g)}}{\text{volume (dm}^3)}$$

WORKED EXAMPLE 4.17

If 10.00 g of sodium hydroxide (NaOH) is dissolved in water and the volume made up to 200.0 cm^3, calculate the concentration in g dm^{-3} and mol dm^{-3}.

Answer

$$\text{concentration } (\text{g dm}^{-3}) = \frac{\text{mass (g)}}{\text{volume } (\text{dm}^3)}$$

$$\text{volume in dm}^3 = \frac{200.0}{1000} = 0.2000 \text{ dm}^3$$

$$\text{concentration} = \frac{10.00}{0.2000} = 50.00 \text{ g dm}^{-3}$$

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CONTINUED

Concentration (mol dm^{-3})

molar mass of NaOH = 40.00 g mol^{-1}

$$\text{amount of substance} = \frac{10.00}{40.00} = 0.2500 \text{ mol}$$

$$\text{concentration } (\text{mol dm}^{-3}) = \frac{\text{amount of substance (mol)}}{\text{volume } (\text{dm}^3)}$$

$$\text{concentration} = \frac{0.2500}{0.2000} = 1.250 \text{ mol dm}^{-3}$$

WORKED EXAMPLE 4.18

Calculate the amount in mol of hydrochloric acid (HCl) present in 50.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

Answer

amount (n) = concentration (C) × volume in dm^3 (V)

$$\text{amount} = 2.00 \times \frac{50}{1000} = 0.100 \text{ mol}$$

Therefore, the amount of HCl is 0.100 mol.

EXAM TIP

The equation $n = CV$ is given in the IB data booklet

Converting between concentrations in mol dm^{-3} and concentrations in g dm^{-3}

To convert a concentration in g dm^{-3} into a concentration in mol dm^{-3}, divide the concentration by the molar mass of the substance.

WORKED EXAMPLE 4.19

A sodium chloride solution has a concentration of 15.00 g dm^{-3}. Calculate the concentration in mol dm^{-3}.

Answer

We know that there are 15.00 g of NaCl present in 1 dm^3, and, if we work out how many moles this is, we will have the concentration in mol dm^{-3}. To work out the number of moles, we divide the mass by the molar mass.

The molar mass of NaCl is 58.44 g mol^{-1}:

$$\frac{15.00}{58.44} = 0.2567$$

Therefore the concentration is 0.2567 mol dm^{-3}

To convert a concentration in mol dm^{-3} into a concentration in g dm^{-3}, multiply the concentration by the molar mass of the substance.

WORKED EXAMPLE 4.20

A sodium thiosulfate ($Na_2S_2O_3$) solution has a concentration of 0.0100 mol dm^{-3}. Calculate the concentration in g dm^{-3}.

Answer

The molar mass of $Na_2S_2O_3$ is 158.12 g mol^{-1}.
The mass of 0.0100 mol is 0.0100 × 158.12 = 1.58 g.
Therefore, there is 1.58 g of $Na_2S_2O_3$ present in each dm^3 of solution, and the concentration is 1.58 g dm^{-3}.

Ways of denoting concentrations

Square brackets are often used to denote concentrations in mol dm^{-3}. So, [HCl] indicates the molar concentration of hydrochloric acid, and we could write [HCl] = 2.00 mol dm^{-3} or [NaOH] = 1.250 mol dm^{-3} in the previous worked examples.

Concentrations are sometimes written with the unit M, which means mol dm^{-3} but is described as 'molar'. Thus, 2 M would refer to a '2 molar solution', i.e., a solution with a concentration of 2 mol dm^{-3}. On the IB syllabus, molar mass is also given the symbol M, and so, it is probably best to avoid using M for mol dm^{-3}.

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Working out the concentration of ions

When ionic substances (see Chapter 6) dissolve in water, the substance breaks apart into its constituent ions. So, for instance, when copper(II) chloride ($CuCl_2$) dissolves in water, it splits apart into Cu^{2+} and Cl^- ions:

$$CuCl_2(aq) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$

From this equation, we can see that each $CuCl_2$ unit will produce one Cu^{2+} ion and two Cl^- ions. Therefore, if we started with 0.10 mol of $CuCl_2$, we would have 0.20 mol of Cl^- ions in solution. If we made a solution that was 0.20 mol dm^{-3} $CuCl_2$, the concentration of chloride ions would be $2 \times 0.20 = 0.40$ mol dm^{-3}, and the total concentration of ions would be $3 \times 0.20 = 0.60$ mol dm^{-3}, since each $CuCl_2$ unit produces three ions.

Water of crystallisation

Some substances crystallise with water as an integral part of the structure. Examples are hydrated copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) and hydrated magnesium chloride ($MgCl_2 \cdot 6H_2O$). Water is necessary for the formation of the crystals and is called the **water of crystallisation**.

Substances that contain water of crystallisation are described as *hydrated*, whereas those that have lost their water of crystallisation are described as *anhydrous*. So, we talk about 'hydrated copper(II) sulfate' ($CuSO_4 \cdot 5H_2O$) and 'anhydrous copper(II) sulfate' ($CuSO_4$). Hydrated copper(II) sulfate can be obtained as large blue crystals, but anhydrous copper(II) sulfate is white and powdery.

When working out the molar mass of a hydrated salt, you must include the water of crystallisation in the calculation:

$$\text{molar mass of } CuSO_4 \cdot 5H_2O = 63.55 + 32.07 + 4 \times 16.00 + 5 \times (2 \times 1.01 + 16.00) = 249.72 \text{ g mol}^{-1}$$

EXAM TIP

Remember, the 5 in front of H_2O means 5 molecules of water and not just 5 times the 'H_2'.

In the case of $CuSO_4 \cdot 5H_2O$, water can be removed by heating:

$$CuSO_4 \cdot 5H_2O \xrightarrow{\text{heat}} CuSO_4 + 5H_2O$$

However, this is not always the case, and when $MgCl_2 \cdot 6H_2O$ is heated, magnesium oxide (MgO) is formed:

$$MgCl_2 \cdot 6H_2O \xrightarrow{\text{heat}} MgO + 2HCl + 5H_2O$$

WORKED EXAMPLE 4.21

Calculate the amount in mol of chloride ions present in 50.0 cm^3 of a 0.0500 mol dm^{-3} solution of iron(III) chloride ($FeCl_3$) and the total concentration of all the ions present.

Answer

amount of substance (number of moles) = concentration × volume in dm^3

$$\text{amount in mol of } FeCl_3 = \frac{50.0}{1000} \times 0.0500 = 2.50 \times 10^{-3} \text{ mol } FeCl_3$$

$$FeCl_3(aq) \rightarrow Fe^{3+}(aq) + 3Cl^-(aq)$$

So, dissolving 2.50×10^{-3} mol $FeCl_3$ produces $3 \times 2.50 \times 10^{-3}$ mol $Cl^-(aq)$, i.e., 7.50×10^{-3} mol $Cl^-(aq)$.
The amount of chloride ions present is 7.50×10^{-3} mol.

When one $FeCl_3$ unit dissolves in water, four ions are produced ($Fe^{3+} + 3Cl^-$).

So, the total concentration of ions present is four times the concentration of $FeCl_3$, i.e., $4 \times 0.0500 = 0.200$ mol dm^{-3}.

The total concentration of ions present is 0.200 mol dm^{-3}.

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When hydrated substances are dissolved in water, the water of crystallisation just becomes part of the water in the solution and, for example, solutions made up from equivalent numbers of moles (but not masses) of hydrated and anhydrous copper(II) sulfate would be identical.

WORKED EXAMPLE 4.22

When 2.00 g $MgSO_4 \cdot xH_2O$ is heated, 0.98 g of anhydrous magnesium sulfate is formed. Determine the value of x.

Answer

The difference between the masses is due to the water given off; therefore:

mass of water lost = 2.00 – 0.98 = 1.02 g

This is now basically just an empirical formula question, but, instead of finding the ratio between the number of moles of elements, we need to find the ratio between the number of moles of $MgSO_4$ and H_2O.

	$MgSO_4$	H_2O
amount / mol	$0.98 \div 120.38 = 8.14 \times 10^{-3}$	$1.02 \div 18.02 = 5.66 \times 10^{-2}$
divide by smaller number	$8.14 \times 10^{-3} / 8.14 \times 10^{-3}$	$5.66 \times 10^{-2} / 8.14 \times 10^{-3}$
ratio	1	6.95

This ratio should be a whole number, so we can round 6.95 up to 7, which is the value of x.

The formula of hydrated magnesium sulfate is, therefore, $MgSO_4 \cdot 7H_2O$.

WORKED EXAMPLE 4.23

If 10.00 g of hydrated copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) is dissolved in water and made up to a volume of 250.0 cm^3, what is the concentration of the solution?

Answer

molar mass of $CuSO_4 \cdot 5H_2O = 249.72 \text{ g mol}^{-1}$

$$\text{amount in mol of } CuSO_4 \cdot 5H_2O = \frac{10.00}{249.72} = 0.04004 \text{ mol}$$

$$\text{concentration} = \frac{\text{amount in mol}}{\text{volume in dm}^3} = \frac{0.04004}{0.2500} = 0.1602 \text{ mol dm}^{-3}$$

So, dissolving 10.00 g of $CuSO_4 \cdot 5H_2O$ in water and making up the solution to 250.0 cm^3 produces a $CuSO_4$ solution with a concentration of 0.1602 mol dm^{-3}.

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TEST YOUR UNDERSTANDING

27 Calculate the concentration of each of the following solutions in mol dm^{-3}:

	Amount of solute / mol	Volume of solution
a	0.100	2.00 dm^3
b	1.20×10^{-3}	10.0 cm^3
c	0.0560	250.0 cm^3

28 Calculate the concentration of each of the following solutions in g dm^{-3}:

	Mass of solute / g	Volume of solution
a	50.0	10.00 dm^3
b	2.00	100.0 cm^3
c	0.780	25.0 cm^3

29 Work out the amount, in mol, of solute present in

a 20.0 cm^3 of 0.220 mol dm^{-3} NaOH(aq)

b 27.8 cm^3 of 0.0840 mol dm^{-3} HCl(aq)

c 540 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$(aq)

d 2.50 dm^3 of 0.140 mol dm^{-3} NaCl(aq).

30 Convert the following concentrations in g dm^{-3} to concentrations in mol dm^{-3}:

a 20.0 g dm^{-3} NaOH

b 10.0 g dm^{-3} KNO_3

c 2.50 g dm^{-3} $CuSO_4$.

31 Convert the following concentrations in mol dm^{-3} to concentrations in g dm^{-3}:

a 0.0200 mol dm^{-3} NaCl

b 0.150 mol dm^{-3} Na_2CO_3

c 0.500 mol dm^{-3} H_2SO_4.

32 Work out the mass of solute that must be used to make up the following solutions:

a 50.0 cm^3 of 0.100 mol dm^{-3} NaOH

b 75.0 cm^3 of 0.0100 mol dm^{-3} $Na_2Cr_2O_7$

c 50.0 cm^3 of 0.200 mol $Na_2S_2O_3 \cdot 5H_2O$.

33 12.50 g of hydrated sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) is dissolved in water and made up to a total volume of 100.0 cm^3. What is the concentration of the solution in mol dm^{-3}?

34 What is the total concentration of ions in each of the following solutions?

a 0.100 mol dm^{-3} NaCl

b 0.200 mol dm^{-3} Na_2SO_4 (forms Na^+ and SO_4^{2-} ions)

c 0.125 mol dm^{-3} $CrCl_3$

35 Calculate the concentration of sodium ions in each of the following:

a a solution made by dissolving 2.00 g of NaOH in water and making up to a total volume of 100.0 cm^3

b a solution made by dissolving 4.50 g of Na_2CO_3 in water and making up to a total volume of 250.0 cm^3

c a solution made by dissolving 5.00 g of $Na_2S_2O_3 \cdot 5H_2O$ in water and making up to a total volume of 500.0 cm^3

d a solution made by dissolving 1.00 g of Na_3PO_4 in water and making up to a total volume of 50.0 cm^3.

36 **a** 3.00 g of $FeSO_4 \cdot xH_2O$ is heated and 1.64 g of $FeSO_4$ is obtained. Determine the value of *x*.

b 2.50 g of $Na_2SO_4 \cdot xH_2O$ is heated and 1.10 g of Na_2SO_4 is obtained. Determine the value of *x*.

c 1.20 g of $BaCl_2 \cdot xH_2O$ is heated and 1.02 g of $BaCl_2$ is obtained. Determine the value of *x*.

d $CuSO_4 \cdot 5H_2O$ is heated to partially dehydrate it. 3.76 g of $CuSO_4 \cdot 5H_2O$ is heated and 3.33 g of $CuSO_4 \cdot xH_2O$ is obtained. Determine the average value of *x*.

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Standard solutions

KEY POINT

A **standard solution** is one for which the concentration is known.

The concentration of a solution can be known if it has been made up accurately from a solid using volumetric glassware or because it has been standardised by reacting it with another standard solution.

How to make a standard solution

A certain mass of the solute is weighed out accurately and then transferred to a beaker. A small amount of distilled water is added, and the mixture is stirred until all the solid has dissolved. This solution is then transferred to a volumetric flask (washing out the beaker with several lots of distilled water to ensure that all the solute is transferred). Finally, distilled water is added to the volumetric flask to make the solution up to the mark so that the total volume of the solution is known. This is summarised in Figure 4.9.

A volumetric flask is used instead of measuring cylinders because it is both more accurate and more precise. It is more accurate because of how it is manufactured; for example, with a 250 cm^3 volumetric flask, the volume should be, at worst, within about 0.3 cm^3 of 250.0 cm^3, but for a 250 cm^3 measuring cylinder, the tolerance could be about +/– 2 cm^3. The reading of the volume in a 250 cm^3 volumetric flask can also be made more precisely than for the same size measuring cylinder because it has a narrower neck – the measurement will have a smaller uncertainty.

Dilution of solutions

Once we have a solution of known concentration, we often need to dilute it to make solutions of other (lower) concentrations. To do this accurately, we would use volumetric apparatus, such as a pipette and volumetric flask.

The concentration of a diluted solution can be worked out using the equation:

$$C_{dil} = \frac{V_{und}}{V_{dil}} \times C_{und}$$

where

C_{dil} = concentration of diluted solution

V_{und} = volume of original (undiluted) solution used

V_{dil} = total volume of diluted solution

C_{und} = concentration of original (undiluted) solution

NOTE: the units of V_{und} and V_{dil} must be the same.

If we have made a standard solution of concentration 0.100 mol dm^{-3}, this could be diluted to a concentration of 0.0100 mol dm^{-3} by measuring out 10.0 cm^3 of the solution using a pipette, transferring it to a 100 cm^3 volumetric flask and making up to 100.0 cm^3 with distilled water.

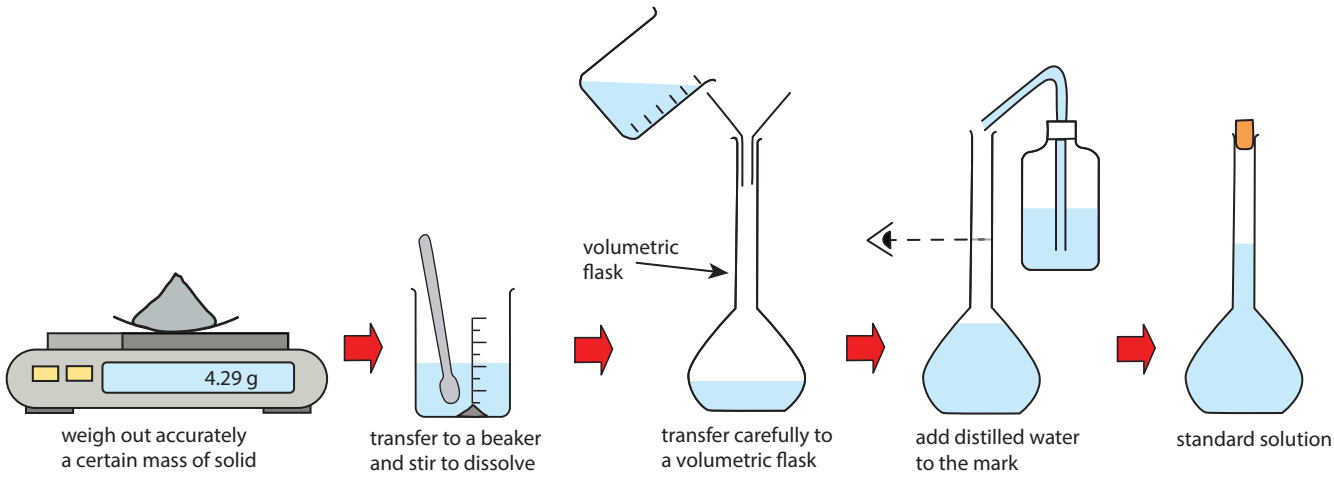

Figure 4.9: Making a standard solution.

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$V_{und} = 10.0\ cm^3$

$C_{und} = 0.100\ mol\ dm^{-3}$

$V_{dil} = 100.0\ cm^3$

$C_{dil} = \frac{10.0}{100.0} \times 0.100 = 0.0100\ mol\ dm^{-3}$

We can see here that the concentration of the diluted solution is one-tenth of that of the original solution, so we say that the original solution was diluted by a factor of ten.

Serial dilutions

This technique can be useful for producing solutions of very low concentrations. Imagine that we wanted to make a solution of lithium chloride (LiCl) with a concentration of 0.100 mg dm^{-3} for analysis, and all we had available was an electronic balance that reads to two decimal places. 0.100 mg is 0.000100 g, and so we cannot measure that on the balance. The smallest mass we can measure out on this balance is 0.01 g and then this would have to be dissolved in 100 dm^3 of water to produce the correct concentration. Not only is 100 dm^3 an extremely large volume (we are likely to only need a few cm^3 of the sample at most), but the uncertainty on a two-decimal-place balance is ±0.01 g, and so, our percentage uncertainty on this mass is ±100%!

We can make up this solution more precisely using **serial dilutions**, which are successive dilutions of a solution.

If we weigh out 1.00 g of LiCl with a two decimal place balance, the percentage uncertainty on this is only 1%: $\frac{0.01}{1.00} \times 100 = 1\%$ This sample is then dissolved in water and made up to a total volume of 1000 cm^3 in a volumetric flask to give a 1.00 g dm^{-3} solution. We then measure out 10.0 cm^3 of this solution using a 10 cm^3 pipette, transfer it to another 1000 cm^3 volumetric flask and make up to the mark with distilled water. We have diluted the original solution by a factor of 100, and so, the concentration of the new solution is 0.0100 g dm^{-3}. If we take 10.0 cm^3 of this 0.0100 g dm^{-3} solution using a 10 cm^3 pipette, transfer it to another 1000 cm^3 volumetric flask, and then make it up to the mark with distilled water, we will have made a 0.000100 g dm^{-3} solution. We have used accurate and precise measuring apparatus and quite large quantities each time, so our percentage uncertainty on the final concentration will be quite low, and we have only used a total of about 3 dm^3 of water! This is summarized in Figure 4.10.

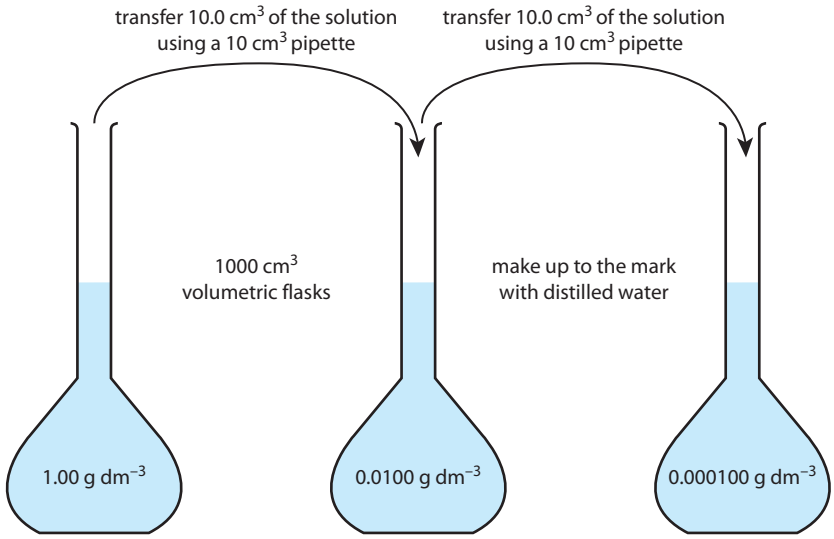

Figure 4.10: Serial dilutions

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SCIENCE IN CONTEXT

Monkshood or wolfsbane (*Aconitum napellus*; Figure 4.11) is a beautiful but toxic plant that has been notorious throughout history as a poison and has even been called 'the queen of poisons'.

Figure 4.11: Monkshood in flower.

The main poison it contains is aconitine ($C_{34}H_{47}NO_{11}$), which is a powerful cardiotoxin and neurotoxin, and ingesting as little as 1 or 2 mg of pure aconitine could be fatal. There are many cases throughout history of accidental and intentional poisoning with aconitine; however, it is also used in Chinese medicine and homeopathy. Homeopathy is a form of treatment where very dilute solutions (as solutions or usually tablets) of substances, many of which are poisons, are administered with the idea 'like cures like'. 30C *Aconite napellus* homeopathic remedy is readily available and is used to treat anxiety or fevers. Many people believe in homeopathic remedies, but there are a lot of sceptics because of the dilutions that are used. A 30C dilution means that the original substance is diluted by a factor of 100 (C) 30 times, which corresponds to diluting it by a factor of 10^{60}, so imagine that we started with 1 cm^3 of pure aconitine – this corresponds to about 0.002 mol. If this is diluted by a factor of 10^{60}, the concentration becomes 2×10^{-60} mol dm^{-3} (the first dilution involves adding it to a suitable solvent and making up to 100 cm^3, so, after the first dilution, the concentration is 0.02 mol dm^{-3}). The number of molecules of aconitine in 1 mol is 6.02×10^{23}, so the number of molecules present in 1 dm^3 of a 2×10^{-60} mol dm^{-3} solution is 1.2×10^{-36}, that is, zero molecules! To consume one molecule, you would have to drink 10^{36} dm^3 of this solution, but the total volume of all the water on the Earth is only about 1.4×10^{21} dm^3!

Determination of the concentration of a coloured solution

We can work out the concentration of a coloured solution, such as copper(II) sulfate solution, using a colorimeter or a visible spectrophotometer. The basic principles of a colorimeter are shown in Figure 4.12.

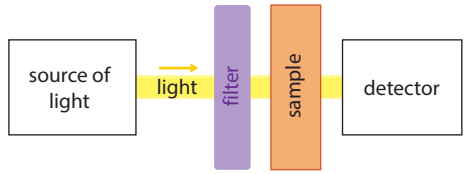

Figure 4.12: A colorimeter can be used to measure the amount of light absorbed at a particular wavelength. The darker the colour of the sample, the more light is absorbed.

We pass monochromatic (of one wavelength) light through the sample and measure how much is absorbed. The higher the concentration of the coloured substance, the more light absorbed.

Before we can measure how much light is absorbed, we must first determine which wavelengths of light are absorbed by the solution. Copper(II) sulfate solution is blue-green, and so, absorbs at the orange–red end of the spectrum. We would usually use the wavelength at which the substance has the highest absorbance (called λ_{max}), but, for copper sulfate, this occurs in the infrared region of the spectrum. Most colorimeters also only have a very limited range of wavelengths available, so we will carry out the experiment at 635 nm, which is the longest wavelength available on our colorimeter.

The quantity that we measure with a colorimeter is called absorbance (A).

To determine the relationship between absorbance and concentration, we need to generate a **calibration curve**.

We start by making up a solution of copper(II) sulfate with a concentration of 0.200 mol dm^{-3} and measuring the absorbance at 635 nm. The solution is then diluted using volumetric apparatus, and the absorbance of each of the diluted solutions is measured at 635 nm (Table 4.2).

The concentration of the diluted solution (C_{Dil}) can be worked out using the equation:

$$C_{dil} = \frac{V_{und}}{V_{dil}} \times C_{und}$$

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Volume of 0.200 mol dm^{-3} $CuSO_4(aq)$ / cm^3	Total volume / cm^3	Concentration of diluted solution / mol dm^{-3}
20.0	25.0	0.160
15.0	25.0	0.120
10.0	25.0	0.080
5.0	25.0	0.040

Table 4.2: The concentrations used to make the calibration curve.

Therefore, if we measure out 20.0 cm^3 of 0.200 mol dm^{-3} $CuSO_4(aq)$ and make it up to a total volume of 25.0 cm^3, we have

$$\text{concentration of diluted solution} = \frac{20.0}{25.0} \times 0.200 = 0.160 \text{ mol dm}^{-3}$$

A graph of absorbance against concentration can then be plotted – the calibration curve (Figure 4.13).

Once we have the calibration curve, we can use it to work out the concentration of an unknown solution of copper(II) sulfate. If the absorbance of the unknown solution at 635 nm is 0.31, we can use the graph (Figure 4.13) to work out that the concentration of the unknown solution is 0.15 mol dm^{-3}.

This technique can also be applied to substances that are colourless (e.g. solutions of DNA or proteins) if they absorb in the ultraviolet (UV) region of the spectrum and a UV-visible spectrophotometer is used.

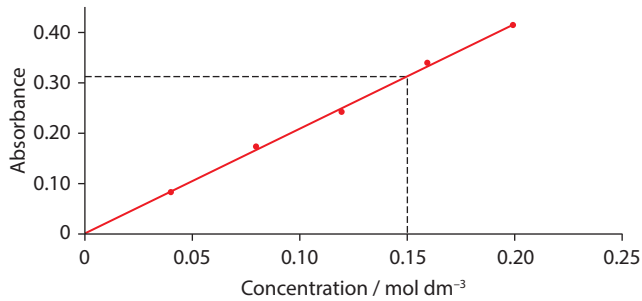


Figure 4.13: Calibration curve for copper(II) sulfate solution at 635 nm

4.6 Avogadro's law

KEY POINT

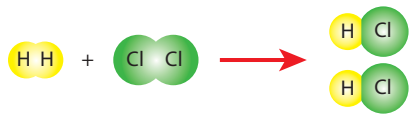
Avogadro's law equal volumes of ideal gases measured at the same temperature and pressure contain the same number of molecules.

In other words, 100 cm^3 of H_2 contains the same number of molecules at 25 °C and 100 kPa pressure as 100 cm^3 of NH_3, if we assume that they both behave as ideal gases. Under the same conditions, 50 cm^3 of CO_2 would contain half as many molecules.

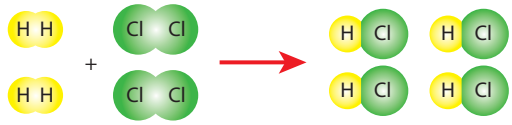
Another way of stating **Avogadro's law** is that the volume of an ideal gas is proportional to the amount of substance (in mol). We will return to this idea and discuss ideal gases in Chapter 5.

The meaning of chemical equations

Consider the reaction between hydrogen gas (H_2) and chlorine gas (Cl_2) to form hydrogen chloride gas (HCl). In this reaction, one molecule of H_2 reacts with one molecule of Cl_2 to form two molecules of HCl:



If we started with two molecules of H_2, then they would combine with two molecules of Cl_2 to form four molecules of HCl:



Four molecules of H_2 would combine with four molecules of Cl_2 to form eight molecules of HCl:

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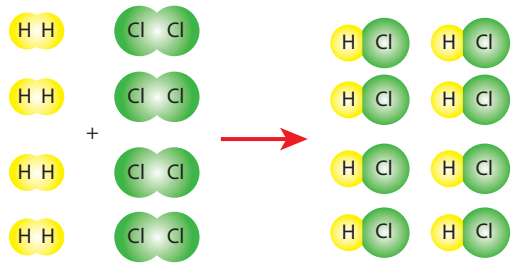
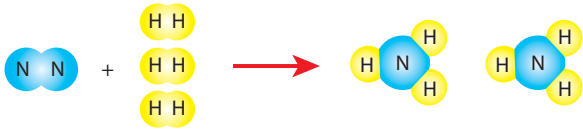


We know from Avogadro's law that, if we have equal numbers of particles, then we have equal volumes of the gases; therefore, we can also say that one volume of H_2 reacts with one volume of Cl_2 to form two volumes of HCl. So, 50 cm^3 of H_2 would react with 50 cm^3 of Cl_2 to form 100 cm^3 of HCl. We can show this relationship in a chemical equation:

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

A chemical equation usually describes how molar quantities combine, and, thus, we can see here that 1 mol H_2 reacts with 1 mol Cl_2 to form 2 mol HCl – remember that the number of moles tells you the number of particles. The term *mole ratio* is used to describe the relationship between the numbers of moles of the various substances in a chemical equation, and this is given by the coefficients (large numbers), so hydrogen and chlorine combine in a mole ratio of 1:1.

One molecule of nitrogen (N_2) combines with three molecules of hydrogen (H_2) to form two molecules of ammonia (NH_3):



Which also means that 1 mol nitrogen (N_2) combines with 3 mol hydrogen (H_2) to form 2 mol of ammonia (NH_3), so we can write the following equation:

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

Nitrogen and hydrogen combine in a mole ratio of 1:3.

The number of moles (amount) is proportional to the volume and, therefore, 20 cm^3 of nitrogen would react with $3 \times 20 = 60$ cm^3 of hydrogen to form $2 \times 20 = 40$ cm^3 of ammonia. In the following worked examples, assume that all gases behave as ideal gases and that all measurements are made under the same conditions of temperature and pressure.

WORKED EXAMPLE 4.24

Consider the following reaction for the synthesis of methanol: $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

a What volume of H_2 reacts exactly with 2.50 dm^3 of CO?

b What volume of CH_3OH is produced?

Answer

a From the equation, we can see that 1 mol CO reacts with 2 mol H_2. Therefore, one volume of CO reacts with two volumes of H_2, and so, 2.50 dm^3 of CO react with 2×2.50, i.e., 5.00 dm^3, of H_2.

b One volume of CO produces one volume of CH_3OH; therefore, the volume of CH_3OH produced is 2.50 dm^3.

WORKED EXAMPLE 4.25

Consider the reaction between ethane and oxygen:

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$$

a What volume of C_2H_6 reacts exactly with 200.0 cm^3 of O_2?

b What volume of CO_2 is produced?

Answer

a From the equation, we can see that two volumes of C_2H_6 will react with seven volumes of O_2; therefore, the ratio between the volume of C_2H_6 and O_2 is 2:7 and the volume of C_2H_6 is $\frac{2}{7}$ of the volume of oxygen:

$$\text{volume of } C_2H_6 = \frac{2}{7} \times 200.0 = 57.14 \text{ cm}^3$$

b From the equation, we can see that seven volumes of O_2 will form four volumes of CO_2; therefore, the ratio between the volume of O_2 and CO_2 is 7:4 and the volume of CO_2 is $\frac{4}{7}$ of the volume of oxygen.

$$\text{volume of } CO_2 = \frac{4}{7} \times 200.0 = 114.3 \text{ cm}^3$$

Note on significant figures: We know that the last zero in 200.*0* is significant because it did not have to be there to hold the position of the 2 – we could have just written 200. The two zeroes in 200 must be there to hold the position of the 2 – otherwise the number would just be 2! These zeroes may be significant or

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CONTINUED

not – we would have to have more information about how the value was measured and/or the uncertainty of the measurement to determine this, so 200 could be 1, 2 or 3 significant figures.

0.0002 is one significant figure because the zero before the decimal point and the three zeros after it are there to hold the position of the 2 – without them we would just have 2! 0.0200 is three significant figures – the last zeroes do not have to be there to hold the position of the 2, so they must be significant.

WORKED EXAMPLE 4.26

If 100 cm^3 of oxygen is put in a container with 30 cm^3 of methane and the mixture ignited, how much oxygen will be left at the end of the reaction?

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

Answer

From the equation, we know that 1 mol CH_4 reacts with 2 mol O_2. Therefore, one volume of CH_4 reacts with two volumes of O_2 – so 30 cm^3 of CH_4 react with 2×30, i.e., 60 cm^3, of O_2.

The original volume of O_2 was 100 cm^3; therefore, if 60 cm^3 reacted, the volume of oxygen gas left over at the end of the reaction would be $100 - 60 = 40$ cm^3.

TEST YOUR UNDERSTANDING

37 Each of these questions uses the following equations, which show the combustion of a hydrocarbon (compound containing C and H only):

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

B $C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

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

D $2C_6H_{10}(g) + 17O_2(g) \rightarrow 12CO_2(g) + 10H_2O(l)$

a Work out the volume of the hydrocarbon that reacts with 100 cm^3 of oxygen in each of the reactions.

b For each of the reactions, calculate the volume of CO_2 produced when 100 cm^3 of the hydrocarbon is reacted with excess (more than enough to react with all the hydrocarbon) oxygen.

c For each of the reactions, calculate the volume of CO_2 produced when 1.00 dm^3 of oxygen is reacted with excess hydrocarbon.

d For each of the reactions, calculate the volume of O_2 left over if, in each case, 20.0 cm^3 of the hydrocarbon is put into a container with 200.0 cm^3 of oxygen and the mixture ignited.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
calculate relative formula masses from relative atomic masses	4.1			
understand what a mole is	4.2			
calculate amount of substance in mol from masses and vice versa	4.3			
calculate the number of particles from the amount of substance in mol and masses and vice versa	4.3			
deduce empirical and molecular formulas from experimental data	4.4			
carry out calculations involving concentrations in mol dm^{-3} and g dm^{-3}	4.4			
solve problems involving gases using Avogadro's law.	4.6			

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REFLECTION

How confident do you feel with the mathematical aspects of this chapter? Where do you think further practice is required? Could you try making up some empirical formula questions for another student and get them to do the same for you? If you looked at the periodic table, could you explain to someone how to work out the mass of an atom of any element? Dilutions are something that students often find difficult; could you explain to another student how to make up 200 cm^3 of 0.10 mol dm^{-3} sodium hydroxide solution, starting with a 0.40 mol dm^{-3} solution?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 5
Ideal gases

LEARNING OBJECTIVES

In this chapter you will:

- understand the assumptions of the ideal gas model
- understand under what conditions a real gas is most different to an ideal gas
- describe the relationships between pressure, volume and temperature for an ideal gas
- carry out calculations using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- carry out calculations involving the ideal gas equation
- understand what is meant by the molar volume of a gas.

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GUIDING QUESTIONS

- What is an ideal gas?
- How do real gases differ from an ideal gas?
- What is the connection between the temperature, pressure, volume and amount of an ideal gas?

Introduction

Eleven of the naturally occurring elements are gases at room temperature and pressure, and these range from the most reactive of all elements, fluorine, to the least reactive, helium. There are many more gases that are compounds, and several of these are associated with environmental issues – carbon dioxide and methane (climate change), ozone (the ozone hole), sulfur dioxide and nitrogen oxides (acid rain), etc. The atmosphere consists of mostly nitrogen (about 78%) and oxygen (about 21%), but changes in the concentrations of the other gases can have severe consequences for the existence of life as we know it on Earth.

5.1 Real gases and ideal gases

If we take 1 mol of three gases, say nitrogen, helium and carbon dioxide, and measure their volumes at 273 K and 100 kPa, we find that they have almost identical volumes. If we compress the gases by doubling the pressure at constant temperature, we find that they all behave in almost exactly the same way – for each of them, the volume that they occupy will, to a very good approximation, halve.

Each gas will behave in a very slightly different way, but under normal conditions [pressures around 100 kPa (approximately atmospheric pressure) and temperatures around room temperature] these variations are negligible, and we can model the behaviour of all these *real gases* by defining an **ideal gas**.

KEY POINT

All the gases around us are real gases, but we model their behaviour using the concept of an ideal gas.

An ideal gas can be defined in terms of microscopic (in terms of the particles) or macroscopic (properties of the gas on a large scale, such as pressure and volume) properties of the gas. We will consider microscopic properties here and macroscopic properties below.

The assumptions of the ideal gas model are as follows:

- An ideal gas consists of particles in constant, random motion.
- The particles have no volume (they are point masses).
- No forces exist between particles (except when they collide).
- All collisions between particles and between particles and the walls of the container are perfectly elastic (there is no change in the total kinetic energy of the colliding particles when they collide).

Why do we need the concept of an ideal gas?

The properties of an ideal gas can be described by a relatively simple set of equations, which are quite straightforward to use. This set of equations is applied in the same way to all gases. The equations allow us to work out what happens to the volume, pressure or temperature of the gas as we change the other two quantities. The predictions we make for these properties, as long as we are working at around room temperature and pressure, agree very well with experimental measurements.

For more advanced work, the properties of real gases can be modelled with much more complicated equations [the van der Waals equation (see below) is one of the simpler ones!], and certain values used in these equations (a and b in the van der Waals equation) are different for each gas.

Deviation of real gases from ideal-gas-beahaviour

KEY POINT

Gases deviate the most from ideal behaviour at high pressure and low temperature.

If we look at two of the assumptions about an ideal gas, in turn, we can understand this.

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Molecules occupy zero volume

We can calculate the volume of 1 mol He atoms as about 3×10^{-3} dm^3. If we compare this to the volume occupied by 1 mol He gas at 273.15 K and 100 kPa, which is 22.7 dm^3 if we assume that it acts as an ideal gas, we can see that the volume actually occupied by the atoms is negligible (approximately 0.01%) compared to the volume occupied by the gas.

We can do the same calculation for He at a higher pressure of 10^4 kPa. One mole of an ideal gas occupies 0.227 dm^3 at this pressure and 273.15 K, and the volume of the atoms is about 1% of the volume of the gas. The volume due to the atoms themselves is no longer negligible and the volume actually occupied by the gas is larger than that predicted using the ideal gas model. However, for helium, even at 10^4 kPa, our model is not too bad. For CO_2 at 100 kPa and 273.15 K, the volume of the molecules is about 0.1% of the volume of the gas but it is about 10% at 10^4 kPa – for CO_2, our model agrees reasonably well with experimental observations at around atmospheric pressure but breaks down significantly at higher pressures. At 10^4 kPa there is a significant difference between the volume predicted by the ideal gas model and the actual volume of CO_2.

At high pressures, the volumes of real gases are higher than those predicted by the ideal gas model, due to the volume of the particles themselves.

There are no forces between particles

The average distance between particles of CO_2 at 273.15 K and 100 kPa is approximately 10 times the diameter of a molecule, but at 100 K and 10^4 kPa this distance is less than twice the molecular diameter of CO_2 (assuming it remains as a gas). At these distances, the forces between particles become more significant. Also, at lower temperatures, the particles are moving more slowly, and so are more influenced by attractive forces from other particles. The intermolecular forces will tend to pull the particles closer together, and so the volume occupied by the gas will be lower than that predicted by the ideal gas model.

For most gases at low temperatures and moderate pressures, the volume occupied is lower than that

SCIENCE IN CONTEXT

Helium

Helium is the second most abundant element in the universe, but the concentration in the Earth's atmosphere is very low, at about 5×10^{-4} %. The reason for this is that helium is a very light atom, and so, many more of the atoms (compared to heavier molecules) will be moving fast enough to escape the gravitational pull of the Earth. Helium in the early atmosphere of the Earth would, therefore, have just escaped off into space. The helium that is present on Earth nowadays comes from radioactive decay. When some nuclei (e.g. uranium and thorium) decay, they produce alpha particles, which are helium nuclei (He^{2+}). These nuclei pick up electrons, as they interact with matter, to form helium atoms. Some of this helium collects in natural gas fields, and helium is a by-product of natural gas production. Only very few countries in the world produce helium, and by far the largest producer is the USA, but other countries, such as Algeria, Qatar and Russia, are also becoming important producers. A major use of helium is in magnetic resonance imaging (MRI) scanners, which are used in medicine to provide images of the body for diagnostic purposes. Helium has the lowest boiling point of any substance (4.2 K, –269 °C) and does not freeze at atmospheric pressure; it is used to cool the electromagnets in MRI scanners, so that they superconduct. Helium is the least reactive element, and it finds uses in welding, scientific research, deep sea diving and rocket engines. Over the last few years, there have been increasing worries about reduced supplies of helium and shortages. Helium is probably most familiar from being used in party balloons (Figure 5.1) and, although this accounts for under 10% of helium used annually, is the gas too valuable to be wasted?

Figure 5.1: It is a strange thought that these party balloons contain helium that came from the radioactive decay of uranium.

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THEORY OF KNOWLEDGE

Imagine a possible news headline:

Scientists have revealed that the helium in children's party balloons comes from the highly radioactive element uranium, which is used in nuclear weapons and was responsible for the deaths of thousands of people in Hiroshima.

Is there anything that is untrue in this headline? How do you think that this would affect people's perception of helium and the sales of party balloons?

predicted by the ideal gas model due to intermolecular forces being significant. This is especially true for larger/more polar molecules (e.g. SF_6, NH_3), which would be expected to have stronger intermolecular forces.

The two effects here oppose each other and whether the volume occupied by a real gas is higher or lower than that predicted by the ideal gas model depends on the gas, the temperature and the pressure. At low temperatures, the effect of intermolecular forces tends to dominate, and the volumes of real gases are generally lower than that predicted by the ideal gas model. At high pressures, the volume of real gases tends to be higher than that predicted due to the volume of the molecules themselves becoming more significant.

A way of remembering the conditions under which a real gas deviates most from the ideal gas model is to think what conditions would make the gas into a liquid – as temperature is decreased and/or pressure is increased, a real gas would eventually become a liquid and then will be least like our predictions for an ideal gas. Under the assumptions of the ideal gas model, it is not possible for a gas to become a liquid because there are no intermolecular forces.

Helium, which exists as individual, small atoms with very weak intermolecular forces, is the gas that most closely approaches ideal gas behaviour over a range of temperatures and pressures.

5.2 Macroscopic properties of ideal gases

In this section, we will look at the relationship between the pressure, temperature and volume of an ideal gas.

The relationship between pressure and volume of an ideal gas (Boyle's law)

KEY POINT

At a constant temperature, the volume of a fixed mass of an ideal gas is inversely proportional to its pressure.

$$P \propto \frac{1}{V}$$

This means that, if the pressure of a gas is doubled at constant temperature, then the volume will be halved and vice versa. This relationship is illustrated in Figure 5.2.

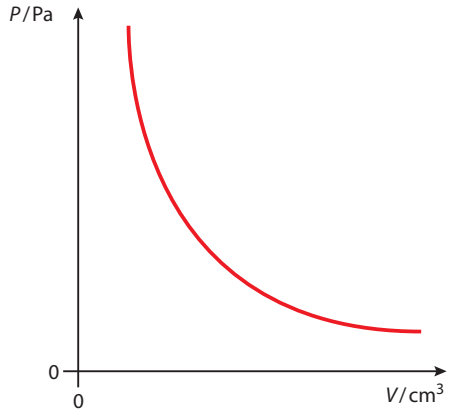

Figure 5.2: The relationship between pressure and volume of a fixed mass of an ideal gas at constant temperature. The pressure and volume could also be in other units, e.g. m^3 or dm^3 for volume.

A constant of proportionality (k) can be introduced into the above relationship between pressure and volume of an ideal gas:

$$P = \frac{k}{V}$$

This can be rearranged to give

$$PV = k$$

This means that the product of the pressure and volume of an ideal gas at a particular temperature is a constant and does not change as the pressure and the volume change. A graph of PV against pressure (or volume)

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will, therefore, be a straight, horizontal line. This is shown in Figure 5.3.

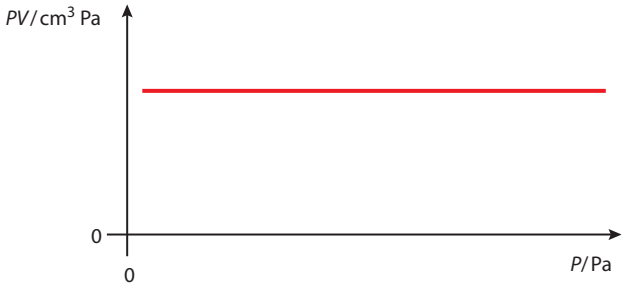

Figure 5.3: The relationship between PV and *P* for a fixed mass of an ideal gas at constant temperature.

Because pressure is proportional to $\frac{1}{\text{volume}}$, a graph of pressure against $\frac{1}{\text{volume}}$ would be a straight-line graph that would pass through the origin (although this graph will never actually pass through the origin – the gas would have to have infinite volume at zero pressure). This relationship is shown in Figure 5.4.

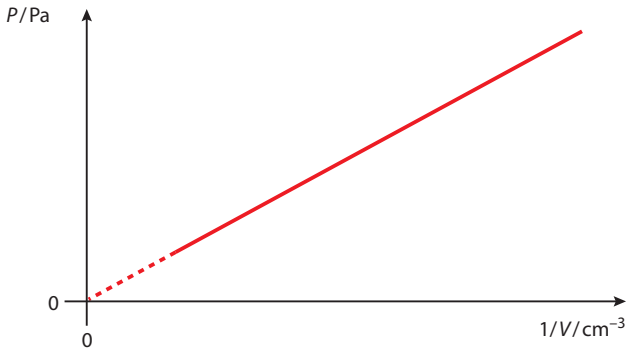

Figure 5.4: The relationship between the pressure and $\frac{1}{\text{volume}}$ of a fixed mass of an ideal gas at constant temperature.

NATURE OF SCIENCE

A scientific *law* is a general statement (often in mathematical form) based on observation/experiment of some aspect of the physical world. It will often involve the relationship between various quantities under specified conditions. For example, Boyle's law describes the relationship between the volume and pressure of a fixed mass of an ideal gas at constant temperature. A law does not explain anything – it is just a description of what happens.

CONTINUED

A *theory* is a way of explaining scientific observations or laws. To be accepted, a theory will have been rigorously tested by experiments and observations – for example, the particle theories and kinetic molecular theory can be used to explain Boyle's law. There is no progression from a theory to a law – they are different things.

The relationship between volume and temperature of an ideal gas (Charles' law)

If the temperature is in kelvin, the following relationship exists between the volume and the temperature:

KEY POINT

The volume of a fixed mass of an ideal gas at constant pressure is directly proportional to its absolute (kelvin) temperature:

$$V \propto T$$

Therefore, if the temperature in kelvin is doubled and the pressure remains constant, the volume of the gas is doubled and vice versa. This means that, if an ideal gas has a volume of 200 cm^3 at 120 K, it will have a volume of 400 cm^3 at 240 K if the pressure remains constant. This is illustrated in Figure 5.5.

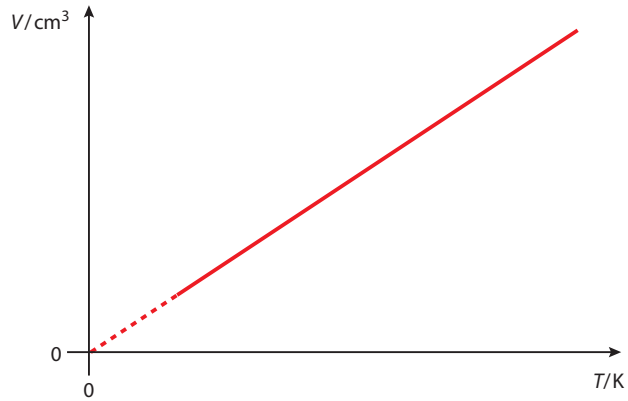

Figure 5.5: The relationship between the volume and temperature (in kelvin) of a fixed mass of an ideal gas at constant pressure. The graph is dashed at the end because we cannot actually get to absolute zero.

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A real gas would behave very differently at low temperatures because it would liquefy and then freeze (which would result in a large decrease in volume), but an ideal gas can never liquefy because there are no forces between the molecules.

This relationship does not work for temperatures in °C (Figure 5.6). For instance, if the volume of an ideal gas at 25 °C is 500 cm^3, the volume it will occupy at 50 °C will be about 560 cm^3.

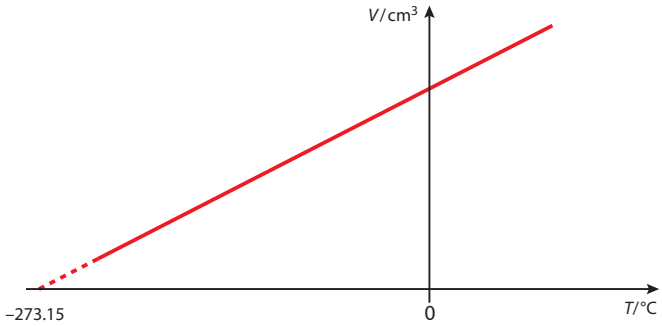

Figure 5.6: The relationship between the volume and temperature (in °C) of a fixed mass of an ideal gas at constant pressure. As can be seen, the temperature at which the volume of an ideal gas is zero will be –273.15 °C. This temperature is absolute zero.

This is a linear relationship but not a proportional one because the graph does not pass through the origin.

The relationship between pressure and temperature of an ideal gas (Gay-Lussac's law)

KEY POINT

For a fixed mass of an ideal gas at constant volume, the pressure is directly proportional to its absolute (kelvin) temperature:

$$P \propto T$$

If the temperature in kelvin of a fixed volume of an ideal gas is doubled, the pressure will also double (Figure 5.7).

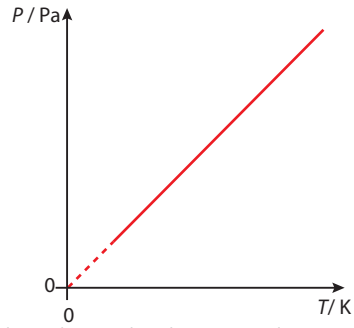

Figure 5.7: The relationship between the pressure and temperature (kelvin) of a fixed mass of an ideal gas at constant volume.

As stated earlier in the chapter, an ideal gas can also be defined in terms of macroscopic properties:

KEY POINT

An ideal gas is one that obeys all three of the laws above ($P \propto 1/V$, $V \propto T$, $P \propto T$) exactly.

5.3 Calculations involving ideal gases

The combined gas law equation

The three relationships discussed above can be combined to produce the following equation:

KEY POINT

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The temperature must be always be in kelvin.

With any calculations involving gases, you have to be extremely careful to use the correct units. In all calculations, it is important to remember that the temperature must always be in kelvin. In this equation, any units may be used for P and V, so long as they are consistent on both sides of the equation.

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WORKED EXAMPLE 5.1

If the volume of an ideal gas collected at 0.00 °C and 100 kPa, is 50.0 cm^3, what would be the volume at 60.00 °C and 108 kPa?

Answer

It is a good idea to write out all the quantities that you have been given so that you can keep track of which one is P_1, P_2, etc., and you can see clearly if the units are consistent.

$P_1 = 100$ kPa $\qquad P_2 = 108$ kPa

The units of P_1 and P_2 are consistent with each other.

$V_1 = 50.0\ cm^3 \qquad V_2 = ?$

$T_1 = 0.00\ °C \Rightarrow 273.15\ K$

$T_2 = 60.00\ °C \Rightarrow 60.00 + 273.15 = 333.15\ K$

Remember: temperature must be in K. $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Substituting in the values, we get $\frac{100 \times 50.0}{273.15} = \frac{108 \times V_2}{333.15}$

Rearranging the equation:

$V_2 = \frac{100 \times 50.0 \times 333.15}{273.15 \times 108} = 56.5\ cm^3$

The units of V_2 are the same as those of V_1.

Therefore, the volume occupied by the gas at 60 °C and 108 kPa is 56.5 cm^3.

KEY POINT

Pascal (Pa) is the SI unit of pressure: 1 Pa is equivalent to 1 N m^{-2}. We will also tend to use kPa as a convenient unit, where 1 kPa = 1000 Pa. Normal atmospheric pressure is approximately 101 kPa.

WORKED EXAMPLE 5.2

What temperature (in °C) is required to cause an ideal gas to occupy 1.34 dm^3 at a pressure of 200 kPa if it occupies 756 cm^3 at 100 kPa and 273.15 K?

Answer

$P_1 = 200$ kPa $\qquad P_2 = 100$ kPa

The units of P_1 are the same as those of P_2.

$V_1 = 1.34\ dm^3$

$V_2 = 756\ cm^3$, i.e. $\frac{756}{1000} = 0.756\ dm^3$

The units of V_1 and V_2 must be made consistent with each other. We could have also changed V_1 to cm^3.

$T_1 = ? \qquad T_2 = 273.15$ K

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\frac{200 \times 1.34}{T_1} = \frac{100 \times 0.756}{273.15}$

Rearranging the equation:

$200 \times 1.34 \times 273.15 = 100 \times 0.756 \times T_1$

$T_1 = \frac{200 \times 1.34 \times 273.15}{100 \times 0.756} = 968$ K

Now convert the temperate into °C by subtracting 273.15.

temperature = 968 – 273.15 = 695 °C

The temperature must be 695 °C for the gas to occupy a volume of 1.34 dm^3.

EXAM TIP

When we add/subtract numbers stated to different numbers of decimal places we use the fewest number of decimal places in the answer. 968 has zero decimal places and 273.15 has 2, so we give our answer to zero decimal places.

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TEST YOUR UNDERSTANDING

1 If a certain mass of an ideal gas occupies 20.0 cm^3 at 273 K and 1.01×10^5 Pa, what volume would it occupy at 311 K and 1.06×10^5 Pa?

2 A certain mass of an ideal gas occupies 250.00 cm^3 at 20.00 °C and 9.8900×10^4 Pa. At what temperature (in °C) will it occupy 400.00 cm^3 if the pressure remains the same?

3 A certain mass of an ideal gas occupies a volume of 8.90 dm^3 at 50.00 °C and 120 kPa. What pressure is required to compress it to 5.00 dm^3 at 100.00 °C?

4 If a certain mass of an ideal gas occupies 1.50 dm^3 at 249.85 °C and 1.56×10^5 Pa, what volume would it occupy at 119.85 °C and 2.45×10^5 Pa?

5 The temperature of a certain mass of an ideal gas is increased from 25.00 to 50.00 °C at constant pressure. What is the ratio of the final volume to the initial volume?

6 An ideal gas is sealed into a container of volume 1.00 dm^3. By what factor does the pressure of the gas change if the container is heated from 100.00 to 500.00 °C?

7 a The pressure of a fixed mass of an ideal gas is doubled and the temperature in K is halved. By what factor does the volume change?

b The pressure of a fixed mass of an ideal gas is increased by a factor of ten and the temperature in K is increased by a factor of five. By what factor does the volume change?

Avogadro's law

Link

Avogadro's law was covered in Chapter 4.

Avogadro's law: equal volumes of ideal gases measured at the same temperature and pressure contain the same number of particles.

Another way of thinking about this is that, as long as the pressure and temperature are constant, the volume of an ideal gas only depends on the number of particles present. This leads us to the following relationship:

number of particles $\propto$ volume

or

amount in mol (n) $\propto$ volume (V)

The ideal gas equation

If the relationships between P, V and T are combined with Avogadro's law, the ideal gas equation is obtained:

$$PV = nRT$$

where R is the *gas constant*. Although R is a universal constant, it can be quoted with various units and its value depends on these units. The SI units for the gas constant are J K^{-1} mol^{-1} and this requires the units shown in the Key Point box:

KEY POINT

A consistent set of units must be used.

R = 8.31 J K^{-1} mol^{-1}

pressure: Pa

volume: m^3

temperature: K

It is important to remember that, if you use pressure in Pa, the volume must be in m^3. The interconversion between the units of volume that you may meet is shown in Figure 5.8.

Remember:

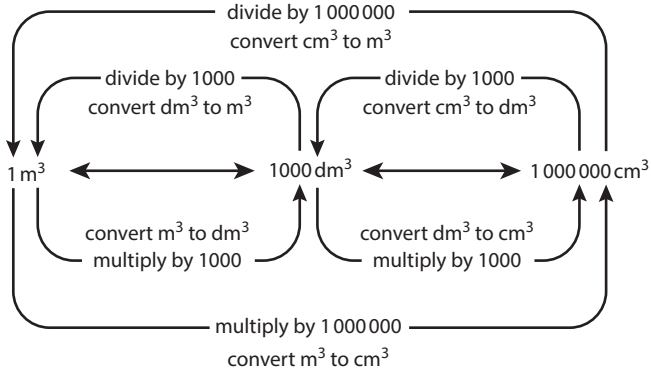

Figure 5.8: Converting between m^3, dm^3 and cm^3.

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WORKED EXAMPLE 5.3

An ideal gas occupies 590 cm^3 at 120 °C and 202 kPa. What amount of gas (in moles) is present?

Answer

All values must be converted into the appropriate set of units:

$P = 202 \text{ kPa} \Rightarrow 202 \times 1000 = 2.02 \times 10^5 \text{ Pa}$

$V = 590 \text{ cm}^3 \Rightarrow \frac{590}{1\,000\,000} = 5.90 \times 10^{-4} \text{ m}^3$

$n = ?$

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

$T = 120 \text{ °C} \Rightarrow 120 + 273.15 = 393.15 \text{ K}$

$PV = nRT$

$2.02 \times 10^5 \times 5.90 \times 10^{-4} = n \times 8.31 \times 393.15$

Rearranging the equation:

$n = \frac{2.02 \times 10^5 \times 5.90 \times 10^{-4}}{8.31 \times 393.15} = 0.0365 \text{ mol}$

The amount of gas is 0.0365 mol.

EXAM TIP

A set of units that also works for $PV = nRT$ is volume in dm^3 and pressure in kPa – if you use these units, you can avoid the problem of converting volumes into m^3.

TEST YOUR UNDERSTANDING

In all questions, take the value of the ideal gas constant as 8.31 $J K^{-1} mol^{-1}$.

8 What amount in mol of an ideal gas is present in a container if the gas occupies a volume of 0.0500 m^3 at a pressure of 1.00×10^5 Pa and a temperature of 300 K?

9 What amount in mol of an ideal gas is present in a container if the gas occupies a volume of 1.50 dm^3 at a pressure of 1.10×10^5 Pa and a temperature of 30.00 °C?

CONTINUED

10 Calculate the volume (in dm^3) occupied by 0.600 mol of an ideal gas at a temperature of 250 K and a pressure of 1.20×10^5 Pa.

11 What is the volume (in cm^3) occupied by 2.50×10^{-3} mol of an ideal gas at 98 kPa and 15.00 °C?

12 1.25×10^{-3} mol of an ideal gas occupies a volume of 128 cm^3 at a temperature of 25.00 °C. Calculate the pressure of the gas.

Molar volume of an ideal gas

Rearranging the ideal gas equation, we get $V = n \times \frac{RT}{P}$.

Therefore, we can deduce that, if the temperature and pressure are constant, the volume occupied by an ideal gas depends only on the number of particles present (the amount in mol) and not on the nature of the particles. Assuming that gases behave ideally, the volume occupied by one mole of *any* gas under a certain set of conditions will, therefore, always be the same. The volume occupied by one mole of a gas is called the **molar volume**.

When carrying out calculations involving gases, we often refer to a specific set of conditions and most commonly we use **standard temperature and pressure**, **STP**.

KEY POINT

STP = standard temperature and pressure:
273.15 K, 100 000 Pa (100 kPa, 1 bar)

molar volume of an ideal gas at STP
= 22.7 $dm^3 mol^{-1}$ or 2.27×10^{-2} $m^3 mol^{-1}$

EXAM TIP

You need to be careful with units – the volume must be in dm^3 if the molar volume is in $dm^3 mol^{-1}$.

Therefore, under the same set of conditions, the volume occupied by one mole of NH_3 is the same as the volume occupied by one mole of CO_2 and one mole of H_2, and this volume is 22.7 dm^3 at STP, assuming that each gas behaves ideally.

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Converting volumes of gases into number of moles

The relationship between the amount in mol of a gas and its volume at constant temperature and pressure is as follows:

$$\text{amount of substance in mol} = \frac{\text{volume}}{\text{molar volume}}$$

This is summarised in Figure 5.9.

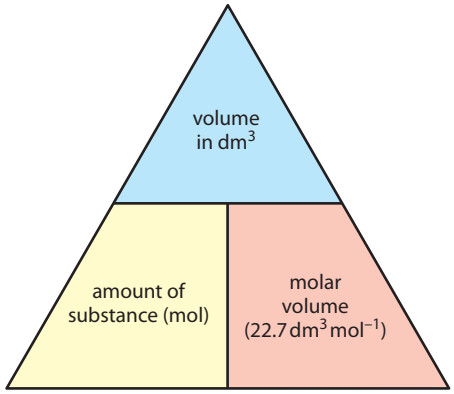

Figure 5.9: The relationship between the amount (number of moles) of a gas and its volume.

WORKED EXAMPLE 5.4

Calculate the amount in mol of 250 cm^3 of O_2 at STP.

Answer

$$\text{amount in mol} = \frac{\text{volume in dm}^3}{22.7}$$

The volume is in cm^3, so it must be converted into dm^3:

$$\frac{250}{1000} = 0.250 \text{ dm}^3$$

$$\text{amount in mol} = \frac{0.250}{22.7} = 0.0110 \text{ mol}$$

WORKED EXAMPLE 5.5

Calculate the volume of 0.135 mol CO_2 at STP.

Answer

$$\text{volume} = \text{amount in mol} \times 22.7 = 0.135 \times 22.7 = 3.06 \text{ dm}^3$$

TEST YOUR UNDERSTANDING

13 Determine the amount in mol present in each of the following at standard temperature and pressure (STP):

- **a** 0.240 dm^3 of N_2
- **b** 2.00 dm^3 of CH_4
- **c** 0.100 dm^3 of SO_2
- **d** 400.0 cm^3 of N_2
- **e** 250.0 cm^3 of CO_2.

14 Work out the volume of each of the following at standard temperature and pressure (STP):

- **a** 0.100 mol C_3H_8
- **b** 100.0 mol SO_3
- **c** 0.270 mol N_2.

The molar volume under other conditions

The value of the molar volume varies with temperature and pressure – you may have come across other values, e.g. 24 $dm^3\ mol^{-1}$ at room temperature and pressure (298.15 K and 1 atmosphere pressure), or 24.8 $dm^3\ mol^{-1}$ at 298.15 K and 100 kPa or 22.4 $dm^3\ mol^{-1}$, using the former definition of STP as 273.15 K and 1 atmosphere pressure (10 1325 Pa).

To work out the molar volume under other conditions, we must use the ideal gas equation.

WORKED EXAMPLE 5.6

What is the molar volume of an ideal gas at 18.00 °C and 1.10×10^5 Pa? (Give your answer in $m^3\ mol^{-1}$ and $dm^3\ mol^{-1}$.)

Answer

The molar volume of a gas is the volume occupied by one mole of the gas.

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CONTINUED

We will be using $PV = nRT$ and so need to ensure a consistent set of units:

$P = 1.10 \times 10^5$ Pa $n = 1.00$ mol

$T = 18.00$ °C $\Rightarrow 18.00 + 273.15 = 291.15$ K

$V = ?$

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

Rearranging $PV = nRT$ we get

$$V = \frac{nRT}{P} = \frac{1.00 \times 8.31 \times 291.15}{1.10 \times 10^5} = 0.0220 \text{ m}^3$$

The molar volume is 0.0220 m^3 mol^{-1} at 18.00 °C and 1.10×10^5 Pa.

This value must be multiplied by 1000 to convert it into dm^3 i.e., 22.0 dm^3 mol^{-1}.

At this point, it is always worth checking whether your answer looks sensible. In the previous section, we met the value for the molar volume of a gas at STP, which is 22.7 dm^3 mol^{-1}. The temperature and pressure here are not very different from STP – the increase in temperature would cause the molar volume to increase slightly and the increase in pressure would cause it to decrease slightly, so we would expect a value not very different from 22.7 dm^3 mol^{-1}, which is what we found.

TEST YOUR UNDERSTANDING

In all questions, take the value of the gas constant as 8.31 J K^{-1} mol^{-1}.

15 Calculate the molar volume of an ideal gas at a temperature of 25.00 °C and a pressure of 1.01×10^5 Pa.

16 Calculate the molar volume of an ideal gas at a temperature of 21.85 °C and a pressure of 9.97×10^5 Pa.

Mixtures of gases

Two of the assumptions of the ideal gas model are that the particles have no volume and there are no forces between particles. These assumptions mean that all gases behave the same in the ideal gas model and we can carry out calculations on mixtures of gases in exactly the same way as on individual gases.

WORKED EXAMPLE 5.7

Calculate the volume (in dm^3) occupied by a mixture of 8.00 g of oxygen and 16.00 g of nitrogen gas at 120 kPa and 280 K. Assume that the gases do not react with each other and behave ideally.

Answer

First, we must work out the amount in mol of each gas:

$$\text{amount in mol of oxygen} = \frac{\text{mass}}{\text{molar mass}} = \frac{8.00}{32.00} = 0.250 \text{ mol}$$

$$\text{amount in mol of nitrogen} = \frac{16.00}{28.02} = 0.571 \text{ mol}$$

Now we could work with each gas individually, calculating the volume occupied by each one and adding the volumes at the end to give the total volume, but it is much easier just to add up the number of moles and do the calculation once instead of twice.

total amount $= n = 0.250 + 0.571 = 0.821$ mol

All values must be converted into the appropriate set of units:

$P = 120$ kPa $\Rightarrow 1.20 \times 10^5$ Pa

$V = ?$

$n = 0.821$ mol

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

$T = 280$ K

$PV = nRT$

$1.20 \times 10^5 \times V = 0.821 \times 8.31 \times 280$

Rearranging the equation:

$$V = \frac{0.821 \times 8.31 \times 280}{1.20 \times 10^5} = 0.0159 \text{ m}^3$$

The volume comes out in units of m^3 since we are using pressure in Pa.

To convert m^3 into dm^3, we multiply by 1000:

volume in dm^3 $= 0.0159 \times 1000 = 15.9$ dm^3

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TEST YOUR UNDERSTANDING

In all questions, take the value of the gas constant as 8.31 J K^{-1} mol^{-1}.

17 Calculate the volume in dm^3 occupied by a mixture of 1.00 g of helium and 1.00 g of neon at 9.85 °C and a pressure of 103 kPa.

18 Calculate the volume in dm^3 occupied by a mixture of 2.20 g of hydrogen, 10.00 g of argon and 25.60 g of nitrogen at 19.85 °C and a pressure of 99 kPa.

Calculating the molar mass of a gas

WORKED EXAMPLE 5.8

0.143 g of an ideal gas occupies a volume of 220 cm^3 at 298 K and a pressure of 1.00×10^5 Pa. Calculate the molar mass of the gas.

Answer

$P = 1.00 \times 10^5$ Pa

$V = 220$ cm^3

This must be converted into m^3: $\frac{220}{10^6} = 2.20 \times 10^{-4}$ m^3

$n = ?$

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

$T = 298$ K

$PV = nRT$, which can be rearranged to $n = \frac{PV}{RT}$

$$n = \frac{1.00 \times 10^5 \times 2.20 \times 10^{-4}}{8.31 \times 298} = 8.88 \times 10^{-3} \text{ mol}$$

We saw in Chapter 4 that the relationship between the amount in mol (n) and the molar mass (M) was:

$$\text{amount in mol}(n) = \frac{\text{mass } (m)}{\text{molar mass } (M)}$$

We have been given the mass of the gas; therefore,

$$8.88 \times 10^{-3} = \frac{0.143}{M}$$

rearranging this, we get $M = 16.1$ g mol^{-1}

WORKED EXAMPLE 5.9

A gas has a density of 1.24 g dm^{-3} at 0.00 °C and 1.00×10^5 Pa. Calculate its molar mass.

Answer

This question looks a bit more difficult because we do not seem to have enough information (neither a mass nor a volume); however, we know the density is 1.24 g dm^{-3}, which means that the mass of 1 dm^3 of the gas is 1.24 g.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

If we can find the number of moles in 1 dm^3, we can work out the molar mass because we know the mass of 1 dm^3.

$P = 1.00 \times 10^5$ Pa

$V = 1.00$ dm^3, which must be converted into m^3:

$\frac{1.00}{1000} = 1.00 \times 10^{-3}$ m^3

$n = ?$

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

$T = 0.00$ °C, which must be converted into K:
$0.00 + 273.15 = 273.15$ K

Using $PV = nRT$ and rearranging:

$$n = \frac{1.00 \times 10^5 \times 1.00 \times 10^{-3}}{8.31 \times 273.15} = 0.0441 \text{ mol}$$

This number of moles has a mass of 1.24 g.

$$M = \frac{m}{n} = \frac{1.24}{0.0441} = 28.1 \text{ g mol}^{-1}$$

Therefore, the molar mass is 28.1 g mol^{-1}.

Experiment to determine the molar mass of a gas

The molar mass of a gas, such as that used for lighter refills, can be determined using the following procedure (Figure 5.10).

- Weigh a lighter gas refill canister.
- Release some gas into the measuring cylinder and record the volume of gas produced.
- Dry the gas canister and re-weigh.

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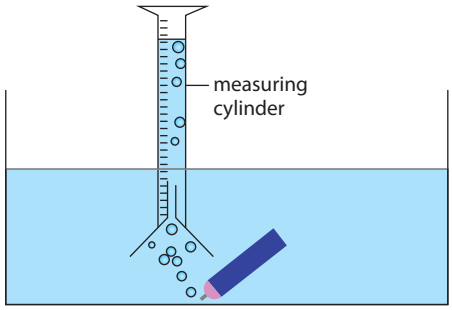

Figure 5.10: Determining the molar mass of the gas in a lighter refill canister.

Other measurements that must be made are the temperature of the gas (if the gas is left long enough, this can be assumed to be the same as room temperature) and the pressure (this can be assumed to be the same as the pressure in the laboratory). The results are shown in Table 5.1.

	Results
initial mass of canister / g	35.54
final mass of canister / g	35.12
initial reading on measuring cylinder / cm^3	12
final reading on measuring cylinder / cm^3	188
temperature / °C	19.00
pressure / Pa	9.98×10^4

Table 5.1: Experimental results.

Calculation:

$P = 9.98 \times 10^4$ Pa

$V = 188 - 12 = 176$ cm^3

This must be converted into m^3: $\frac{176}{1 \times 10^6} = 1.76 \times 10^{-4}$ m^3

$n = ?$

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

$T = 19.00$ °C $\Rightarrow$ 292.15 K

Assuming that the gas behaves ideally, we use $PV = nRT$ to determine the amount in mol of the gas:

$$n = \frac{9.98 \times 10^4 \times 1.76 \times 10^{-4}}{8.31 \times 292.15} = 7.23 \times 10^{-3} \text{ mol}$$

The mass of the gas is found by subtracting the final mass of the gas canister from the initial mass:

mass of gas (m) = 35.54 – 35.12 = 0.42 g

We, therefore, know that 7.24×10^{-3} mol of this gas has a mass of 0.42 g:

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

$$M = \frac{0.42}{7.23 \times 10^{-3}} = 58 \text{ g mol}^{-1}$$

Therefore, the molar mass is 58 g mol^{-1}.

We can only quote the answer to two significant figures because the mass of gas was given to two significant figures. A more precise answer could have been obtained by using a three decimal place electronic balance or by collecting a larger volume of gas.

Let's consider two possible sources of systematic error in this experiment. A systematic error is an error introduced into an experiment by the apparatus or the procedure. Systematic errors result in a loss of accuracy, i.e., the measured value is further away from the true value of a quantity.

If we rearrange the two equations that we have used, we can derive an overall equation for the molar mass (M) of the gas, which will allow us to predict the effects of systematic errors on the final value:

$$n = \frac{m}{M} \text{ and } n = \frac{PV}{RT}$$

$$M = \frac{mRT}{PV}$$

Some gas escaped – this means that the recorded volume was lower than expected. Dividing by a smaller value of V will give a value for M that is larger than 58 g mol^{-1}.

The canister was not dried completely after removing it from the water – there would be extra mass due to the water and, therefore, the mass of gas would appear to be smaller than the mass actually released from the canister. Multiplying by a smaller value of m would give a value of M that is smaller than 58 g mol^{-1}.

Can you think of any more systematic errors?

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TEST YOUR UNDERSTANDING

In all questions, take the value of the gas constant as 8.31 J K^{-1} mol^{-1}.

19 Calculate the molar mass of an ideal gas if 0.197 g of the gas occupies a volume of 1.58×10^{-4} m^3 at a pressure of 1.01×10^5 Pa and a temperature of 292 K.

20 Calculate the molar mass of an ideal gas if 0.586 g of the gas occupies a volume of 282 cm^3 at a pressure of 1.02×10^5 Pa and a temperature of –18.15 °C.

21 Calculate the molar mass of an ideal gas if 0.201 g of the gas occupies a volume of 1.75 dm^3 at a pressure of 9.88×10^4 Pa and a temperature of 39.85 °C. Suggest the identity of the gas.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the assumptions of the ideal gas model	5.1			
explain under what conditions a real gas is most different to an ideal gas	5.1			
describe the relationships between pressure, volume and temperature for an ideal gas	5.2			
carry out calculations using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	5.3			
carry out calculations involving the ideal gas equation	5.3			
convert between volumes and amount of substance using the molar volume of a gas.	5.3			

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REFLECTION

- There are qualitative and quantitative ideas in this chapter. How would you assess your understanding of these?
  - I understand the theory and am confident with the calculations.
  - I understand the theory but need more practise with the calculations.
  - I need to go through the theory again and practise the calculations.
- Do you think that you could explain the concept of an ideal gas to another student?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Unit 2

Bonding and structure

INTRODUCTION

Have you ever thought what chemistry is? How would you define it or explain to another student how it is different from other sciences? One way of looking at it is that chemistry is about chemical reactions. These chemical reactions involve atoms/ions/molecules interacting with each other and joining together in different ways. So, it could be argued that chemistry is about structure and bonding and how atoms combine to form the world around us, from the simplest diatomic molecules to DNA molecules containing millions of atoms.

A study of bonding allows us to understand the structures of molecules and how they interact with each other, but why do we do this? You may now be thinking about what chemistry is, but that is not the same as why you should study chemistry. One reason, of course, is just for the sake of it: it is fascinating – there is such variety within chemistry, and it is remarkable that we can use just a few basic principles to understand the structure and bonding in substances as widely different from each other as a lump of iron or a sample of DNA. Without simplifying things too much, you can explain quite a lot in chemistry just using the basic ideas that opposite charges attract and like charges repel.

Is the search for knowledge, however, a sufficient reason for studying a subject? Many people would argue that it is, but a great deal of research is also carried out for commercial reasons. Governments and companies pour large amounts of money into scientific research where the aim is to make discoveries that are of benefit to society (and to make a profit). Chemistry is fundamental in the drive to design new materials with highly desirable properties for specific uses. These new materials could be stronger and lighter than existing materials or they could have specific properties, such as superconductivity at room temperature or resistance to corrosion, but they could also result in unforeseen environmental problems.

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Chapter 6
The ionic model

LEARNING OBJECTIVES

In this chapter you will:

- understand the formation of anions and cations
- deduce the charges on ions from their position in the periodic table
- know the charges of commonly encountered ions
- deduce the formulas of ionic compounds
- understand ionic bonding
- describe the structure of ionic compounds
- explain the properties of ionic compounds in terms of structure and bonding
- discuss the connection between the lattice enthalpy and the strength of ionic bonding.

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GUIDING QUESTIONS

- What is ionic bonding?
- What are the characteristics of compounds with ionic bonding?

Introduction

There are many compounds with **ionic bonding** that we encounter in everyday life, for example, sodium hydrogencarbonate (baking soda) and calcium carbonate (chalk, marble, limestone), but easily the most familiar is sodium chloride, common salt. Salt (in moderation) is an essential part of our diet and pre-refrigeration it was useful in preserving food. It is hard to believe now, but salt was once a highly valued commodity and wars were even fought over it. Throughout history, salt has played a significant role in many economies, political systems and everyday life, and its importance persists in the names of many towns and cities, for example, Salzburg and Hallein in Austria, Marsala in Italy and Poza de la Sal in Spain, to name just a few. Words derived from salt include salad (from the Roman tendency to eat salted greens), salami, sausage, salacious, etc.

6.1 Ionic and covalent bonding

Compounds can be divided into two main classes according to the bonding in them – they are either ionic or covalent. The type of bonding present can usually be deduced by looking at the formula of the compound. *Covalent compounds* are those formed between two or more non-metallic elements, whereas *ionic compounds* are usually formed between a metallic element and a non-metallic one.

For example, NaCl is an ionic compound, but CH_4 is covalent. Some more ionic and covalent compounds are shown in Table 6.1.

Ionic	Covalent
MgO, KF, $NiCl_2$, CuO, Li_3N, FeS	H_2O, CCl_4, H_2S, PH_3, CO_2, N_2H_4

Table 6.1 Some ionic and covalent compounds.

There are some compounds for which the distinction is not so clear. For instance, ammonium chloride does not contain any metallic elements but has ionic bonding between the ammonium ions (NH_4^+) and the chloride ions (Cl^-). There is also covalent bonding within the NH_4^+ ion.

Generally, as a rough rule of thumb, elements that are close together in the periodic table form covalent compounds, but elements that are far apart in the periodic table form ionic compounds. Thus, elements from Groups 1 and 17 combine to form ionic compounds (CsF being the most ionic), but elements from Groups 14, 15, 16 and 17 combine to form covalent compounds.

6.2 Formation of ions

Positive and negative ions

Positive ions are usually formed by metallic elements by the loss of electrons from the highest main energy level – these are often called the *valence* or *outer-shell* electrons. A magnesium atom has two electrons in its highest main energy level (outer shell) and loses these two electrons to form a 2+ ion (Figure 6.1). The Mg^{2+} ion that is formed is **isoelectronic** (same number of electrons) with the noble gas atom neon.

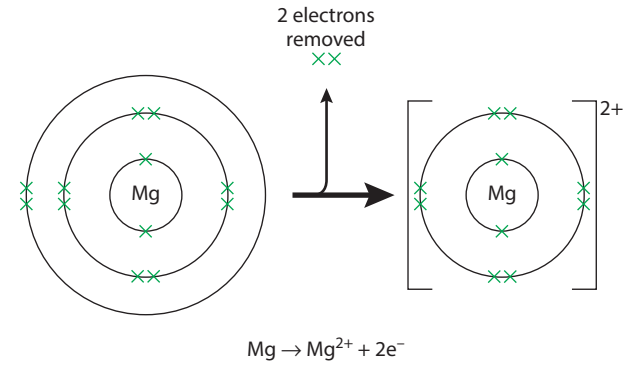

Figure 6.1: An Mg atom loses its two outer-shell electrons to form an Mg^{2+} ion. The equation here could have also be written as $Mg - 2e^- \rightarrow Mg^{2+}$, but we do not usually write equations with negative signs in chemistry.

KEY POINT

Positive ions are called *cations*.

Negative ions are usually formed by non-metallic elements by the gain of electrons. For example, an oxygen atom has six electrons in its highest main energy level and gains two electrons (Figure 6.2).

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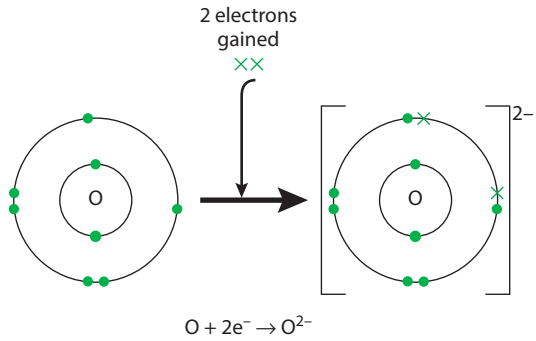

Figure 6.2: The O^{2-} ion is isoelectronic with an Ne atom.

KEY POINT

Negative ions are called *anions*.

The number of electrons lost/gained when ions are formed

The electron configuration of ions was discussed in Chapter 3.

KEY POINT

The number of electrons lost or gained is determined by the electron configuration of an atom.

The number of electrons lost by elements in Groups 1 and 2 when they form positive ions is given by the group number. For instance, sodium, in Group 1 of the periodic table, has one electron in its highest main energy level (outer shell) and, therefore, forms a 1+ ion; calcium is in Group 2, has 2 outer-shell electrons, and forms a 2+ ion. The electron configurations of some Group 1 atoms and their ions are shown in Table 6.2.

Atom	Full electron configuration	Ion	Full electron configuration
Li	$1s^2\ 2s^1$	Li^+	$1s^2$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	Na^+	$1s^2\ 2s^2\ 2p^6$
K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	K^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Table 6.2: Li, Na and K all have one outer-shell electron (red), which is lost when they form a 1+ ion.

The elements in Group 13 have three outer-shell electrons, which can be lost to form ions, so, for example, aluminium forms a 3+ ion. The number of electrons lost by elements in Group 13 is, therefore, given by the group number minus ten.

The number of electrons gained by elements in Groups 15 to 17 when they form negative ions is given by 18 minus the group number. For instance, fluorine, in Group 17 of the periodic table, has seven electrons in its highest main energy level (seven outer-shell electrons) and gains one electron (18 – 17 = 1) to form a 1– ion; sulfur is in Group 16, has six electrons in its highest main energy level (six outer-shell electrons) and gains two electrons to form a 2– ion. The electron configurations of some Group 17 atoms and their ions are shown in Table 6.3.

Atom	Full electron configuration	Ion	Full electron configuration
F	$1s^2\ 2s^2\ 2p^5$	F^-	$1s^2\ 2s^2\ 2p^6$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	Cl^-	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Br	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$	Br^-	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

Table 6.3: The electron configurations of some atoms and ions of Group 17 elements.

When elements in the main groups of the periodic table [Groups 1, 2, 13 (to a certain extent), 15, 16 and 17] form ions, electrons are gained or lost to produce the electron configuration of the nearest noble gas. That is, electrons are gained or lost to make an ion that is isoelectronic (same number of electrons) with the nearest noble gas. The electron configurations of some noble gas (Group 18) atoms are shown in Table 6.4.

Atom	Full electron configuration
He	$1s^2$
Ne	$1s^2\ 2s^2\ 2p^6$
Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Kr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

Table 6.4: The electron configurations of some noble gas (Group 18) atoms.

It can be seen that Li^+ is isoelectronic with He, the nearest noble gas atom, Na^+ is isoelectronic with Ne, and K^+ is isoelectronic with Ar. All the ions formed by the atoms in Group 17 are also isoelectronic with noble gas atoms.

For the first 20 elements, we can also say that electrons are lost or gained to achieve a full outer shell of electrons.

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Although these two points are true for the first 20 elements, there are many exceptions after that because of the presence of d and f sub-shells.

For example, Br^- ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$) is isoelectronic with a noble gas atom (Kr), but does not have a full outer shell of electrons, because the fourth shell is not full (the maximum number of electrons in the fourth shell is 32). Ga^{3+} ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$) has a full outer shell but is not isoelectronic with a noble gas atom.

Ions formed by transition metal atoms

KEY POINTS

The transition metals can form more than one ion. For instance, iron can form iron(II), Fe^{2+}, and iron(III), Fe^{3+}.

The ions formed by transition metals do not generally have noble gas electron configurations or full outer shells of electrons.

Remember that the 4s electrons are lost first when a transition metal atom forms an ion. The full electron configurations of Fe^{2+} and Fe^{3+} are shown in Table 6.6, and it can be seen that neither has a full outer shell of electrons nor is isoelectronic with a noble gas atom.

Atom	Full electron configuration	Ion	Full electron configuration
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	Fe^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
		Fe^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Table 6.6: The 4s electrons are lost before the 3d electrons when transition metal atoms form ions.

The formulas of ions

The formulas of commonly encountered positive ions are given in Table 6.7 and of some negative ions in Table 6.8.

Ion	Symbol
lithium	Li^+
sodium	Na^+
potassium	K^+
rubidium	Rb^+
caesium	Cs^+
silver	Ag^+
ammonium	NH_4^+
hydrogen	H^+
magnesium	Mg^{2+}
calcium	Ca^{2+}
barium	Ba^{2+}
iron(II)	Fe^{2+}
copper(II)	Cu^{2+}
zinc	Zn^{2+}
nickel(II)	Ni^{2+}
iron(III)	Fe^{3+}
aluminium	Al^{3+}

Table 6.7: Positive ions.

Ion	Symbol
fluoride	F^-
chloride	Cl^-
bromide	Br^-
iodide	I^-
hydroxide	OH^-
hydrogencarbonate	HCO_3^-
nitrate(V)	NO_3^-
oxide	O^{2-}
sulfide	S^{2-}
carbonate	CO_3^{2-}
sulfate(VI)	SO_4^{2-}
nitride	N^{3-}
phosphate(V)	PO_4^{3-}

Table 6.8: Negative ions. Ions such as NO_3^- are most properly named including the oxidation state [i.e. nitrate(V)] but this is often omitted.

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The formulas of some ions can be worked out from the periodic table, as discussed previously, but others have to be learned. When there is a number in Roman numerals after the name of a positive ion, this is the *oxidation state* of the metal ion and indicates the charge on the ion, so iron(II) is Fe^{2+} and iron(III) is Fe^{3+}. The Roman numerals in the names of the negative ions do not help in the same way, and these are probably best ignored until Chapter 10.

6.3 The formation of ionic compounds

Transfer of electrons

KEY POINT

When an ionic compound is formed, electrons are transferred from one atom (the metal atom) to another (the non-metal atom) to form positive and negative ions.

Electrons cannot be created or destroyed; therefore, the total number of electrons lost must always equal the total number gained. In Figure 6.3, you can see that a magnesium atom loses its two outer-shell electrons to form a 2+ ion and an oxygen atom is able to gain both of them to form a 2– ion.

A magnesium atom, therefore, combines with an oxygen atom in a 1:1 ratio to form the ionic compound MgO. In the formation of magnesium fluoride

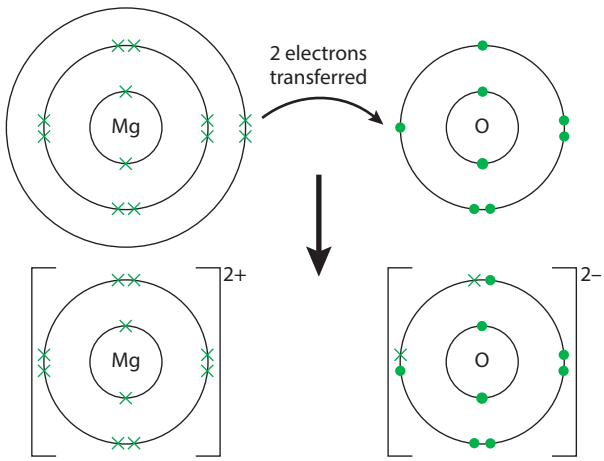

Figure 6.3: Electron transfer in ionic bonding.

(Figure 6.4), one magnesium atom must combine with two fluorine atoms, because magnesium loses two electrons when it forms an ion but each fluorine atom can gain only one electron. So, the formula of magnesium fluoride is MgF_2.

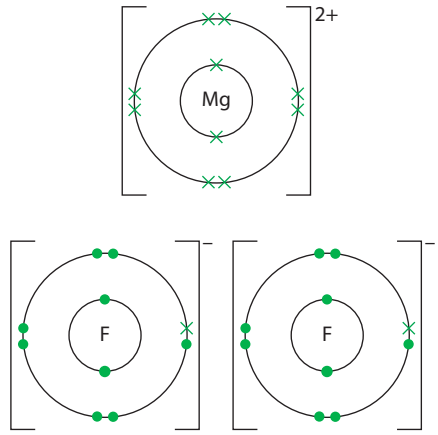

Figure 6.4: The ions in magnesium fluoride.

Link

It takes the input of over 2000 kJ mol^{-1} of energy (ionisation energy) to remove two electrons from a magnesium atom to form an Mg^{2+} ion but only about 650 kJ mol^{-1} is released when 2 F^- ions are formed, so why do ionic compounds such as this form? See Chapter 13 for a discussion of the energy terms involved in the formation of ionic compounds.

Naming ionic compounds

Ionic compounds are named with the cation (usually a metal) first followed by the name of the anion. The name of the anion (negative ion) is different from the name of the element that it is derived from; for example, oxygen forms an *oxide* ion, fluorine forms a *fluoride* ion and sulfur forms a *sulfide* ion.

Take care with the difference between sulfate (SO_4^{2-}) and sulfide (S^{2-}) and between nitrate (NO_3^-) and nitride (N^{3-}). The ending '-ate' usually indicates the presence of oxygen.

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Working out the formulas of ionic compounds

One approach to working out the formulas of ionic compounds, is to look at the numbers of electrons lost when a positive ion forms, and the number of electrons gained when a negative ion forms, and match these up.

Alternatively, we use the fact that the overall charge on the compound is zero, and so the total charge of the positive ions must be cancelled out by the total charge of the negative ions.

WORKED EXAMPLE 6.1

Deduce the formula of aluminium fluoride.

Answer

We need to consider the number of electrons lost by aluminium and gained by fluorine.

Aluminium is in Group 13 of the periodic table, and so, forms a 3+ ion by the loss of three electrons, whereas fluorine, in Group 17, gains one electron to generate a 1– ion. The three electrons transferred from the aluminium must be gained by three separate fluorine atoms; therefore, the formula of aluminium fluoride is AlF_3.

Alternatively: the overall charge on the compound is zero, so the 3+ charge on the Al^{3+} ion must be cancelled out by the $3 \times 1-$ charge on $3F^-$ ions, i.e. $Al^{3+}(F^-)_3$.

WORKED EXAMPLE 6.2

Deduce the formula of sodium oxide.

Answer

Each sodium atom loses one electron to form a 1+ ion, but an oxygen atom gains two electrons to form a 2– ion; therefore, two sodium atoms combine with one oxygen atom and the formula is Na_2O. Alternatively: the formula of the ions formed by sodium and oxygen are Na^+ and O^{2-}; therefore, two Na^+ ions must combine with one O^{2-} ion to cancel out the charges.

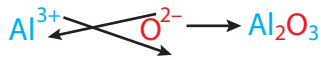
WORKED EXAMPLE 6.3

Deduce the formula of magnesium hydroxide.

Answer

When we are dealing with polyatomic (containing more than one atom) ions, we just use the method with the charges. The charges on the ions are: Mg^{2+} and OH^-. The 2+ charge on the Mg^{2+} ion is cancelled out by the $2 \times 1-$ charge on two OH^- ions; therefore, the formula is $Mg(OH)_2$. The brackets around OH are essential because, otherwise, the formula would read $MgOH_2$, which would indicate the presence of only one oxygen atom.

A shortcut to working out formulas is to switch over the charges on the ions, for example:



You would, only, however, do this when the charges on the positive and negative ions are not the same, so, for example, calcium oxide does not have the formula Ca_2O_2.

The formulas of some other ionic compounds are shown in Table 6.9.

Name	Positive ion	Negative ion	Formula
sodium sulfate	Na^+	SO_4^{2-}	Na_2SO_4
lithium carbonate	Li^+	CO_3^{2-}	Li_2CO_3
iron(II) sulfate	Fe^{2+}	SO_4^{2-}	$FeSO_4$
iron(II) sulfide	Fe^{2+}	S^{2-}	FeS
iron(III) nitrate	Fe^{3+}	NO_3^-	$Fe(NO_3)_3$
magnesium nitride	Mg^{2+}	N^{3-}	Mg_3N_2
ammonium sulfate	NH_4^+	SO_4^{2-}	$(NH_4)_2SO_4$

Table 6.9: The formulas of some ionic compounds.

TEST YOUR UNDERSTANDING

1 State whether the following compounds have ionic or covalent bonding:

a LiF **b** CF_4

c CaO **d** NH_3

e PCl_3 **f** $CuCl_2$.

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CONTINUED

2 Write the formulas of the following compounds:

- **a** potassium chloride
- **b** barium sulfate
- **c** calcium hydroxide
- **d** sodium hydrogencarbonate
- **e** strontium sulfide
- **f** magnesium nitrate
- **g** lithium nitride
- **h** magnesium phosphate
- **i** magnesium fluoride
- **j** potassium sulfate
- **k** ammonium carbonate
- **l** silver sulfide
- **m** silver nitrate
- **n** ammonium chloride
- **o** copper(II) nitrate
- **p** rubidium carbonate.

SCIENCE IN CONTEXT

Cement is made by heating limestone, which is mostly calcium carbonate ($CaCO_3$) with clay/shale [mainly silica (SiO_2) and alumina (Al_2O_3)] and various other substances. During the process, the mixture is heated so that calcium carbonate decomposes to form calcium oxide (lime):

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Calcium oxide then combines with the other material present to form substances such as tricalcium silicate ($3CaO \cdot SiO_2$). When cement is mixed with water, sand and gravel, it produces concrete, the most-used material in the world (Figure 6.5). The global cement and concrete industry is worth over $600 billion (USD), but it is estimated that it could produce up to 8% of the annual global CO_2 emissions, and so contributes significantly to climate change. The main contributions to the emission of carbon dioxide come from the high temperature required (therefore, lots of energy needed) for the production of cement and CO_2 produced when limestone decomposes.

6.4 Ionic bonding and the structure of ionic compounds

A crystal of sodium chloride consists of a three-dimensional lattice of Na^+ and Cl^- ions (Figure 6.6).

A **lattice** has a regular repeating pattern. Each Na^+ ion is surrounded by six Cl^- ions and vice versa. All the Na^+ ions in the crystal attract all the Cl^- ions and vice versa – it is these electrostatic attractions between oppositely charged ions that hold the crystal together.

KEY POINT

Ionic bonding is the electrostatic attraction between oppositely charged ions.

Electrostatic attraction just means that positive charges attract negative charges and vice versa.

Substances are described as having either a **giant structure** or a *molecular structure*. Ionic compounds have a giant structure – there are no individual molecules of sodium chloride – all the positive ions attract all the negative ions, so the bonding extends fairly uniformly

SCIENCE IN CONTEXT

Figure 6.5: Concrete is everywhere, but what is the environmental impact?

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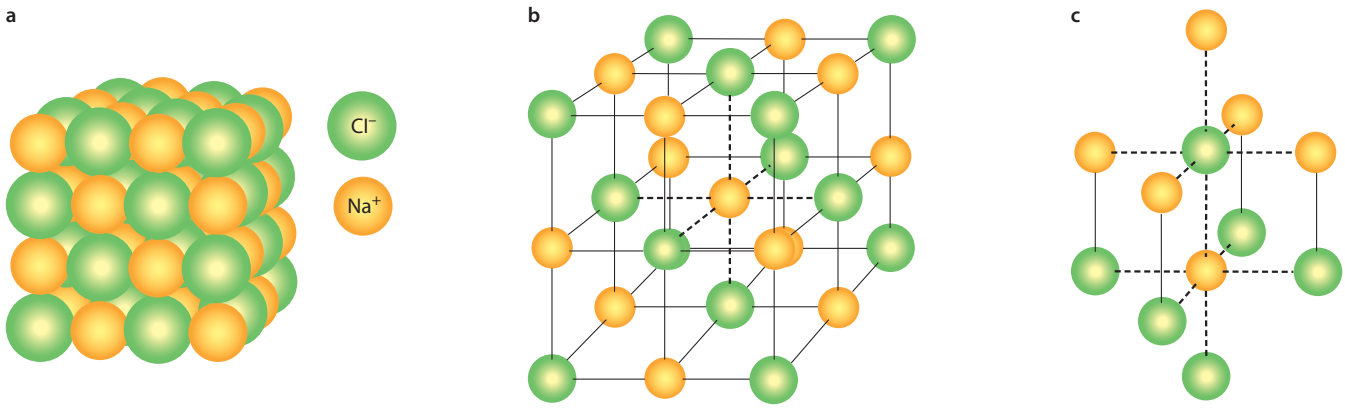

Figure 6.6: a A space-filling diagram of the NaCl lattice. The lattice keeps on going in three dimensions – only a tiny part of the structure is shown. **b** An expanded view of the NaCl lattice. **c** Each Na^+ ion is surrounded by six Cl^- ions in an octahedral array and vice versa. The **coordination number** (number of nearest neighbours) of each ion is six.

throughout the whole structure. Most covalent compounds (Chapter 7) consist of individual molecules and have molecular structures.

It is usually better to avoid the term 'ionic bond' and talk about 'ionic bonding' as a whole – the lines in Figure 6.6b and 6.6c are not ionic bonds, they are simply there to give a better idea of the shape. Ionic bonding (electrostatic attractions between oppositely charged ions) extends throughout the whole structure in all directions – all the positive ions in the structure attract all the negative ions – there are no individual ionic bonds.

THEORY OF KNOWLEDGE

It states on the IB syllabus that ionic compounds exist as three-dimensional lattice structures, represented by empirical formulas. Let us look at evaluating the second part of this statement. It is always difficult in science to make statements like this because you have to think whether it is true in every situation. If we look at all the formulas of ionic compounds mentioned so far, e.g., NaCl, $CuCl_2$ and $Mg(NO_3)_2$, they are all empirical formulas – they show the simplest whole number ratio of atoms present in the compound – but is this always true? If we can find one exception, does this make the statement false? Examples of exceptions are sodium ethanedioate ($Na_2C_2O_4$), which contains the ethanedioate ion, $C_2O_4^{2-}$; and sodium peroxide, Na_2O_2, which contains the peroxide ion (O_2^{2-})… there are others!

6.5 Physical properties of ionic compounds

Remember: examples of physical properties are melting point, solubility, electrical conductivity, etc. Chemical properties are how a substance reacts.

Melting points and boiling points

KEY POINT

Ionic compounds usually have high melting points and boiling points and are, therefore, usually solids at room temperature.

For instance, sodium chloride has a melting point of 801 °C and a boiling point of over 1400 °C, while magnesium oxide has a melting point of over 2800 °C and a boiling point of about 3600 °C.

The high melting and boiling points of ionic solids are due to the fact that the electrostatic forces between the oppositely charged ions are strong. When an ionic solid is melted, the electrostatic forces throughout the giant lattice must be (partially) overcome and, because these are so strong, a lot of energy is required.

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Magnesium oxide has a much higher melting point than sodium chloride because the electrostatic attractions between the 2+ and 2– ions in the magnesium oxide lattice are much stronger than those between the 1+ and 1– ions in sodium chloride. A higher temperature is required to provide sufficient energy to separate the ions in magnesium oxide.

Not all ionic compounds have high melting points and there are some ionic compounds, such as ethylammonium nitrate, that are liquids at room temperature. These *ionic liquids* are finding important uses as solvents.

Volatility

Volatility refers to how readily a substance turns into a gas. Ionic compounds have low volatility – they do not turn into a gas easily. The volatility of ionic substances is low because the electrostatic forces between the ions are strong and, therefore, require a lot of energy to overcome.

Solubility in water

KEY POINT

Ionic substances are often soluble in water.

When ionic substances dissolve, they are present in solution as individual ions, and so, the lattice structure has to be broken apart. A lot of energy is required to break apart the lattice structure because of the strong electrostatic forces of attraction between the oppositely charged ions. Water is, however, a *polar solvent* and energy is released when the ions are hydrated by being surrounded (ion–dipole attractions) by water molecules (Figure 6.7). This energy pays back the energy required to break apart the ionic lattice.

Link

See Chapter 7 for a discussion of polar molecules.

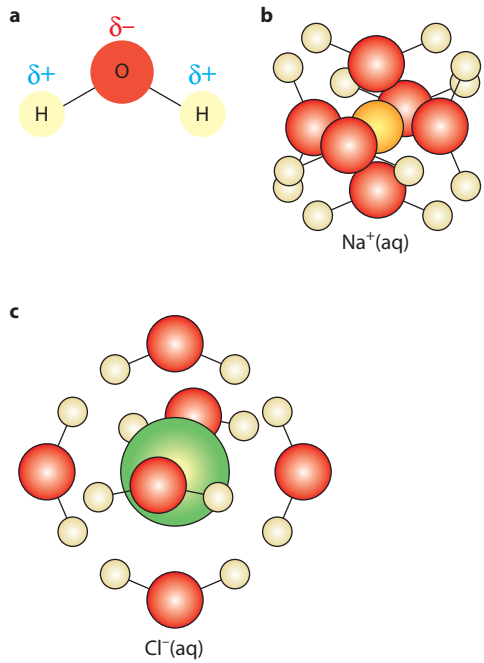

Figure 6.7: a A water molecule is polar. **b** A hydrated sodium ion. **c** A hydrated chloride ion.

It is important to remember that not all ionic compounds are soluble in water and, for example, most carbonates (e.g. calcium carbonate), most oxides [e.g. copper(II) oxide], most hydroxides [e.g. iron(II) hydroxide], most silver salts (except silver nitrate and silver fluoride) and most lead(II) salts [except lead(II) nitrate and lead(II) ethanoate] are essentially insoluble in water.

Solubility in non-polar solvents

KEY POINT

Ionic solids are not usually soluble in non-polar solvents, such as hexane.

Only very weak forces would be formed between Na^+ and Cl^- ions and the molecules of a non-polar solvent. A great deal of energy is required to break apart the ionic lattice, and this would not be paid back by the small amount of energy released when the non-polar solvent forms interactions with the ions.

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Electrical conductivity of ionic compounds

Electricity is a flow of charged particles. These charged particles can be either electrons or ions. A substance conducts electricity if the charged particles are free to move.

KEY POINT

Ionic substances do not conduct electricity when solid.

In the solid state, the ions are held tightly in position in the lattice structure so that they are not free to move around (other than vibrate).

KEY POINT

Ionic substances conduct electricity when molten (in the liquid state).

When an ionic substance is melted, the forces between the ions are partially overcome and the ions are able to move freely throughout the liquid.

KEY POINT

Ionic substances conduct electricity when dissolved in water.

This is because the ions are now separate from each other and free to move around (Figure 6.8). Positive ions can move towards a negative electrode and negative ions move towards a positive electrode, so allowing the conduction of electricity.

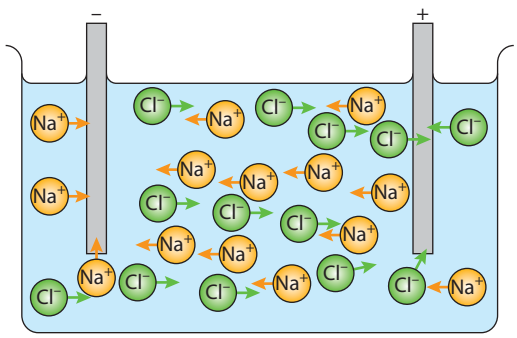

Figure 6.8: Ions move towards the oppositely charged electrode.

EXAM TIP

It is important to be clear that *ions* are moving, not electrons, when an ionic substance conducts electricity.

NATURE OF SCIENCE

Scientists use models to explain and predict the properties of substances. We can use our model of the bonding in ionic compounds to explain their properties, for instance, the fact that they have high melting points, conduct electricity when molten, etc.

Our model for bonding in ionic substances predicts that all ionic substances have a common set of properties. Therefore, we can predict the properties of any new ionic compound and use experimental observations to test the model.

6.6 Lattice enthalpy and strength of ionic bonding

Enthalpy changes will be discussed in more detail in Chapters 12 and 13. For the treatment here, enthalpy and energy can be regarded as the same thing.
The **lattice enthalpy** represents the energy required to break apart 1 mol of an ionic solid into its constituent gaseous ions (it will be defined fully in Chapter 13).

For example, for NaCl, it is for the following process:

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

The energy required to break apart 1 mol NaCl(s) into gaseous ions is 771 kJ mol^{-1}.

For ammonium nitrate, the equation is

$NH_4NO_3(s) \rightarrow NH_4^+(g) + NO_3^-(g)$

The 'constituent ions' for ammonium nitrate are the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-) and not, for instance, the N^{3-} and O^{2-} ions.

Energy has to be supplied to break apart the lattice because of the electrostatic attractions between oppositely charged ions, and so, the value of the lattice

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Substance	Lattice enthalpy / kJ mol^{-1}	Melting point / °C
NaCl	+771	801
MgO	+3791	2852
KCl	+711	770
CaO	+3401	2614
CsCl	+645	646
BaO	+3054	1918

Table 6.10: The lattice enthalpies and melting points of some substances. The positive value for the lattice enthalpy indicates that the process of breaking apart the lattice is endothermic: energy must be supplied to break apart the lattice.

	NaCl		$MgCl_2$		MgO	
lattice enthalpy / kJ mol^{-1}	+771		+2526		+3791	
charges on ions	1+	1–	2+	1–	2+	2–
radius of metal ion / pm	95		65		65	
	CsCl		$BaCl_2$		BaO	
lattice enthalpy / kJ mol^{-1}	+645		+2056		+3054	
charges on ions	1–	2+	2+	1–	2+	2–
radius of metal ion / pm	169		135		135	

Table 6.11: The lattice enthalpy depends on the charge and size of the ions. 1 pm ≡ 1 × 10^{-12} m.

enthalpy can be regarded as a guide to the strength of ionic bonding. The greater the electrostatic attraction between the ions, the more energy has to be supplied to break the lattice apart.

Because the melting point of an ionic substance also depends on the force of attraction between ions, a substance with a high lattice enthalpy would also be expected to have a high melting point (Table 6.10).

The effect of charge and size on lattice enthalpies

Some lattice enthalpies are shown in Table 6.11.

KEY POINT

The strength of the electrostatic attraction between ions depends on the charge on the ions and the size of the ions (ionic radii).

The effect of charge

KEY POINT

The higher the charges on the ions, the more strongly they will attract each other and, therefore, the greater the lattice enthalpy.

The force between ions is proportional to the product of the charges, so the force of attraction increases along the series: 1+/1– < 1+/2– < 2+/2–.

$MgCl_2$ has a higher lattice enthalpy than NaCl (Figure 6.9).

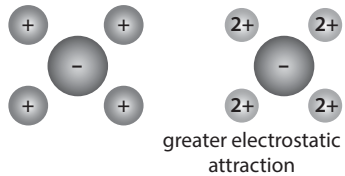

Figure 6.9: NaCl contains 1+ and 1– ions, whereas $MgCl_2$ contains 2+ and 1– ions. There is a stronger electrostatic attraction between 2+ and 1– ions than between 1+ and 1– ions, therefore more energy is required to break apart the lattice in $MgCl_2$.

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The effect of size

KEY POINT

The larger the ions, the weaker the forces of attraction between them and the smaller the lattice enthalpy (everything else being equal).

The larger the ions (bigger ionic radii), the greater the distance between the centres of the ions (an ion acts essentially like a point charge at its centre) and, therefore, the weaker the electrostatic attraction between the ions and the smaller the lattice enthalpy (Figure 6.10).

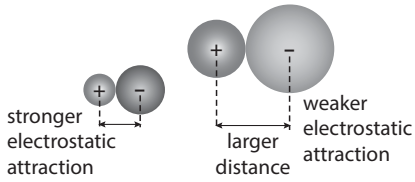

Figure 6.10: Smaller ions have a greater attraction between them.

The Cs^+ ion is larger than the Na^+ ion; therefore, CsCl has a smaller lattice enthalpy than NaCl – there is a weaker attraction between the ions in CsCl.

$MgCl_2$, therefore, has a larger lattice enthalpy than NaCl, not just because the Mg^{2+} ion has a higher charge than the Na^+ ion, but also because the Mg^{2+} ion is smaller. Some people talk about the **charge density** of an ion, which is the charge on the ion divided by its volume. Smaller/more highly charged ions have a higher charge density than larger/less highly charged ions. Mg^{2+} therefore has a higher charge density than Na^+.

Link

The connection between melting point and lattice energy is, not straightforward and NaCl has a higher melting point than $MgCl_2$, because of more covalent character in the bonding in $MgCl_2$ due to the higher charge density. It gets even more complicated with $AlCl_3$, which has a significantly lower melting point than both of them and changes structure to a covalent molecular one as it melts.

WORKED EXAMPLE 6.4

Arrange the following compounds in order of increasing lattice enthalpy: $BaCl_2$, LiF, MgS, KCl.

Answer

As a general rule, the effect of changes in the charge on the ions will be larger than variations in the radii of ions. MgS contains 2+ and 2– ions, $BaCl_2$ contains 2+ and 1– ions, and LiF and KCl both contain 1+ and 1– ions. The attraction between 2+/2– ions in MgS is greater than that between 2+/1– ions in $BaCl_2$, which is greater than that between 1+/1– ions in LiF/KCl. In terms of charges, then the order of increasing lattice enthalpy is as follows:

$KCl/LiF < BaCl_2 < MgS$

To decide whether LiF or KCl has a higher lattice enthalpy, we have to look at the variation in the sizes of the ions down Group 1 and Group 17. Down any group in the periodic table, the atoms get bigger (there are more shells of electrons), and this also means that the ions get larger. Therefore, K^+ is larger than Li^+ and Cl^- is larger than F^-. The greater the distance between the centres of ions, the weaker the attraction; therefore, KCl will have a lower lattice enthalpy than LiF and the overall order is as follows:

$KCl < LiF < BaCl_2 < MgS$

EXAM TIP

The largest lattice enthalpy is obtained for small, highly charged ions – ions with greatest charge density. When comparing different compounds, the effect of charge will be a more important factor than size variations.

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TEST YOUR UNDERSTANDING

3 State whether each of the following statements is TRUE or FALSE.

- **a** Ionic compounds are usually solids at room temperature.
- **b** Ionic compounds conduct electricity when solid.
- **c** Ionic compounds conduct electricity when molten because electrons are free to move.
- **d** Calcium fluoride has a higher melting point than potassium fluoride.
- **e** Sodium chloride is soluble in hexane (C_6H_{14}).

4 Arrange the following in order of increasing lattice enthalpy (smallest first):

LiF, KCl, CaO, CaS, $CaCl_2$.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
understand the formation of anions and cations	6.1			
deduce the charges on ions from their position in the periodic table	6.2			
recall the charges of commonly encountered ions	6.2			
deduce the formulas of ionic compounds	6.3			
explain ionic bonding	6.4			
describe the structure of ionic compounds	6.5			
explain the properties of ionic compounds in terms of structure and bonding	6.5, 6.6			
discuss the connection between the lattice enthalpy and the strength of ionic bonding.	6.6			

REFLECTION

- To what extent do you feel that your progress in this chapter has been limited because you need to learn the charges on ions?
- Do you feel that your understanding of this chapter would be enhanced if you read through it again after looking at Chapter 7, which deals with covalent bonding?
- Do you think that you could explain ionic bonding to another student?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 7

The covalent model

LEARNING OBJECTIVES

In this chapter you will:

- explain the term 'covalent bond'
- explain the relationship between bond strength and length for multiple bonds
- explain what a coordination bond is
- deduce Lewis formulas (structures) for covalent molecules
- understand what is meant by the 'octet rule'
- deduce the shapes of molecules/ions with up to four electron domains
- understand what makes a molecule polar
- describe and explain the bonding and structure of substances with covalent network structures
- explain the formation of intermolecular forces
- explain the influence of intermolecular forces on the melting/boiling point of covalent substances
- explain the physical properties of covalent substances
- explain how mixtures can be separated using paper chromatography and thin-layer chromatography

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CONTINUED

- explain resonance and delocalisation of electrons
- deduce Lewis formulas and shapes for molecules and ions with expanded octets of electrons
- use formal charge to distinguish between possible Lewis formulas
- explain the formation of σ and π bonds
- explain hybridisation
- describe and explain the structure of benzene.

GUIDING QUESTIONS

- What is covalent bonding?
- How can the structures, shapes and characteristics of covalent molecules be predicted?
- How does the structure of covalent substances influence the properties?

Introduction

There are many, many, more covalent compounds than ionic compounds. These range from the simplest covalent molecule, H_2, to the complex molecules that carry our genetic information. Many of the substances that we are familiar with from everyday life have covalent bonding – water, oxygen, nitrogen, carbon dioxide, ethanol (alcohol), paracetamol, caffeine… the list is endless.

7.1 Covalent bonds

KEY POINT

Covalent bonding occurs when atoms share electrons.

The simplest covalent molecule is hydrogen, H_2. A hydrogen atom has one electron in its outer shell, and a **covalent bond** is formed when it shares this electron with another hydrogen atom in an H_2 molecule (Figure 7.1).

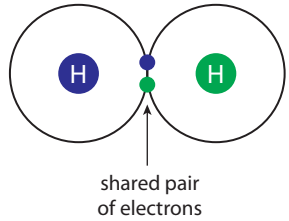

Figure 7.1: A covalent bond is a shared pair of electrons.

The electrons are shown in different colours to illustrate the fact that they come from different atoms, but all electrons are identical.

We often show a covalent bond as a line between atoms, for example, in H_2 (Figure 7.2).

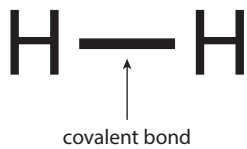

Figure 7.2: A covalent bond between two H atoms.

What holds the atoms together in a covalent bond?

KEY POINT

A covalent bond is the electrostatic interaction between the positively charged nuclei of both atoms and the shared pair of electrons.

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The electrons are negatively charged and because the shared electrons are attracted to the nuclei (positively charged) of *both* atoms simultaneously, this holds the atoms together (Figure 7.3).

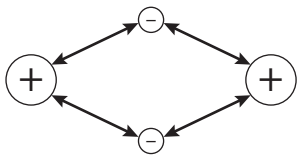

Figure 7.3: The positively charged nuclei attract the negatively charged electrons in the bond.

INTERNATIONAL MINDEDNESS

Probably the most common and familiar covalent compound is water (H_2O). The human body is made up of about 60% water and recommendations for drinking water usually advise about 2 – 3 litres per day. Bottled water is a very common way of consuming water, and the global bottled water market is worth about $300 billion (USD) annually, but there has been increasing controversy in recent years about the consumption of bottled water and its effect on the environment, both in terms of the use and disposal of plastic bottles but also the carbon footprint of transporting water around the world. Some estimates suggest that one million plastic bottles (not just containing water) are sold globally every minute, with most of these not being recycled.

Lewis formulas

Lewis formulas are diagrams showing all the valence (outer-shell) electrons in a molecule (or ion). Lewis formulas are also called Lewis structures or electron dot structures (or dot and cross diagrams).

The covalent bonding in a molecule of methane (CH_4) is shown in Figure 7.4. A carbon atom has four electrons in its outer shell (highest occupied energy level), and it shares these electrons with four separate hydrogen atoms to form four covalent bonds.

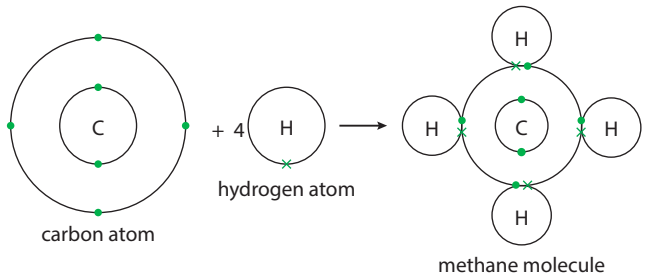

Figure 7.4: The covalent bonding in CH_4.

Various ways of showing the Lewis formula for methane are given in Figure 7.5.

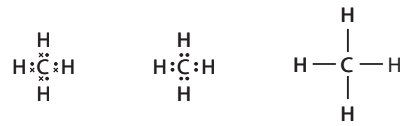

Figure 7.5: Three different types of Lewis formulas for methane.

In the first structure, the electrons from H are shown as a cross and those from C as a dot. In the last structure, all pairs of electrons are shown as lines. When you are still learning Lewis formulas, it is probably better to stick to the first way of drawing them and then only move on to the structures with the lines when you are more confident.

The octet rule

How do we know how many electrons are shared when atoms combine to form covalent molecules? The **octet rule** can help here.

KEY POINT

Octet rule: electrons will be shared so that the central atom has eight electrons in its outer (valence) shell.

This rule holds for the majority of molecules/ions where the central atom is from Period 2 (Li – Ne). There are no molecules/ions where the central atom is from Period 2 and has more than eight electrons in its outer shell, but

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there are some where it has fewer than eight electrons (these will be discussed below or in the next section). For a Period 2 atom, the octet of electrons corresponds to the outer shell being full – the maximum number of electrons in the second main energy level is eight.

The octet rule also holds for many molecules/ions when the central atom is from Period 3 or below – exceptions to the octet rule will be discussed in the Higher Level section.

Consider the bonding in water (H_2O) – an oxygen atom has six electrons in its outer shell, and so will share two electrons to generate an octet of electrons (full outer shell). A hydrogen atom will always just form one covalent bond – it shares one electron to have a full outer shell (the first main energy level can take a maximum of two electrons). The formation of a water molecule is shown in Figure 7.6 and Lewis formulas are in Figure 7.7.

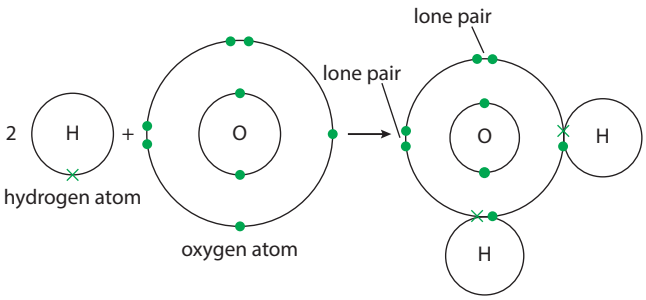


Figure 7.6: The formation of a water molecule.

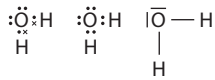


Figure 7.7: Lewis formulas for water. In the third one, the pairs of electrons are represented by lines.

A **lone pair of electrons** (often just 'lone pair') is a pair of electrons in the outer shell of an atom in a molecule that is not involved in covalent bonding. There are two lone pairs of electrons on the oxygen atom in a water molecule. These are shown in Figures 7.6 and 7.7.

Molecules where the central atom does not have a complete octet

It is not always the case that the formation of covalent bonds results in each atom attaining an octet of electrons. In BF_3 (Figure 7.8a), boron has only six electrons in its outer shell. This is because a boron atom has only three electrons in its outer shell and can, therefore, share a maximum of three electrons. Similarly, in gaseous $BeCl_2$, the beryllium atom only has a total of four electrons in its outer shell (Figure 7.8b).

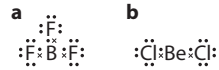


Figure 7.8: Lewis formulas of **a** BF_3 and **b** $BeCl_2$.

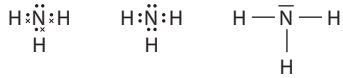
WORKED EXAMPLE 7.1

Deduce the molecular formula and the Lewis formula for the simplest compound formed between nitrogen and hydrogen and state how many lone pairs of electrons are in the molecule.

Answer

A nitrogen atom has the electron configuration $1s^2\ 2s^2\ 2p^3$, so there are five electrons in the outer shell. To attain a complete octet, a nitrogen atom must share three electrons. An H atom has one electron in its outer shell and, therefore, will share one electron to gain a full outer shell. This means that a nitrogen atom will combine with three hydrogen atoms, and the molecular formula of the simplest compound formed will be NH_3.

Three different versions of the Lewis formula are:



All three are correct Lewis formulas for NH_3 and any one of them will score full marks in the examination. There is one pair of electrons not involved in covalent bonding in the outer shell of the nitrogen atom, so there is one lone pair of electrons in the molecule.

Multiple covalent bonds

It is possible for more than one pair of electrons to be shared between two atoms. A double covalent bond results from the sharing of two pairs of electrons, and a triple bond arises when three pairs of electrons are shared.

O_2

Oxygen is in Group 16 of the periodic table and, therefore, an oxygen atom has six electrons in its outer shell. An oxygen atom must, therefore, share two electrons to complete its octet. In O_2, each oxygen shares

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two electrons with the other oxygen atom, and so, there are two shared pairs of electrons – a double bond – between the oxygen atoms. Various Lewis formulas for O_2 are shown in Figure 7.9.

Figure 7.9: Lewis formulas for O_2. Any one of these is an acceptable way of representing the Lewis formula.

N_2

Nitrogen is in Group 15, and so, has five electrons in its outer shell. A nitrogen atom will, therefore, share three electrons to generate a complete octet, so six electrons are shared when two nitrogen atoms combine to form N_2. Three shared pairs of electrons between two atoms form a triple bond (Figure 7.10).

Figure 7.10: Lewis formulas for N_2.

More examples of molecules with multiple bonding are shown in Figure 7.11.

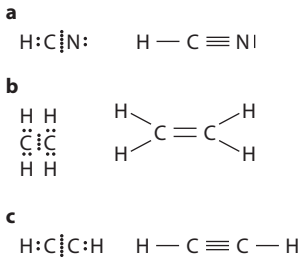


Figure 7.11: Lewis formulas for **a** HCN, **b** C_2H_4 (ethene) and **c** C_2H_2 (ethyne).

The strength and length of single, double and triple bonds

We can quantify the strength of a covalent bond using the *bond energy*. The bond energy is the energy required to break a covalent bond. A more detailed definition is given in Chapter 13.

The length of a covalent bond is called the *bond length*. More precisely, the bond length is the distance between the nuclei of the atoms making up a covalent bond.

Bond	Bond length / pm	Bond energy / kJ mol^{-1}
C—C	154	346
C=C	134	614
C≡C	120	839
C—O	143	358
C=O	122	804
C≡O	113	1077

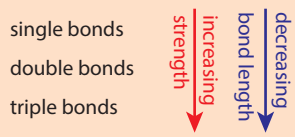
Table 7.1: The relationship between number of bonds and bond length/strength. 1 pm is 10^{-12} m.

As can be seen from Table 7.1, when comparing the same pair of atoms bonded together, triple bonds are stronger (higher bond energy) than double bonds, which are stronger than a single bond.

This is because the attraction of the two nuclei for three electron pairs (six electrons) in a triple bond is greater than the attraction for two electron pairs (four electrons) in a double bond, which is greater than the attraction for one electron pair (two electrons) in a single bond (Figure 7.12).

It can also be seen in Table 7.1 that, when we consider bonds between the same types of atoms, triple bonds are shorter than double bonds, which are shorter than single bonds. This is, again, due to stronger attraction between the bonding electrons and the nuclei when there are more electrons in the bond.

KEY POINT



It is important to consider only bonds between the same type of atoms because the bond length also depends on the size of the atom, so the H—H single bond, at 74 pm, is significantly shorter than the C≡C triple bond.

The relationship between bond length and bond strength

In general, when we are comparing just single bonds, the longer the bond, the weaker it is. Data for two groups in the periodic table are shown in Table 7.2.

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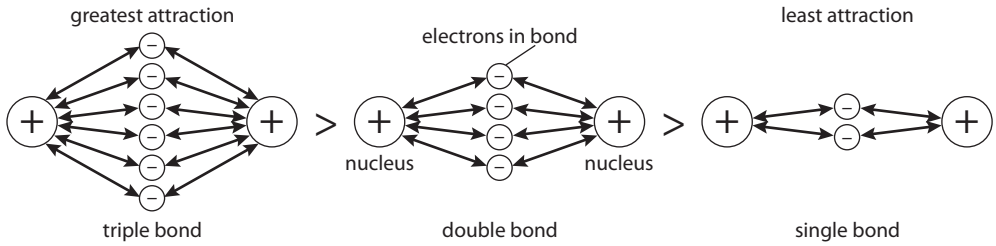

Figure 7.12: The more electrons that make up a covalent bond, the greater the attraction between the electrons and the nuclei and, therefore, the stronger the bond.

Group 14			Group 17		
Bond	Length / pm	Bond energy / kJ mol^{-1}	Bond	Length / pm	Bond energy / kJ mol^{-1}
C—C	154	348	Cl—Cl	199	242
Si—Si	233	226	Br—Br	228	193
Ge—Ge	240	188	I—I	267	151

Table 7.2: The relationship between the lengths of bonds and bond strength.

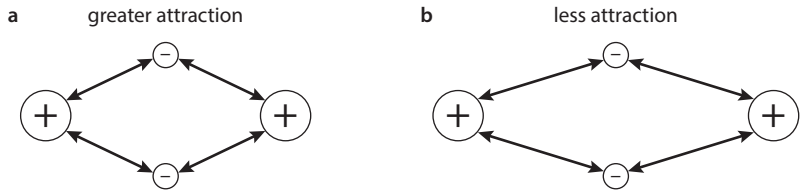

Figure 7.13: The bond in **a** is a shorter bond, in which the bonding electrons are closer to the nuclei than in **b**.

If we consider data for Group 14, it can be seen that the single bond between the elements gets weaker as the bond gets longer. This is because, as the atoms get bigger, the electron pair in the covalent bond is further away from the nuclei of the atoms making up the bond. If the electron pair is further away from the nuclei, it is less strongly attracted, and the covalent bond is weaker (Figure 7.13). A similar trend can be seen down Group 17.

Trends should only be compared down a group because elements in the same group have the same number of outer-shell electrons and, therefore, the bonding will be most similar. In general, comparisons such as this are most useful and valid when similar molecules, bonds or compounds are considered.

NATURE OF SCIENCE

Not all trends are perfect in chemistry; for instance the F—F bond length is 142 pm, but the bond energy is only 159 kJ mol^{-1}. A good motto in chemistry is 'never assume anything – always check'! Simple models have to be refined to include explanations of exceptions to expected trends.

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Coordination bonds

KEY POINTS

A coordination bond is a type of covalent bond in which both electrons come from the same atom.

Once a coordination bond has been formed, it is identical to an 'ordinary' covalent bond.

Coordination bonds are also called coordinate covalent bonds or dative covalent bonds.

For example, a coordination bond is formed when H^+ bonds to NH_3:

$$NH_3 + H^+ \rightarrow NH_4^+$$

H^+ does not have any electrons with which to form a covalent bond, but NH_3 has a lone pair of electrons that can be used to form a covalent bond (Figure 7.14). When a covalent bond is formed between the N and the H, both electrons for the covalent bond are supplied by the nitrogen atom – a coordination bond.

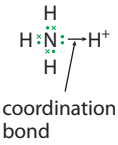

Figure 7.14: Formation of a coordination bond in NH_4^+.

The formation of a coordination bond is sometimes shown using an arrow (Figure 7.14). Figure 7.15a shows a Lewis formula for the ammonium ion in which we can see clearly which is the coordination bond. Once it has been formed, the coordination bond is, however, the same as the other three N—H bonds, and no distinction is generally made in Lewis formulas (Figure 7.15b).

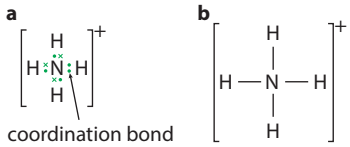

Figure 7.15: The ammonium ion **a** with the coordination bond shown and **b** with no distinction between the types of bonds.

EXAM TIP

If N forms 4 bonds in a molecule/ion, one of the bonds is almost certainly a coordination bond.

H_3O^+ (the hydronium ion) is formed when a lone pair of electrons is donated from O in H_2O to H^+ (Figure 7.16).

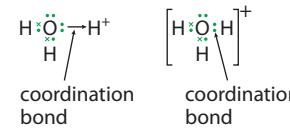

Figure 7.16: The formation of H_3O^+ involves a coordination bond.

In BF_3, there are only six electrons in the outer shell of the boron atom – so there is space for boron to accept a pair of electrons. NH_3 and BF_3 can combine to form an *adduct* (two molecules bonded together), see Figure 7.17.

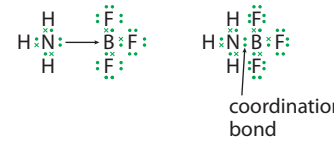

Figure 7.17: A coordination bond is formed when NH_3 reacts with BF_3.

Link

The reactions on this page are examples of Lewis acid – base reactions – the electron-pair donor is the Lewis base, and the electron-pair acceptor is the Lewis acid (see Chapter 22).

Carbon monoxide (CO)

Normally carbon shares four electrons to form four covalent bonds, and oxygen shares two electrons to form two covalent bonds. If a carbon atom combines with an oxygen atom with the formation of two covalent bonds, we get the structure:

However, in this structure, although the oxygen atom has a complete octet, the carbon atom has only six electrons in its outer shell. Both atoms can attain an octet if the oxygen atom donates a pair of electrons to carbon in the formation of a coordination bond. There is now a triple bond between the two atoms

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made up of two 'ordinary' covalent bonds and one coordination bond (Figure 7.18). Both atoms have a lone pair of electrons.

Figure 7.18: Carbon monoxide has a triple bond: two 'ordinary' covalent bonds and one coordination bond.

The bonding in carbon monoxide can also be represented as shown in Figure 7.19.

Figure 7.19: An alternative Lewis formula for carbon monoxide.

It is not immediately obvious in Figure 7.19 that there is a coordination bond between C and O. A clue, however, is the fact that O forms 3 bonds – when O forms 3 bonds, you can usually assume that one of them is a coordination bond.

Link

Coordination bonds are important in the formation of transition metal complexes – see Chapter 10.

How to work out Lewis formulas

We have seen several Lewis formulas already in this chapter, but now we will develop a more systematic approach to working out Lewis formulas where the central atom does not expand its octet (have more than eight electrons in the outer shell). Examples where expansion of the octet does occur will be covered in the Higher Level section.

A set of guidelines for working out Lewis formulas is as follows:

- Start with the outer atoms.
- All outer atoms (except hydrogen, which should have two) have eight electrons in their outer shell. This is achieved by forming single bonds, double bonds, triple bonds and/or having + or – charges.
- The outer atoms will form the maximum number of bonds they can (e.g. oxygen will form double bonds wherever possible), up to a maximum limited by the fact that the central atom can form a maximum of four bonds.
- The central atom will usually have eight electrons in its outer shell. It cannot have more than eight electrons but it can have fewer than eight.

NF_3

The central atom is nitrogen, and the three outer atoms are fluorine.

If we start with the outer atoms – fluorine is in Group 17, so a fluorine atom has seven electrons in its outer shell and will form one single bond to have a full outer shell. Therefore, for each fluorine atom to have eight electrons in its outer shell, three single bonds between nitrogen and fluorine must be formed. A nitrogen atom has five electrons in its outer shell, and so, when it shares one electron with each fluorine atom, it will have eight electrons in its outer shell. Figure 7.20 shows the Lewis formula for NF_3.

Figure 7.20: The Lewis structure for NF_3. Each atom has a complete octet.

Dots and crosses are used in Figure 7.20, but you do not need to distinguish between electrons in a Lewis formula (Figure 7.21).

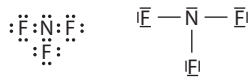

Figure 7.21: Different ways of representing the Lewis formula of NF_3.

It is important to remember that a Lewis formula must show all the outer-shell electrons, including those on the outer atoms, so the representation in Figure 7.22 is *not* a Lewis formula because the lone pairs on F are not shown.

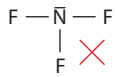

Figure 7.22: Always remember to show the lone pairs on outer atoms. This is not a Lewis formula.

Note that, because the elements in Group 17 (the halogens) have seven electrons in their outer shells, they will always form just a single bond when they are the outer atoms. The halogens, other than F, can form more than one bond when they are the central atom, but F

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never does anything other than forming a single covalent bond in covalent molecules.

CO_2

Carbon is the central atom, and the oxygens are the outer atoms. Oxygen is in Group 16, and so has six electrons in its outer shell. To complete its octet, each O atom needs two more electrons, which it will gain, wherever possible, by forming two bonds. A carbon atom has four electrons in its outer shell, and so will be able to form double bonds to both oxygen atoms. Each atom in CO_2 then has a complete octet (Figure 7.23).

Figure 7.23: Lewis formulas for CO_2.

CO_3^{2-}

Carbon is the central atom, and the oxygens are the outer atoms. Each oxygen can complete its octet by forming a double bond (Figure 7.24).

Figure 7.24: Oxygen can complete its octet by forming a double bond to carbon.

Formation of three double bonds to the C atoms would, however, cause C to have more than eight electrons in its outer shell, which is not possible (Figure 7.25).

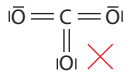

Figure 7.25: This structure is not possible because a Period 2 atom cannot have more than eight electrons in its outer shell. Carbon here has 12 electrons (6 pairs) in its outer shell.

The next best solution for an oxygen atom is that it forms a single bond and completes its octet by gaining an extra electron (one of the negative charges) (Figure 7.26). The electron for the negative charge will come from sodium, calcium, etc. – the CO_3^{2-} ion cannot be formed in isolation – another atom must lose electrons at the same time to form the 2– charge.

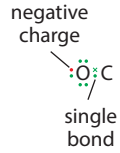

Figure 7.26: Oxygen can complete its octet by forming a single bond to carbon and gaining an extra electron.

Carbon can form a maximum of four bonds; therefore, one oxygen atom will form a double bond and the other two form single bonds.

The Lewis formula for CO_3^{2-} is shown in Figure 7.27.

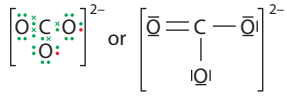

Figure 7.27: Two representations of the Lewis formula of the carbonate ion.

The overall charge on the ion must be included and square brackets drawn around the ion. We do not generally show the individual charges on the O atoms for reasons that will be discussed in the section on resonance. As a final check, you should make sure that the central atom has no more than eight electrons in its outer shell, because it is from Period 2.

EXAM TIP

You must remember to show lone pairs in Lewis formulas. For ions, you also need to include brackets and charges.

Alternative method for working out Lewis formulas

This approach is useful for working out the Lewis formulas of molecules/ions just containing Period 2 atoms.

1. Add up the total number of valence (outer-shell) electrons of all the atoms in the molecule/ion.
2. Divide by two to get the total number of valence electron pairs.
3. Each pair of electrons is represented by a line.

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4 Arrange the lines (electron pairs) so that all the atoms are joined together by at least single bonds and the outer atoms have full outer shells, i.e., are connected to four lines.

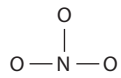
5 Rearrange the lines (electron pairs) so that every Period 2 atom has four pairs of electrons.
The outer atoms already have four pairs, so this should normally involve moving only lone pairs so that they become bonding pairs of electrons.

NO_3^-

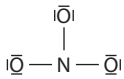
total no. electrons = 5 (N) + 3 × 6 (O) + 1 (– charge) = 24 e^-

There are, therefore, 24 ÷ 2 = 12 pairs of electrons, which means that there will be 12 lines in the Lewis formula.

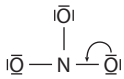
Three lines must be used to join all the atoms together:



This leaves nine lines (electron pairs) that will be distributed as lone pairs of electrons on the outer atoms (the O atoms) to give each a complete octet:



Now each O has four lines attached (four pairs of electrons in its outer shell), and all the electron pairs (lines) have been used. The nitrogen, however, has only three pairs of electrons in its outer shell, and one of the lines needs to be moved from being a lone pair on oxygen to make a double bond between nitrogen and oxygen. This does not change the number of electrons in the outer shell of O but will increase the number of electrons in the outer shell of N to eight.



The final Lewis formula for the NO_3^- ion is shown in Figure 7.28.

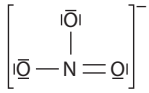


Figure 7.28: The final Lewis formula for NO_3^-.

This is a purely mechanical technique for working out the Lewis structure and does not really involve any understanding of the bonding in the ion. The Lewis structure showing the electrons as dots and crosses is probably clearer (Figure 7.29).

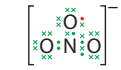


Figure 7.29: The Lewis formula of NO_3^- with the electrons shown individually. This representation also shows that one of the N–O bonds is a coordination bond.

NO_2^-

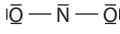
total no. electrons = 5 (N) + 2 × 6 (O) + 1 (– charge) = 18 e^-

There are, therefore, $\frac{18}{2}$ = 9 pairs of electrons, i.e., 9 lines.

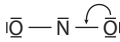
The atoms are joined together using two lines:

More lines are added to the outer atoms to give each a complete octet:

So far, only eight lines (electron pairs) have been used and the last line must be put as a lone pair on nitrogen. It cannot be put anywhere else, as the oxygens already have four electron pairs each.



Nitrogen only has three electron pairs, and so, a lone pair is moved from an oxygen to form a double bond:



This results in the Lewis formula for NO_2^- shown in Figure 7.30.

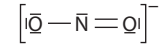


Figure 7.30: The final Lewis formula for NO_2^-.

It is important to note that the Lewis formula could be drawn the other way round with the double bond to the other O atom – these two structures are entirely equivalent (Figure 7.31).

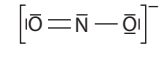


Figure 7.31: An alternative structure for NO_2^-.

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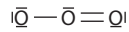
Link

NO_2 has been asked about in examinations. It has an odd number of electrons and, therefore, an unpaired electron. The Lewis structure can be shown with an N=O double bond and an N→O coordination bond. The unpaired electron would then be on N. Species with unpaired electrons are called radicals and are discussed in Chapter 21.

O_3 (ozone)

Ozone is isoelectronic (has the same number of electrons) with NO_2^- and its Lewis formula could be worked out in the same way to give a structure with the same distribution of bonds and lone pairs:



Again, it can be drawn with the double bond on either side.

A difference, however, between the structures of O_3 and NO_2^- is that O_3 contains a coordination bond but NO_2^- does not (Figure 7.32).

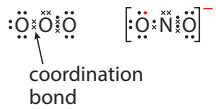


Figure 7.32: O_3 contains a coordination bond but NO_2^- does not.

The technique of just drawing electron pairs as lines does not make it obvious which bonds are coordination bonds. We could, however, have deduced this from the Lewis formula of O_3 as the left-hand O has three lone pairs, which accounts for all of its outer-shell electrons; therefore, the left-hand O atom does not contribute any electrons to the single bond between it and the central O atom, so this must be a coordination bond.

NO_2^+ and CO_2

NO_2^+ and CO_2 are isoelectronic and have the same number of atoms. Once we realise this, drawing the Lewis formula of NO_2^+ is straightforward, as it is the same as that of CO_2 (Figure 7.33).

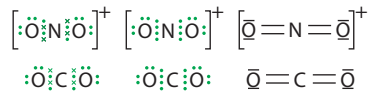


Figure 7.33: The Lewis formulas of NO_2^+ and CO_2 are the same, but do not forget the brackets and charge for NO_2^+!

This technique for drawing Lewis formulas is useful for molecules/ions involving just Period 2 elements, but it also works for compounds involving Period 3 elements (and those in Periods 4, 5, 6, 7) if the atoms do not expand their octet.

TEST YOUR UNDERSTANDING

1 Work out Lewis formulas for the following:

a	H_2S	**b**	PCl_3	**c**	CCl_4
d	COF_2	**e**	HCN	**f**	CS_2
g	FNO	**h**	N_2H_4	**i**	H_2O_2
j	PCl_4^+	**k**	NO^+	**l**	OCN^-.

2 Which of the following has the shortest C—O bond length?

HCHO, CO, CH_3OH, CO_2

3 Which of the following has the longest C—C bond length?

HCCH, H_3CCH_3, H_2CCH_2

4 Which of the following has the shortest N—N bond length?

N_2, N_2H_2, N_2H_4

5 Which of the following contain a coordination bond?

H_3O^+, O_2, CO_2, CO, O_3, NH_4^+

6 In which of the following does the central atom not have a complete octet?

CH_3^+, NO_2^+, BF_3, NF_3, $BeCl_2$

7 What is the total number of lone pairs of electrons in each of the following?

H_2O, OF_2, CH_3Cl, NH_4^+, Br_2, $SiCl_4$, PH_3

8 Draw Lewis formulas for the following nitrogen-containing molecules/ions:

NO_2^+, NO_2^-, NO_3^-, HNO_3, NH_2OH, FNO_2, NNO (more than one is possible).

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7.2 Shapes of molecules: VSEPR theory

The shapes of molecules can be predicted using the valence shell electron-pair repulsion (VSEPR) theory. The basic principle of VSEPR is:

KEY POINT

Pairs of electrons (electron domains) in the valence (outer) shell of the central atom repel each other and will, therefore, take up positions in space to minimise these repulsions – to be as far apart in space as possible.

The pairs of electrons may be either non-bonding pairs (lone pairs) or bonding pairs (pairs of electrons involved in covalent bonds). We will use the term **electron domain** instead of electron pair from now on to avoid confusion when we have structures involving multiple bonds. A double bond is made up of two pairs of electrons, but these electrons are constrained to occupy the same region of space, so a double bond behaves, in terms of repulsion, as if it were just one electron domain. Similarly, a triple bond, made up of three electron pairs, is also one electron domain for the purpose of working out the shapes of molecules.

Electron domain geometries

The shape of a molecule depends on the number of electron domains in the outer shell of the central atom.

Consider a molecule with formula XY_2, where there are single bonds between X and Y and no lone pairs on X, so there are two electron domains around the central atom. These two electron domains will repel each other and, therefore, take up positions in space to get as far away from each other as possible – this is the linear arrangement shown in Figure 7.34a.

Imagine now that they did not take up this arrangement but that the molecule was instead bent, as in Figure 7.34b. With this shape, there will be more repulsion between the electron pairs on one side of the molecule and less on the other side – the greater repulsion will push the molecule back into the linear shape.

KEY POINT

How the electron domains are arranged in space around the central atom is called the electron domain geometry.

There are five possible electron domain geometries (for two to six electron domains), which are derived from the idea of how a number of objects, joined to a central point, can be arranged in space to be as far apart from each other as possible.

In this section, only molecules/ions with up to four electron domains around the central atom will be considered (see Higher Level Section 7.13 for five and six electron domains). The electron domain geometries and bond angles are shown in Table 7.3.

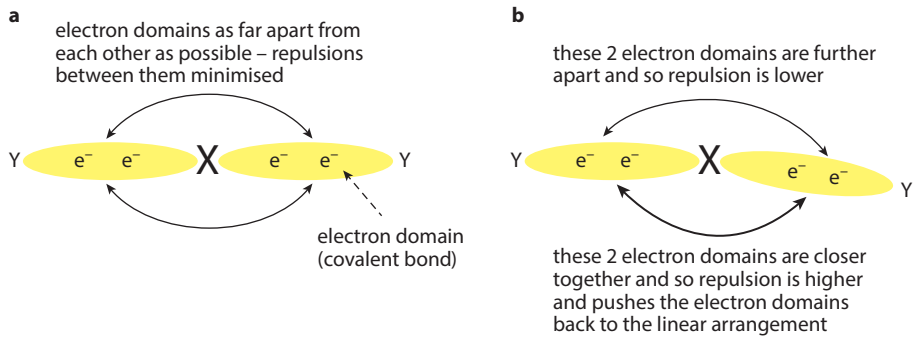

Figure 7.34: Electron domains will take up positions in space to minimise repulsions. **a** The electron domain geometry for two electron domains is linear; **b** this arrangement has more repulsion on one side of the molecule and the shape will change until the repulsions balance.

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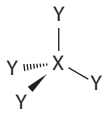
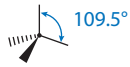
No. of electron domains	Electron domain geometry	Bond angle	Example
2	linear Y — X — Y		$BeCl_2(g)$
3	trigonal planar 		BF_3
4	tetrahedral 		CH_4

Table 7.3: Electron domain geometries and bond angles.

How to draw molecules in 3-D

We use a convention for drawing molecules when we need to show their shape. This is shown in Figure 7.35.

Figure 7.35: a This symbol indicates a bond in the plane of the paper. **b** This symbol indicates a bond coming out of a plane. **c** This symbol indicates a bond going into a plane.

How to predict the shapes of molecules

1. Draw a Lewis formula for the molecule or ion.
2. Count the number of electron domains around the central atom (total of single bonds + lone pairs + multiple bonds).
3. Look at Table 7.3 to get the electron domain geometry.
4. Imagine the shape with the lone pairs removed but all the bonds staying in place. A lone pair is just an electron pair in the outer shell of an atom and, as such, it contributes to the overall shape of the molecule but cannot itself be 'seen' (detected directly by a physical technique) and is not included in the description of the actual shape.
5. State the actual shape of the molecule – the molecular geometry.

CH_4

The Lewis formula for CH_4 is shown in Figure 7.36.

Figure 7.36: The Lewis formula for CH_4.

We must now count the number of electron domains around the central atom:

Single bonds:	4
Multiple bonds:	0
Lone pairs:	0

Total number of electron domains: 4

These four electron domains repel each other and take up positions in space as far away from each other as possible to minimise repulsions. The shape that allows four objects to be as far away from each other as possible is a tetrahedron. Therefore, the four electron domains are arranged tetrahedrally around the C atom. The shape (molecular geometry) of the methane molecule is tetrahedral and the H—C—H bond angle is 109.5° (Figure 7.37).

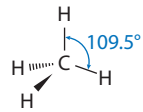


Figure 7.37: CH_4 is tetrahedral.

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Remember: we need to think in three dimensions and not just two. If the shape were square planar, as shown in Figure 7.38, the angle between the electron domains would be only 90°, so there would be greater repulsion. The tetrahedral shape minimises the repulsions.

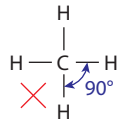

Figure 7.38: CH_4 does *not* adopt a square planar shape because this has greater repulsion between electron domains.

NH_3

The Lewis formula of NH_3 is shown in Figure 7.39.

Figure 7.39: The Lewis formula of NH_3.

Single bonds:	3
Multiple bonds:	0
Lone pairs:	1
Total number of electron domains:	4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible, the electron domains are distributed in a tetrahedral arrangement. The electron domain geometry is tetrahedral – but a lone pair is just a pair of electrons in the outer shell of the central atom and, although it repels the other pairs of electrons and influences the shape, it cannot be 'seen'. It is important to remember that the shape of a molecule is the arrangement of the atoms in space – not the electrons. The arrangement of the atoms here is, therefore, trigonal pyramidal (a pyramid with a triangular base) (Figure 7.40).

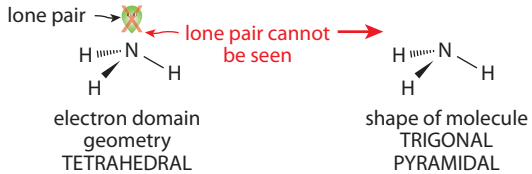

Figure 7.40: The electron domain geometry of the NH_3 molecule is tetrahedral, but the shape of the molecule is trigonal pyramidal.

THEORY OF KNOWLEDGE

Here, we talk about it not being possible to 'see' a lone pair of electrons, but, of course, it is not possible to see any of these molecules. There are various techniques for determining the shapes of molecules experimentally. Probably the most important of these is X-ray crystallography, in which a crystal of the substance is placed in an X-ray diffractometer and, from the position and intensity of diffracted X-ray beams, the shape of the molecules, and all the angles and bond lengths can be calculated. The lone pairs of electrons cannot be detected by this technique. Do we know or believe the shapes of molecules stated here? Which ways of knowing do we use to interact with this microscopic world? In biology, microscopes are used to 'view' things that are too small to be seen with the naked eye. Is there a difference between the use of a microscope to interact with this invisible world and the use of an X-ray diffractometer? What about the use of electron microscopes?

The H—N—H bond angle in NH_3 is 107.3° (Figure 7.41), which is smaller than in a perfect tetrahedron, because the lone pair repels the bonding pairs of electrons more than the bonding pairs of electrons repel each other. This will be considered in more detail later.

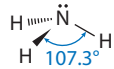

Figure 7.41: The bond angle in NH_3. Note: the bond angle is between *bonds* and not between a bond and a lone pair.

CO_2

The Lewis formula for CO_2 is shown in Figure 7.42.

Figure 7.42: The Lewis formula for CO_2.

Looking at the *central atom*:	
Single bonds:	0
Multiple bonds:	2
Lone pairs:	0
Total number of electron domains:	2

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Because these two electron domains repel each other and take up positions in space to be as far apart as possible, the electron domains are distributed in a linear arrangement (Figure 7.43), and the shape adopted by the atoms is linear.

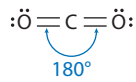

Figure 7.43: The linear CO_2 molecule.

O_3

The Lewis formula for O_3 is shown in Figure 7.44.

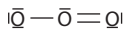

Figure 7.44: The Lewis formula of O_3.

Looking at the central atom:

Single bonds:	1
Multiple bonds:	1
Lone pairs:	1
Electron domains:	3

The three electron domains on the central atom repel each other and take up positions in space to be as far apart as possible – the electron domains are distributed in a trigonal planar (flat triangle) arrangement (Figure 7.45). The lone pair on the central O is just a pair of electrons in its outer shell and cannot be 'seen'. The shape (molecular geometry) adopted by the atoms is, therefore, bent (also called 'angular', or 'V-shaped').

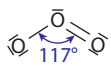

Figure 7.45: The shape of an O_3 molecule.

Again, the bond angle is slightly less than the ideal angle in a regular trigonal planar structure (120°), and this results from the extra repulsion of the lone pair, so that the bonding pairs are pushed closer together and the bond angle is reduced.

7.3 Lone pairs and bond angles

KEY POINTS

The order of repulsion strength for pairs of electrons is as follows:

lone pair – lone pair > lone pair – bonding pair > bonding pair – bonding pair.

This is because lone pairs are held closer (Figure 7.46) to the central nucleus than bonding pairs (lone pairs are in the outer shell of the central atom, whereas a bonding pair can be imagined as being, on average, halfway between the bonded atoms). The lone pairs are thus closer to the bonding pairs of electrons than the bonding pairs are to each other and repel them more strongly. This will cause the angle between the bonds to become smaller. As the bonds get closer, the repulsion between them increases and the repulsion to the lone pair decreases (because it is further away) until everything balances out.

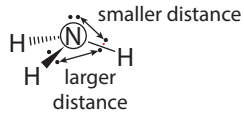

Figure 7.46: Lone pairs lie closer to the bonding pairs than the bonding pairs are to each other.

Consider CH_4, NH_3 and H_2O, each of which has four electron pairs in the outer shell of the central atom, and, therefore, the electron domain geometry in each case is tetrahedral. From Table 7.4, we can see that the more lone pairs are present, the smaller the H—X—H bond angle is. This is due to greater repulsion from lone pairs than from bonding pairs of electrons. Two lone pairs cause greater repulsion than one, so the bond angle gets smaller as the number of lone pairs increases.

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Molecule	Lewis formula	Bonding pairs	Lone pairs	Electron domain geometry	Molecular geometry/shape	H—X—H bond angle
CH_4		4	0	tetrahedral	tetrahedral	109.5°
NH_3		3	1		trigonal pyramidal	107.3°
H_2O		2	2		bent	104.5°

Table 7.4: Bond angles of CH_4, NH_3 and H_2O showing the influence of lone pairs.

EXAM TIP

If you are asked to predict a bond angle in a molecule/ion, just take two or three degrees off the bond angle in the perfect shape (electron domain geometry) for each lone pair present on the central atom. For example, a bent molecule based on a trigonal planar structure (one lone pair on the central atom) could have a bond angle of 120 – 3 = 117°. There is no scientific basis for doing this, but it is useful for answering examination questions!

7.4 Multiple bonds and bond angles

A double bond consists of four electrons and a single bond consists of two electrons; therefore:

KEY POINT

A double bond will repel single bonds more than they repel each other.

Methanal (CH_2O) has three electron domains around the central carbon: one double bond and two single bonds. The shape is trigonal planar and, if all repulsions were equal, the bond angle would be 120°. However, the double bond, with four electrons, repels the single bonds more than the double bonds repel each other, so the O—C—H bond angles are opened up and the H—C—H bond angles close up until all the repulsions balance (Figure 7.47).

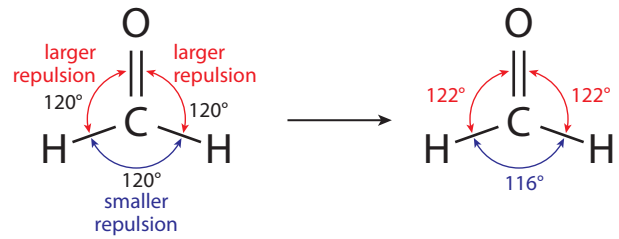

Figure 7.47: A double bond repels single bonds more than they repel each other, so that the H—C—H bond angle in methanal is 116° rather than 120°.

A triple bond (six electrons) will cause greater repulsion than a double bond (four electrons). However, all commonly encountered compounds containing a triple bond have a linear structure (Figure 7.48), and so, the extra repulsion from the triple bond will make no difference to the bond angles, which will be 180°.

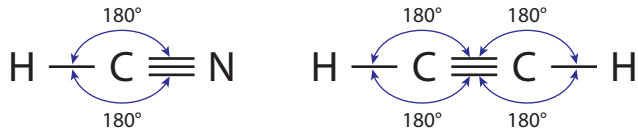

Figure 7.48: The shapes and bond angles of hydrogen cyanide (HCN) and ethyne (C_2H_2).

KEY POINT

Lone pairs repel double bonds more than they repel each other.

The shape of sulfur dioxide is shown is Figure 7.49. The lone pair has caused the O—S—O bond angle to close up slightly from the trigonal planar bond angle of 120°.

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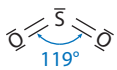

Figure 7.49: The shape and bond angle in SO_2.

Note that S has more than eight electrons in its outer shell – it has expanded its octet. Molecules where the central atom has expanded its octet will be considered in the Higher Level section.

The reasoning in this section must be applied with caution – there are always exceptions! Sometimes the exceptions are just due to some factors associated with a particular molecule/ion, but they may also be due to a more advanced concept not having been covered yet. Looking at the structure of the carbonate ion (CO_3^{2-}) in Figure 7.50, we would not expect the bond angles to all be 120°, however, they are. The reasons for this will be covered in Higher Level Section 7.16.

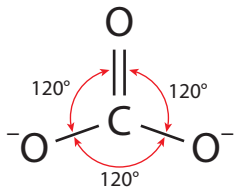

Figure 7.50: All the bond angles in the carbonate ion are 120°.

Predicting the shapes of ions

The approach to predicting the shapes of ions is exactly the same as for neutral molecules.

NH_4^+

The Lewis formula for NH_4^+ is shown in Figure 7.51.

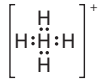

Figure 7.51: The Lewis formula for NH_4^+.

Single bonds:	4
Multiple bonds:	0
Lone pairs:	0
Electron domains:	4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible (Figure 7.52), the electron domains are distributed in a tetrahedral arrangement.

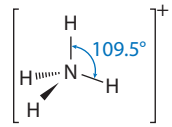

Figure 7.52: Tetrahedral NH_4^+.

NO_2^-

The Lewis structure for NO_2^- is shown in Figure 7.53.

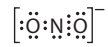

Figure 7.53: The Lewis structure for NO_2^-.

Single bonds:	1
Multiple bonds:	1
Lone pairs:	1
Electron domains:	3

Because these three electron domains repel each other and take up positions in space to be as far apart as possible, the electron domains are distributed in a trigonal planar arrangement. One of the electron domains is a lone pair, so the actual shape of the ion is bent (Figure 7.54). This structure is based on trigonal planar (bond angle 120°) with one lone pair, so a bond angle of about 117° could be predicted.

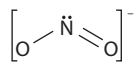

Figure 7.54: NO_2^- is bent.

Molecules with more than one central atom

The approach to predicting the shapes of molecules with more than one central atom is the same as for other molecules, except that each 'central atom' must be considered separately.

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N_2H_4

The Lewis formula for N_2H_4 is shown in Figure 7.55.

Figure 7.55: The Lewis formula for N_2H_4.

In this molecule, the two N atoms are 'central atoms' and each one must be considered separately (Table 7.5).

Left-hand nitrogen	Right-hand nitrogen
single bonds: 3	single bonds: 3
multiple bonds: 0	multiple bonds: 0
lone pairs: 1	lone pairs: 1
electron domains: 4	electron domains: 4

Table 7.5: Counting electron domains around the nitrogen atoms in N_2H_4.

We can see (Figure 7.56) that the arrangement of electron domains around each nitrogen is tetrahedral and, with one lone pair on each nitrogen, the shape about each nitrogen atom is trigonal pyramidal.

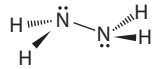

Figure 7.56: The structure of N_2H_4. Note: VSEPR does not predict how the NH_2 groups are arranged relative to each other.

C_2H_2

The Lewis formula for C_2H_2 is shown in Figure 7.57.

Figure 7.57: The Lewis formula of C_2H_2.

In ethyne, each C should be considered separately, but each one is identical; therefore, we have for each C:

Single bonds:	1
Multiple bonds:	1
Lone pairs:	0
Electron domains:	2

The triple bond counts as one electron domain, so, with two electron domains around each C, the shape is linear (Figure 7.58) about each C and, therefore, linear overall.

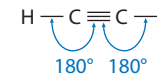

Figure 7.58: Linear C_2H_2.

VSEPR summary

The shapes adopted by molecules depend on the number of *pairs* of electrons in the outer shell of the central atom. To take account of molecules containing multiple bonds, this is often expressed in terms of electron domains, where one multiple bond counts as one electron domain.

- Electron domains in the outer shell of the central atom repel each other.
- The electron domains may be either electrons involved in bonds or lone pairs.
- The electron domains take up positions in space to minimise repulsions in a molecule/ion, i.e., to be as far apart from each other as possible.
- Lone pairs influence the shapes of molecules/ions but cannot be 'seen'.
- Lone pairs repel bonding pairs of electrons more than the bonding pairs repel each other. Therefore, the presence of lone pairs results in a closing up of bond angles.
- Triple bonds repel more than double bonds, which repel more than single bonds.

The shapes of some specific molecules/ions are shown in Table 7.6.

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Total number of electron domains	Bonding pairs	Lone pairs	Electron domain geometry	Shape	Example
2	2	0	linear	linear	CO_2, NO_2^+, HCN, $BeCl_2(g)$
3	3	0	trigonal planar	trigonal planar	BF_3, SO_3, NO_3^-, CO_3^{2-}
3	2	1	trigonal planar	bent, V-shaped, angular	SO_2, O_3, NO_2^-
4	4	0	tetrahedral	tetrahedral	CCl_4, XeO_4, NH_4^+, BCl_4^-, SO_4^{2-}, PO_4^{3-}
4	3	1	tetrahedral	trigonal pyramidal	NH_3, PCl_3, XeO_3, H_3O^+, ClO_3^-, $SOCl_2$
4	2	2	tetrahedral	bent, V-shaped, angular	H_2O, SCl_2, ClF_2^+, I_3^+

Table 7.6 The electron domain geometries and shapes of some specific molecules/ions. Some of the molecules/ions have central atoms with expanded octets – these are highlighted in red.

TEST YOUR UNDERSTANDING

9 Work out the shapes of the following molecules or ions and predict their bond angles.

Where ambiguity could arise, the central atom has been highlighted in blue.

a H_2S **b** PBr_3 **c** CF_4

d HCN **e** COF_2 **f** CS_2

g FNO **h** PCl_4^+ **i** OCN^-

j NNO **k** C_2Cl_4 **l** NO_2^+

10 Identify the species with the smaller H—X—H bond angle:

a H_3O^+ or H_2O **b** NH_3 or NH_4^+

c NH_3 or HNNH **d** H_3CCH_3 or H_2CCH_2

e H_2CO or H_3COH **f** CH_3^+ or CH_4

g NH_2^- or NH_3.

11 Identify species with a trigonal planar electron domain geometry:

CO_2, O_3, NO_2^+, BCl_3, NO_2^-, CO_3^{2-}, NH_2^-, NF_3.

7.5 Polarity

Electronegativity

In an F_2 molecule, the two fluorine atoms attract the electrons in the bond equally, and so, the electrons lie symmetrically between the two nuclei (Figure 7.59). This molecule is non-polar.

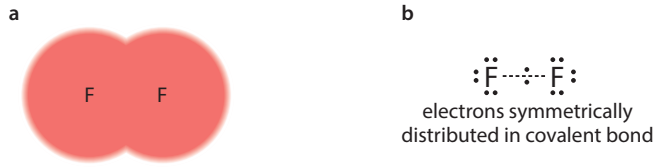

Figure 7.59: a The electron density in F_2; **b** F_2 is a non-polar molecule.

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In a covalent bond between two different atoms, the atoms do not attract the electron pair in the bond equally. How strongly the electrons are attracted depends on the size of the individual atoms and their nuclear charge.

KEY POINT

Electronegativity is a measure of the attraction of an atom in a molecule for the electron pair in the covalent bond of which it is a part.

In HF, fluorine is more **electronegative** than hydrogen and attracts the electrons in the H—F bond more strongly than the hydrogen atom does. The electrons in the bond lie closer to fluorine than to hydrogen (Figure 7.60).

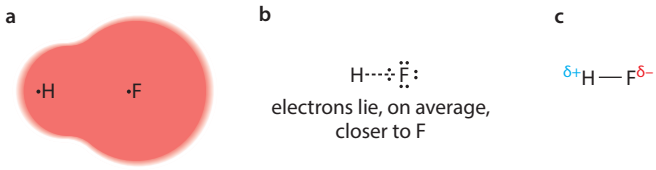

Figure 7.60: a The electron density in HF; **b** HF is a polar molecule; **c** usual representation of HF.

The unsymmetrical distribution of electron density results in small charges on the atoms indicated by δ+ (delta positive) or δ– (delta negative). Fluorine is δ– because the electrons in the bond lie closer to F, whereas electron density has been pulled away from hydrogen, so H is δ+. When charges are separated like this it is called a *dipole* and, because the overall HF molecule is a dipole (with a positive end and a negative end), it is called a **polar molecule**.

7.6 Pauling electronegativities

There are various scales of electronegativity, and it is important to realise that, although they are derived from physical quantities (such as bond energies), the numbers themselves are not physical quantities – they have no units and must only be used in a comparative way. The most commonly used scale of electronegativity is that developed by Linus Pauling. The electronegativity values for some elements, worked out using the Pauling method, are shown in Table 7.7.

H 2.20							
Li 0.98	Be 1.57		B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31		Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00		Ga 1.81	Ge 2.01	As 2.01	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95		In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66

Table 7.7 Pauling electronegativities for some elements.

General things to notice about this table are that:

- non-metals have higher electronegativities than metals
- electronegativity generally decreases down a group
- electronegativity increases across a period
- the most electronegative elements are F, O, Cl and N in the top-right corner of the periodic table.

Link

Trends in electronegativity will be explained in Chapter 10.

Most noble gases do not have electronegativity values because they do not (generally) form compounds. Xenon (Xe) does, however, form a variety of compounds, usually with oxygen and fluorine, and is assigned an electronegativity value of 2.60.

EXAM TIP

To remember the trends in electronegativity, just remember that fluorine is the atom with the highest electronegativity. Electronegativity must then increase across a period towards fluorine and decrease down a group from fluorine.

In general, atoms with similar electronegativities will form covalent bonds and atoms with widely different electronegativities will form ionic bonds. So, LiF (electronegativity difference: 3.00) is ionic, but CH_4 (electronegativity difference: 0.35) has covalent bonding.

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The difference in electronegativity can be taken as a guide to how ionic or how covalent the bond between two atoms is likely to be.

Linus Pauling related the electronegativity difference between two atoms to the ionic character of a bond. He suggested that an electronegativity difference of 1.7 corresponded to 50% ionic character in a bond and reasoned that a higher electronegativity difference than this corresponded to a structure that was more ionic than covalent, whereas if the difference was less than 1.7, the bonding was more covalent than ionic. This is a useful idea, but it must be used with great caution. For instance, KI (electronegativity difference: 1.7) would come out of this discussion as having 50% ionic and 50% covalent character, and NaI (difference of 1.6) would appear to be mostly covalent, whereas both behave as predominantly ionic compounds. Pauling, in his original discussion of this, was actually referring to diatomic molecules and not to macroscopic compounds, but his ideas are often used out of context, and you will sometimes see statements that suggest that the bonding in a compound is ionic if the difference in electronegativity is more than 1.7, and covalent if the difference is less than 1.7. This will be discussed again in Chapter 9.

Polar molecules

The electronegativity difference between two atoms covalently bonded together results in the electrons lying more towards one atom than the other. We call such a bond polar or say that it is a dipole.

KEY POINTS

Polar bonds arise when there is a difference in electronegativity between the atoms making up the bond.

Although individual bonds may be polar, a molecule may be non-polar overall if, because of the symmetry of the molecule, the dipoles of the individual bonds cancel out.

All the bonds in the molecules in Figure 7.61 are polar. However, whether a molecule is polar overall also depends on the shape of the molecule. For a molecule to be polar, it must have a positive end to the molecule and a negative end. For instance, HCl, NH_3 and H_2O in Figure 7.63 are polar, but CO_2 is non-polar. HCl, NH_3 and H_2O all have an overall dipole (or net dipole moment), and the arrow indicates the direction of the dipole.

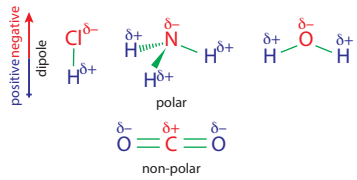

Figure 7.61: Each individual bond in these molecules is polar. HCl, NH_3 and H_2O are polar molecules – one end of the molecule is slightly positive compared with the other end. CO_2 is non-polar.

CO_2 is a non-polar molecule (Figure 7.62). Each C=O bond is polar, because oxygen is more electronegative than carbon, but, overall, the bond dipoles cancel so that there is no net dipole moment and the molecule is non-polar.

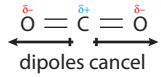

Figure 7.62: Bond polarities can cancel out, making CO_2 non-polar. The dipoles can be thought of as vectors – here the resultant vector is zero.

BF_3 is also non-polar. Again, each individual bond is polar, but the bond dipoles cancel (Figure 7.63).

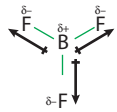

Figure 7.63: Bond dipoles cancel out, making BF_3 non-polar. Again, in terms of vectors, the resultant vector is zero.

CCl_4 is non-polar, but $CHCl_3$ is polar (Figure 7.64).

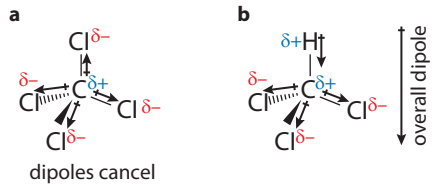

Figure 7.64: a CCl_4 is non-polar because the individual bond dipoles cancel. **b** $CHCl_3$ is polar because the bond dipoles do not cancel out; there is a positive end to the molecule and a negative end. Although the C in $CHCl_3$ is shown as δ+, it is not as positive as H (C is more electronegative than H); therefore, C is slightly negative compared with H, although it is relatively positive overall in the molecule.

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EXAM TIP

The examination answer as to why CCl_4 is non-polar is 'although each individual bond is polar due to the difference in electronegativity of the atoms, because of the symmetry of the molecule, the bond dipoles cancel'.

Some polar and non-polar molecules are shown in Table 7.8.

Polar	Non-polar
HCl, H_2O, NH_3, SO_2, $CHCl_3$, CH_2Cl_2, CH_3Cl, SCl_2, XeO_3, PCl_3, $SOCl_2$, $POCl_3$	CO_2, C_2H_2, C_2Cl_4, BF_3, XeF_2, XeF_4, SF_6, PF_5, XeO_4, SO_3
	these molecules are non-polar, because, due to the symmetry of the molecules, the individual dipoles of the bonds cancel out

Table 7.8: Some polar and non-polar molecules. Molecules where the central atom has an expanded octet are highlighted in red.

EXAM TIP

There are many ways you can be asked whether something is polar:

Is the molecule polar?

Does the molecule have a dipole moment?

Does the molecule have a non-zero dipole moment?

Does the molecule have a net dipole moment?

TEST YOUR UNDERSTANDING

12 Arrange the following atoms in order of electronegativity (lowest first):

Cl, O, H, Br, Na.

13 Select the polar molecules from the following list. For the polar molecules, draw diagrams showing the overall dipole of the molecule.

HBr, HCN, PH_3, SCl_2, CF_4, N_2, OCl_2, BCl_3, C_2Cl_2, H_2S, CH_2Cl_2

The polarity of ions

The IB Chemistry syllabus states that you should be able to deduce the net dipole moment of ions. This is a far more difficult problem. First of all, because an ion is charged, we do not really talk about an ion being polar or not – it has an overall charge. One thing we can look at with ions is the distribution of the charge within the ion. For instance, with the CO_3^{2-} ion, the negative charge is going to be more on the O atoms than on the C atoms. However, calculation of the charge density within an ion is not simple, and it does not just rely on electronegativity values. For instance, in the cyanate ion (OCN^-), electronegativities would suggest that O would be more negative than N; however, calculations and experimental work suggest that it is the other way round.

7.7 Intermolecular forces

The nature of intermolecular forces

Br_2 is a liquid at room temperature. It consists of discrete molecules in which the two Br atoms are joined by a covalent bond (an **intramolecular force**). But if Br_2 is to be a liquid, there must be some forces between molecules holding them in the liquid state (otherwise, it would be a gas). These forces are **intermolecular forces** (Figure 7.65).

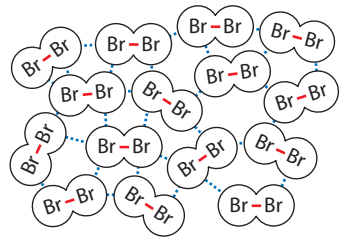

Figure 7.65: Intermolecular and intramolecular forces in liquid bromine. Intramolecular forces (covalent bonds) are shown in red and intermolecular forces are the dashed lines in blue.

There are various types of intermolecular force. The main type between non-polar atoms/molecules is the **London (dispersion) force**. London forces are much weaker than covalent bonds. Therefore, when bromine is heated gently, the London forces are overcome first,

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and the Br_2 molecules (with Br atoms held together by covalent bonds) remain intact (Figure 7.66).

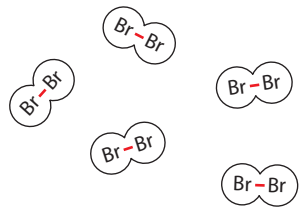

Figure 7.66: Gaseous bromine. Intramolecular forces (covalent bonds) are still present, but the intermolecular forces have been overcome – the intermolecular forces are weaker than covalent bonds and therefore less energy is required to overcome them.

The covalent bonds between the Br atoms can also be broken by heating, but then the bromine would have to be heated to a much higher temperature – much more energy would have to be supplied. The weaker, intermolecular, forces are overcome more easily.

KEY POINTS

London forces are present between all molecules in solid and liquid states.

Intermolecular forces are much weaker than covalent bonds.

How London forces arise

KEY POINT

London forces are temporary (instantaneous) dipole-induced dipole interactions.

Consider liquid argon. The electrons in an atom are in constant motion, and, at any one time, it is likely that they will not be symmetrically distributed about the nucleus, so one side of the atom will be slightly positive (fewer electrons) and the other slightly negative (more electrons). This is a temporary (instantaneous) dipole. This dipole will induce an opposite dipole in a neighbouring atom – the δ+ part will more strongly attract the electrons in a neighbouring atom, making that part of the neighbouring atom slightly negative. These dipoles will attract each other so that there is an attractive force between atoms (Figure 7.67). Although

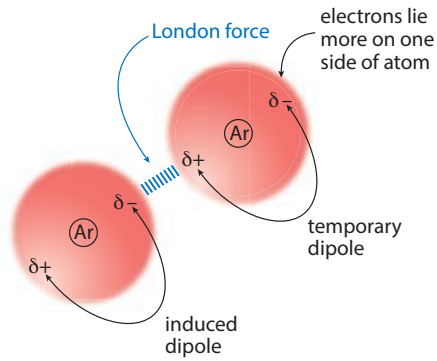

Figure 7.67: The origin of London forces.

the dipoles are constantly disappearing and reappearing, the overall force between the argon atoms is always attractive because one dipole always induces an opposite dipole in the neighbouring atom.

KEY POINT

London forces get stronger as relative molecular mass increases.

In general, London forces are stronger between molecules with more electrons. As the number of electrons increases, the relative molecular mass also increases, and we normally talk about 'an increase in the strength of London forces as the relative molecular mass increases'.

To boil a non-polar liquid, the London forces between the molecules must be broken (no covalent bonds are broken). We can, therefore, use the boiling point of a non-polar liquid as an indicator of the strength of London forces – the stronger the forces, the more energy must be supplied to overcome them and, therefore, the higher the boiling point.

A clear correlation between boiling point and relative molecular/atomic mass can be seen down Group 17 (blue line) and down Group 18 (red line) in Figure 7.68.

Relative atomic mass is used for the elements in Group 18 because they exist as individual atoms, with London forces between them, and not molecules.

Consider Group 17: fluorine (M_r 38.00) is a gas at room temperature, but iodine (M_r 253.80) is a solid. This is because there are more electrons in an iodine molecule, and the atoms making up the molecule are larger. More electrons moving around means that the temporary dipoles will be larger. Larger atoms in the molecule mean that the outer electrons will be less strongly held

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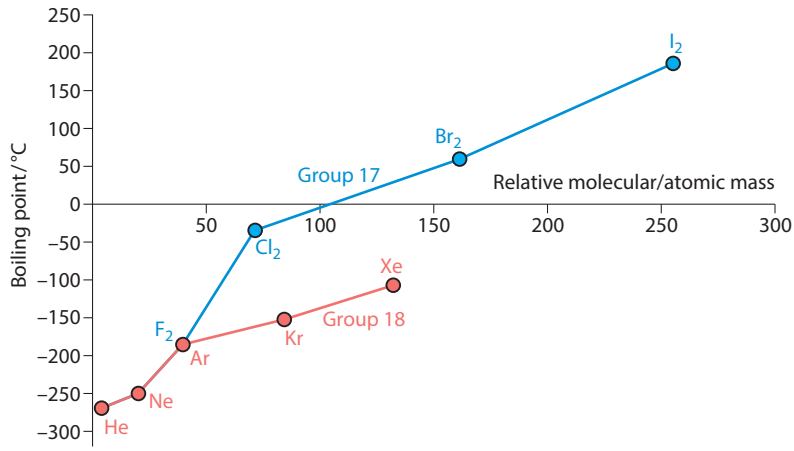

Figure 7.68: Variation in boiling points of elements in Groups 17 and 18.

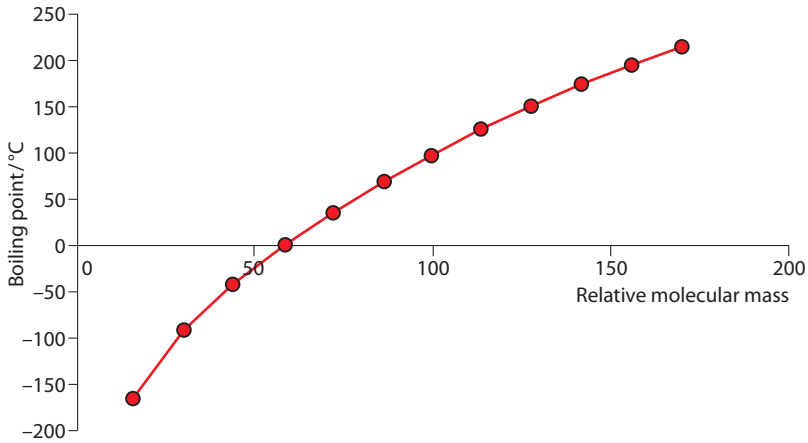

Figure 7.69: Boiling points of alkanes.

(further from the nucleus), so the molecule is more polarisable and, therefore, the induced dipoles will be larger. More polarisable means that it is easier to deform the electron cloud around an atom/molecule.

Care must be exercised when relating boiling point to relative mass. We can see in Figure 7.68 that Cl_2 has a higher boiling point than Xe although it has a lower relative mass. As with several other things we have seen in this chapter, comparisons are most useful when comparing species that are as similar as possible – for instance, the elements within a group or a series of similar compounds.

Figure 7.69 shows how the boiling point of the alkane series of compounds (Chapter 11) varies with relative molecular mass. As the relative molecular mass (and the length of the hydrocarbon chain) increases, so do the boiling points – e.g. butane (C_4H_{10}) has a higher boiling point than ethane (C_2H_6). A higher boiling point means that the London forces between molecules are stronger. The forces between the molecules are stronger because there are more atoms and, therefore, more electrons, present in butane than in ethane and more points of contact between the chains.

Polar molecules and dipole–dipole forces

Because of the electronegativity difference between H and Cl, H—Cl molecules are polar.

London forces are present between the molecules in HCl(l), but, because of the polarity of the molecules, there are also other intermolecular forces present (Figure 7.70). These are called permanent dipole–permanent dipole interactions, or usually just dipole–dipole forces/interactions.

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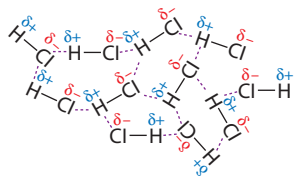


Figure 7.70: Permanent dipole – permanent dipole interactions exist between molecules. These are shown as purple dotted lines.

The intermolecular forces between molecules that are polar (dipole–dipole interactions as well as London forces) are stronger than those between non-polar molecules (only London forces), all other things being equal.

In general, all other things being equal, these permanent dipole–dipole interactions would be expected to cause melting points and boiling points to be higher for polar molecules. All other things being equal basically means that we should compare compounds with relative molecular masses as similar as possible (so that London forces are a similar as possible).

KEY POINT

If molecules with similar relative molecular masses are compared, polar molecules have higher melting and boiling points than non-polar molecules.

If we compare propane and ethanal (Table 7.9), both have a relative molecular mass of 44 and, therefore, the strength of London forces should be similar. However, ethanal is a polar molecule and has dipole–dipole interactions as well as London forces. The intermolecular forces between molecules of ethanal are stronger than those between propane molecules, and ethanal has a significantly higher boiling point, indicating more energy must be supplied to overcome the forces between molecules.

A similar situation is seen when we compare Br_2 with ICl (Table 7.10).

The relative molecular masses of these two molecules are very similar, and so, the strengths of the London forces are similar. However, ICl is polar (Cl is more electronegative than I), whereas Br_2 is non-polar. The intermolecular forces are stronger in ICl because of the dipole–dipole interactions. Stronger intermolecular forces mean that the boiling point of ICl is higher than that of Br_2.

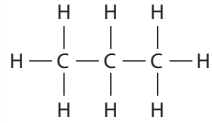
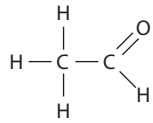
Molecule	Structure	M_r	Boiling point / °C
propane		44.11	−42
ethanal		44.06	21

Table 7.9: Comparing ethanal and propane.

Compound	M_r	Boiling point / °C
Br_2	159.80	59
ICl	162.35	100

Table 7.10: Comparing bromine and iodine chloride.

We cannot simply say that polar molecules have stronger intermolecular forces and higher boiling points than non-polar molecules, and this can be seen if we compare Br_2 with three other interhalogen compounds (Table 7.11).

Compound	M_r	Boiling point / °C	Polar / non-polar
Br_2	159.80	59	non-polar
ClF	54.45	−100	polar
BrF	98.90	20	polar
ClBr	115.35	5	polar

Table 7.11: Comparing bromine with interhalogen compounds.

Br_2 is the only molecule here that is non-polar, but it has the highest boiling point, as a result of its highest relative molecular mass and, therefore, strongest London forces.

BrF has a higher boiling point than ClBr, despite having a lower relative molecular mass, because it is more polar than ClBr due to a bigger difference in electronegativity between Br and F compared to Cl and Br.

Dipole-induced dipole forces

If liquid HCl is mixed with liquid chlorine, the polar HCl molecule will induce a dipole in the non-polar Cl_2 molecule. In Figure 7.71, the slightly positive H of HCl will attract the electrons more on the side

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of the Cl_2 molecule closest to it, making that side of Cl_2 slightly negative and the other side slightly positive – an induced dipole. Because an opposite dipole will always be induced, the dipole-induced dipole forces will always be attractive.

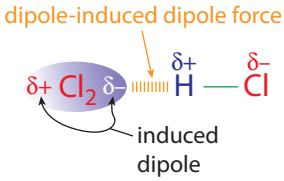

Figure 7.71: Dipole-induced dipole interactions.

van der Waals forces

van der Waals forces is the collective name given to forces between molecules and includes London (dispersion) forces, dipole–dipole interactions and dipole–induced dipole interactions. Hydrogen bonding (see next section) and ion–dipole interactions are not counted as van der Waals forces.

Hydrogen bonding

Hydrogen bonding is an intermolecular force that influences many properties of substances, and it could be argued that life as we know it would not exist on Earth without it.

Evidence for hydrogen bonding

Table 7.12 and Figure 7.72 compare the boiling points of the hydrides of Group 16 elements.

The boiling point increases from H_2S to H_2Te, as would be expected from the increase in the strength of London forces as the relative molecular mass increases.

Group 16 hydride	Boiling point / °C
H_2O	100
H_2S	–60
H_2Se	–41
H_2Te	–4

Table 7.12: Boiling points of some hydrides.

H_2O has, however, a much higher boiling point than would be expected from its relative molecular mass. Even if we allow for the fact that H_2O is the most polar molecule, we cannot explain such a large difference in boiling points. This suggests that there must be intermolecular forces other than London forces and dipole–dipole interactions between H_2O molecules and that these intermolecular forces are significantly stronger than the other forces. These extra intermolecular forces between H_2O molecules are called *hydrogen bonds*.

The nature of hydrogen bonds

A hydrogen bond between two water molecules is shown in Figure 7.73.

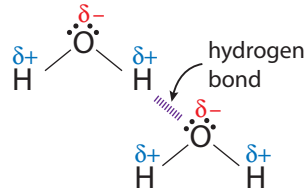

Figure 7.73: A hydrogen bond between two water molecules. The hydrogen bond is the dashed purple line between the lone pair of the δ– oxygen on one molecule and a δ+ hydrogen on the other molecule.

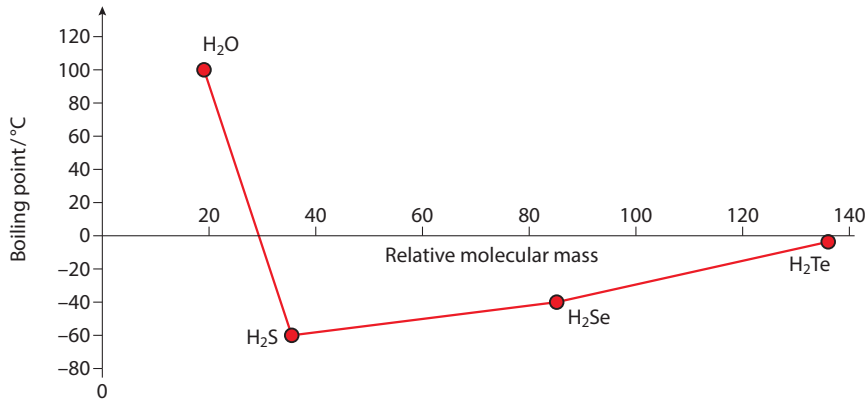

Figure 7.72: Boiling points of Group 16 hydrides.

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Hydrogen bonding occurs between molecules when a very electronegative atom (N, O, F) is joined to a hydrogen atom in the molecule. The electronegative atom withdraws electron density from the hydrogen, polarising the bond so that H is δ+ and the other atom is δ–. The δ+ H in one molecule will be strongly attracted to the δ– atom in a neighbouring molecule.

However, if hydrogen bonding between molecules just involved dipole–dipole interactions, then Cl, with a higher electronegativity than N, would also be expected to participate in hydrogen bonding; but, there is very little hydrogen bonding in liquid HCl. There must, therefore, be more to hydrogen bonding than just an electrostatic interaction between dipoles.

When H is attached to a very electronegative atom, the electron density is pulled away strongly from H so that there is little electron density around the nucleus (H has no inner shells of electrons). The electron density of the lone pair on N, O or F in one molecule can then interact with the H nucleus in a different molecule. There is thus a directional component to hydrogen bonds and the formation of a partial bond between the H atom in one molecule and the N/O/F atom in another molecule. Because of this directional component, a hydrogen bond should always be drawn in line with the H—X bond (Figure 7.74) – the linear arrangement maximises the strength of the interaction. It is important to realise, however, that, although hydrogen bonding is the strongest of the intermolecular forces, it is much weaker than covalent bonding.

Hydrogen bonding between ammonia molecules and hydrogen fluoride molecules is shown in Figure 7.75.

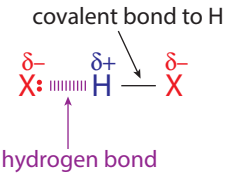

Figure 7.74: A hydrogen bond should be in line with the H—X covalent bond.

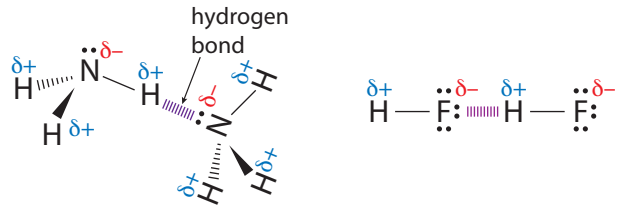

Figure 7.75: Hydrogen bonding between ammonia molecules and between hydrogen fluoride molecules. Note how the hydrogen bonds are drawn in line with the H—X bond.

Deciding whether there is hydrogen bonding between molecules

We can work out whether there will be hydrogen bonding between molecules simply by looking at whether the molecule contains N/O/F joined directly to a hydrogen atom. Table 7.13 shows some molecules that have hydrogen bonding between them and others that do not.

KEY POINT

The requirements for hydrogen bonding are that the H atom is attached to a very electronegative atom – N, O or F – which possesses at least one lone pair of electrons.

Hydrogen bonding between molecules	No hydrogen bonding between molecules
HF	HCl
H_2O	H_2S
NH_3	PH_3
CH_3CH_2OH	CH_3OCH_3
$CH_3CH_2NH_2$	CH_3CH_2F
hydrogen bonding between molecules, because there is an H joined directly to an N, O or F atom	no hydrogen bonding between molecules, because H is not joined to N, O or F

Table 7.13: Hydrogen bonding or no hydrogen bonding?

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Methoxymethane (CH_3OCH_3) has the structure shown in Figure 7.76a.

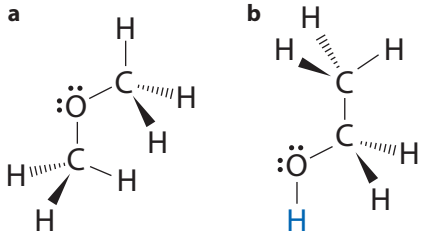

Figure 7.76: a The structure of methoxymethane. **b** The structure of ethanol.

It is a polar molecule, but there is no hydrogen bonding between molecules because it does not have an H joined directly to an O. The structure of ethanol (CH_3CH_2OH), which has the same molecular formula as methoxymethane, is shown in Figure 7.76b. Ethanol will have hydrogen bonding between molecules because it has an H joined directly to the O – this is highlighted in blue. Hydrogen bonding between some molecules of ethanol is shown in Figure 7.77.

There is no hydrogen bonding between molecules of CH_3CH_2F because H is not joined directly to an F atom, but there would be hydrogen bonding between molecules of $CH_3CH_2NH_2$ because two H atoms (in blue) are joined directly to N (Figure 7.78).

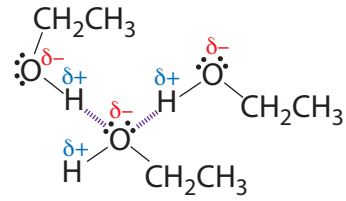

Figure 7.77: Hydrogen bonding in ethanol.

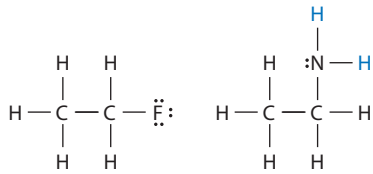

Figure 7.78: Lewis formulas of fluoroethane and ethylamine (ethanamine).

EXAM TIP

Remember, hydrogen bonding is an *intermolecular* force – you should usually try to include the words 'between molecules' in an answer about hydrogen bonding.

SCIENCE IN CONTEXT

Is hydrogen bonding essential for life on Earth? Hydrogen bonding is one of the main forces responsible for the three-dimensional structure of proteins and holds together the strands of DNA, but, probably more than anything else, the importance of hydrogen bonding comes from the influence it has on the properties of water. Perhaps the most important of these is that water ($M_r = 18.02$) has an extremely high boiling point for its relative molecular mass, which means that it is a liquid at the temperature of the Earth – methane (CH_4, $M_r = 16.05$) has a boiling point of –162 °C and ethane (C_2H_6, $M_r = 30.08$) has a boiling point of –89 °C.

If you have ever looked at an ice cube in a drink, you will notice that it floats – this is very unusual – usually the solid form of a substance is denser than the liquid. However, to achieve the maximum amount of hydrogen bonding, ice has a very open structure

Figure 7.79: Without hydrogen bonding, water would not be a liquid at the temperature of the Earth.

that makes it less dense. This structure collapses slightly as ice melts, making the water denser. A consequence of this is that water freezes from the top down rather than the bottom up; if it were the

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CONTINUED

other way round, many more bodies of water would freeze completely, killing everything in them.

Hydrogen bonding is also one of the reasons that water is a very good solvent, so that enzymes, which catalyse the reactions of life, are soluble in the water in cells. It also causes ethanol to be soluble in water in all proportions. Ethanol is the alcohol in alcoholic drinks – these are not pure ethanol but solutions of ethanol in water. Beers are usually around 5%, wines about 10 – 15% and spirits 40% solutions of ethanol in water (although some spirits are much more concentrated solutions than this). Although the consumption of alcoholic drinks is a socially acceptable activity in many countries and cultures, there is a negative side to alcohol and the World Health Organization estimates that annually about three million deaths (over 5% of all deaths) worldwide result from the harmful use of alcohol.

Figure 7.80: Icebergs float.

7.8 Melting points and boiling points

Melting/boiling points and intermolecular forces

All the substances we are looking at in this section consist of individual molecules with intermolecular forces between them. It is really important to remember:

KEY POINT

Only intermolecular forces are broken when covalent molecular substances are melted or boiled – covalent bonds are not broken.

The stronger the intermolecular forces, the more energy must be supplied to overcome them and the higher the boiling point.

The effect of relative molecular mass

This will often be the most important factor in determining the melting/boiling points of covalent molecular substances.

KEY POINT

Generally, substances with higher relative molecular masses have higher melting points and boiling points due to stronger London forces.

Consider the four compounds in Table 7.14, which all have the formula CH_3X, where X is a halogen.

	CH_3F	CH_3Cl	CH_3Br	CH_3I
boiling point (°C)	–78	–24	4	42
M_r	34.04	50.49	94.94	141.94

Table 7.14: The effect of M_r on boiling point

CH_3I has the strongest London forces because it has the highest relative molecular mass (most electrons) and, therefore, the highest boiling point.

Of these molecules, CH_3F will be the most polar and CH_3I the least polar, because F is the most electronegative of the halogens and I is the least electronegative. It can be seen, however, that any effect due to differences in the strength of dipole–dipole interactions is far outweighed by the effect of London forces.

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The effect of different intermolecular forces

On the IB syllabus, the following statement is made about intermolecular forces of attraction:

London forces < dipole–dipole forces < hydrogen bonding

WEAKEST → STRONGEST

However, London forces are present between all molecules and, if hydrogen bonding is present, there will also be dipole–dipole interactions, so the key thing to look at is the *total* of all the intermolecular forces present. We have also seen that the relative molecular mass is often the key factor in determining the strength of intermolecular forces.

Therefore, if the *relative molecular masses are similar*, then perhaps a better statement about the strength of intermolecular forces is:

London forces between molecules < dipole–dipole forces + London forces < hydrogen bonding + dipole–dipole forces + London forces

WEAKEST → STRONGEST

The effect of the presence of different types of intermolecular forces on the boiling point is summarised in Table 7.15.

Type of substance		Intermolecular forces
substances containing H bonded to N, O or F	decreasing boiling point	hydrogen bonding, permanent dipole–dipole, London forces
polar substances		permanent dipole–dipole, London forces
non-polar substances		London forces

Table 7.15: If relative molecular masses are approximately equal, then the boiling points usually change in the order shown.

Hydrogen bonding is a particularly strong intermolecular force and the influence of this can be considerable and outweigh significant differences in relative molecular mass – this will be considered next.

WORKED EXAMPLE 7.2

Compare the boiling points of propane ($CH_3CH_2CH_3$), methoxymethane (CH_3OCH_3) and ethanol (CH_3CH_2OH).

Answer

Let us compare the relative molecular masses of these substances:

$CH_3CH_2CH_3$: 44.11, CH_3OCH_3: 46.08, CH_3CH_2OH: 46.08

The relative molecular masses are all very similar and, therefore, the strengths of the London forces are going to be similar. The next thing we can look at is whether any of the molecules are polar:

$CH_3CH_2CH_3$: non-polar, CH_3OCH_3: polar, CH_3CH_2OH: polar

The presence of the very electronegative O atom in CH_3OCH_3 and CH_3CH_2OH means that these substances are polar. $CH_3CH_2CH_3$ is the only non-polar molecule and will have the lowest boiling point because the only forces between molecules are London forces. CH_3OCH_3 and CH_3CH_2OH have dipole–dipole forces as well as London forces.

CH_3OCH_3 and CH_3CH_2OH are both polar and have the same relative molecular mass, but CH_3CH_2OH has an H joined to an O and, therefore, there is also hydrogen bonding between molecules.

CH_3CH_2OH, therefore, has hydrogen bonding, dipole–dipole forces and London forces between molecules, whereas CH_3OCH_3 only has dipole–dipole and London forces between molecules. Hydrogen bonding is also a particularly strong intermolecular force; therefore, overall, the intermolecular forces are stronger between molecules of CH_3CH_2OH than between molecules of CH_3OCH_3, and CH_3CH_2OH has a higher boiling point than CH_3OCH_3.

The boiling points of these compounds are as follows:

$CH_3CH_2CH_3$: –42 °C, CH_3OCH_3: –25 °C, CH_3CH_2OH: 78 °C

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WORKED EXAMPLE 7.3

The boiling points of three hydrides of Group 15 are shown in the table:

	NH_3	PH_3	AsH_3
Boiling point / °C	–33	–134	–116

Explain this order in terms of intermolecular forces.

Answer

NH_3 has a significantly lower relative molecular mass (17.04) than AsH_3 (77.95) and, therefore, would be expected to have a lower boiling point because the London forces between molecules are weaker. However, because NH_3 has an H joined directly to an N atom, there is hydrogen bonding between molecules. Hydrogen bonding between NH_3 molecules is stronger than the London forces between PH_3 and AsH_3 molecules; therefore, more energy is required to overcome the intermolecular forces between NH_3 molecules, and it has the highest boiling point.

Both PH_3 and AsH_3 are only very slightly polar and the main reason that AsH_3 has a higher boiling point than PH_3 is because AsH_3 has a higher relative molecular mass and, therefore, stronger London forces between molecules. Higher relative molecular mass means that there are more electrons in an AsH_3 molecule (an As atom is also larger and, therefore, more polarisable than a P atom); therefore, instantaneous dipoles and induced dipoles will be larger, leading to stronger London forces.

7.9 Solubility

It is often said, when referring to solubility, that 'like dissolves like'.

KEY POINT

Generally, a substance will dissolve in a solvent if the intermolecular forces in the solute and solvent are similar.

Whether or not a covalent molecular substance dissolves depends (in part) on how much energy is needed to overcome intermolecular forces in the solvent and solute and then how much energy is released, to pay back this energy, when intermolecular forces are formed between solvent and solute molecules in the solution.

Link

Solubility is discussed here from the point of view of energy. The influence of entropy on solubility will be considered in Chapter 15.

Pentane is readily soluble in hexane but insoluble in water

Pentane (C_5H_{12}) and hexane (C_6H_{14}) are both non-polar organic liquids with only London forces between molecules. The amount of energy required to overcome the London forces in pure hexane and pure pentane is

TEST YOUR UNDERSTANDING

14 For each of the following pairs, deduce which has the higher boiling point:

a Cl_2 or Br_2 **b** CH_3Cl or CH_3Br

c N_2 or CO **d** NO or O_2.

15 Draw a diagram to show the hydrogen bonding between molecules of water.

16 Which of the following will have hydrogen bonding between molecules?

HF, H_2, CH_3F, CH_3OH, H_2CO, N_2H_4, H_2S

17 Arrange the molecules in the following sets in order of increasing boiling point (lowest first):

a CH_4, CCl_4, CF_4 **b** HF, HCl

c NH_3, N_2H_4, CH_4 **d** CH_3OH, CH_3F, C_2H_4

e H_2O, H_2S, H_2O_2

f $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2OCH_2CH_3$, $CH_3CH_2CH_2CH_2CH_3$

g N_2, F_2, HF, Ne.

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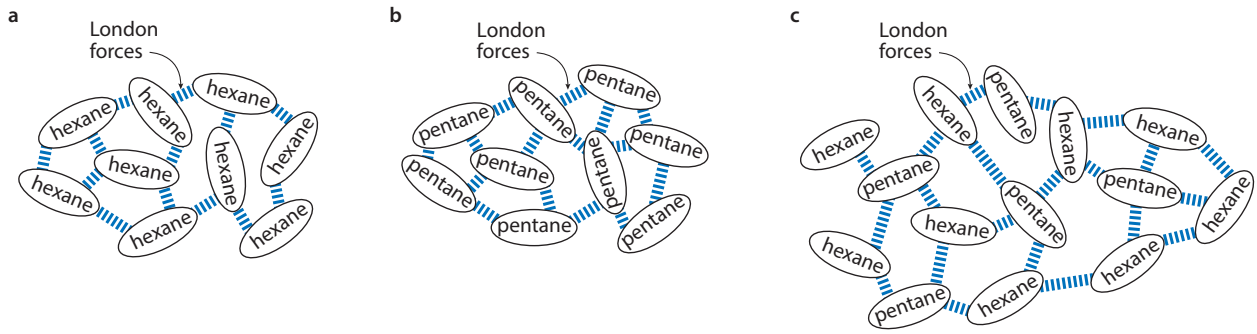

Figure 7.81: a There are London forces between hexane molecules; **b** there are London forces between pentane molecules; **c** there are London forces between hexane and pentane molecules when pentane dissolves in hexane.

paid back when London forces are formed between the molecules of hexane and pentane (Figure 7.81).

Pentane does not dissolve in water because there is hydrogen bonding between water molecules. If pentane were to dissolve in water, there would only be London forces/dipole–induced dipole forces between water molecules and pentane. The energy released if London forces/dipole–induced dipole forces were to form between water molecules and pentane molecules would not pay back the energy required to break the hydrogen bonds between water molecules, because the hydrogen bonds between the water molecules are significantly stronger than London forces/dipole–induced dipole forces between water and pentane molecules.

Hydrogen bonding and solubility

KEY POINT

Substances that are able to participate in hydrogen bonding will generally be soluble in water, because they are able to hydrogen bond to water.

Solubility of alcohols in water

Ethanol (C_2H_5OH) is very soluble in water because ethanol is able to hydrogen bond to water (Figure 7.82). The formation of hydrogen bonds between water molecules and ethanol molecules in solution releases energy and pays back the energy to break hydrogen bonds in pure water and pure ethanol.

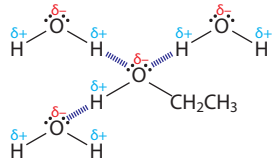

Figure 7.82: Hydrogen bonding between water and ethanol.

KEY POINT

Longer chain alcohols become progressively less soluble in water.

Octan-1-ol is insoluble in water. Although there is some hydrogen bonding between the OH group of the alcohol and water molecules, the long, non-polar, hydrocarbon chain prevents water molecules on either side from hydrogen bonding to each other (Figure 7.83). Energy

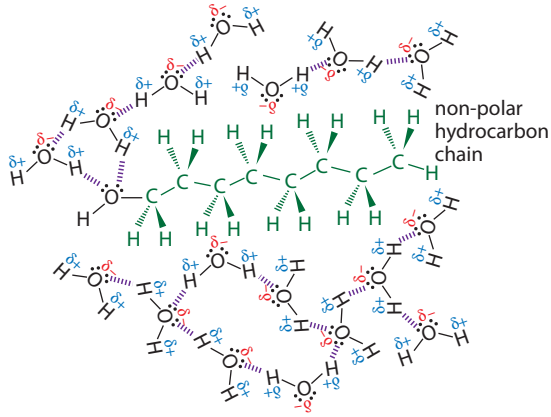

Figure 7.83: The hydrocarbon chain in octan-1-ol prevents hydrogen bonding between water molecules on either side.

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is needed to break the hydrogen bonds between water molecules, but this is not paid back, as only London/dipole–induced dipole forces form between the water molecules and the hydrocarbon part of the molecule.

Chromatography and intermolecular forces

Paper chromatography as a means of separating the components of a mixture has already been discussed in Chapter 1.

Thin-layer chromatography (TLC) is a very similar technique to paper chromatography, and the experiment is carried out in basically the same way, but instead of a piece of paper, a plate (a piece of plastic, glass or metal) coated in silica gel or alumina (the adsorbent) is used.

TLC may be used for similar separations to those for paper chromatography. TLC has many advantages over paper chromatography; for example, it is faster and gives better resolution (better separation of spots).

KEY POINT

All chromatography techniques involve a **stationary phase** and a **mobile phase**. The components in a mixture are separated because of their differences in affinity for (attraction to) the stationary and mobile phases. Affinity for/attraction to mobile and stationary phases depends on intermolecular forces.

Paper chromatography and partition

The fibres that make up the chromatography paper are coated with water – this water is not free to move – it is the **stationary phase** in paper chromatography; the **mobile phase** is the solvent moving up the paper. Separation is due to **partition** of the various substances between the stationary and mobile phases according to their solubility in each. Compounds more soluble in the water on the fibres (stationary phase) will move up the paper more slowly, whereas compounds more soluble in the mobile phase will move up the paper more quickly.

Partition

Partition is the tendency of a solute to be distributed between two immiscible solvents according to its solubility in each solvent. For instance, if an aqueous solution of bromine is shaken with hexane (Figure 7.84),

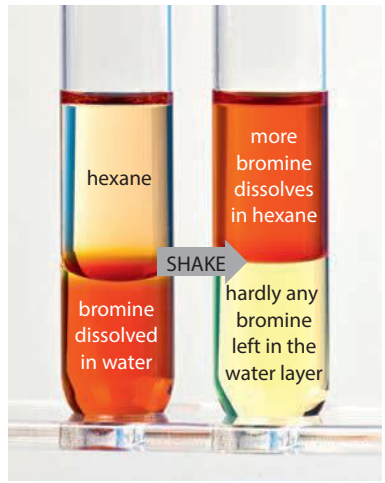

Figure 7.84: Bromine is more soluble in hexane than water.

most of the bromine moves into the hexane layer, as bromine (non-polar) is more soluble in hexane (non-polar). The intermolecular forces are more similar between bromine and hexane than between bromine and water.

TLC and adsorption

Separation in TLC is due to **adsorption** – the components of the mixture are either dissolved in the solvent or adsorbed onto the stationary phase (the plate coated with silica or alumina). The greater the tendency of a solute molecule to be adsorbed onto the stationary phase, the more slowly it moves along the plate.

Note: the process is *ad*sorption and not *ab*sorption – particles stay on the surface, they do not go into the stationary phase.

In Figure 7.85, the red particles have a greater tendency to be adsorbed on the solid particles, and so spend less time dissolved in the solvent moving up the TLC plate. The yellow particles have very little tendency to be adsorbed on the solid particles, and so spend more time dissolved in the mobile phase. The yellow particles thus travel more quickly up the plate.

Adsorption relies on the formation of intermolecular forces between solute molecules and the silica surface. The nature of the groups at the surface of silica is such that stronger interactions are formed with polar molecules rather than non-polar molecules. In Figure 7.85, the red particles are more polar than the yellow ones.

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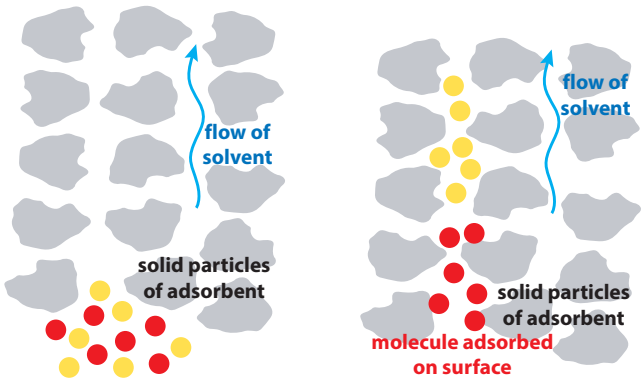

Figure 7.85: In general, the more polar the solute particles, the greater tendency they will have to be adsorbed on the stationary phase. The red particles are more polar than the yellow ones.

R_F value

We can describe the position of spots on a paper chromatogram/TLC plate using the **R_F (retardation factor) value**:

KEY POINT

$$R_F = \frac{\text{distance solute moves}}{\text{distance solvent front moves}}$$

These distances can be measured on the paper or TLC plate from the position of the original pencil line (not from the bottom of the paper or plate) (Figure 7.86).

$$R_F = \frac{b}{a}$$

$$R_F = \frac{27}{59} = 0.46$$

The R_F value is a ratio, so it has no units.

EXAM TIP

You will need a ruler in the examination to measure these values. Remember to measure from the baseline/pencil line (not the bottom of the paper/plate). There will always be some tolerance allowed in the examination (e.g. +/–0.02) on the R_F value.

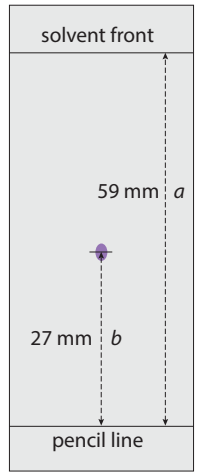

Figure 7.86: Measure from the pencil line to the middle of the spot.

An R_F value close to 1 indicates that a component has a very high solubility in the mobile phase, whereas a very low R_F value means that the component hardly moves at all from the baseline and has a very high affinity for the stationary phase/low solubility in the mobile phase.

Consider a paper chromatography/TLC experiment using a non-polar solvent. A spot of a mixture of two components, X (polar) and Y (non-polar), is put on the chromatography paper/TLC plate and the solvent allowed to travel up the paper/plate until it gets to within about 1 cm of the top (Figure 7.87). The paper/plate is then withdrawn from the solvent, the position of the solvent front marked with a pencil, and allowed to dry (the solvent evaporates).

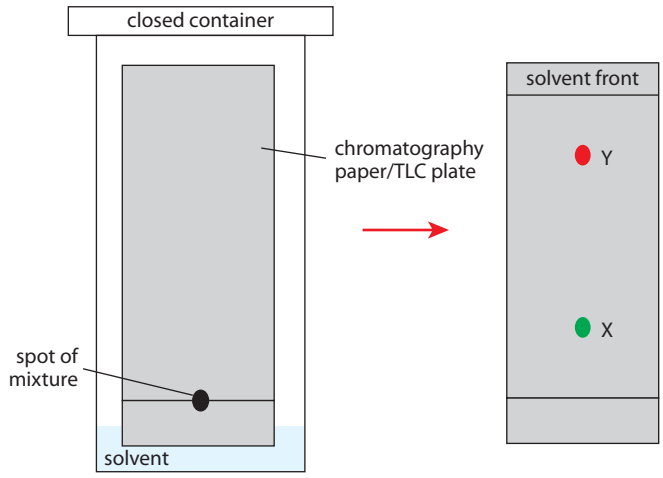

Figure 7.87: Paper chromatography/TLC experiment to separate X and Y.

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Measuring the distances X and Y have travelled from the baseline we get:

R_F value of X = 0.23

R_F value of Y = 0.80

The R_F value depends strongly on the solvent used as the mobile phase but is also affected by the type of paper or plate used.

Paper chromatography

Because X is polar, it is more soluble in the stationary phase (water on the fibres) and less soluble in the non-polar solvent. This is because the intermolecular forces are more similar between X and water than between X and the non-polar solvent. X spends more time dissolved in the stationary phase and less time dissolved in the mobile phase; therefore, it travels a smaller distance up the paper and has a lower R_F value.

TLC

Because X is polar, it is adsorbed more strongly onto the stationary phase and is less soluble in the non-polar solvent. This is because the forces between X and the groups at the surface of the adsorbent are stronger. X spends more time adsorbed on the stationary phase and less time dissolved in the mobile phase; therefore, it travels a smaller distance up the plate and has a lower R_F value.

Using the R_F value to identify the components of a mixture

The R_F value may be useful in identifying the components of a mixture. Consider an experiment in which we wish to determine the dyes present in a mixture: we suspect that the mixture, Z, contains some or all of the dyes A, B, C and D. The mixture is spotted onto a piece of chromatography paper or a TLC plate together with pure samples of each of the dyes A–D (Figure 7.88).

The results show that Z contains three components, and as the spots of A, B and C have moved the same distance as the individual components of Z, we can be reasonably sure that Z is a mixture of A, B and C. No component of Z moves the same distance as D, so Z does not seem to contain D.

The experiment could also have been conducted using separate plates/pieces of chromatography paper and comparing the R_F values of the pure dyes with each component of Z. If the R_F values were the same using the same solvent and the same type of TLC plate or chromatography paper, it would be likely that the substances were the same.

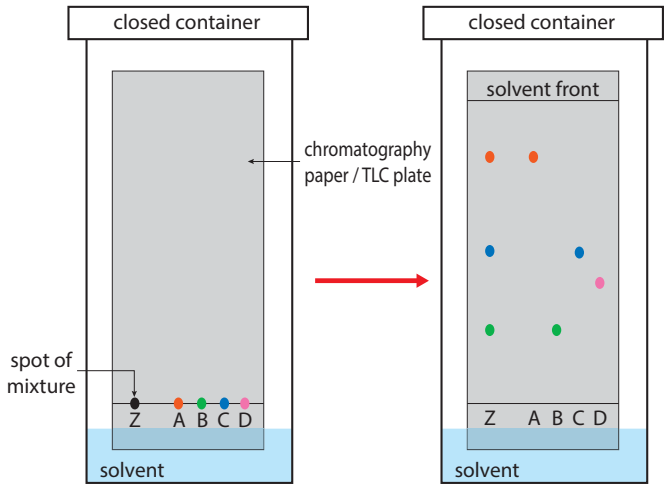


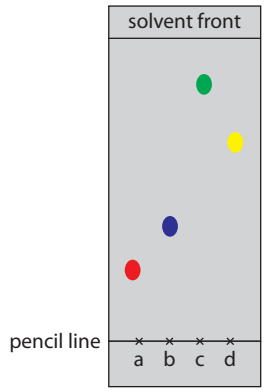
Figure 7.88: Using chromatography to identify the components of a mixture, Z.

TEST YOUR UNDERSTANDING

18 Which will be more soluble in water?

- **a** NaCl or CCl_4
- **b** CH_3OH or CH_3Cl
- **c** CH_3CH_2OH or $CH_3CH_2CH_2CH_2CH_2CH_2OH$
- **d** $CH_3CH_2CH_2CH_2CH_2CH_2OH$ or $CH_2(OH)CH_2CH_2CH_2CH_2CH_2OH$

19 Calculate the R_F value of each of the spots on the TLC plate.



20 Arrange the substances in question 19 in order of polarity (least polar first) if the experiment was carried out using a non-polar solvent.

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7.10 Covalent network structures

So far, we have looked at covalent *molecular* substances. For instance, carbon dioxide is a covalent molecular substance – in all states it exists as individual CO_2 molecules. In the solid state (below –78 °C), the individual CO_2 molecules are arranged in a regular array with intermolecular forces between them (Figure 7.89).

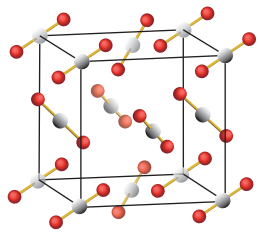

Figure 7.89: Arrangement of CO_2 molecules.

There are other covalent substances that exist as *networks* in the solid state; each atom is joined to neighbouring atoms by covalent bonds and there are no individual molecules. These substances are said to have **covalent network structures** or giant covalent structures. Solids with covalent network structures usually have much higher melting/boiling points than molecular solids because, to melt/boil a network solid, covalent bonds have to be broken – these are much stronger than the intermolecular forces that are broken when a molecular solid is melted/boiled.

Allotropes

Allotropes are different forms of the same element. For instance, diamond, graphite, graphene and fullerenes are all allotropes of carbon. They all contain only carbon atoms, but these atoms are joined together differently in each structure. Because the structure and bonding of allotropes are different, they have different physical and chemical properties, for example, tin has a metallic allotrope (white tin) and a non-metallic one (grey tin).

Other elements that exist as allotropes include oxygen (O_2 and O_3) and phosphorus.

Diamond

Diamond has a covalent network structure. There are no individual molecules – the whole structure continues in three dimensions with each carbon atom joined to four others, in a tetrahedral array, by covalent bonds (Figure 7.90). The structure of diamond is based on puckered hexagonal rings.

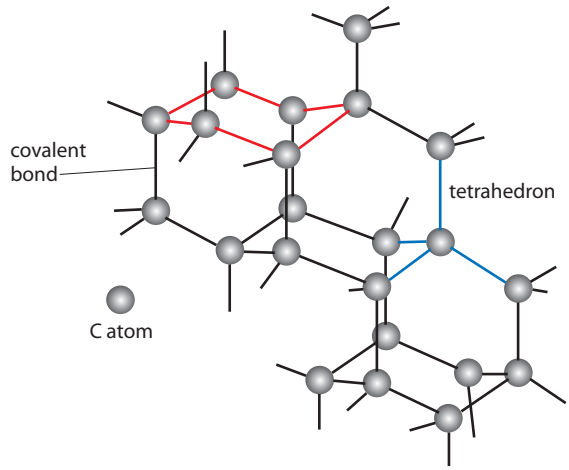

Figure 7.90: Part of the diamond structure, which is based on *puckered* hexagonal rings. One hexagon is highlighted in red.

EXAM TIP

Remember, the structure of diamond is a *covalent network*. *Tetrahedral* is the arrangement of atoms around each carbon and not the name of the structure.

Diamond has a very high melting point and boiling point (about 4000 °C) because covalent bonds must be broken when diamond is melted/boiled; this requires a lot of energy because the bonds are very strong. Diamond is very hard for the same reason.

Diamond does not conduct electricity, because all the electrons are held tightly in covalent bonds and are, therefore, not free to move through the structure.

Diamond is not soluble in water or organic solvents because the forces between the atoms are too strong. The energy to break these covalent bonds would not be paid back when the C atoms formed interactions with solvent molecules.

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Graphite

Like diamond, graphite has a covalent network structure. Unlike diamond, however, it has a layer structure (Figure 7.91).

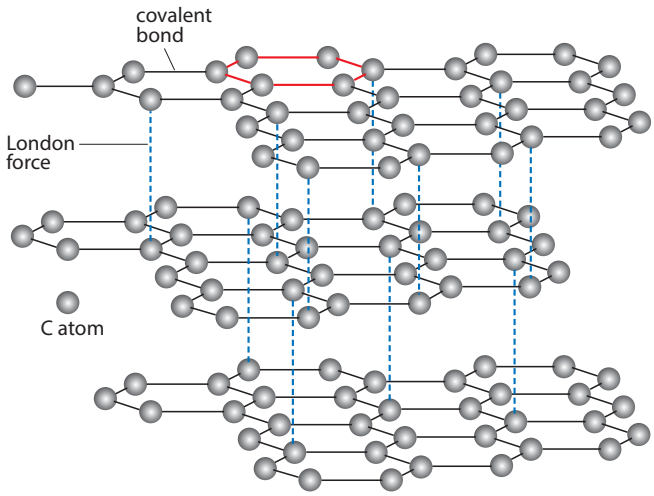

Figure 7.91: Part of the structure of graphite, which is based on *planar* hexagonal rings. One hexagon is highlighted in red.

Each C is covalently bonded to three others in a trigonal planar array. The structure is also based on hexagons, but here the hexagons are planar.

There are covalent bonds between the C atoms within a layer but only London forces between the layers (some of these are shown in blue in Figure 7.91). The presence of weak forces between the layers is usually given as the explanation that graphite is a good lubricant (used in pencils, for example) – not much force is required to separate the layers.

Although the lubricant properties of graphite are usually explained as being due to the weak forces between layers of carbon atoms, graphite is a poor lubricant in a vacuum, and the lubricant properties actually come from water molecules adsorbed on the surface.

Graphite has a very high melting/boiling point because strong covalent bonds within the layers must be broken when it is melted/boiled and this requires a lot of energy.

Graphite is not soluble in water or non-polar solvents. This is because of the strong covalent bonds between atoms. The energy to break these covalent bonds would not be paid back when the C atoms formed interactions with solvent molecules.

Graphite conducts electricity because *delocalised* electrons are free to move. Each C atom forms only three covalent bonds – the extra electrons not used in these bonds (carbon has four outer-shell electrons) are delocalised (spread) over the whole structure and able to move within the layers.

What are delocalised electrons?

When the three covalent bonds are formed by each carbon atom in the layers in graphite, there is one p orbital, containing one electron, left over. (These p orbitals are perpendicular to the plane of the layers (Figure 7.92) and can overlap side-on to give a π system (see Higher Level Section 7.16) extending over the whole layer. The electrons can move throughout this system and because they do not belong to one atom in particular are said to be delocalised. Movement of delocalised electrons within this π system allows the conduction of electricity within layers. Graphite is, however, an electrical insulator perpendicular to the plane of the layers because the electrons cannot move between the layers.

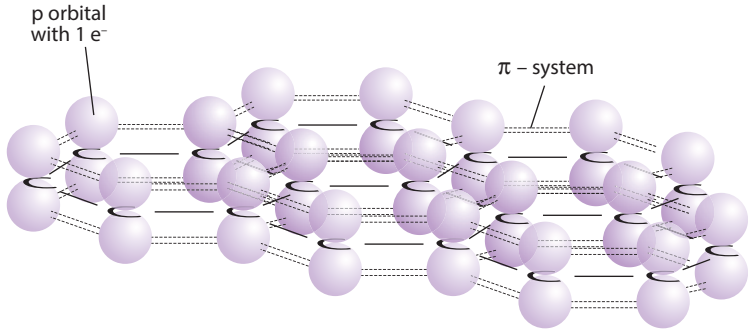

Figure 7.92: Delocalisation in graphite.

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Graphene

Graphene is a relatively new form of carbon that consists of a single layer of graphite. It is difficult to make large sheets of graphene and especially large single crystals, but the technology is developing, and graphene has some interesting properties that could make it very important in the near future as a new material in the electronics industry.

Graphene has a very high tensile strength and would be expected to have a very high melting point because covalent bonds need to be broken to break the sheet. It is also a very good electrical (C forms only three bonds) and thermal conductor.

NATURE OF SCIENCE

Science is a highly collaborative subject. The study of graphene lies on the boundary between chemistry and physics. The isolation of graphene was the result of collaboration between scientists of different nationalities and at universities in different countries. Scientists working in universities publish work in peer-reviewed journals and present their findings at conferences, which makes the knowledge available to others working in the same field; however, scientists also work for commercial companies and a lot of the work on graphene will be kept secret.

C_{60} fullerene (buckminsterfullerene)

The fourth allotrope of carbon that will be considered here has a molecular rather than a network structure. It consists of individual C_{60} molecules, with covalent bonds within the molecule and London forces between the molecules (Figure 7.93).

C_{60} is insoluble in water but soluble in some organic solvents, such as benzene. The energy to overcome the London forces between C_{60} molecules is paid back by the energy released when London forces are formed between C_{60} molecules and the solvent. C_{60} does not conduct electricity. Although each C forms three bonds in the C_{60} molecule, so that there is delocalisation of electrons over the molecule, the molecular structure means that electrons are not able to move from one molecule to the next.

Diamond and graphite have network structures, but C_{60} has a molecular structure. The melting points of diamond and graphite (around 4000 °C) are, therefore, substantially higher than that of C_{60}, because strong covalent bonds must be broken when diamond and graphite are melted, but only much weaker intermolecular forces (London forces) must be overcome when C_{60} melts (it actually sublimes at about 530 °C).

Silicon

Silicon, like carbon, is in Group 14 of the periodic table. Silicon has the same structure as diamond – a covalent network structure in which each Si atom is joined to four others by covalent bonds in a tetrahedral array. Silicon has a high melting point because it takes a lot of energy to break the strong covalent bonds in the network structure. The melting point (1414 °C) is substantially lower than that of diamond (around 4000 °C). If we look at the bond lengths in silicon and diamond, we can see the reason for this:

Si—Si bond length: 235.2 pm

C—C bond length: 154.5 pm

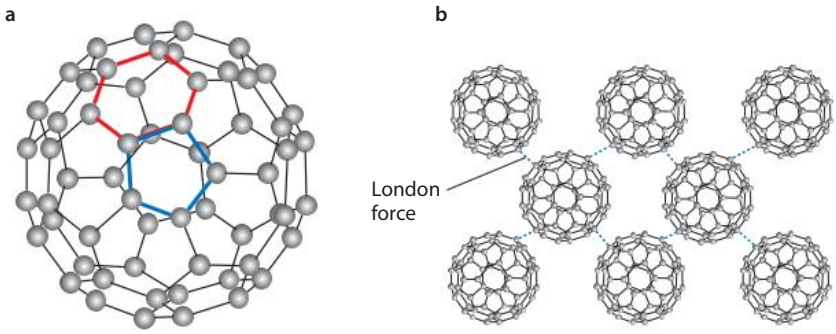

Figure 7.93: a One molecule of C_{60}. The structure is based on hexagons (one highlighted in red) and pentagons (one highlighted in blue). **b** London forces exist between C_{60} molecules in the solid state.

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The Si—Si bond length is substantially longer than the C—C bond length. This means that the electron pair in the bond is further away from the nuclei of the atoms making up the bond and, therefore, the electrostatic attraction is weaker. Less energy is required to break the Si—Si bond and, therefore, the melting point is lower.

Silicon is a semiconductor – it conducts electricity significantly less well than metals and graphite but much better than diamond. Unlike metals, where the electrical conductivity decreases as temperature is increased, silicon conducts electricity better as temperature is increased. Although, the electrons in silicon appear to be all held tightly in chemical bonds and, therefore, not free to move around, the bonds are weaker in silicon than in diamond, which means that the energy gap to the next available set of vacant orbitals is lower and electrons can be promoted to these higher orbitals (more electrons are promoted at higher temperatures). The electrons in this higher set of orbitals are free to move around and carry electricity.

Silicon dioxide

SiO_2 (quartz) is a compound with a covalent network structure (Figure 7.94). Each silicon atom is bonded to four oxygen atoms in a tetrahedral array. Each oxygen is bonded to two silicon atoms. Due to two lone pairs (and two bonding pairs) on each oxygen atom each Si—O—Si unit is bent (electron domain geometry is tetrahedral).

It is hard to see from diagrams of the structure that the formula is SiO_2 because there are no individual molecules. However, if you pick one particular Si atom, you can see that each Si has a half share of four O atoms, i.e., $Si\left(O_{\frac{1}{2}}\right)_4 = SiO_2$ (Figure 7.95).

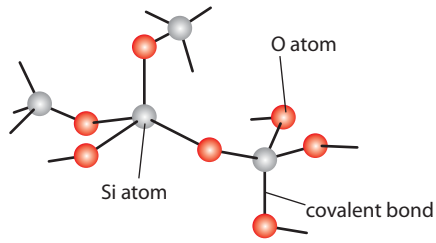

Figure 7.94: Part of the structure of silicon dioxide.

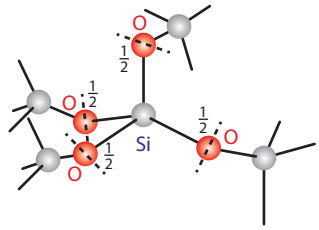

Figure 7.95: How to work out the formula of silicon dioxide from the structure.

SiO_2 has high melting and boiling points, because covalent bonds between atoms must be broken to melt/boil it, and this requires a lot of energy.

Comparison of the physical properties of ionic and covalent substances

Ionic bonding was discussed in Chapter 6. Table 7.16 shows a comparison of the physical properties of ionic, covalent molecular and covalent network substances.

	Ionic	Covalent molecular	Covalent network
melting point	usually solids with high melting points	may be solid, liquid or gas at room temperature	solids with high melting points
	strong electrostatic forces of attraction between oppositely charged ions in the giant lattice structure must be overcome	only intermolecular forces are overcome when the substances are melted or boiled; intermolecular forces are weaker than the electrostatic forces in an ionic lattice; no covalent bonds are broken when covalent molecular substances are melted or boiled	strong covalent bonds in the network structure must be broken
volatility	non-volatile	many are volatile	non-volatile
	strong electrostatic forces in the lattice	weak intermolecular forces	strong covalent bonds in the network structure

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	Ionic	Covalent molecular	Covalent network
solubility	many are soluble in water and usually insoluble in organic solvents	not usually soluble in water, but soluble in organic solvents	not soluble in water or organic solvents
	strong interactions between the ions and the polar water molecules provide energy to break apart the lattice structure	substances dissolve when intermolecular forces in the solvent and solute are similar; molecules that are able to hydrogen bond to water are usually soluble in water	a lot of energy to break strong covalent bonds, but only weak London forces would be formed between atoms and solvent molecules
conduction of electricity	do not conduct electricity in the solid state, but do conduct when molten or in aqueous solution because of mobile ions	do not conduct electricity in any state	some conduct electricity, some do not
	ions not free to move in solid state because they are held tightly in the lattice structure; ions free to move around when molten or dissolved in water	no ions or free electrons present – only neutral molecules. Some substances, such as HCl, dissolve in water with ionisation – HCl(aq) conducts electricity	Diamond – electrons held tightly in covalent bonds – does not conduct electricity. Graphite conducts due to delocalised electrons that are free to move.

Table 7.16: A comparison of the properties of ionic and covalent substances.

TEST YOUR UNDERSTANDING

21 Arrange the following sets of substances in order of increasing boiling point:

a $NaCl$, $SiCl_4$, CCl_4, HCl

b Br_2, HBr, $CaBr_2$, PBr_3

c C_4H_{10}, C_3H_7OH, C_3H_8, C_4H_9OH

d SO_2, SiO_2, CO_2.

22 Arrange the following sets of substances in order of solubility in water (least soluble first):

a $NaCl$, C_6H_{12}, $C_5H_{11}OH$

b CH_3Cl, $CaCl_2$, CH_4.

7.11 The expanded octet

We met the octet rule before: the idea that the central atom in a molecule/ion can have a maximum of eight electrons in its outer shell. There are, however, many molecules and ions where the central atom has more than eight electrons in its outer shell. In this case, we say that the central atom has *expanded its octet*. The Lewis formula for sulfur(VI) fluoride, SF_6, is shown in Figure 7.96. In this structure, the sulfur atom has 12 electrons in its outer shell.

Figure 7.96: The Lewis formula of SF_6.

Similarly, in noble gas compounds, such as XeF_4, the central atom will have an expanded octet (Figure 7.97).

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Figure 7.97: The Lewis formula for XeF_4. The Xe atom has 12 electrons in its outer shell.

If the central atom is from Period 2, the outer shell (highest main energy level) is the second shell, which can hold a maximum of eight electrons, but if the central atom is from Period 3, 4, etc., the outer shell can hold more than eight electrons because d orbitals are available for bonding.

7.12 Formal charge

We can use the concept of **formal charge** (FC) to decide between alternative Lewis formulas, including whether or not the central atom in a molecule/ion will have an expanded octet.

KEY POINT

Formal charge is the charge that an atom in a molecule/ion would have, if we assume that the electrons in a covalent bond are equally shared between the atoms that are bonded; i.e., we assume that all atoms have the same electronegativity.

Atoms in a molecule can gain a formal charge either if a coordination bond is formed or if the molecule has an overall charge (it is an ion).

A coordination bond is formed when both shared electrons come from the same atom. When the bond forms, it can be imagined that the donor atom gives an electron to the receiver atom, so that each now has one electron, which can be used to form a covalent bond. Because the donor atom has given away an electron, it now has an FC of +1 and the receiver atom has an FC of −1 (Figure 7.98).

The FC on an atom can be worked out from the Lewis formula using the following equation:

$$FC = v - \frac{b}{2} - n$$

where

v = number of valence electrons in the uncombined atom
b = number of bonding electrons
n = number of non-bonding electrons

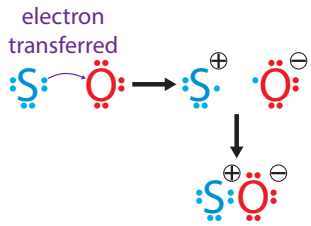

Figure 7.98: Formation of a coordination bond results in a formal charge on each atom.

Using FC to decide between alternative Lewis formulas for sulfur dioxide

Two different Lewis formulas are possible for SO_2, depending on whether the octet on S is expanded or not.

Approach 1:

Sulfur does not expand its octet.

Sulfur has six electrons in its outer shell and can, therefore, form a maximum of two normal covalent bonds. If these are both formed to the same oxygen atom, we get the structure shown:

However, in this structure, there is no bond between sulfur and the right-hand oxygen atom. The structure can be completed by a coordination bond between sulfur and the second oxygen so that all atoms have eight electrons in their outer shell:

Approach 2:

Sulfur expands its octet.

Each oxygen atom can achieve an octet by forming a double bond.

If a sulfur atom forms two double bonds, it will have ten electrons in its outer shell – it has expanded its octet:

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Structure A (no expansion of octet)	Structure B (expansion of octet)
	
S FC = $6 - \left(\frac{6}{2}\right) - 2 = +1$	S FC = $6 - \left(\frac{8}{2}\right) - 2 = 0$
O1 FC = $6 - \left(\frac{4}{2}\right) - 4 = 0$	O1 FC = $6 - \left(\frac{4}{2}\right) - 4 = 0$
O2 FC = $6 - \left(\frac{2}{2}\right) - 6 = -1$	O2 FC = $6 - \left(\frac{4}{2}\right) - 4 = 0$

Table 7.17: Calculating FCs in SO_2.

The calculations of FCs in the two possible structures for SO_2 are shown in Table 7.17. The FC on the sulfur atom in structure A was worked out as follows:

- An unbonded S atom has six electrons in its outer shell because it is in Group 16, therefore $v = 6$; there are six electrons involved in covalent bonds (S forms three bonds), therefore $b = 6$, and there are two non-bonding electrons (one lone pair), so $n = 2$.

$$FC = v - \frac{b}{2} - n$$

$$= 6 - \left(\frac{6}{2}\right) - 2 = +1$$

The FCs on the atoms in SO_2 are shown in Figure 7.99.

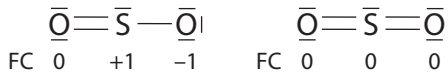

Figure 7.99: FCs on the atoms in alternative Lewis structures for SO_2.

KEY POINT

In general, the preferred Lewis structure is the one in which the FCs are closest to zero.

This means that the preferred structure will be the one where the absolute value of the charges is smallest, so, for instance, a structure with FCs +1, 0, −1 would be preferred over one with FCs +2, −1, −1.

Therefore, for SO_2, we can see that the preferred structure is structure B, the one with two double bonds, because this has the lowest absolute values of FC. In general, the structure with the fewest coordination bonds will be preferred.

FC closest to zero means that there will be the most even distribution of charge in the molecule/ion.

There are various ways that we can rationalise the idea that a structure with an FC closest to zero is most likely:

- It is more difficult to remove extra electrons from an atom to form a 2+ ion (second ionisation energy is higher than the first), and it takes quite a bit of energy to force an extra electron onto an atom that is already negatively charged, to form a 2− ion, against the repulsion between the electrons (see electron affinity in Chapter 10).
- If an atom already has a positive FC, it will have a lower tendency to donate any further electrons in a coordination bond.
- It is highly unlikely that a structure would exist with atoms with high FCs because the positively charged atom would just attract electrons from the negatively charged atom to form an extra bond, if at all possible.

The sulfate(VI) ion

Consider the alternative Lewis formulas for the sulfate(VI) ion shown in Figure 7.100. The FCs are worked out in Table 7.18. The absolute values of the FCs are closer to zero in structure Y, so this is the preferred structure. In both cases, the sum of the FCs is 2−, which is the overall charge on the ion.

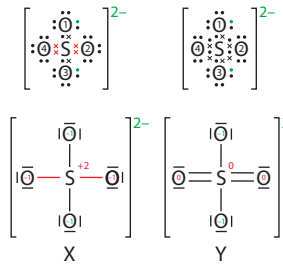

Figure 7.100: Two possible Lewis formulas and FCs for SO_4^{2-}. Coordination bonds are shown in red.

EXAM TIP

Remember, the sum of the FCs on all atoms must add up to zero, if you are looking at a neutral molecule, and equal the overall charge, if it is an ion.

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Structure X	Structure Y
In the first structure, S has not expanded its octet, and there are two coordination bonds; the FCs are	In the second structure, S has expanded its octet, and there are no coordination bonds; the FCs are
S: $FC = 6 - \frac{8}{2} - 0 = +2$	S: $FC = 6 - \frac{12}{2} - 0 = 0$
O1: $FC = 6 - \frac{2}{2} - 6 = -1$	O1: $FC = 6 - \frac{2}{2} - 6 = -1$
O2: $FC = 6 - \frac{2}{2} - 6 = -1$	O2: $FC = 6 - \frac{4}{2} - 4 = 0$
O3: $FC = 6 - \frac{2}{2} - 6 = -1$	O3: $FC = 6 - \frac{2}{2} - 6 = -1$
O4: $FC = 6 - \frac{2}{2} - 6 = -1$	O4: $FC = 6 - \frac{4}{2} - 4 = 0$

Table 7.18: Calculating FCs in SO_4^{2-}.

What if FCs in two possible structures are the same?

Consider N_2O. We can draw two possible Lewis formulas for this (Figure 7.101).

Figure 7.101: Two possible Lewis formulas for N_2O. The coordination bonds are shown in red.

The FCs can be worked out using the method previously described (Figure 7.102).

Figure 7.102: The FCs on the atoms in N_2O. The coordination bonds are shown in red.

In both formulas, the FCs are the same, and so, we cannot distinguish between them like this. The negative charge is, however, more likely to be on the more electronegative atom, that is, O, therefore we can select the structure with a triple bond (the left-hand structure) as the preferred structure. In reality, the structure is somewhere between the two shown (see Section 7.16 on resonance), but calculations suggest that the N—N bond is closer to a triple bond than a double bond.

Using FC to decide which is the central atom

In the previous discussion, how did we know that the structure of N_2O was NNO and not NON? We can use FC to decide which is more likely. The Lewis formulas and FCs for NON are shown in Figure 7.103.

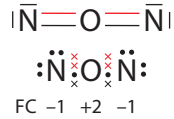


Figure 7.103: Lewis formulas and FCs for NON.

It can be seen that the absolute values of FCs are higher in this structure since O forms two coordination bonds and, therefore, has a +2 FC. The structure NNO is, therefore, preferred to NON, and this is the one that is adopted by the molecule.

TEST YOUR UNDERSTANDING

23 What is the formal charge on N in each of the following?

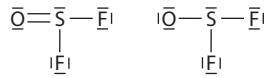
a NH_3 **b** NH_4^+

c NO_2^+ **d** NO_2^-

e NO_3^- **f** HCN

g CH_3NO_2

24 Two possible Lewis formulas for SOF_2 are shown here. Use formal charge to decide which is probably a better representation of the structure.



25 Draw alternative Lewis formulas with and without an expanded octet on the central atom for each of the following molecules/ions. Use the concept of formal charge to decide which structure is probably the best representation of the actual structure.

a $POCl_3$ **b** ClO_4^-

c XeO_4

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Link

The concept of formal charge assumes that the bonding in a molecule/ion is purely covalent. The concept of oxidation state, which will be introduced in Chapter 10, assumes that the bonding in a molecule/ion is purely ionic. Neither provides a complete picture of the bonding; why do we use them?

Working out Lewis formulas for molecules/ions where the central atom has an expanded octet

We can put the rules that we learned earlier about drawing Lewis formulas and the discussion of FC together to come up with a set of guidelines for drawing Lewis formulas for molecules where the central atom comes from Period 3 or below and, therefore, can expand its octet.

1. The outer atoms are usually the more electronegative atoms, unless H is present, in which case, H will be the outer atom. The central atom is usually the largest one, but not always, e.g., Cl_2O.
2. Always make sure that the outer atoms have a complete octet or, if the outer atom is a hydrogen atom, that it has two electrons in its outer shell. Therefore, when H or halogens are the outer atoms, they will always form a single bond to the central atom.
3. Oxygen will form a double bond, wherever possible.
4. The maximum number of bonds that the central atom can form is usually equal to the number of electrons in the outer shell of the uncombined atom, i.e., P will form a maximum of five bonds, S six bonds and Cl seven bonds. There are a few exceptions to this, where a coordination bond is formed to the central atom, as in the formation of PCl_6^- (but this could also be viewed as a Cl^- donating an electron to a P atom to enable it to form six bonds).

XeF_2

This has Xe as the central atom and two F atoms as the outer atoms. Fluorine will form a single bond to complete its octet. The Lewis formula is shown in Figure 7.104. There are three lone pairs on xenon, giving it a total of ten electrons in its outer shell.

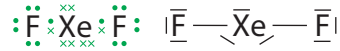

Figure 7.104: Two different ways of drawing the Lewis formula of XeF_2.

SO_3

Sulfur is the central atom and oxygen is the outer atom. Oxygen needs two electrons to complete its octet. If possible, it will complete its octet by forming double bonds to the S. Three double bonds to the O atoms would require six electrons from the S atom. Sulfur is in Group 16, so it has six outer-shell electrons, which is enough for three double bonds. The Lewis formula of SO_3 is shown in Figure 7.105.

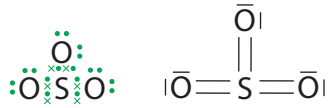

Figure 7.105: Two different ways of drawing the Lewis formula of SO_3.

$HClO_4$

Chlorine is the central atom, and hydrogen and oxygen are the outer atoms. Hydrogen always completes its outer shell by forming a single bond and oxygen atoms will, wherever possible, complete their octets by forming two bonds. Chlorine is in Group 17, so it has seven outer-shell electrons and will form a maximum of seven bonds. The formation of four double bonds to O and a single bond to H would be nine bonds. Here, the solution relies on realising that H is joined to O and not Cl, so that one of the oxygens completes its octet by forming one bond to Cl and one to H (Figure 7.106).

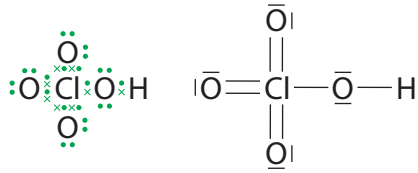

Figure 7.106: Two different ways of drawing the Lewis formula of $HClO_4$.

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EXAM TIP

Ions with the formula XO_n^{m-}

There are lots of ions with this general formula, for instance, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}. When drawing Lewis formulas for these ions, a handy thing to remember is that, in virtually every case (an exception is NO_3^- – see below), the value of the charge (m in XO_n^{m-}) gives the number of O atoms that are singly bonded. The other O atoms will have double bonds. Therefore, in ClO_3^-, there is one single bond; in SO_4^{2-}, there are two single bonds; and in PO_4^{3-}, there are three single bonds (Figure 7.107).

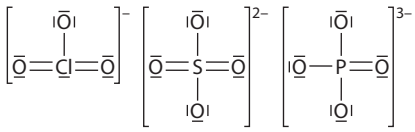


Figure 7.107: The charge tells you how many X—O single bonds there are in the structure.

When the charge is zero ($m = 0$), then the number of X—O single bonds is zero. So, in XeO_3, XeO_4, SO_2 and SO_3, there are just double bonds to oxygen.

NO_3^- is an exception and has two single bonds, one of which is a coordination bond (Figure 7.108).

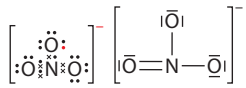


Figure 7.108: NO_3^- has two oxygen atoms that are joined to the central atom with single bonds.

TEST YOUR UNDERSTANDING

26 Draw Lewis formulas for the following molecules/ions:

a	PCl_5	**b**	SO_2Cl_2
c	XeF_4	**d**	PCl_6^-
e	BrF_5	**f**	ClF_3
g	XeO_4	**h**	SF_4
i	ClO_4^-	**j**	N_3^-
k	H_3PO_4	**l**	SbF_5^{2-}.

7.13 Shapes of molecules and ions with an expanded octet

We have already used VSEPR to explain and predict the shapes of molecules and ions with up to four electron domains (Section 7.2). Here, we will extend the technique to include molecules and ions with five or six electron domains.

The electron domain geometries for five and six electron domains are shown in Table 7.19.

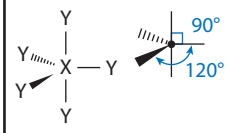
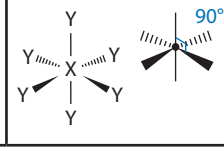
Electron domains	Electron domain geometry	Shape	Example
5	trigonal bipyramid		PF_5
6	octahedral		SF_6

Table 7.19 The electron domain geometries for molecules with five or six electron domains.

Five electron domains

PF_5

The Lewis formula of phosphorus(V) fluoride is shown in Figure 7.109.

Figure 7.109: Lewis formula of PF_5

Single bonds:	5
Multiple bonds:	0
Lone pairs:	0
Electron domains:	5

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The five electron domains repel each other and, therefore, take up positions in space to be as far apart as possible – the electrons domains are distributed in a trigonal bipyramidal arrangement. The molecular geometry (shape adopted by the atoms) is also trigonal bipyramidal – two triangular-based pyramids on top of each other (Figure 7.110).

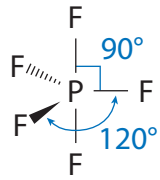

Figure 7.110: The shape and bond angles of PF_5.

Trigonal bipyramids and lone pairs

There are two different bond angles in a trigonal bipyramid.

The positions around the middle plane of a trigonal bipyramid are described as *equatorial* (Figure 7.111); the positions above and below the central triangle are described as *axial*.

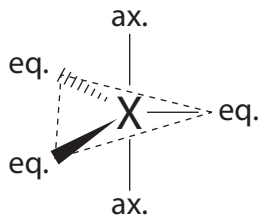

Figure 7.111: Axial and equatorial positions.

KEY POINT

In a trigonal bipyramid, the axial and equatorial positions are not equivalent. Lone pairs always occupy an equatorial position. This applies only to trigonal bipyramidal structures.

SF_4

The Lewis formula of sulfur(IV) fluoride is shown in Figure 7.112.

Figure 7.112: Lewis formula of SF_4.

Single bonds:	4
Multiple bonds:	0
Lone pairs:	1
Electron domains:	5

The five electron domains repel each other and take up positions in space to be as far apart as possible – the electron domains are distributed in a trigonal bipyramidal arrangement. One of these electron pairs is a lone pair, and this adopts an equatorial position in a trigonal bipyramid (Figure 7.113).

Figure 7.113: The seesaw shape of SF_4.

The molecule is often described as having a 'seesaw' shape. The extra repulsion from the lone pair causes the other bonding pairs to bend away from it, and a better representation of the shape is shown in Figure 7.114. It can be seen that, in this case, the lone pair has a very large influence on the bond angles – more than just a couple of degrees.

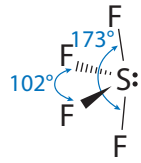

Figure 7.114: F atoms bend back away from the lone pair.

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EXAM TIP

Care must be exercised here – if you write the angle 102° for the bond angle in your answer, it could be marked incorrect, even though it is the correct answer because it is quite a bit less than 120°. When predicting bond angles in the exam, it is best just to take two to three degrees off the ideal bond angle for each lone pair present.

Link

Lone pairs always going in an equatorial position is often discussed in terms of the repulsion between the pairs of electrons. The repulsion between electron pairs at 90° to each other is greater than between pairs at 120° to each other. Having one lone pair (which causes greater repulsion than bonding pairs of electrons) in an equatorial position limits the number of 90° repulsions to two. Having one lone pair in an axial position would mean that there would be three 90° repulsions – i.e., greater repulsion overall and a less stable molecule.

An alternative explanation is in terms of the hybridisation of the central atom (see Section 7.14). A trigonal bipyramid involves two different hybridisation schemes – sp^2 for the equatorial positions and pd for the axial positions. An s orbital has lower energy than a p orbital or a d orbital and, therefore, if a lone pair occupies an sp^2 orbital, it is lower in energy than if it were in a pd orbital. Because a lone pair exists solely on the central atom, this should be in the orbital with the lowest energy – an sp^2 orbital – in the equatorial position.

ClF_3

The Lewis formula of chlorine(III) fluoride is

Figure 7.115: Lewis formula of chlorine(III) fluoride

Single bonds:	3
Multiple bonds:	0
Lone pairs:	2
Electron domains:	5

Two of the electron pairs are lone pairs and take up equatorial positions in the trigonal bipyramid (Figure 7.116).

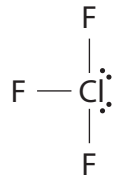

Figure 7.116: ClF_3 is a T-shaped molecule.

The actual shape adopted by the molecule is usually described as 'T-shaped'. The lone pairs cause the bonding pairs to bend away from them, and if you are asked to predict Cl—F bond angles, 85° would be a suitable exam answer (Figure 7.117) – the actual bond angle is 87°.

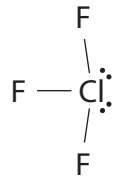

Figure 7.117: F atoms in ClF_3 bend back away from the lone pairs.

I_3^-

The Lewis formula of the triiodide ion is shown in Figure 7.118.

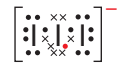

Figure 7.118: The Lewis formula of I_3^-.

Single bonds:	2
Multiple bonds:	0
Lone pairs:	3
Electron domains:	5

The ion has three lone pairs and two bonding pairs around the central atom, so the electron pairs are distributed in a trigonal bipyramidal arrangement. The shape is linear, with three lone pairs around the middle of the trigonal bipyramid (Figure 7.119).

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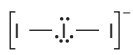

Figure 7.119: I_3^- is a linear ion.

Six electron domains

XeF_4

Xenon(IV) fluoride has four bonding pairs and two lone pairs around the central atom. Its Lewis formula is shown in Figure 7.120.

Figure 7.120: Lewis formula of XeF_4.

Single bonds:	4
Multiple bonds:	0
Lone pairs:	2
Electron domains:	6

The arrangement of electron domains is octahedral, and the two lone pairs take up positions opposite each other to minimise repulsion. The shape adopted by the molecule is described as square planar (Figure 7.121).

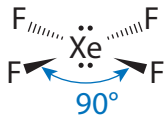

Figure 7.121: XeF_4 is a square planar molecule.

BrF_5

Bromine(V) fluoride has five bonding pairs and one lone pair around the central atom (Figure 7.122).

Figure 7.122: Lewis formula of BrF_5.

Single bonds	5
Multiple bonds	0
Lone pairs	1
Electron domains	6

The arrangement of the electron domains is octahedral, and the shape of the molecule is square pyramidal. The lone pair causes the four fluorine atoms on the base of the pyramid to bend away from it slightly due to greater repulsion between a lone pair and a bonding pair than between two bonding pairs (Figure 7.123).

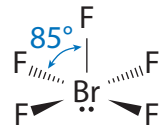

Figure 7.123: BrF_5 is a slightly distorted square pyramidal molecule. The actual F—Br—F bond angle is 85°, but if you predict 87°/88° in the exam (taking off two to three degrees for a lone pair), that will be fine.

Table 7.20 summarises the shapes of molecules and ions with five and six electron domains.

Electron domains	Single + multiple bonds	Lone pairs	Electron domain geometry	Molecular geometry	Examples
5	5	0	trigonal bipyramidal	trigonal bipyramidal	PF_5, XeO_3F_2
5	4	1	trigonal bipyramidal	seesaw	SF_4, XeO_2F_2
5	3	2	trigonal bipyramidal	T-shape	ClF_3, $XeOF_2$
5	2	3	trigonal bipyramidal	linear	I_3^-
6	6	0	octahedral	octahedral	SF_6, PF_6^-, XeO_6^{4-}, IO_6^{5-}
6	5	1	octahedral	square pyramidal	SF_5^-, BrF_5, XeF_5^+, $XeOF_4$
6	4	2	octahedral	square planar	XeF_4, SF_4^{2-}

Table 7.20: The shapes of molecules and ions with more than four electron domains.

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TEST YOUR UNDERSTANDING

27 Work out the shapes of the following molecules and ions and predict their bond angles:

- **a** BrF_3
- **b** ClF_5
- **c** SO_2Cl_2 (S central atom)
- **d** SeF_4
- **e** XeF_2
- **f** AsF_6^-
- **g** TeF_5^-
- **h** $F_2ClO_2^-$ (Cl central atom)
- **i** I_3^+
- **j** ICl_2^-
- **k** SbF_5^{2-}
- **l** $FBrO_3$.

28 Sort the following molecules into polar and non-polar molecules. For the polar molecules, draw diagrams showing the dipoles.

XeF_6, XeF_4, SF_4, PCl_5, SF_2, SF_6, ClF_5, BrF_3, $SOCl_2$

7.14 Hybridisation

The formation of covalent bonds

A covalent bond is usually formed by the overlap of two atomic orbitals, each containing one electron. These *atomic* orbitals overlap to form a *molecular* orbital (Figure 7.124). The electrons are unpaired in the atomic orbitals but are paired up in the molecular orbital. We do not, however, use the term molecular orbital at this level and usually just talk about the electrons being paired up in the covalent bond.

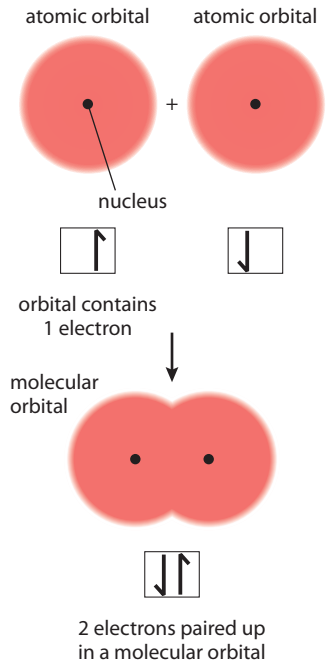
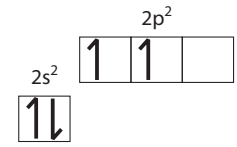


Figure 7.124: The overlap of two s orbitals to form a covalent bond.

Because an unpaired electron in an orbital is required to form a bond, the number of bonds that are formed by an atom should depend on the number of unpaired electrons. Therefore, fluorine, with one unpaired electron, forms one bond; oxygen, with two unpaired electrons, forms two bonds; and nitrogen, with three unpaired electrons, forms three bonds.

Carbon has the outer-shell electron configuration $2s^2\ 2p^2$:



Because it has only two unpaired electrons, carbon should only form two covalent bonds. However, carbon virtually always forms four covalent bonds.

Promotion of electrons to generate more unpaired electrons

If one of the electrons in the 2s orbital of carbon is promoted to the 2p sub-level, this produces four unpaired electrons.

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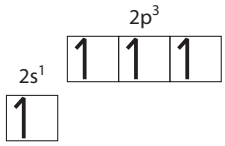

This requires energy, since an electron is being moved from a lower energy orbital to a higher one. However, the formation of covalent bonds releases energy, and the subsequent formation of four bonds instead of two more than pays back the energy needed to promote an electron to a higher sub-level.

Mixing of orbitals

Carbon now has four unpaired electrons and can form four covalent bonds. When carbon forms four single bonds, as in methane, CH_4, the shape around the carbon atom is tetrahedral with bond angles of 109.5°. Covalent bonds are formed when orbitals overlap, but the p atomic orbitals (at 90° to each other) on C do not point in the correct direction to overlap with the H atomic orbitals (Figure 7.125).

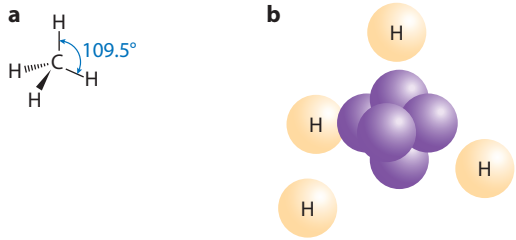

Figure 7.125: a Bond angles and **b** p orbitals in CH_4.

To form methane, the four atomic orbitals in the outer (valence) shell of carbon (one s and three p) *mix* to form a new set of four orbitals – sp^3 hybrid orbitals – which point to the vertices of a tetrahedron. This mixing of orbitals is called **hybridisation** and the *hybrid orbitals* formed are shown in Figure 7.126.

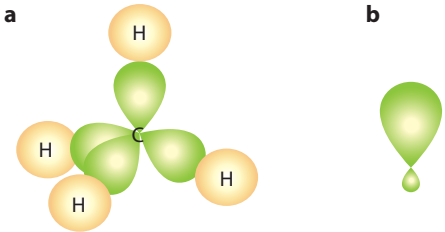

Figure 7.126: a Four sp^3 hybrid orbitals point towards the vertices of a tetrahedron and are better set up for bonding to the H atoms. **b** One sp^3 hybrid orbital.

KEY POINT

Hybridisation is the mixing of atomic orbitals in a particular atom to produce a new set of orbitals (the same number as originally) that are better arranged in space for covalent bonding.

The four sp^3 hybrid orbitals have the same energy (Figure 7.127) – they are degenerate. The overall energy of the s and p orbitals does not change when they undergo hybridisation, so the energy of one sp^3 hybrid orbital is the average of the energies of the s and three p orbitals they were formed from. The sp^3 orbitals are, therefore, much closer in energy to the p orbitals than to the s orbitals.

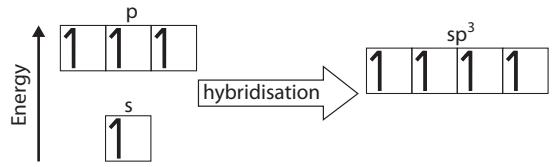

Figure 7.127: The new sp^3 orbitals are degenerate.

Different hybridisation schemes

Hybridisation involves the mixing of orbitals on an atom when it forms a molecule. There are three different types of hybridisation that we look at: sp, sp^2 and sp^3 hybridisation. Hybridisation is determined by the electron domain geometry. Mixing of orbitals produces the arrangement that minimises the repulsion between electron domains and maximises the bonding to the outer atoms.

The s and p orbitals in the outer shell of an atom are shown in Figure 7.128.

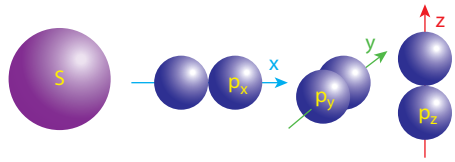

Figure 7.128: s and p orbitals.

sp^3 hybridisation

We have already seen that one s orbital is mixed with all three p orbitals to produce four sp^3 orbitals that point towards the corners of a tetrahedron. This hybridisation scheme will be adopted by any

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molecule/ion with four electron domains, therefore, a tetrahedral electron domain geometry. Thus, the C atom in CH_4 and the O atom in H_2O have sp^3 hybridisation (Figure 7.129).

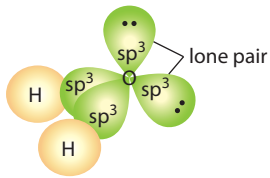

Figure 7.129: The hybrid orbitals in water.

sp^2 hybridisation

Mixing together the s, p_x and p_z orbitals in Figure 7.127 produces three sp^2 hybrid orbitals all in one plane. The sp^2 hybrid orbitals have a trigonal planar distribution in space – at 120° to each other (Figure 7.130).

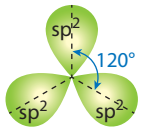

Figure 7.130: There are 3 sp^2 hybrid orbitals, and they are at 120° to each other.

The p_y orbital is in a different plane to the other p orbitals and is not involved in hybridisation. This hybridisation scheme will be adopted by any molecule/ion with three electron domains, therefore, a trigonal planar electron domain geometry. The B atom in BCl_3 has sp^2 hybridisation (Figure 7.131).

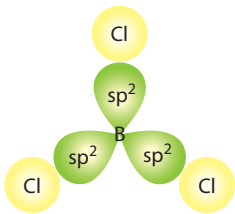

Figure 7.131: The B atom in BCl_3 is sp^2 hybridised.

sp hybridisation

Mixing together the s and p_x orbitals in Figure 7.128 produces two sp hybrid orbitals that have a linear distribution in space – at 180° to each other (Figure 7.132).

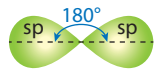

Figure 7.132: There are two sp hybrid orbitals, and they are at 180° to each other.

This hybridisation scheme will be adopted by any molecule/ion with two electron domains, therefore, a linear electron domain geometry. The Be atom in gaseous $BeCl_2$ has sp hybridisation (Figure 7.133).

Figure 7.133: The Be atom in gaseous $BeCl_2$ is sp hybridised.

Table 7.21 shows a summary of the orbitals used in hybridisation. It is important to remember that the number of hybrid orbitals is always the same as the number of atomic orbitals from which they were produced.

Hybridisation	Orbitals used	Hybrid orbitals produced	Spatial distribution of orbitals
sp	1 × s, 1 × p	2	linear
sp^2	1 × s, 2 × p	3	trigonal planar
sp^3	1 × s, 3 × p	4	tetrahedral

Table 7.21. Hybrid orbitals summary.

Predicting the hybridisation of an atom

NH_3

The Lewis formula for ammonia is:

Figure 7.134: Lewis formula for ammonia

There are four electron domains – three bonding pairs of electrons and one lone pair. So, the electron domain geometry is tetrahedral, and the hybridisation of the nitrogen atom is sp^3 (Figure 7.135).

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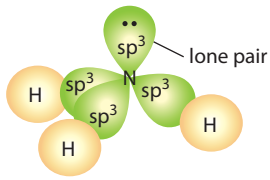

Figure 7.135: The N in NH_3 is sp^3 hybridised.

CO_2

The Lewis formula for carbon dioxide is shown in Figure 7.136.

Figure 7.136: The Lewis formula of CO_2.

There are two electron domains around the carbon atom – two double bonds. So, the electron domain geometry is linear, and the hybridisation of the carbon atom is sp.

O_3

The Lewis formula for ozone is shown in Figure 7.137.

Figure 7.137: The Lewis formula of O_3.

There are three electron domains around the central oxygen atom, and so, the electron domain geometry is trigonal planar, and the hybridisation of the central atom is sp^2.

Table 7.22 shows the hybridisation of the central atom in several molecules and ions.

Other hybridisation schemes, involving d orbitals, can be used to rationalise the bonding in five- and six-coordinate molecules – sp^3d^2 for an octahedral shape, for example.

With organic molecules (see Chapter 11), the hybridisation of C can be worked out just by looking at the number of bonds formed:

- when a carbon atom forms just single bonds, the shape is tetrahedral and the hybridisation is sp^3
- when a carbon atom forms one double bond, the shape is trigonal planar and the hybridisation is sp^2
- when a carbon atom forms a triple bond, the shape is linear and the hybridisation is sp.

Electron domains	Electron domain geometry	Hybridisation	Examples
2	linear	sp	CO_2, HCN, C_2H_2, NO_2^+
3	trigonal planar	sp^2	BF_3, SO_3, NO_3^-, CO_3^{2-}, SO_2, BF_3, NO_2^-
4	tetrahedral	sp^3	CCl_4, XeO_4, NH_4^+, BCl_4^-, SO_4^{2-}, PO_4^{3-}, NH_3, PCl_3, XeO_3, H_3O^+, ClO_3^-, $SOCl_2$, H_2O, SCl_2, ClF_2^+

Table 7.22: Hybridisation of central atoms.

THEORY OF KNOWLEDGE

Is hybridisation real? There is evidence from ultraviolet photoelectron spectroscopy to suggest that it is not. Why then do we still use this theory? There is a more advanced theory of bonding called molecular orbital theory, but this is much more complicated and does not allow us to draw lines (bonds) between atoms in the same way.
Is a more advanced theory always more useful?

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TEST YOUR UNDERSTANDING

29 Predict the hybridisation of the central atom in each of the following:

a BCl_3 **b** NCl_3 **c** OCl_2 **d** CCl_4 **e** $BeCl_2$

f H_2S **g** PCl_4^+ **h** OCN^- **i** SeO_3 **j** FNO.

30 What is the hybridisation of the nitrogen atoms in each of the following?

a N_2H_4 **b** N_2H_2

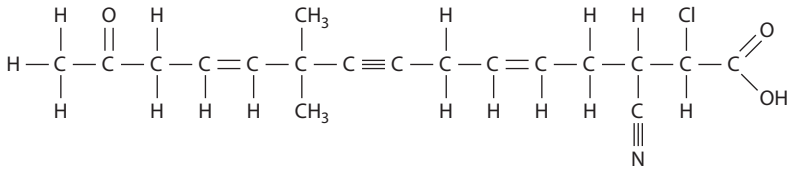
31 What is the hybridisation of the carbon atoms in each of the following?

a C_2F_4 **b** C_2F_2 **c** C_2F_6 **d** COF_2

32 The structure of an organic molecule is shown below.

Deduce how many C atoms are

a sp^3 hybridised **b** sp^2 hybridised **c** sp hybridised.



7.15 Sigma and pi bonds

A covalent bond is formed when two atomic orbitals, each containing one electron, overlap. When these orbitals overlap (are combined) head-on, the bond formed is a 'normal' single bond and is called a **sigma (σ) bond** (Figure 7.138).

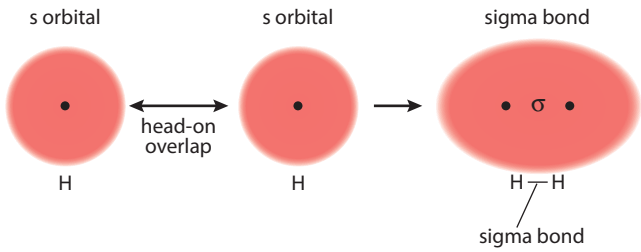


Figure 7.138: The overlap/combination of two s orbitals to form a σ bond. The orbitals are shown in cross-section for clarity.

A covalent bond can also be formed when an atomic orbital containing two electrons overlaps with an empty orbital. This is a coordination bond.

Sigma σ bonds are formed by the head-on overlap of any two orbitals – this can be two p orbitals; an s orbital and a p orbital; an sp^3 hybrid orbital and an s orbital; a d orbital and a p orbital, and so on. Figure 7.139 shows a sigma bond formed from overlap of two p orbitals.

KEY POINTS

Sigma (σ) bonds result from the head-on (axial) overlap (combination) of atomic orbitals. The electron density in a sigma bond lies mostly along the internuclear (bond) axis.

A pi (π) bond is formed by the sideways (lateral) overlap (combination) of parallel p orbitals. The electron density in the π bond lies above and below the internuclear axis.

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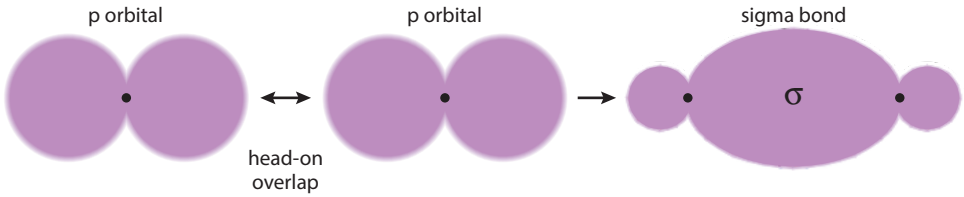

Figure 7.139: A sigma bond formed by head-on overlap of p orbitals. The electron density in the bond lies mostly along the internuclear axis.

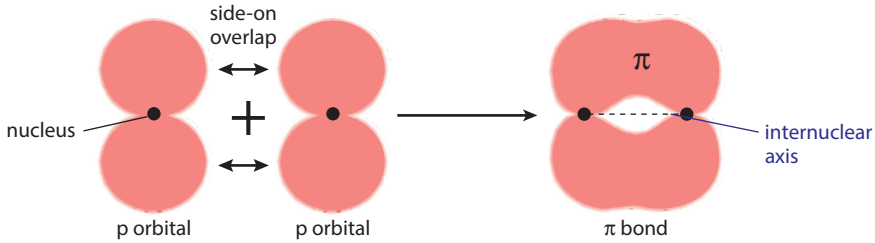

Figure 7.140: A π bond is formed when p orbitals overlap side-on. The electron density in the bond lies above and below the internuclear axis.

A **pi (π) bond** is formed when two parallel p orbitals overlap (are combined) side-on (lateral overlap) (Figure 7.140). π bonds are involved in the formation of double and triple bonds.

The π bonds can also be formed when two d orbitals overlap side-on or a d orbital overlaps side-on with a p orbital.

Bonding in methane, CH_4

Methane contains only single bonds between carbon atoms (Figure 7.141). These are σ bonds formed when sp^3 hybrid orbitals on the carbon atom overlap head-on with the s orbitals of each H atom.

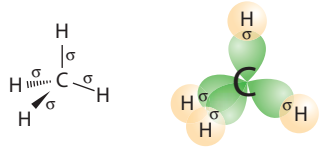

Figure 7.141: Bonding in methane.

Bonding in ethene, C_2H_4

The Lewis formula for ethene is shown in Figure 7.1.142.

Figure 7.142: Lewis formula for ethene

The arrangement of atoms around each carbon atom is trigonal planar (three electron domains), and the molecule is planar overall (Figure 7.143).

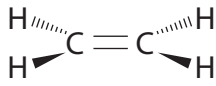

Figure 7.143: The shape of ethene.

The electron domain geometry about each C is trigonal planar, and so, each C atom is sp^2 hybridised. Mixing the two p orbitals and one s orbital, all in the same plane, produces three sp^2 orbitals pointing towards the corners of an triangle (Figure 7.144).

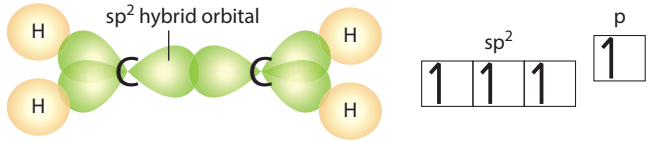

Figure 7.144: The sp^2 hybrid orbitals on each C contain one electron, leaving one electron in a p orbital on each C.

This leaves one p orbital, containing one electron, perpendicular to the single bond (σ) framework on each C atom (Figure 7.145). The perpendicular p orbitals, each containing 1 electron, overlap side-on to form a π bond. The π bond, like the σ bond, therefore involves two shared electrons.

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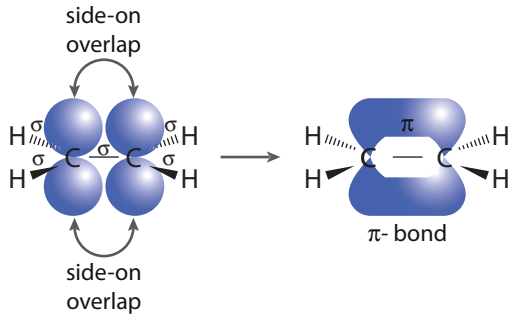
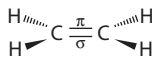


Figure 7.145: The formation of a π bond in ethene.

The double bond thus has two different components – a sigma bond, which results from the head-on overlap of two sp^2 orbitals, and a pi bond, which arises from the side-on overlap of two parallel p orbitals:



That these components are different can be seen from the bond energies in Table 7.23. A C=C bond has less than twice the strength of a C—C single bond, meaning that the π bond in ethene is not as strong as the C—C σ bond. Side-on overlap (π bond) is not as effective as head-on overlap – there is a more direct attraction between the electron pair and the nuclei in a σ bond.

	Bond energy / kJ mol^{-1}
C—C	348
C=C	612

Table 7.23: Bond energies in single and double C–C bonds.

Link

The presence of a double C=C bond makes alkenes much more reactive than alkanes, which only contain C—C; see Chapter 22. The reactions of alkenes usually involve the C=C bond breaking to form a C—C bond. Because the second component (π bond) of the C=C bond is weaker than a C—C single bond (σ bond), it is more easily broken.

The bonding in ethyne, C_2H_2

The Lewis formula for ethyne is H:C⋮C:H

There are two electron domains around each C; therefore, the shape is linear. The linear shape means that one s and one p orbital on each carbon atom are hybridised to produce two sp hybrid orbitals at 180° to each other (Figure 7.144). These are used to form σ bonds between the carbon atoms and between the carbon atoms and the hydrogen atoms (Figure 7.146). The two p orbitals at 90° to the C—H bonds are not involved in hybridisation. These p orbitals overlap side-on to produce two π bonds (Figure 7.147).

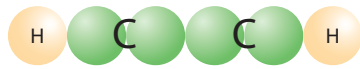


Figure 7.146: Only the p orbitals that point towards the hydrogen atoms are involved in hybridisation.

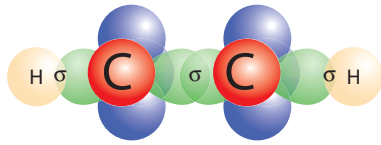


Figure 7.147: The formation of σ bonds in ethyne.

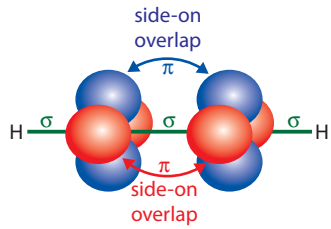
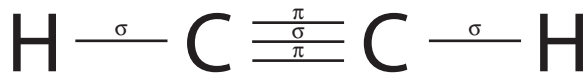


Figure 7.148: Formation of a triple bond.

A triple bond thus consists of a one σ bond and two π bonds (Figure 1.148).



Counting σ and π bonds

- a single bond consists of a σ bond
- a double bond consists of a σ bond and a π bond
- a triple bond consists of a σ bond and two π bonds.

All covalent bonds (single, double and triple), therefore, contain one σ bond.

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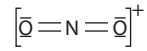
WORKED EXAMPLE 7.4

Deduce the number of sigma and pi bonds in NO_2^+.

Answer

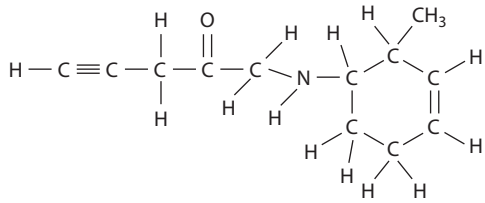
To tackle this, we have to draw the Lewis formula for NO_2^+.



We can see that there are two double bonds. A double bond is made up of a σ bond and a π bond and, therefore, there are two σ bonds and two π bonds in NO_2^+.

WORKED EXAMPLE 7.5

The structure of an organic molecule is shown.



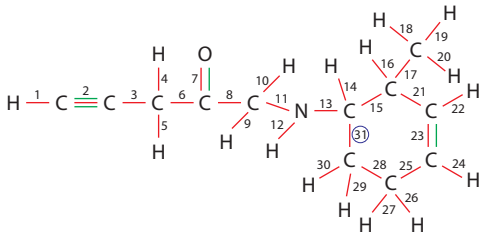
a Deduce the number of σ and π bonds in this molecule.

b Deduce how many C atoms are sp^3 hybridised.

c Explain what the hybridisation of the N atom is.

Answer

a To work this out, we need to remember that each single bond is a σ bond and that a double bond consists of a π bond and a σ bond, and a triple bond consists of a σ bond and two π bonds. We must also be careful to expand CH_3 because the H atoms are joined to C by single bonds. All the σ bonds have been highlighted in red in the diagram below and the π bonds in green. Especially in an exam, it is very easy lose count of this number of σ bonds (hopefully you will not get as many as this!), and so, it is often good to go through crossing them out or numbering them.



There are 31 σ bonds in this molecule and 4 π bonds.

b C is sp^3 hybridised when it only forms single bonds (when it forms double bonds it is sp^2 hybridised and sp for triple bonds). So, all the C atoms, except those that form a π bond (in green), are sp^3 hybridised. This gives a total of seven C atoms that are sp^3 hybridised.

c This diagram shows the structure of the molecule, rather than a Lewis formula, so it is important to realise that not all valence electrons are shown. Nitrogen forms three bonds, therefore it will also have a lone pair. With three single bonds and one lone pair, there is a total of four electron domains, which means that the hybridisation of N is sp^3.

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TEST YOUR UNDERSTANDING

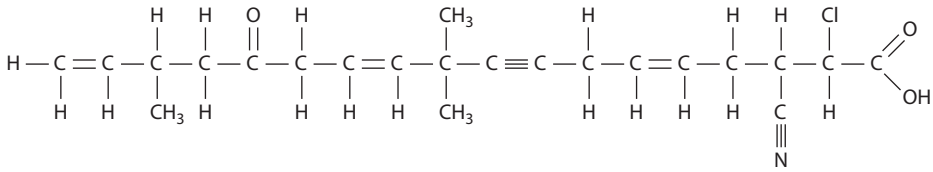
33 Work out the number of sigma and pi bonds in each of the following:

a O_2 **b** N_2 **c** BCl_3 **d** CO_2

e H_2CO **f** HCN **g** N_2F_2 **h** CO

i $CH_3CH{=}CH_2$ **j** $SOCl_2$ **k** $HC{\equiv}C{-}CH_3$ **l** H_2SO_4

m



7.16 Resonance and delocalisation

The Lewis formula of ozone, O_3, is shown in Figure 7.149.

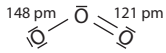


Figure 7.149: The Lewis structure for O_3 with expected bond lengths.

It would be expected from this structure that there would be one short (O=O) and one long (O—O) bond. If we had to predict values, the IB data booklet gives us an O=O bond length of 121 pm and and O—O bond length of 148 pm. However, both bond lengths are equal, at 128 pm, in an ozone molecule. The first attempt at explaining the equality of bond lengths in molecules such as O_3 involved the idea of **resonance structures** and **resonance hybrids**.

It is possible to draw an alternative Lewis formula (resonance structure) for O_3 with the double bond between the other two atoms (Figure 7.150).

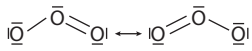


Figure 7.150: Resonance structures for O_3.

Neither of these structures alone can explain the equal O—O bond lengths, but, if we say that the actual structure is not one structure nor the other, but somewhere in between, then we can rationalise the equal bond lengths. The individual Lewis formulas are called resonance structures, and we imagine the actual structure as being a hybrid (resonance hybrid) of these two; in this case, with equal contributions from both resonance forms, the bond lengths in the resonance hybrid would be expected to be equal. The double-headed arrow between the resonance structures indicates that the actual structure is a resonance hybrid of the two resonance structures.

What we are basically saying with the idea of resonance is that the structure of a molecule/ion cannot be adequately described by just drawing one Lewis formula – more than one is required. The term 'resonance' is an unfortunate one because it is used in other contexts in conjunction with vibrations. It is important to note that the structure is not constantly flipping between the different resonance forms but is a mixture of them – rather like a mule is a hybrid of a donkey and a horse; it is not a horse one second and a donkey the next.

THEORY OF KNOWLEDGE

Why have chemists developed the idea of resonance? To what extent is it just an attempt to rescue an inadequate approach to the bonding in molecules/ions? Is resonance complete nonsense? The concept of resonance seems quite bizarre, but it is actually very useful, and chemists can rationalise structural data and make accurate predictions about chemical reactions using it. Does something have to be 'correct' to be useful?

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How to work out whether a molecule/ion has resonance forms

The key thing that we are looking for when deciding whether a molecule has resonance structures is whether it is possible to draw another Lewis formula where the only difference is in the position of double bonds (and lone pairs) and everything else remains the same. These alternative formulas, the resonance structures, will generally look exactly the same as the original except the molecule/ion will look as if it has been flipped/rotated around.

NO_2^-

If you look at the left-hand formula in Figure 7.151, you can see that we can convert it into an entirely equivalent form by just moving the lone pair on the left-hand O to become a double bond and moving the π component of the double bond to become a lone pair.

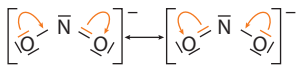

Figure 7.151: The two possible Lewis structures for NO_2^-. The curly arrows (showing movement of a pair of electrons) indicate how one resonance form can be converted into the other.

The actual structure of NO_2^- cannot be adequately described by just one of these structures (the N—O bond lengths are equal), the actual structure is somewhere in between – the structure of NO_2^- is a resonance hybrid of the two resonance forms shown.

CO_3^{2-}

To describe the structure of the carbonate ions requires three separate resonance forms – it is a resonance hybrid with equal contributions from these forms (Figure 7.152).

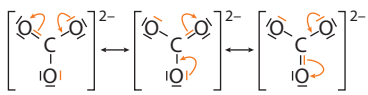

Figure 7.152: The resonance structures (Lewis formulas) for CO_3^{2-}.

Again, these look entirely equivalent – you could imagine just rotating one onto the next. The three bonds in CO_3^{2-} are, therefore, entirely equivalent and all C—O bonds length are equal. This also explains why the bond angle is exactly 120° – all three bonds repel equally – this would not be the case if one were a double bond and the other two single bonds.

SO_4^{2-} and H_2SO_4

SO_4^{2-} has resonance forms but H_2SO_4 does not.

Two resonance forms for SO_4^{2-} are shown in Figure 7.153.

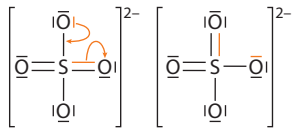

Figure 7.153: Two resonance forms for SO_4^{2-}… there are four more.

These are entirely equivalent and only differ in the position of the double bond and lone pair. Although it does not look like one could just be rotated into the other, do not forget that the ions are actually tetrahedral – they have just been drawn square planar for convenience. There are four more equivalent resonance forms of SO_4^{2-} (all with two double bonds and two single bonds), and the actual structure is a hybrid of these. All S—O bond lengths and angles in SO_4^{2-} are equal (149 pm, 109.5°).

If we try moving the double bond in H_2SO_4, the form generated is not equivalent to the first one – the O joined to the H has three bonds (Figure 7.154).

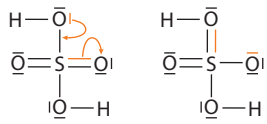

Figure 7.154: These two forms are not equivalent.

H_2SO_4 does not exhibit resonance and can be perfectly adequately described by the Lewis formula shown on the left in Figure 7.154. There are different bond lengths (S=O is 142 pm and S—O is 157 pm) and O—S—O bond angles in H_2SO_4.

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KEY POINT

All ions with the formula XO_n^{m-} will have resonance forms and equal X—O bond lengths.

Bond order

Bond order is a term we use to compare the bonds between atoms (see Table 7.24).

	Bond order
single bond	1
double bond	2
triple bond	3

Table 7.24

When molecules/ions are best described as resonance hybrids, the bond orders will involve fractions, for instance, the O—O bond order in ozone is $1\frac{1}{2}$ and the C—O bond order in CO_3^{2-} is $1\frac{1}{3}$. We can work out the bond orders by looking at how many bonded pairs of atoms the π component of a bond is shared between.

In NO_2^-, the π component of the double bond (shown in orange) is shared between two pairs of bonded N—O atoms, and so, each can be regarded as having a half share (Figure 7.155).

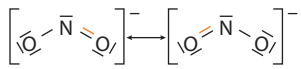

Figure 7.155: The orange bond is shared between two bonded pairs of atoms, so each has a half share. Alternatively, we can say that there are three bonds (lines) shared between two bonded groups of atoms (the two N—O groups) and so the bond order is $\frac{3}{2}$.

When the single bond order is added in, we have a bond order of 1 + 0.5 = 1.5. Because the bond order is between that of a single bond and a double bond, we would expect the N—O bond length to be between that of an N—O single bond (140 pm) and an N=O double bond (114 pm). The N—O bond length in the NO_2^- ion is 118 pm.

Link

Ozone (O_3) and oxygen (O_2) are important in protecting the surface of the Earth from the damaging effects of ultraviolet radiation. UV radiation is absorbed by molecules of O_2 or O_3 causing dissociation:

$O_2 \Rightarrow 2O\bullet$ and $O_3 \Rightarrow O\bullet + O_2$

The bond between the atoms in an O_2 molecule is a double bond (bond order 2), but O_3 has a bond order of 1.5. This means that the bond between the oxygen atoms in O_2 is stronger than that in O_3 and so higher energy (shorter wavelength) radiation is required to dissociate O_2.

In NO_3^-, the π component of the double bond (shown in orange) is shared between three N—O bonds (Figure 7.156), and so, the bond order is 1.33; 1 from the σ bond and 0.33 from the π component. Alternatively, there are 4 bonds shared between 3 N—O groups and so the bond order is $\frac{4}{3}$.

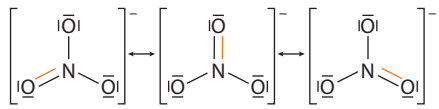

Figure 7.156: The orange bond is shared between three pairs of bonded N—O atoms, so each has a one-third share.

We would, therefore, predict that the N—O bond length in NO_3^- is between the N=O bond length and the N—O bond length. We would also predict that it would be longer than the N—O bond length in NO_2^- (bond order 1.5). The N—O bond length in NO_3^- is 124 pm, which is, indeed, longer than the N—O bond length of 118 pm in NO_2^-.

Some other bond orders are shown in Table 7.25:

	Bond order
PO_4^{3-}	1.25
SO_4^{2-}	1.5
ClO_4^-	1.75

Table 7.25

We previously used formal charge to distinguish between the possible Lewis structures of N_2O. The actual structure is somewhere in between the two – a resonance hybrid of the structures (Figure 7.157).

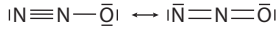

Figure 7.157: Resonance structures for N_2O.

Here, the structures are not equivalent to each other (we cannot just flip one around to make the other one),

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and it will not be the case then that these will contribute equally to the resonance hybrid. Calculations suggest an N—N bond order of about 2.7, which would suggest a larger contribution to the resonance hybrid from the form with the N≡N triple bond.

TEST YOUR UNDERSTANDING

34 Which of the following are best described as a resonance hybrid of more than one resonance structure?

HCN, IO_3^-, PCl_3, HNO_3, NO_2^+, AsO_4^-, $HCOO^-$ (H joined to C)

35 In which of the following would all the X—O bond lengths be equal?

SO_4^{2-}, H_2SO_3 (2 H atoms joined to O atoms), CH_3COO^-, HNO_2 (H joined to an O atom), H_2CO_3, PO_4^{3-}

36 Work out the X—O bond order in each of the following:

a SO_3^{2-} **b** ClO_3^- **c** HSO_4^-.

37 Arrange ClO_2^-, ClO_3^- and ClO_4^- in order of increasing Cl—O bond length.

Delocalisation

The concept of resonance structures and a resonance hybrid was developed to try to rationalise the structures of molecules/ions where experimental observations of bond lengths/angles could not be explained by just drawing one Lewis formula. The concept of resonance can be useful, and many predictions can be made using it, but a more satisfying explanation for experimental observations comes from the idea of **delocalisation** of electrons.

KEY POINT

Delocalisation is the sharing of a pair of electrons between three or more atoms.

In ozone, O_3, each oxygen atom can be regarded as being sp^2 hybridised with three sp^2 orbitals at 120° to each other and a p orbital on each oxygen atom that is perpendicular to the plane of the molecule. If we look at one of the resonance structures of O_3, where the double bond is between oxygen atom 2 and 3, there is side-on overlap between the p orbital on O2 and O3 to form the π bond (Figure 7.158).

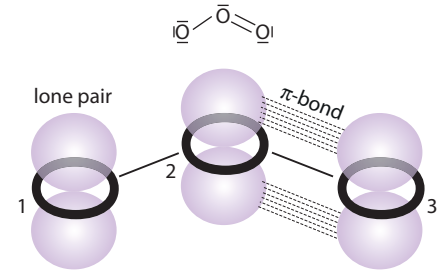

Figure 7.158: The p orbitals of O_3.

The p orbital on oxygen atom 1 can, however, also overlap side-on with the p orbital on oxygen atom 2, which is part of the π bond. In this way, the electron pair of the π bond is spread (delocalised) over all three oxygen atoms (Figure 7.159).

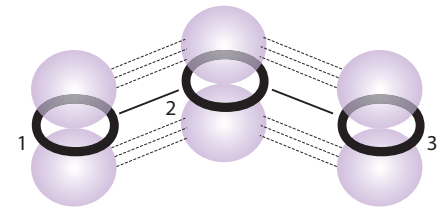

Figure 7.159: O_3 has a delocalised π system.

The delocalised system can be shown using dashed lines between atoms (Figure 7.160). The O—O bonds are identical and somewhere between a single bond and a double bond. Because the π bond is shared over two O—O bonds, each can be regarded as having a half share and the O—O bond order is 1.5.

Figure 7.160: Two equivalent representations of the delocalisation in ozone. The dashed lines represent the delocalisation of electrons. These diagrams are also sometimes called *resonance hybrids*.

All the molecules/ions that we have identified so far as having resonance forms can also be discussed in terms of a delocalised π system. The overlap of the p orbitals and delocalised structure of the carbonate (CO_3^{2-}) ion are shown in Figure 7.161.

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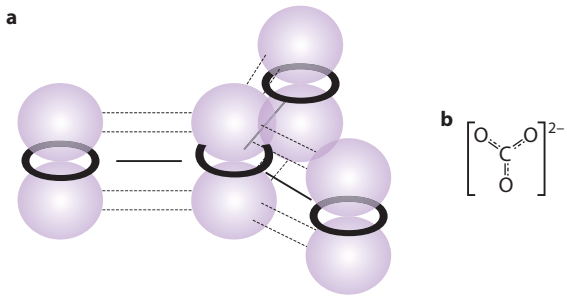

Figure 7.161: a Overlap of p orbitals in the carbonate ion. **b** Representation of the delocalisation in the carbonate ion.

There is a p orbital on each atom, and these overlap side-on to form the π delocalised system. The electrons in this system do not belong to any one atom but are delocalised over the whole ion.

NO_2^- is isoelectronic with ozone, and the delocalised system can be shown in a similar way (Figure 7.162).

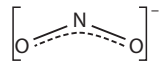

Figure 7.162: The delocalised structure of NO_2^-.

EXAM TIP

If asked for a Lewis formula/structure or resonance structure of a species such as O_3 in an examination, you must show a structure with all its bonds and lone pairs – one of the structures shown in Figure 7.150. You must not show the delocalised structure, unless specifically asked for this. If you are asked for the delocalised structure, you should not include lone pairs of electrons. The delocalised structure is sometimes called a resonance hybrid.

TEST YOUR UNDERSTANDING

38 Draw diagrams showing delocalisation in each of the following:

ClO_2^-, IO_3^-, SO_4^{2-}, $HCOO^-$, ClO_4^-.

Benzene

Benzene (molecular formula C_6H_6) was first isolated in 1825 by Michael Faraday, and its formula was known early on, but it was 40 years before a plausible structure was suggested. The structure consists of a planar, hexagonal ring of carbon atoms, with a hydrogen atom joined to each carbon atom. A ring structure for this molecule, with alternating double and single bonds, was originally proposed by Friedrich Auguste Kekulé. The structure is often shown without the atoms (Figure 7.163).

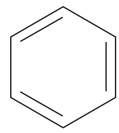

Figure 7.163: The benzene structure, with alternating single and double bonds, is still known as 'Kekulé benzene', but more systematic names for this would be cyclohexa-1,3,5-triene or 1,3,5-cyclohexatriene.

One piece of evidence (other evidence is discussed next) against the structure shown being the best representation of the structure of benzene came when it became possible to measure bond lengths. All the carbon–carbon bond lengths in benzene are equal and, at 140 pm, are between the C=C bond length of 133 pm and the single bond length of 154 pm. This can be explained by the structure of benzene being a resonance hybrid with equal contributions from the two resonance structures shown in Figure 7.164.

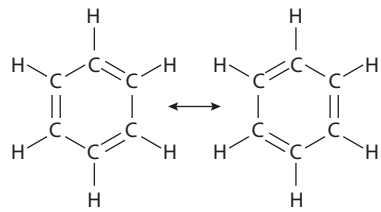

Figure 7.164: The resonance structures of benzene.

All the bonds between the C atoms are, therefore, equivalent. Because the π components of three double bonds are shared between six pairs of bonded C—C atoms, the bond order is 1.5, which explains the C—C bond length being between that of a C—C single bond and C=C.

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The structure of benzene is nowadays better represented as in Figure 7.165b.

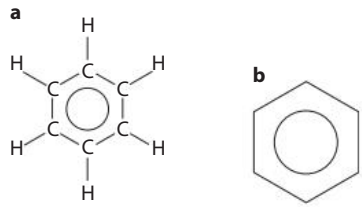
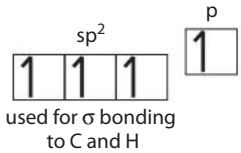


Figure 7.165: Benzene ring showing **a** all the atoms; **b** the usual representation.

The circle represents a π system of delocalised electrons. Each carbon atom is sp^2 hybridised and forms σ bonds to the two adjacent C atoms and the H atom. This leaves a p orbital containing one electron on each C perpendicular to the ring:



The sigma framework and p orbitals on each C atom are shown in Figure 7.166.

Figure 7.166: The sigma framework for C_6H_6.

Figure 7.167 shows that, instead of the p orbitals just overlapping side-on between adjacent C atoms to give three localised π bonds, delocalisation can occur over the whole structure.

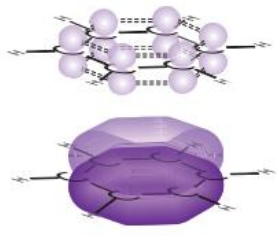


Figure 7.167: Formation of the benzene delocalised system.

So, benzene has a π ring of six delocalised electrons that extends all around the ring of carbon atoms. Because there are six electrons in the π system, this is equivalent to one π electron ($\frac{1}{2}$ a bond) per C—C bond and, therefore, a bond order of 1.5 for each pair of C—C atoms in the ring.

Evidence for benzene's delocalised structure

In the next sections, we will look at the evidence for benzene being represented as a resonance hybrid/delocalised structure, rather than by just one Lewis formula with alternating C—C and C=C (Kekulé benzene). Remember, Kekulé benzene does not actually exist – it is just a proposed structure, and we are evaluating it on the grounds of experimental evidence.

All the carbon – carbon bond lengths are equal

All C—C bond lengths are equal in benzene and intermediate in length between a C—C single bond and a C=C double bond (Table 7.26). If the structure of benzene were that of Kekulé benzene, then it would be expected that there would be three short C=C bonds (approximately 133 pm) and three longer C—C bonds (approximately 154 pm). The delocalised/resonance hybrid structure of benzene suggests all C—C bond lengths are equal with a C—C bond length between that of a C—C bond and a C=C double bond.

Bond	Compound	Bond length pm
C=C	cyclohexene	133
C—C	cyclohexane	154
C┈C	benzene	140

Table 7.26: Bond lengths in cyclohexane, cyclohexene and benzene. The bond lengths in cyclohexane and cyclohexene were chosen for comparison because these molecules (see structures in Figure 7.165) also contain a ring of six C atoms. Bond lengths can be determined by X-ray crystallography.

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Less energy is given out than predicted when benzene reacts with hydrogen

When cyclohexene (C_6H_{10}) is heated with hydrogen in the presence of a nickel catalyst, cyclohexane (C_6H_{12}) is formed. This is an addition reaction (see Chapter 22) in which hydrogen adds across the C=C bond of cyclohexene (Figure 7.168) – the enthalpy change is approximately –120 kJ mol^{-1}.

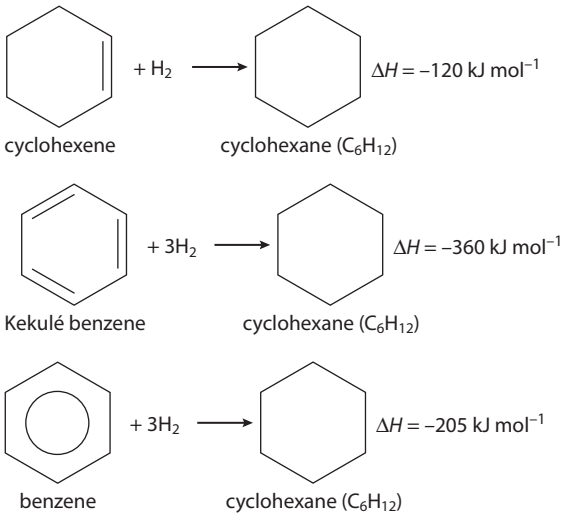

Figure 7.168: Comparing enthalpies of hydrogenation.

For more information about enthalpy changes, see Chapter 12. A negative value indicates that energy is given out (in the form of heat), so the products have lower energy than the reactants – the products are more stable than the reactants.

Cyclohexene molecules contain one C=C bond, whereas Kekulé benzene contains three. It would, therefore, be expected that the enthalpy change for the complete hydrogenation of Kekulé benzene to cyclohexane would be 3 × –120, i.e., –360 kJ mol^{-1}. However, the enthalpy change when benzene undergoes complete hydrogenation to cyclohexane is only –205 kJ mol^{-1}.

If an enthalpy level diagram (Figure 7.169) is drawn for the hydrogenation reactions of benzene and Kekulé benzene, it is seen that benzene is 155 kJ mol^{-1} more stable than would be predicted if it had the structure with alternating single and double carbon–carbon bonds (less energy is given out forming the same product, so benzene must have started with less energy than Kekulé benzene).

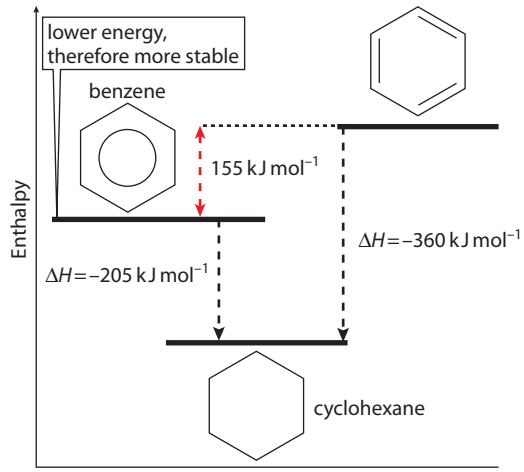

Figure 7.169: Comparative enthalpy changes for the hydrogenation reactions of benzene and Kekulé benzene.

The extra stability of benzene compared with the structure with alternating double and single bonds is due to the delocalisation of electrons. This is also sometimes called the **resonance energy**.

There are only three isomers of $C_6H_4Cl_2$

Further evidence for a delocalised structure for benzene comes from examining the number of isomers that are possible for $C_6H_4X_2$, assuming a Kekulé structure and a delocalised structure (Figure 7.170). Isomers are compounds that have the same molecular formula but different structures. For more details, see Chapter 11.

Only three isomers have ever been found for $C_6H_4Cl_2$, but the structure with alternating double and single bonds suggests that there should be four. The difference

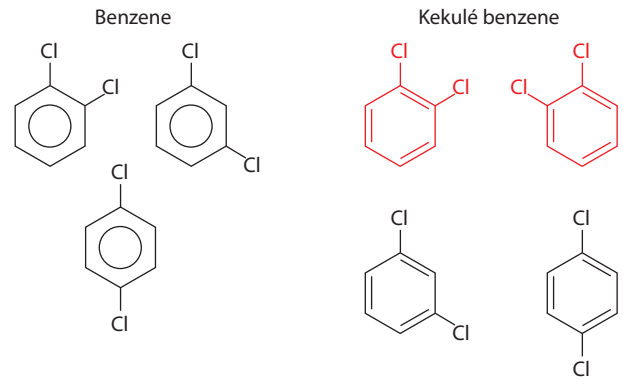

Figure 7.170: Possible isomers for $C_6H_4Cl_2$.

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arises because two chlorine atoms that are on adjacent carbon atoms in the ring can either be separated by a C—C single bond or a C=C double bond, if benzene is assumed to have the Kekulé structure. These are highlighted in Figure 7.170.

Benzene undergoes substitution rather than addition reactions

Kekulé benzene would be expected to undergo addition reactions like alkenes (compounds with a C=C) and to decolorise bromine water. However, benzene does not react like alkenes – it does not undergo addition reactions under normal conditions and will not decolorise bromine water. An addition reaction would involve the destruction of the delocalised system and the loss of the extra stability (resonance energy) associated with it. Therefore, benzene undergoes *substitution* reactions, which involve replacement of one or more H atoms on the ring with another atom or group but no loss of the delocalised system. For example, benzene reacts with chlorine in the presence of a catalyst, such as aluminium chloride, to form chlorobenzene, C_6H_5Cl (Figure 7.171)

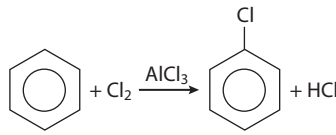

Figure 7.171

Although the delocalised ring may be temporarily disrupted in reactions, it is restored so that the extra stability is not lost. For more information about the reactions of alkenes and benzene, see Chapter 22.

EXAM TIP

The evidence for the structure of benzene can be classified as either chemical (enthalpy changes of hydrogenation and substitution reactions) or physical (C—C bond lengths, number of isomers).

NATURE OF SCIENCE

Science is an ever-changing body of knowledge. When new and conflicting evidence comes to light, such as bond length data, theories must be modified. Theories can be superseded by new ones that provide a better explanation of experimental data. The theory of resonance has been largely replaced by the theory of delocalisation.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the term 'covalent bond'	7.1			
explain the relationship between bond strength and length for multiple bonds	7.1			
explain what a coordination bond is	7.1			
deduce Lewis formulas (structures) for covalent molecules/ions with up to four electron pairs in the outer shell of the central atom	7.1			

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CONTINUED

I can...	Section	Needs more work	Nearly there	Confident to move on
use the 'octet rule' when deducing Lewis formulas (structures)	7.1			
use VSEPR to work out the shapes and bond angles in molecules/ions with up to four electron domains on the central atom	7.2			
deduce whether a molecule is polar or not	7.5			
explain the formation of intermolecular forces	7.7			
understand the influence of intermolecular forces on the melting/boiling point of covalent substances	7.8			
explain how mixtures are separated using paper chromatography and thin-layer chromatography	7.9			
explain the physical properties of covalent substances	7.10			
describe and explain the bonding and structure of substances with covalent network structures	7.10			
deduce Lewis formulas and shapes for molecules and ions with expanded octets of electrons	7.11			
use formal charge to distinguish between Lewis formulas	7.12			
explain hybridisation and determine the hybridisation of an atom in a molecule/ion	7.14			
explain the formation of σ and π bonds	7.15			
explain resonance and delocalisation of electrons and recognise molecules/ions that exhibit it	7.16			
describe and explain the structure of benzene.	7.16			

REFLECTION

- In which areas do you feel that you need most practice?
- Can you draw up your own set of rules for drawing Lewis formulas?
- Do you feel confident that you could draw the Lewis formula for any molecule/ion?
- Can you explain how to work out shapes of molecules to another student?
- Do you feel that you could explain hybridisation and delocalisation to another student? If not, can you identify where the gaps in your understanding are?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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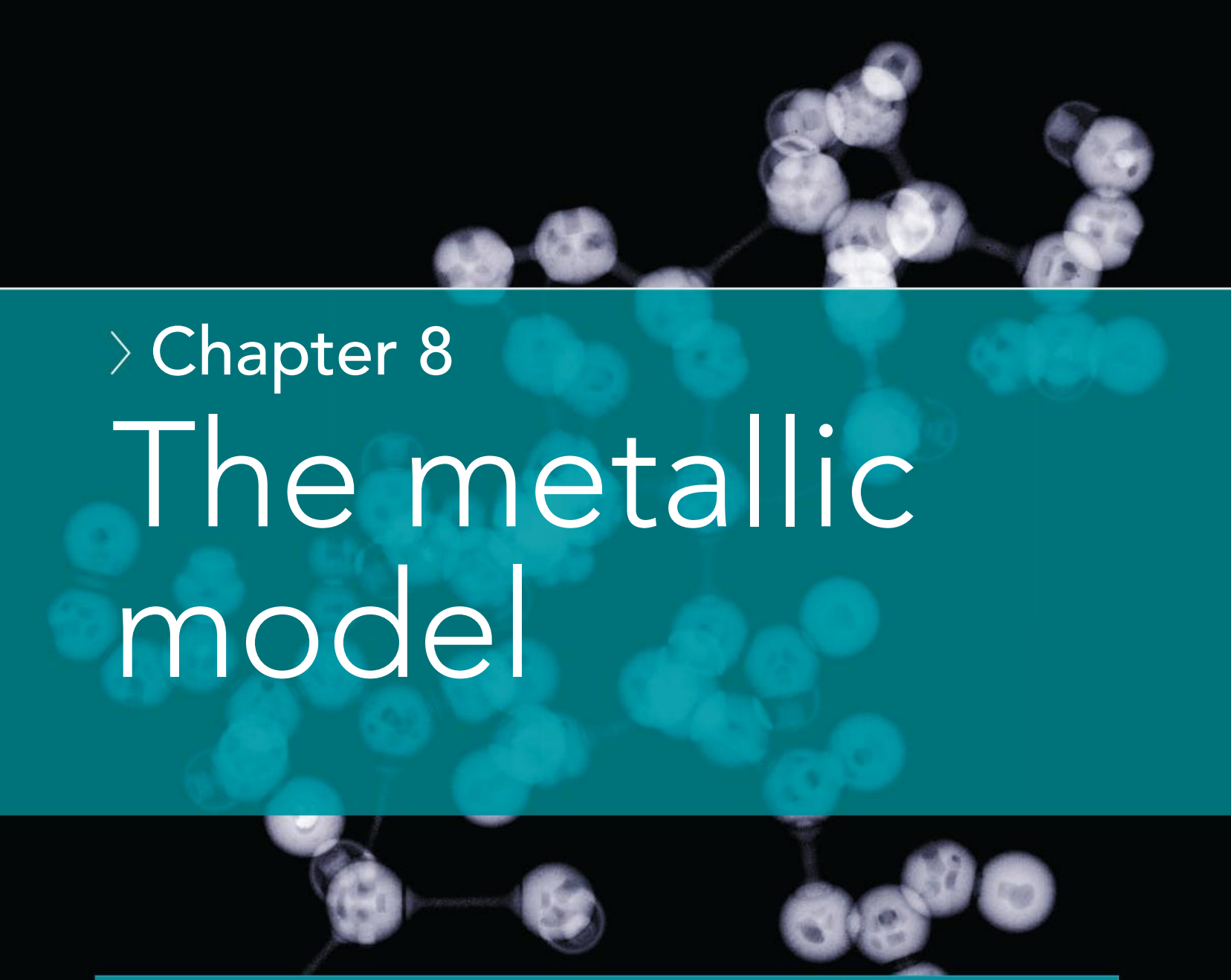

Chapter 8

The metallic model

LEARNING OBJECTIVES

In this chapter you will:

- explain metallic bonding
- explain the factors that affect the strength of metallic bonding
- explain the variation in the melting point of main group metals down a group and across a period
- describe and explain the characteristic properties of metals
- understand the connection between the properties of a metal and its uses

- understand that transition metals have delocalised d electrons
- explain the melting points and electrical conductivity of transition metals.

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GUIDING QUESTIONS

- What makes something a metal?
- What is metallic bonding?
- How can the properties of metals be explained in terms of structure and bonding?

Introduction

About three-quarters of the known elements are metals. These metals have a variety of properties and uses, for example:

- mercury is a liquid at room temperature and is most familiar from its use in thermometers, but is extremely toxic
- sodium is a soft, highly reactive metal that is less dense than water and is used in street lighting
- iron is a high melting point and strong metal, which is used extensively in construction, usually in the form of steel
- gold is a highly unreactive and very dense metal that is used in jewellery.

These all seem very different, so what is it about them that means we recognise them as metals?

8.1 Classifying elements as metals

Metals are found on the left-hand side, middle and towards the bottom of the periodic table (Figure 8.1).

Metals share common properties

Elements can be classified as metals or non-metals according to their properties. Characteristic physical properties of metals are shown in Table 8.1.

In the sections that follow, we will look at explaining these properties in terms of the structure and bonding in metals.

Metals also have characteristic chemical properties:

- form positive ions (cations)
- usually form ionic compounds
- their oxides are usually basic (will react with acids to form salts or form alkaline solutions if soluble in water).

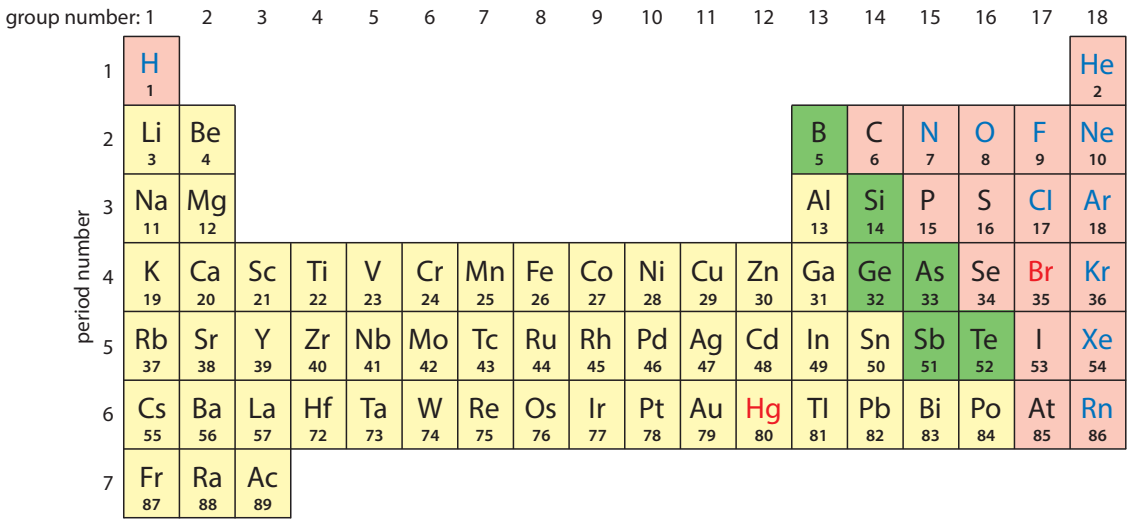

Figure 8.1: The periodic table showing the distribution of metals (yellow), metalloids (green) and non-metals (pink). Metallic character and the periodic table will be discussed further in Chapter 10.

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Physical property	Comment
lustrous	shiny when freshly scratched/cut
good conductors of electricity	metals conduct electricity when solid or liquid; conduction decreases as temperature increases
good conductors of heat	although the best conductor is diamond
ductile	may be drawn into wires
malleable	may be hammered into shape – many uses arise from the ability to easily shape metals, e.g. making car bodies

Table 8.1: Some physical properties of metals.

8.2 Metallic bonding

KEY POINT

Metals contain a regular lattice arrangement of positive ions (cations) surrounded by a 'sea' of delocalised electrons.

The structure of a typical metal is shown in Figure 8.2.

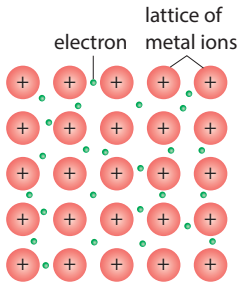

Figure 8.2: A metallic structure. This is a giant structure – there are no individual molecules.

When atoms come together to form a metallic structure, positive ions are formed as the outer-shell electrons become free to move over the whole structure. The electrons are described as *delocalised* – they do not belong to any one metal atom but move between all the metal ions in the lattice.

KEY POINT

Metallic bonding is the electrostatic attraction between positive ions and delocalised electrons.

Each delocalised electron is attracted by all the positive ions in the lattice structure and vice versa, so the whole lattice is held together (Figure 8.3).

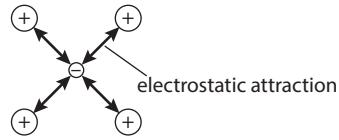

Figure 8.3: The attraction between metal ions and a delocalised electron.

Link

To form a metal, an atom must relatively easily be able to form a positive ion. Therefore, the elements that are metals are those where the atom has a relatively low ionisation energy (the energy to remove an electron from an atom). Ionisation energy generally decreases down a group and increases across a period; therefore, the metals are found to the left and the bottom of the periodic table, see Chapter 10.

The strength of metallic bonding

KEY POINTS

The strength of metallic bonding depends on the charge on the metal ion and the size (radius) of the metal ion.

Metallic bonding is strongest when the ions are small and highly charged (greatest charge density).

The effects of these factors on the melting point of metals down a group and across a period will be discussed in the sections that follow.

Melting point of metals

The variation in melting point down Group 1 (the alkali metals) is shown in Figure 8.4.

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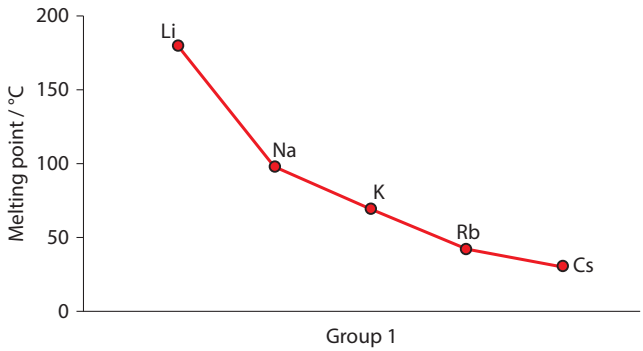

Figure 8.4: Variation in melting point in Group 1.

All the elements in Group 1 have one electron in their outer shell and, therefore, form 1+ ions in the metallic lattice. The attraction for delocalised electrons is actually due to the nucleus of the positive ion (another way of saying this is that the ion acts as if it is a point charge at its centre). The positive ion gets larger as we go down the group; therefore, the nucleus is further from the delocalised electrons and the attraction becomes weaker (Figure 8.5). Weaker attractions between the positive ions and delocalised electrons (weaker metallic bonding) means that less energy is required to break apart the lattice as we go down Group 1, and the melting point decreases.

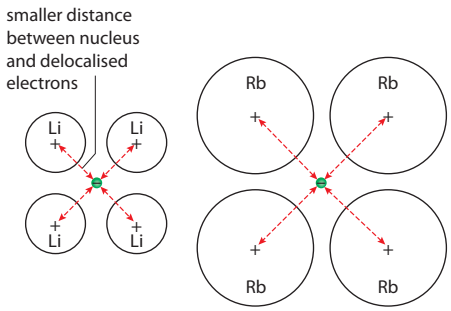

Figure 8.5: The delocalised electrons are attracted more strongly in lithium than in rubidium.

Sodium, magnesium and aluminium are three consecutive metallic elements going from left to right across Period 3 in the periodic table. The melting and boiling points of sodium, magnesium and aluminium are shown in Table 8.2.

	Na	Mg	Al
melting point / °C	98	649	660
boiling point / °C	883	1090	2467

Table 8.2: The melting and boiling points of sodium, magnesium and aluminium.

There are three main reasons why magnesium has a higher melting point than sodium:

1 Magnesium has two outer-shell electrons and forms a 2+ ion, but sodium, which has one outer-shell electron, forms a 1+ ion (Figure 8.6). The electrostatic attraction between a 2+ ion and a delocalised electron is stronger than that between a 1+ ion and a delocalised electron.

2 The Mg^{2+} ion (72 pm) is smaller than the Na^{+} ion (102 pm) and, therefore, the delocalised electrons are closer to the nucleus of the positive ion in magnesium and are more strongly attracted. Why Mg^{2+} is smaller than Na^{+} is explained in Chapter 10.

3 In magnesium, there are more delocalised electrons per atom since it forms a 2+ ion, but sodium only forms a 1+ ion.

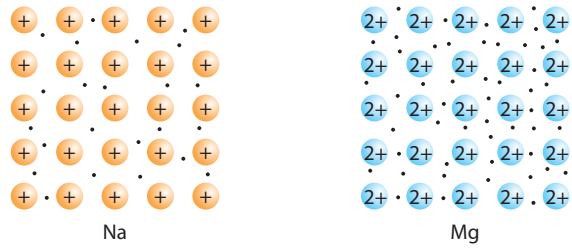

Figure 8.6: Metallic bonding in sodium and magnesium.

Overall, these three factors mean that there will be stronger electrostatic attractions between the positive ions and the delocalised electrons (metallic bonding) in magnesium than in sodium.

Aluminium has only a slightly higher melting point than magnesium, but the boiling points (that of Al is significantly higher) show the expected increase in the strength of metallic bonding as the charge on the ion increases (Al^{3+}) and the radius of the ion decreases (54 pm).

Charge density

The charge density of an ion is the charge divided by the volume of the ion. The higher the charge density on an ion, the more strongly it will attract the delocalised electrons.

The trends in melting point can also be described in terms of charge density: Mg^{2+} has a higher charge density (higher charge and smaller volume) than Na^{+} and, therefore, attracts the delocalised electrons more strongly.

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8.3 Properties of metals and their uses

Physical properties of metals

KEY POINT

Metals are good conductors of electricity.

Metals conduct electricity in the solid state and liquid state. Electricity is a flow of charge. Metals conduct electricity because the delocalised electrons are free to move – they will move in a particular direction if a voltage is applied to a piece of metal.

Link

Metals conduct electricity when solid or liquid, but, remember, ionic compounds do not conduct in the solid state. Ionic compounds conduct in the liquid state because *ions* are free to move, see Chapter 6.

KEY POINT

Metals are good conductors of heat (thermal conductors).

Metals are very good conductors of heat because of the delocalised electrons. If one end of a piece of a metal is heated, the delocalised electrons there gain kinetic energy and move faster. These electrons are able to move throughout the lattice and transfer this kinetic energy quickly to other electrons and metal ions in the lattice.

KEY POINT

Metals are malleable.

Metals are **malleable** and **ductile** because, when a force is applied to a piece of metal, the layers of ions can slide over each other without affecting bonding. This is possible because metallic bonding is non-directional – the metal ions in the lattice attract delocalised electrons in all directions and vice versa. So, when one layer is displaced relative to another (Figure 8.7), the positive ions still attract delocalised electrons in the same way.

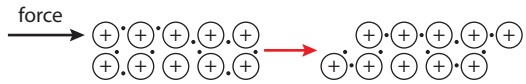

Figure 8.7: Metals are malleable. Displacing one layer makes no difference to the metallic bonding.

This can be compared with ionic solids (Figure 8.8), which are brittle, as displacement of one layer relative to the other results in like charges repelling each other so the solid breaks apart.

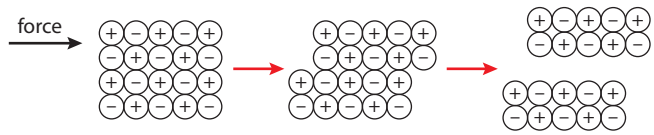

Figure 8.8: Brittleness. Displacement of layers in ionic compounds results in like charges being next to each other.

INTERNATIONAL MINDEDNESS

Metal ores are not distributed evenly in the Earth's crust. For example, Chile has the largest reserves of copper, whereas South Africa has the largest reserves of manganese, and the Democratic Republic of Congo has the largest reserves of cobalt. Mining of metals makes a significant contribution to the gross domestic product (GDP) of many developing countries but can also bring with it environmental and social challenges.

Uses of metals

The characteristic properties of metals make them essential as construction materials. As well as the properties listed above, metals are also usually strong (high tensile strength) and have high melting points. The metals are often used in the form of alloys. Alloys are mixtures of two or more metals or of a metal with a non-metal. Alloys will be discussed in Chapter 9.

Link

Because metallic bonding is non-directional, the introduction of an atom of a different metal when an alloy is formed does not affect the nature of the bonding (Chapter 9).

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Metals such as iron have a wide range of uses, such as in construction (bridges, cars, etc.). Iron is usually used in the form of steel, an alloy of iron and carbon. The fact that mild steel is strong and malleable makes it ideal for the construction of car bodies (Figure 8.9).

Figure 8.9: Mild steel is malleable, which makes it very good for making car bodies – and for crushing them afterwards!

Copper is a very good conductor of electricity and can be drawn out into wires (ductile). It is used in a very close to pure form (not an alloy) in electrical cabling (Figure 8.10). The presence of impurities significantly reduces its electrical conductivity.

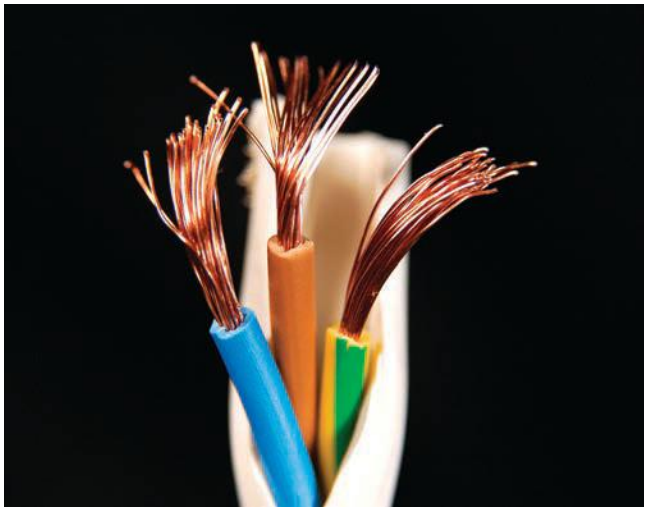

Figure 8.10: Copper is used in electrical cabling.

Aluminium is also a very good conductor of electricity, can be drawn into wires and has a relatively low density (about one-third that of copper), making it ideal for use in overhead power cables (Figure 8.11).

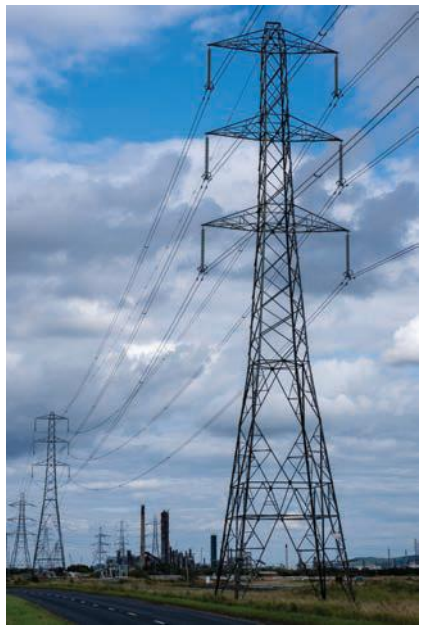

Figure 8.11: Aluminium is used in power transmission.

The high thermal conductivity of metals means that they are used for pots and pans – heat is rapidly transferred from the cooker to the contents of the pan. Stainless steel, cast iron, aluminium and copper are all used for making pans (Figure 8.12). Liquid sodium is used for heat transfer in some types of nuclear reactor.

Figure 8.12: Copper is used for making pots and pans.

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TEST YOUR UNDERSTANDING

1 Are the following statements TRUE or FALSE?

- **a** Metals are found towards the top right of the periodic table.
- **b** Metallic bonding is the attraction between positive ions and delocalised electrons.
- **c** Metals only conduct electricity when molten.
- **d** Metals conduct electricity because positive ions are free to move.
- **e** Metals are malleable because delocalised electrons are free to move.
- **f** Metals are good thermal conductors because delocalised electrons are free to move.

2 Arrange the following sets in order of increasing melting point (lowest first):

- **a** Na, Li, K
- **b** Al, Mg, Na.

SCIENCE IN CONTEXT

Aluminium is probably most familiar to us in everyday life from its use in drinks cans (Figure 8.13) and pots and pans, but its importance is much wider than that, and aluminium is second only to steel as the most used metal globally (although its production is still only less than 5% that of steel).

Figure 8.13: Aluminium is used in drinks cans.

CONTINUED

Its main advantages over steel are that it is resistant to corrosion (it does not rust) and its density is only about a third of that of steel. This means that aluminium finds extensive use in planes, trains and increasingly in cars. Since it is lightweight, less fuel is required and, therefore, less CO_2 is produced per km for cars with internal combustion engines, and electric vehicles can travel further. However, there is a downside to the use of aluminium; since it is a relatively reactive metal, it must be extracted from its ore using electrolysis, which requires huge amounts of energy. The production of aluminium from its ore accounts for about 3–4% of global electricity consumption. It is estimated that the production of 1 tonne of aluminium produces greenhouse gas emissions equivalent to about 15 tonnes of CO_2 and that aluminium production accounts for about 1% of global greenhouse gas emissions. Energy consumption and emissions can be reduced by using renewable energy (this has to be on a huge scale; therefore, hydroelectric power is the main contributor here) and by recycling aluminium, which uses only around 5% of the energy of producing aluminium from its ore.

8.4 Transition metals

The first-row transition metals have the general electron configuration: [Ar] $4s^2$ $3d^n$ (Cr and Cu are exceptions). The chemistry of the transition metals is dominated by the use of d electrons/orbitals in bonding.
When transition metals form ions, the outer-shell s electrons are lost first and then the d electrons; for example, the electron configuration of Fe^{3+} is [Ar] $3d^5$. In the elemental state, the d electrons and the s electrons will be delocalised.

KEY POINTS

Transition metals have delocalised d electrons.

Transition metals have significantly higher melting points than metals in the s and p blocks.

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The significantly higher melting points of transition metals compared to metals such as magnesium or aluminium can be attributed to the delocalisation of d electrons – higher charges on ions and more delocalised electrons result in stronger metallic bonding.

The electron configurations of the first four d-block elements are as follows:

Sc [Ar] $4s^2$ $3d^1$

Ti [Ar] $4s^2$ $3d^2$

V [Ar] $4s^2$ $3d^3$

Cr [Ar] $4s^1$ $3d^5$

Along this series, it would, therefore, be expected that there would be an increase in the charge on the positive ions formed as the two s electrons and increasingly more d electrons are delocalised. Added to this, the ions also get smaller along the series. These effects would result in stronger attraction between positive ions and delocalised electrons, and hence, higher melting points. An increase in melting point is indeed found from Sc to V (Cr has virtually the same melting point as V) (Figure 8.14).

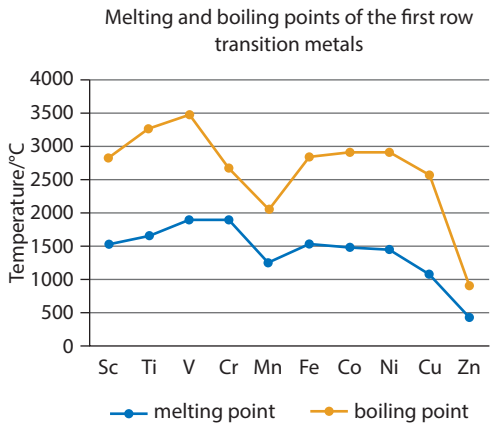

Figure 8.14: The melting and boiling points of the first-row transition metals. Zn is included here for completeness, but it is not usually regarded as a transition metal (see Chapter 10).

It is not, however, the case that vanadium metal contains 5+ ions and Cr metal contains 6+ ions – the quantity of energy to produce these ions would not be paid back by the energy released when the metallic bonds are formed. The actual charges on the ions will be lower than this.

The melting points generally decrease from V to Zn. As we go further along the series, the nuclear charge increases and the size of the atoms decreases, which means that ionisation energy increases, and it becomes more difficult to form more highly charged ions. The lower melting point of Mn and the elements in the second half of the series can therefore be understood in terms of lower charges on the ions actually present in the lattice and fewer delocalised d electrons. The chemistry of nickel and copper is dominated by the formation of 2+ ions, but vanadium has an extensive chemistry in the +4 oxidation state.

The electrical conductivity of transition metals

The transition metals all conduct electricity because delocalised electrons are free to move. The delocalised electrons in transition metals include both the d electrons (3d electrons for the first-row transition metals) and the s electrons (4s for the first row).

The electrical conductivity of the first-row transition metals (with the exception of copper) is lower than that of sodium, magnesium and aluminium and, for many of the transition metals, significantly so (Table 8.3).

Metal	Electrical conductivity at room temperature / S m^{-1}
sodium	2.05×10^7
magnesium	2.23×10^7
aluminium	3.69×10^7
scandium	1.8×10^6
titanium	2.4×10^6
vanadium	4.98×10^6
chromium	7.93×10^6
manganese	6.94×10^6
iron	1.01×10^7
cobalt	1.11×10^7
nickel	1.40×10^7
copper	5.85×10^7

Table 8.3: A comparison of the electrical conductivity of transition metals with some non-transition metals (in turquoise). The unit for electrical conductivity is siemens per metre.

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Many of the transition metals are, therefore, not regarded as terribly good conductors of electricity for metals. Scandium and aluminium, for example, both have three electrons that could be delocalised ($4s^2$ and $3d^1$ for Sc and $3s^2$ $3p^1$ for Al), but the electrical conductivity of Sc is only about 5% that of Al. It would, therefore, seem that the tendency of d electrons to become delocalised is less than that of s and p electrons. The delocalisation of d electrons in the transition metals does, to a certain extent, contribute to their electrical conductivity, although the very high electrical conductivity of copper is usually explained solely in terms of the delocalisation of the outer s electron.

KEY POINTS

Transition metals generally have higher melting points than non-transition metals (e.g. Na and Mg).

Transition metals generally have lower electrical conductivity than non-transition metals (copper is an important exception).

The physical properties of transition metals can be explained in terms of delocalised d electrons.

TEST YOUR UNDERSTANDING

3 Are the following statements TRUE or FALSE?

a Potassium has a higher melting point than nickel.

b d electrons are delocalised in transition metals.

c Vanadium has a higher melting point than scandium because there is a higher charge on the ion, and there are more delocalised electrons.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain metallic bonding	8.2			
explain the factors that affect the strength of metallic bonding	8.2			
explain the variation in the melting point of main group metals down a group and across a period	8.2			
rationalise a use of a metal in terms of its properties	8.3			
explain that transition metals have delocalised d electrons	8.5			
explain the melting points and electrical conductivity of transition metals.	8.5			

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REFLECTION

- This chapter is only a very short one, but it contains some important ideas.
- Think about the concepts covered in this chapter. Which parts are you most confident with?
- Could you explain metallic bonding to someone else?
- Chapters 6, 7 and 8 all concern bonding. How confident are you at linking the ideas and comparing the types of bonding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 9
From models to materials

LEARNING OBJECTIVES

In this chapter you will:

- understand the continuum between ionic, covalent and metallic bonding
- use electronegativity values to place substances in a bonding triangle
- relate the position of a compound in the bonding triangle to its properties.
- understand the term alloy
- explain the properties of alloys
- understand the term polymer
- explain the properties of polymers (plastics) in terms of structure and bonding
- explain how addition polymers are formed
- deduce the structure of the repeating unit and equations for the formation of addition polymers

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CONTINUED

- explain how condensation polymers are formed
- deduce the structure of the repeating unit of a condensation polymer
- understand that biological macromolecules form by condensation polymerisation and breakdown by hydrolysis

GUIDING QUESTIONS

- How are the different types of bonding interrelated?
- How do structure and bonding relate to the properties of materials?
- What are polymers and how are they made?

Introduction

The prehistory of humankind is often talked about in terms of the materials that were used, so humans transitioned from the Stone Age to the Bronze Age to the Iron Age, as more sophisticated techniques were developed to process metals. Both bronze and the iron that was being used were alloys – the 'iron' was not actually pure iron but an alloy of iron and carbon (mostly what we generally call wrought iron, but also steel). Recent history has seen the unprecedented development of new materials, but will the current period of time be remembered as the 'Plastic Age'? Mass produced plastics have been around for under 100 years, but they have definitely changed the world – for the better?

9.1 Bonding and electronegativity

So far, we have met the three types of bonding (ionic, covalent and metallic) in three different chapters and regarded them as completely separate models for bonding in a substance. However, when we look at the properties of a compound or material, we often find that it does not fit neatly into one category of bonding.

For example, silicon is described as having a network covalent structure but conducts electricity. Metallic bonding and covalent bonding can be regarded as two extremes of the same thing. In the *band theory* of network solids, the orbitals are regarded as overlapping between adjacent atoms throughout the solid. In a metal, the electrons within this set of orbitals are totally delocalised, but in a covalent structure, such as diamond, the electrons are localised between the atoms; in silicon, the situation is somewhere between these two extremes.

A substance such as CsF is fairly close to 100% ionic, and there is complete transfer of electrons from Cs to F, but in LiI the small Li^+ ion attracts the electrons from the large I^- ion quite strongly, and so, more covalent character (sharing of electron density) would be expected. The lattice enthalpies of silver halides are also significantly different from what would be expected from a purely ionic model. So, for LiI and silver halides, the bonding is somewhere between the two extremes of purely covalent or purely ionic bonding.

KEY POINT

Bonding within a substance is best described in terms of a continuum between ionic, covalent and metallic bonding.

Using electronegativity differences to predict the type of bonding in a substance

When Pauling developed his electronegativity scale, he used it to predict the degree of ionic/covalent character in *bonds* – he predicted that the bigger the difference in electronegativity between two atoms, the more ionic the bonding. He tested his model by looking at the dipoles of gaseous molecules of the type XY and tried to estimate the percentage contribution to the structure

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from X^+Y^- (100% ionic) and X—Y (100% covalent). The dipole moment (the product of the charges and the distance between them) could be worked out theoretically for X^+Y^-, and the closer this value was to the experimental value, the more ionic the bonding. If the theoretical values and experimental values were the same, then there would be 100% ionic bonding, but any covalent bonding would cause the experimental dipole moment to be lower than predicted.

Pauling's calculation predicted about 22% ionic character in a bond for an electronegativity difference between X and Y of 1.0, 63% ionic character for an electronegativity difference of 2.0 and 89% ionic character for an electronegativity difference of 3.0. So, using this scale, the percentage ionic character for NaCl is 73%. If, however, we look at the bulk form of NaCl, this description of bonding as being about one-quarter covalent does not seem very useful or realistic; for instance, the lattice enthalpy of NaCl is within 1% of that predicted by a purely ionic model and all the properties of sodium chloride fit the ionic model very well. It is important to remember that, when Pauling was predicting the ionic character of a bond, he was looking at gaseous molecules – gaseous NaCl molecules will behave very differently from solid NaCl.

Substances with approximately 50% ionic and 50% covalent character according to electronegativity values

You will often see it stated that, if the electronegativity difference between two elements is greater than 1.7, then the bonding is ionic, and if it less than 1.7, it is covalent, so let's have a look at some substances with electronegativity differences around 1.7. This would include compounds such as AuF_3 (electronegativity difference: 1.6), LiI (1.7), $MgBr_2$ (1.7), Na_2S (1.7), PF_5 (1.8) and Al_2O_3 (1.8).

Of these substances, some are regarded as having predominantly covalent bonding (e.g. PF_5) and others as having predominantly ionic bonding (e.g. LiI). When trying to decide on the predominant form of bonding in a substance, we have to compare its properties with what we would expect from, say, an 'ionic compound', such as NaCl, or a 'covalent compound', such as CCl_4. A typical ionic compound would be expected to have a high melting point and conduct electricity when molten, whereas a typical covalent compound would be expected to have a low melting point and not conduct electricity in any state. These are, of course, generalisations, but are a good starting point for understanding what the predominant form of bonding is likely to be.

A comparison of experimental lattice energies with what is predicted by a purely ionic model and determination of the structure (using X-ray crystallography) can also be crucial in making judgments about bonding.

Looking at the structures of some of the substances mentioned above: AuF_3 has a polymeric structure with predominantly covalent bonding; LiI is a white crystalline substance with a relatively high melting point and an experimental lattice energy that is very close to that obtained using a purely ionic model – it would generally be regarded as an ionic compound; PF_5 is a molecular gas at room temperature and pressure with predominantly covalent bonding.

From this, it can be seen that just using differences in electronegativities is not perhaps the best way of predicting the type of bonding in a substance, and a bonding triangle provides a better method.

Bonding triangles

A bonding triangle (Figure 9.1) can be used to illustrate the idea that there is a continuum from one type of bonding to the other two – and shows that the idea of purely ionic or purely covalent bonding is an oversimplification.

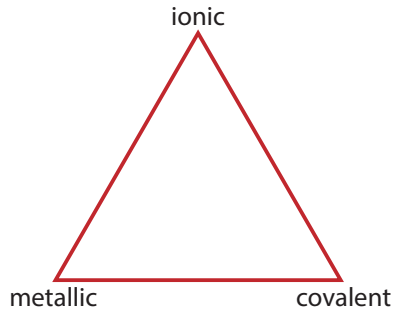

Figure 9.1: A simple bonding triangle.

There is no standard bonding triangle, and lots of different ones can be drawn using different quantities to estimate the contribution from each of the different types of bonding to the overall bonding in a substance. One common way of doing this is in terms of electronegativity (some electronegativity values are given in Table 9.1). These triangles are often called van Arkel–Ketelaar triangles after two scientists who developed the early ideas of bonding triangles.

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H 2.2																
Li 1.0	Be 1.6											B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3											Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.0	Se 2.6	Br 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 2.1	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

Table 9.1: Electronegativity values.

Figure 9.2 shows a bonding triangle where some binary substances (made up of just two elements) or pure elements are arranged according to their electronegativity values. On the vertical axis we have the electronegativity difference between the elements and on the horizontal axis the average electronegativity.

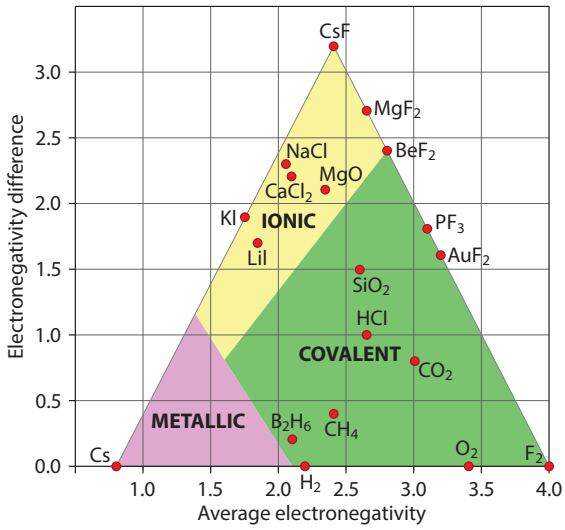

Figure 9.2: A van Arkel–Ketelaar triangle showing some compounds and elements. Electronegativity is sometimes given the symbol χ.

The triangle can be divided up into different regions (shown in different colours in Figure 9.2) by observing the properties of a known substance and making a judgement about the predominant type of bonding. For instance, a substance could be classified as having predominantly metallic bonding if it conducts electricity (and conductivity decreases as temperature increases), conducts heat and is malleable.

In general:

- small difference in electronegativity and low average electronegativity = predominantly metallic bonding
- small difference in electronegativity and high average electronegativity = predominantly covalent bonding
- large difference in electronegativity and mid-range average electronegativity = predominantly ionic bonding.

The vertices of the bonding triangle

The two vertices at the base of the bonding triangle are chosen from the elements with the highest and lowest electronegativity values. Caesium is the element with the lowest electronegativity in the periodic table (francium would be lower, but no one has ever seen a piece of francium!), and fluorine has an electronegativity of 4.0 on the Pauling scale, which is the highest value.

- Caesium has the lowest first ionisation energy of any element and only forms a 1+ ion, so it could be considered the most metallic element, but the assignment of bonding in caesium as 100% metallic is, of course, entirely arbitrary.
- The assignment of 100% covalent character to fluorine is also arbitrary, although we can be fairly sure that bonding in any homonuclear (two atoms

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the same) diatomic molecule (a molecule made up of two atoms) that is a gas at room temperature and pressure is going to be fairly close to 100% covalent.

- CsF is the compound with the biggest difference in electronegativity and, therefore, should be the most ionic compound.

The bonding in CsF is sometimes stated as being of 92% ionic character and 8% covalent character – this is based solely on the differences in electronegativity (see the previous discussion on the difficulty in using differences in electronegativity values).

Putting substances into a bonding triangle

Compounds can be placed in the triangle by using electronegativity values – for example, NaCl:

- Na electronegativity = 0.9
- Cl electronegativity = 3.2

difference in electronegativity = 3.2 − 0.9 = 2.3

$$\text{average electronegativity} = \frac{3.2 + 0.9}{2} = 2.05$$

This would put NaCl firmly in the ionic region of the triangle, and its properties (high melting point, conducts electricity when molten) fit in with this classification.

EXAM TIP

The equations:

difference in electronegativity ($\Delta\chi$) = $|\chi_a - \chi_b|$ where |A| represents the absolute value of A (no sign)

and

$$\text{average electronegativity} = \frac{(\chi_a + \chi_b)}{2}$$

are given in the IB data booklet.

Predicting the type of bonding in a substance

If you are given the formula of a substance you are unfamiliar with, you can use the bonding triangle to give you an idea of the type of bonding that it might have.

WORKED EXAMPLE 9.3

Use the bonding triangle to determine the predominant form of bonding in $SrBr_2$ and $AlBr_3$.

Answer

From Table 9.1:

Al electronegativity = 1.6

Sr electronegativity = 1.0

Br electronegativity = 3.0

$SrBr_2$

difference in electronegativity = 3.0 − 1.0 = 2.0

$$\text{average electronegativity} = \frac{3.0 + 1.0}{2} = 2.0$$

$SrBr_2$ falls into the ionic region of the bonding triangle in Figure 9.2, and its properties, such as a melting point of 643 °C, would support this.

$AlBr_3$

difference in electronegativity = 3.0 − 1.6 = 1.4

$$\text{average electronegativity} = \frac{3.0 + 1.6}{2} = 2.3$$

$AlBr_3$ falls in the covalent region of the triangle, and its properties support this prediction – it has a melting point of 98 °C and consists of Al_2Br_6 molecules in the solid state.

What is the predominant form of bonding?

Let's go back and look at some of the substances discussed previously, which were classified as being approximately 50% ionic and 50% covalent, according to electronegativity values, and see how we can predict the predominant type of bonding using a bonding triangle.

AuF_3: electronegativity difference: 1.6, average electronegativity: 3.2 – covalent region

LiI: electronegativity difference: 1.7, average electronegativity: 1.85 – ionic region

PF_5: electronegativity difference: 1.8, average electronegativity: 3.1 – covalent region

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The predictions made using the bonding triangle, therefore, fit in much better with observed properties than using electronegativity differences by themselves.

Some things to be careful of when using bonding triangles

Bonding triangles are a useful illustration of the continuum between different types of bonding, but the information from them must not be taken too literally. For instance, it would make very little sense to say that the bonding in chlorine is more metallic than the bonding in fluorine because chlorine is further along the axis towards metallic bonding.

Bonding triangles will not always get close to predicting the type of bonding. For instance, there are two different lead chlorides: $PbCl_2$ and $PbCl_4$. These would appear in the same place in the bonding triangle, but $PbCl_2$ has predominantly ionic bonding, whereas $PbCl_4$ is covalent molecular. Similarly, there are two allotropes of tin: one is metallic and one has a covalent network structure.

Bonding triangles do not predict the properties of transition metals or their compounds well. For example, because of its reasonably high electronegativity (2.4), elemental gold would be classified as a substance where the bonding is predominantly covalent. Silver iodide would also come out as covalent, but, although there is undoubtedly covalent character in its bonding, it would usually be regarded as an ionic compound from its properties.

A bonding triangle provides a useful starting point for making a hypothesis about bonding in a substance, but it is only that, and the predominant type of bonding can only really be deduced from a careful examination of the properties and structure of a substance.

EXAM TIP

A bonding triangle is shown in the IB data booklet. This also has a section labeled 'Polar covalent'. Remember that this refers to the type of bond rather than to the properties of the overall molecule. For example, BF_3 would be placed in the polar covalent region – each bond is polar, but due to the symmetry of the molecule it has no net dipole moment.

TEST YOUR UNDERSTANDING

1 Using the electronegativity values given in Table 9.1, determine the average electronegativity and difference in electronegativity for each substance and predict, using Figure 9.2, whether you would expect the bonding to be predominantly covalent, ionic or metallic.

a GeO_2 **b** $BeCl_2$

c GaAs **d** Mg_2Si

e CaS **f** KCl

9.2 Alloys

KEY POINT

Alloys are mixtures of two or more metals or of a metal with a non-metal.

Alloys are often made by dissolving one or more metals in another molten (liquid) metal. Although there is chemical bonding (metallic bonding) between the different atoms in an alloy, alloys are classified as mixtures rather than compounds because the metals can be mixed in various proportions – they have no fixed composition (see Chapter 1).

The majority of metals we come across in everyday life are alloys rather than pure metals. Steel, an alloy of iron and carbon, is used much more than pure iron. Other examples of alloys include brass (Cu and Zn), bronze (Cu and Sn) and pewter (Sn, Sb and Cu).

Alloys are metals and have the same characteristic properties as metals, for example, they conduct electricity and heat and are malleable.

KEY POINT

Alloys have enhanced properties compared to pure metals.

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Brass is mainly an alloy of copper and zinc. Brass, containing about 60% copper and 40% zinc, is almost twice as strong and hard as pure copper or pure zinc. Sometimes small amounts of other metals are also added to brass to further enhance its properties. For example, Naval Brass (typically about 40% zinc) also has a small amount of tin added and has excellent resistance to corrosion in saltwater conditions.

Figure 9.3: Naval Brass has excellent resistance to corrosion.

Steel is harder and stronger than pure iron. The most common form of steel is mild steel, and it is used extensively as a construction material; however, like iron, mild steel rusts. Stainless steel (Figure 9.4) is a form of steel containing typically about 10–20% chromium (and often other metals, especially nickel). The presence of chromium makes the steel very resistant to corrosion.

Figure 9.4: A DeLorean car has a stainless-steel body, so it does not need to be painted to prevent it from rusting.

Aluminium is a light (low density) metal, but it is not strong enough to be used in airplane manufacture until it is alloyed with copper (and smaller amounts of magnesium and manganese) to produce a range of alloys (e.g. Aluminium 2024), which have strengths several times higher than that of the pure metal but densities that are only slightly higher.

Bronze is an alloy based on copper. Traditionally bronze is regarded as an alloy of copper and tin, but the term is also used for other copper alloys that do not necessarily contain any tin. Bronze has, in the past, been used for coins because of its hardness, resistance to wear and resistance to corrosion.

Alloying a metal usually enhances its properties, but it can also produce undesirable properties – e.g. aluminium alloys are more susceptible to corrosion than the pure metal, and the electrical conductivity of copper is reduced by alloying with other metals.

Alloys have metallic bonding

Metallic bonding is the electrostatic attraction between positive ions in a lattice structure and delocalised electrons. The bonding is non-directional – all the metal ions in the lattice attract the delocalised electrons and vice versa. Because of the non-directional bonding, an atom of a different metal can be introduced into the metallic lattice without changing the bonding. The properties of metals/alloys are explained in terms of this bonding model in Chapter 8.

Link

The structure and bonding within a metallic structure mean that a variable number of one type of metal atom can be replaced with a different metal atom without affecting the bonding – the different metal will form a positive ion in the same way, and the outer-shell electrons will become part of the sea of delocalised electrons (see Chapter 8). It will not matter if the new atom forms a 1+, 2+ or 3+ ion. This is not generally possible with ionic compounds (imagine replacing an Na^+ ion with an Mg^{2+} ion in the NaCl lattice) or covalent compounds, where elements can only combine in certain fixed ratios.

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Alloys tend to be stronger and stiffer than pure metals

The reason that alloys are stronger than the pure metals can be explained in terms of the structure of metals. A different-sized atom will disrupt the lattice structure and prevent planes of metal atoms sliding over each other as easily (Figure 9.5).

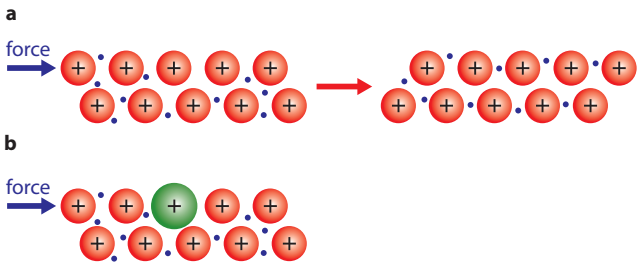

Figure 9.5: **a** Metals are malleable and ductile because the planes of atoms/ions can slide over each other without disrupting bonding. **b** The introduction of a different-sized atom makes it more difficult for the planes of atom/ions to slide over each other, and so, alloys tend to be stronger and stiffer than pure metals.

TEST YOUR UNDERSTANDING

2 Are the following statements TRUE or FALSE?

- **a** Alloys are generally regarded as mixtures and not compounds.
- **b** Alloys are usually softer than the original metals.
- **c** Steel is harder than pure iron.

INTERNATIONAL MINDEDNESS

Steel is by far the metal produced in the largest amount (much more than all other metals combined) and globally about 1.8 billion tonnes of steel are produced every year. This amount has approximately trebled over the last 50 years, but this has not meant equal fortunes for all steel-producing nations, and some countries, such as the UK, have seen a massive decline in the steel industry with closures of plants and

CONTINUED

extensive unemployment. World steel production is now dominated by China, which produces over 50% of all steel. Other major steel producers include India, Japan, the USA, Russia and South Korea.

9.3 Polymers

KEY POINT

Polymers are long-chain molecules, usually based on carbon, which are formed when smaller molecules (monomers) join together through covalent bonding.

The process when **monomers** join together to form polymers is called **polymerisation**. There are two main types of polymerisation: **addition polymerisation** and **condensation polymerisation**. Polymers may be natural or synthetic. Examples of **polymers** are polyethene (polythene), polypropene, nylon and cellulose. Addition polymerisation will be discussed here and condensation polymerisation in the Higher Level section.

EXAM TIP

Polymers, both natural and synthetic, can also be described as macromolecules.

Plastics

The synthetic polymers described here are more commonly known as 'plastics'. They are produced in vast quantities by the petrochemicals industry and come from organic chemicals derived from crude oil. They find extensive use in everyday life: for example, polyethene is used for making plastic bags, bowls and bottles; poly(chloroethene) is used for making insulation for electrical cables and window frames; and polypropene is used for making car bumpers and carpet fibres.

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Figure 9.6: Plastic is everywhere and forever (well, perhaps not forever, but for a long time – it does not biodegrade!).

There are many desirable properties of plastics that make them an essential part of everyday life, but there are also some negative properties, which means that these materials are regarded by many as a huge environmental problem.

Desirable properties of plastics

- Strength and durability: HDPE (high-density polyethene), PVC [poly(vinyl chloride) – poly(chloroethene)], nylon and Perspex™ are particularly strong, rigid and hardwearing.
- Flexibility: LDPE (low-density polyethene) and plasticised PVC are easily rolled into sheets or films and can be used, e.g., for wrapping food (cling film).
- Lack of reactivity: addition polymers contain unreactive, saturated C—C bonds and generally inert side groups. Polyethene containers are used for storage of corrosive substances, such as hydrofluoric acid, which reacts with glass.
- Thermal insulation: polypropene, polyethene and polystyrene have high specific heat capacities and extremely low thermal conductivity, making them excellent thermal insulators.
- Electrical insulation: PVC is a very good electrical insulator and is used as a covering for electrical wires.

KEY POINT

Plastics may consist of individual chains (with intermolecular forces between them) or have cross-links (covalent bonds) between chains.

Most of the plastics we are familiar with consist of individual chains with intermolecular forces between them. When there are just intermolecular forces between the chains, the plastic is called a **thermoplastic**, and can be repeatedly heated and cooled and remoulded into different shapes – the softening–hardening process is reversible. The intermolecular forces are partially overcome when thermoplastic polymers are heated (Figure 9.7) and form again when the polymer cools. Examples of thermoplastics are polyethene and PVC.

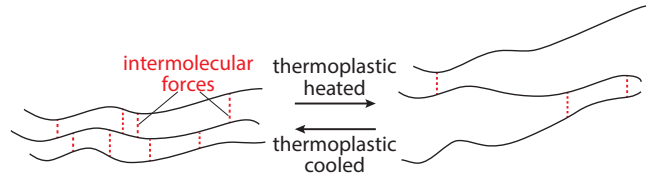

Figure 9.7: Intermolecular forces are broken when a thermoplastic is heated and form again when it is cooled.

Some polymers have covalent bonds (cross-links) between the chains. These tend to make the polymer stronger and more rigid. Natural rubber is a soft and sticky substance that is not very useful until it is processed. The formation of cross-links between chains (covalent bonds involving sulfur atoms) in the process of vulcanisation produces the much stronger and more rigid material that we are familiar with in car tyres. Polymers with extensive cross-linking cannot be remoulded (this would involve breaking covalent bonds) and are called **thermosets**. Examples of thermosets are Bakelite (Figure 9.8) and polyurethanes. Cross-linking can also occur in naturally occurring polymers and cross-linking between chains is a major contributor to the strength of collagen (an important structural protein in the body present in, e.g., bones, skin and tendons).

The structure of plastics

Plastics can be amorphous (completely random structure with chains arranged like in a plate of spaghetti) or semi-crystalline. Semi-crystalline polymers contain some regions where the chains are more ordered and packed more closely together, and some amorphous regions (Figure 9.9).

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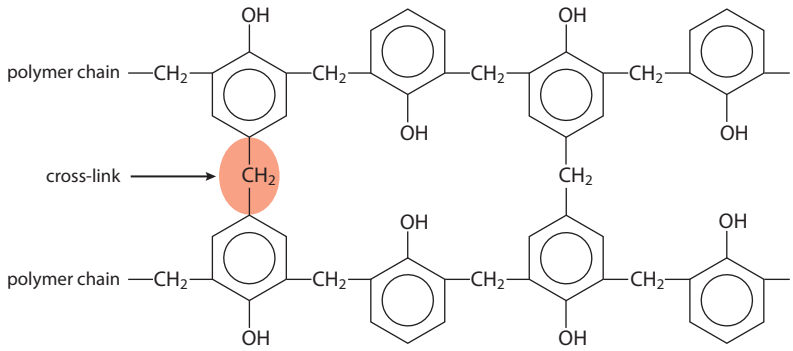

Figure 9.8: Part of the structure of a thermoset showing cross-links.

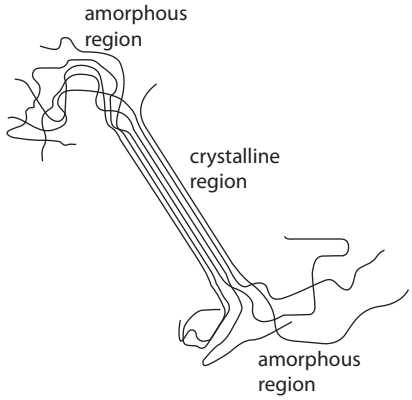

Figure 9.9: Amorphous and crystalline regions in the structure of a plastic.

The mechanical properties of polymers depend on many factors

The length of the polymer chain (relative molecular mass), the degree of branching and the arrangement of groups on the polymer chain are all important in determining how strong a plastic is. Polymers with longer chains and less branching tend to be stronger because there are stronger intermolecular forces (London forces) between chains.

As the relative molecular mass of the polymer increases, the material generally gets stronger. This corresponds to stronger London forces between chains as the relative molecular mass increases. Ultra-high molecular weight polyethene (UHMWPE) is a strong, low density and very tough polymer that is used as body armour.

KEY POINT

Less branching leads to a more crystalline polymer and stronger and stiffer material.

LDPE (low-density polyethene) contains a high proportion of branching (Figure 9.10a). Highly branched polymer chains are less able to pack closely together and, therefore, contact points between chains are reduced – this results in weaker London forces. Because the intermolecular forces between the chains are weaker, the polymer is more flexible and has lower tensile strength. Tensile strength refers to how well a material resists a stretching force without breaking.

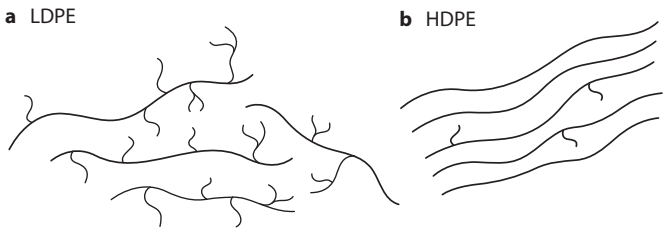

Figure 9.10: The proportion of branching in **a** LDPE is significantly higher than in **b** HDPE and contributes to their different properties and uses.

High-density polyethene (HDPE) has (virtually) no branching (Figure 9.10b). Lack of branching allows these polymer chains to pack together more tightly in a more regular arrangement – the structure is more crystalline and the density is higher. The more efficient packing of the chains increases the strength of London forces, and so, the chains are held together more tightly. This makes the polymer stiffer and increases its tensile strength. HDPE can also be used at a higher operating

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temperature. HDPE and LDPE have different uses because of their different mechanical properties. For example, LDPE is commonly used for plastic bags (more flexible), but HDPE is better for packing crates (more rigid).

Hydrogen bonding between chains increases strength

Kevlar and nylon are both very strong polymers. Nylon and Kevlar are both used for making ropes and Kevlar is used for body armour. Nylon and Kevlar both have comparatively strong intermolecular hydrogen bonds between groups (C═O to H—N) along the whole chain (Figure 9.11).

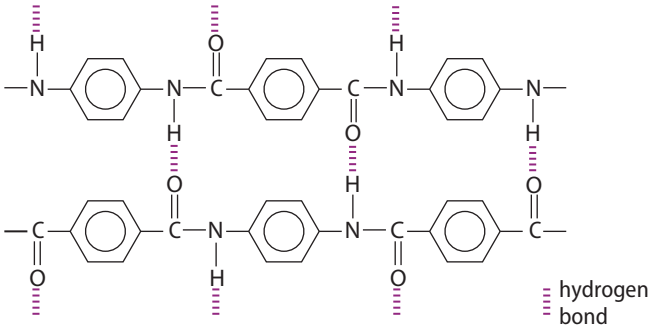

Figure 9.11: Hydrogen bonding in Kevlar.

Cellulose is an important structural polymer in plants – it is a major component of plant cell walls; cotton is almost completely cellulose and wood is about 50% cellulose. A major contribution to the strength of cellulose comes from hydrogen bonding both between polymer chains and within them.

Other properties of plastics

Plastics are usually good thermal insulators

To be a good conductor of heat, kinetic energy must be transmitted rapidly from one end of the substance, which is hotter (more kinetic energy), to other parts of the substance, which are colder (lower kinetic energy). Polymers consist of individual molecules with only weak forces between them, and so, kinetic energy is not transmitted easily from one molecule to the next. They also have no free electrons (as in metals) to carry the kinetic energy. Thermal conductivity is increased if polymers are more crystalline (packed closer together) and have cross-links between chains – both these allow for better transmission of kinetic energy. Some plastics (e.g. expanded polystyrene and extruded polystyrene) are very good insulators because of air trapped in the structure (Figure 9.12).

Figure 9.12: Expanded polystyrene is an excellent thermal insulator and is used in disposable coffee cups and packaging. It is not, however, Styrofoam™, which is extruded polystyrene and is used as building insulation.

Plastics are usually good electrical insulators

The polymer chains are uncharged, and electrons are held tightly in covalent bonds – there are no charged particles free to move, and so, plastics are good electrical insulators. PVC is used extensively as electrical insulation for wires.

Optical properties of polymers

Whether a polymer is transparent or not will depend on the structure. Amorphous polymers are generally transparent, whereas those that are semi-crystalline are often translucent/opaque. Differences in density between different regions in semi-crystalline polymers cause scattering of light. Perspex is used instead of glass in some applications (Figure 9.13).

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Figure 9.13: The use of Perspex screens became more common during the COVID-19 crisis.

Flexibility of polymers

The flexibility of polymers depends on how well the polymer chains slide over each other. Branching generally increases flexibility – the forces between the chains are reduced, whereas cross-linking decreases flexibility – covalent bonds between chains means that they are less able to move relative to each other. Some polymers (e.g. PVC) can be made more flexible by using plasticisers, which are molecules that insert themselves between the polymer chains, forcing them apart, and so reducing the strength of the intermolecular forces between them – this allows the chains to move more freely.

Plastics made by addition polymerisation are usually unreactive and resistant to attack by chemicals

Polyethene is non-polar and has strong non-polar, C—C, bonds throughout the structure, which means that it is not susceptible to attack by acids, etc. Polymers made by condensation polymerisation (see the Higher Level section) that contain polar ester or amide groups are more susceptible to hydrolysis (essentially breaking apart by water, usually in the presence of acids or alkalis). For example, proteins can be broken down into their constituent amino acids by heating with hydrochloric acid, but polyethene bottles can be used to store hydrochloric acid. The susceptibility to hydrolysis makes condensation polymers more likely to be **biodegradable**.

TEST YOUR UNDERSTANDING

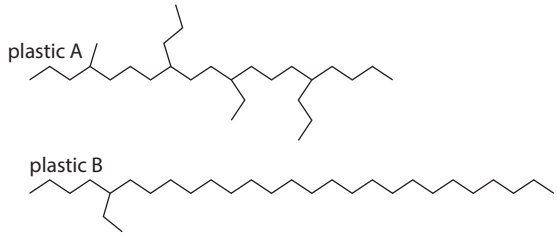
State and explain whether:

3 **a** branching increases or decreases the strength of plastics?

b plastics are thermal insulators or conductors?

c plastics are usually electrical insulators or conductors?

4 The basic structure of the polymer chains in two plastics A and B are shown below. Explain which will be denser and which will be more flexible.



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SCIENCE IN CONTEXT

Environmental impact of the use of plastics

Plastics are extremely useful materials, but there are many environmental concerns associated with their use. The main concern arises from the fact that plastics derived from alkenes, such as polyethene, polypropene and poly(chloroethene), are non-biodegradable, which means that they cannot be broken down by microorganisms when, for instance, they are buried in soil. This means that they can persist in the environment for hundreds of years. They are non-biodegradable because of the strong carbon–carbon covalent bonds throughout the polymer chain.

There are, however, many factors that must be considered when discussing the environmental impact of the use of plastics. It is far from a trivial debate, and we cannot simply say that plastics are bad for the environment. Some relevant points are summarised here:

- Plastics are made from crude oil, which is a finite resource.
- Plastics persist for a long time in the environment.
- Plastics are usually non-biodegradable, so they have to be disposed of by burying in landfill sites or by incineration. Landfill sites can be unsightly, smelly and noisy and take up large areas of land. Incineration is more expensive, contributes to the greenhouse effect by generating CO_2, and can produce toxic gases from halogenated polymers, such as PVC.
- Many plastic containers need less energy to make than an equivalent one in glass or aluminium.
- The use of plastics in making insulation materials reduces energy losses. The energy liberated in the incineration of plastics can be useful, for heating buildings, for example.
- Plastic containers are light and less energy is needed – and, therefore, less CO_2 is generated – to transport them – for example, fizzy drinks in plastic bottles rather than in glass bottles.
- Plastic packaging can reduce food wastage – if less food is wasted, then less energy needs to be used to produce more.
- Plastic pipes for water, gas, sewage and communication cables do not rust and, therefore, do not have to be replaced as often – this reduces energy consumption.
- Plastic debris in the environment can cause harm to birds and marine animals. There is increasing evidence of large amounts of microplastics (pieces of plastic less than 5 mm) in the environment. They have been found in food, drinking water, animals and birds and in human excrement.

There are many reasons that we use plastics and will continue to use them, but the environmental impact has to be closely monitored and controlled. Many governments around world have introduced legislation to help; for instance, microbeads, which are tiny pieces of plastic that are added to cosmetics as an exfoliant have been banned in several countries (Figure 9.14). Natural alternatives that are used instead include ground nut shells and coffee grounds.

Figure 9.14: Microbeads are tiny pieces of plastic that are added to cosmetics in, for example, facial or body scrubs. When these products are washed off, the microbeads go into the environment – whoever thought that this was a good idea?

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Addition polymerisation

Addition polymerisation occurs when alkenes (organic compounds containing a C=C group) join together. The structure of ethene, the simplest alkene, is shown in Figure 9.15a. A more general structure of an alkene is shown in Figure 9.15b. Here, the R groups represent different groups that could be joined to C. The R groups could be, for example, H atoms, CH_3 groups or Cl atoms. The R groups could be all the same or different.

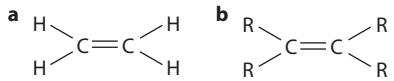


Figure 9.15: The structure of **a** ethene and **b** a more general alkene. The key feature is that they contain C=C.

The general equation for addition polymerisation is shown in Figure 9.16.

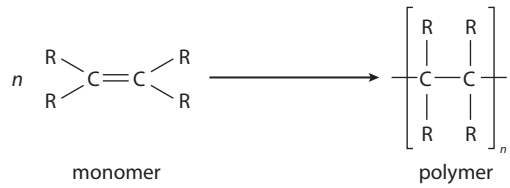


Figure 9.16: A general addition polymerisation reaction.

KEY POINT

In addition polymerisation, a large number of monomer molecules, which are alkenes, are joined together to form a polymer chain.

During the reaction, one component of the C=C double bond breaks, leaving a single bond between the carbon atoms. The other two electrons are used to form bonds to other monomers. It is important to realise that it is only the C=C group that reacts when polymerisation occurs – all the other groups attached to the C=C unit are unaffected.

The structure of the polymer can be represented by the **repeating unit** of the polymer (the term 'repeat unit' is also used). This unit is the part shown in brackets in Figure 9.16, which is repeated to produce the polymer chain. This is shown in Figure 9.17.

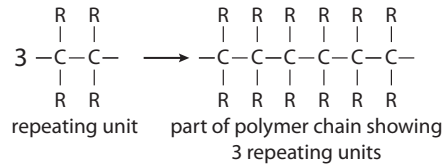


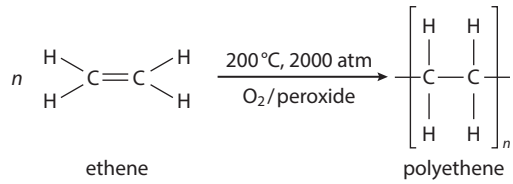
Figure 9.17: The repeating unit present in the structure of a polymer. The number of repeating units present in a polymer chain will usually be in the thousands. The repeating unit is always shown as a two-carbon unit because it comes from a C=C group.

EXAM TIP

When asked to draw the repeating unit, this is just the part inside the brackets (including the continuation bonds) – you should not include the brackets or the '*n*' – that represents the polymer.

Polyethene

In the production of polyethene, ethene molecules react together at high temperature and high pressure in the presence of a small amount of oxygen or an organic peroxide:



In this polymerisation reaction, ethene is the monomer and polyethene is the polymer. This is an example of addition polymerisation, because monomer molecules are simply added to each other without anything else being produced.

Addition polymers are named according to the monomer from which they were made – the name of the polymer just comes from adding *poly* (meaning many) to the name of the monomer. Brackets are used when the name of the monomer is more complex and confusion could arise, e.g. poly(chloroethene). Polyethene is more commonly called polythene.

A section of the polymer chain of polyethene is shown in Figure 9.18.

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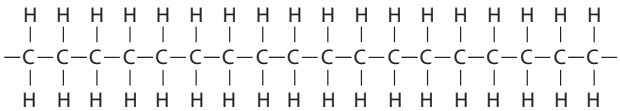


Figure 9.18: A section of the polyethene polymer chain.

Polypropene

It is important to remember that it is only the C=C group that reacts when polymerisation occurs – all the other groups attached to the C=C unit are unaffected. This can be seen if we look at the polymerisation of propene (Figure 9.19). The —CH_3 (methyl group) attached to the C=C unit does not become part of the main polymer chain – it is just a side group on the chain.

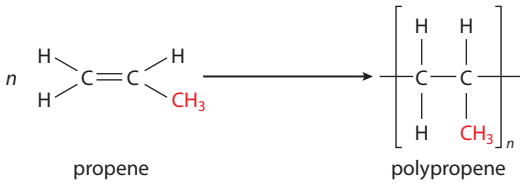


Figure 9.19: Polymerisation of propene.

Working out the repeating unit from the monomer and vice versa

The repeating unit of a polymer is the basic unit from which the whole polymer chain can be made up. In each of the equations used so far, this has been shown in square brackets. The repeating unit can be worked out from a monomer, as shown in Figure 9.20.

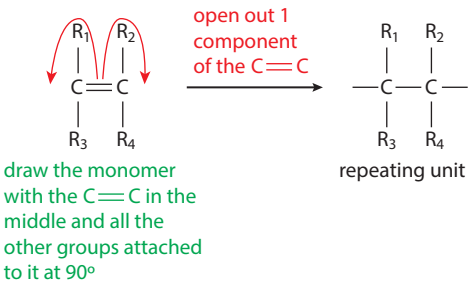


Figure 9.20: How to work out the repeating unit from the monomer.

The repeating unit can be identified from the polymer chain by taking any two adjacent carbon atoms in the main polymer chain (Figure 9.21). The monomer of a polymer can be derived by placing a double bond between the two carbon atoms of the repeating unit.

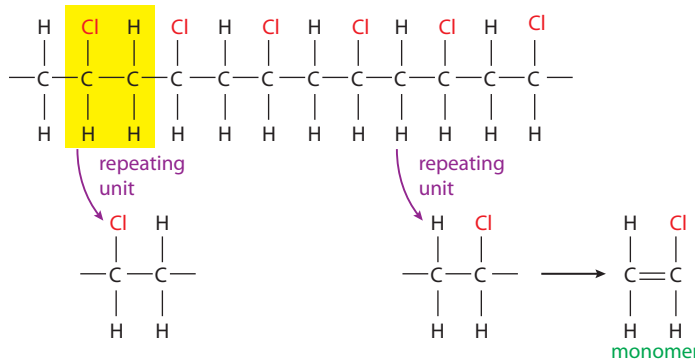
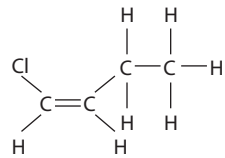


Figure 9.21: Working out the repeating unit and monomer from the polymer chain. The two repeating units shown are identical – one is just flipped around relative to the other.

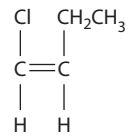
WORKED EXAMPLE 9.1

Draw the repeating unit of the polymer formed from the monomer shown.



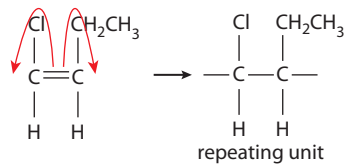
Answer

First of all, re-draw the monomer with the C=C in the middle and the bonds around it at 90°:



The —CH_2CH_3 group has also been shown in condensed form to make everything a bit easier to draw.

Now open out the C=C unit to produce one continuation bond on each side:



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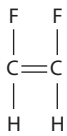
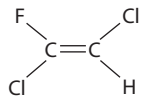
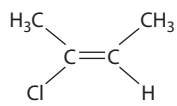
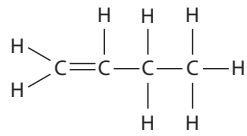
TEST YOUR UNDERSTANDING

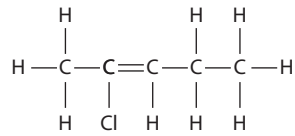
5 Draw the repeating units for the polymers formed from these alkenes:

a 

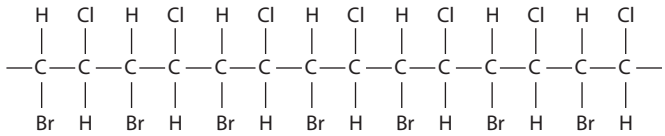
b 

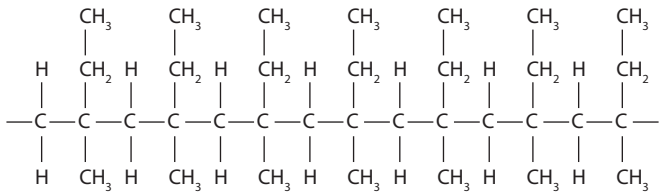
c 

d 

e 

6 Draw the monomers used to make the following polymers:

a 

b 

9.4 Condensation polymerisation

In addition polymerisation, monomers that contain C=C join together to form a polymer chain and no other products are formed. Condensation polymerisation also involves monomers joining together to form a polymer chain, but the monomers do not contain C=C (or, if they do, it is not this group that reacts) and when two monomers join together, a small molecule, such as water, is also formed.

Esters

Esters are a class of organic compound – they are covered in more detail in Chapter 11. They are formed in a condensation (addition–elimination) reaction from a carboxylic acid and an alcohol (Figure 9.22). When the OH of the carboxyl group in the carboxylic acid reacts with the H of the hydroxyl group of an alcohol, the two molecules are joined together via an ester group and a water molecule is also formed. A condensation reaction is one in which two molecules join together with the elimination of a small molecule (often water).

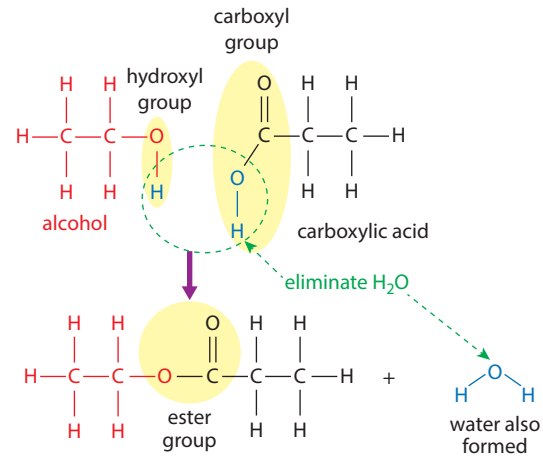


Figure 9.22: Formation of an ester. The reaction usually requires heating in the presence of a catalyst, such as concentrated sulfuric acid.

This reaction will not produce a polymer because there is only one reactive (functional) group on each molecule. If, however, we react a dicarboxylic acid (two COOH groups) with a dihydric alcohol (an alcohol with two OH groups), an ester group can be formed on both sides of both monomers and the chain can keep going. It is the presence of two functional groups on each monomer that allows the production of a polymer chain.

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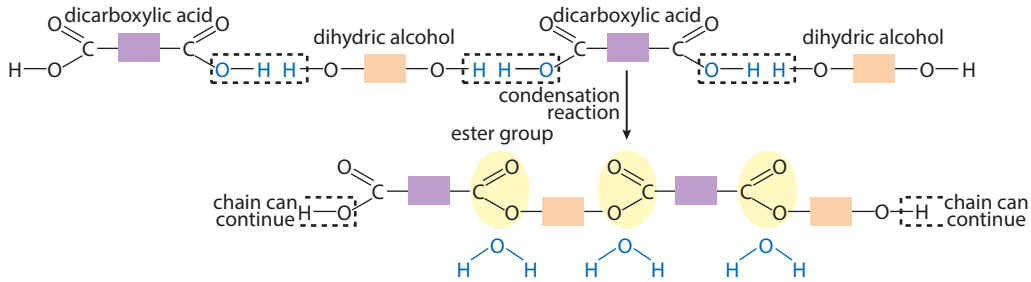

Figure 9.23: Dicarboxylic acid molecules and dihydric alcohol molecules combine together and begin a polymer chain.

A polyester is a type of polymer formed by a condensation polymerisation reaction

The reaction scheme in Figure 9.23 shows a representation of the reaction of two dicarboxylic acid molecules with two dihydric alcohol molecules.

The functional group joining the monomers together is the ester functional group, so this is the beginning of a **polyester** chain. The chain can continue on both sides, because the presence of *two* functional groups in the original monomers means that there will either be a 'free' hydroxyl (—OH) group or a 'free' carboxyl (—COOH) group on each end of the chain that can react further. It can be seen from this reaction scheme that, when four monomer molecules join together, three water molecules are produced. In general, the total number of water molecules is always one fewer than the total number of monomer molecules that join together.

The formation of a polyester from ethane-1,2-diol and benzene-1,4-dicarboxylic acid is shown in Figure 9.24.

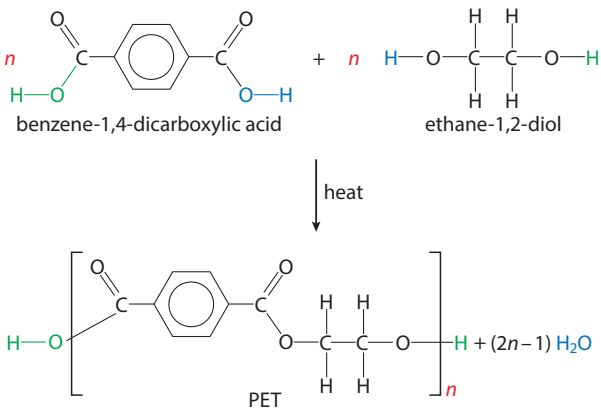

Figure 9.24: Condensation polymerisation.

This polymer is commonly called polyethylene terephthalate, or PET (or PETE), and is used in the manufacture of plastic bottles for drinks and fibres for clothing. Increasingly, PET bottles are being recycled to reduce waste.

The total number of monomers is $n + n = 2n$, and the number of water molecules formed is $2n-1$.

> **EXAM TIP**
>
> If a structure is shown without the terminal H and OH groups (in green in Figure 9.24) the total number of water molecules is $2n$ and not $2n - 1$.

The polymer chain as a whole can be represented by the unit shown in brackets in Figure 9.24 – this is the repeating unit of the polymer. The whole polymer chain could be built up by just joining these units together – a longer section of the chain is shown in Figure 9.25.

Polyamides

Just as a dicarboxylic acid reacts with a dihydric alcohol to form a polyester, a dicarboxylic acid reacts with a diamine (two NH_2 groups) to form a **polyamide**. This time, the monomers are linked together by an amide (amido) group; hence, it is a poly*amide* rather than a poly*ester*. This is also a condensation polymerisation because a water molecule is eliminated every time two monomers are joined. A general scheme for the polymerisation reaction, showing the formation of the repeating unit, is shown in Figure 9.26.

Nylon is a polyamide

Figure 9.27 shows an example of a reaction that makes a polyamide, nylon 6,6.

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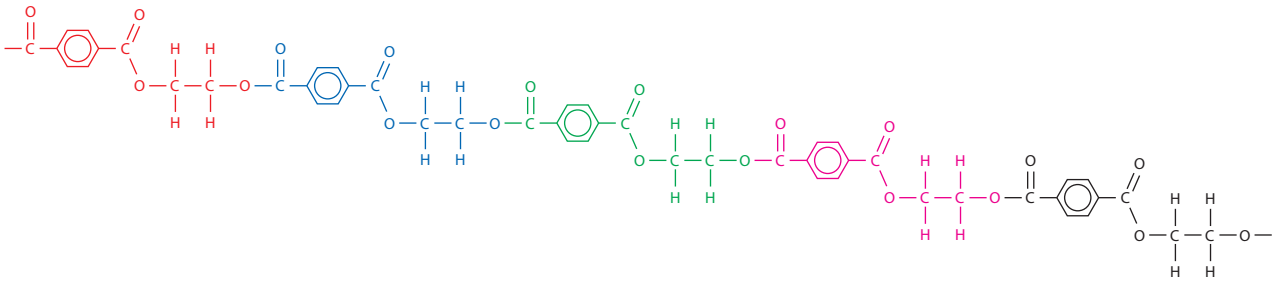

Figure 9.25: Joining the repeating unit to make part of the polymer chain in PET.

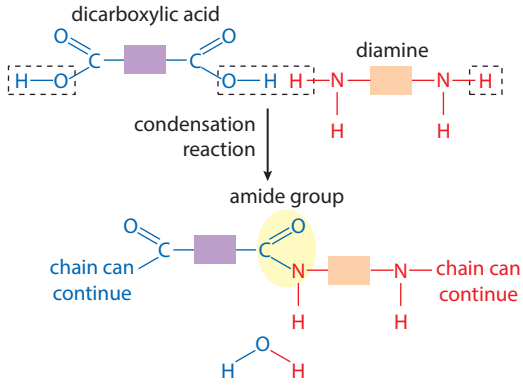

Figure 9.26: Formation of a polyamide.

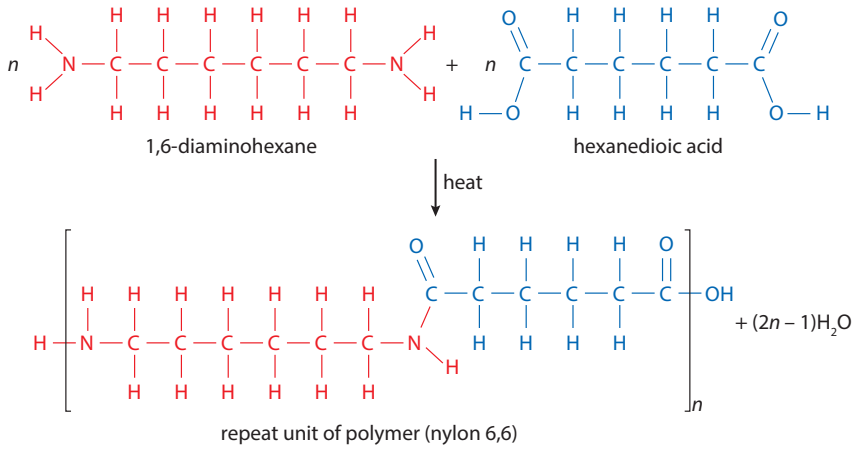

Figure 9.27: Making nylon 6,6 – a polyamide. 1,6-diaminohexane can also be called hexane-1,6-diamine.

The polyamide formed from 1,6-diaminohexane and hexanedioic acid is commonly called 'nylon 6,6' or 'nylon 66'. The '6,6' refers to the number of carbon atoms in each monomer. This polymer is used in the manufacture of car parts, fibres for clothing and carpets, and some types of rope.

How to work out the repeating units of polyesters and polyamides from monomer structures

Figure 9.28 shows how to work out the repeating unit for a polyester from the monomers. The only difference for a polyamide is that only one of the H atoms is removed from the NH_2 group.

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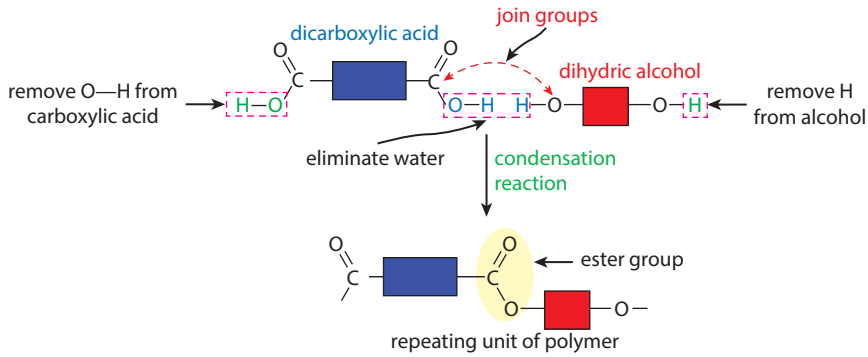
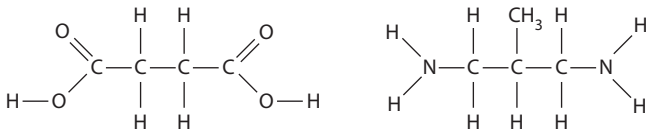


Figure 9.28: How to work out the repeating unit for a condensation polymer.

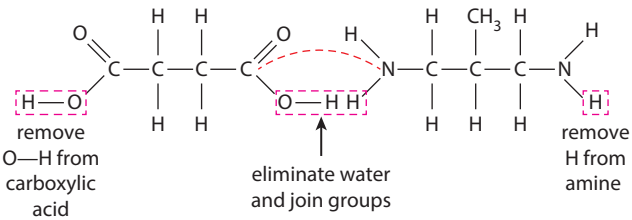
WORKED EXAMPLE 9.2

Deduce the structure of the repeating unit of the polymer formed when the two monomers shown react together to form a polyamide.

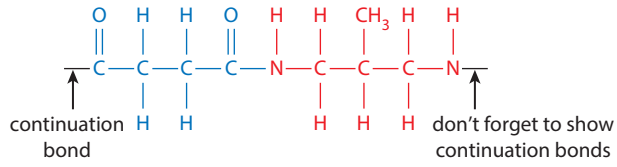


Answer

Put the two monomers together so that the OH of COOH is next to an H of NH_2:



Water is removed, OH from COOH and H from NH_2, and the C of C═O is joined to N to produce the repeating unit:



How to work out the repeating unit when there is only one monomer

A polyamide or polyester can also be formed by one monomer that has two different functional groups; Figure 9.29 shows an example.

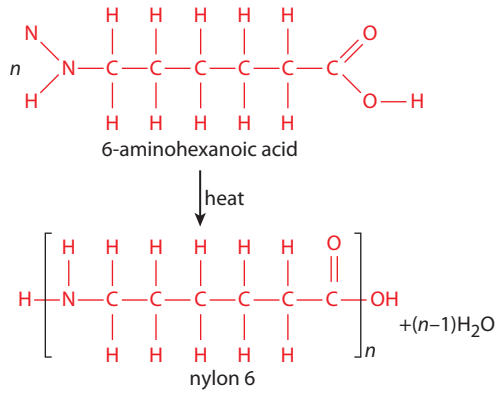


Figure 9.29: A polymerisation equation for a reaction when there is only one monomer. This is not actually how nylon 6 is produced commercially.

To work out the structure of the repeating unit, just remove H from the NH_2 (OH for polyester) group and OH from the COOH group. The repeating unit is shown in brackets in Figure 9.29.

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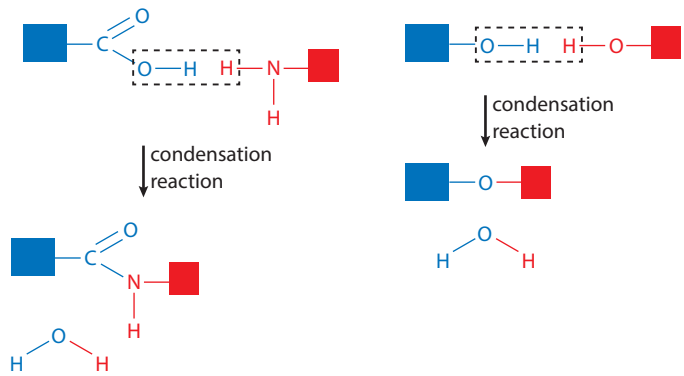

Figure 9.30: Some condensation reactions by which biological macromolecules can be formed – the coloured boxes represent the rest of the molecule.

Biological macromolecules form by condensation reactions

Biological macromolecules including proteins, DNA, starch and cellulose are all formed when monomers join in condensation reactions (Figure 9.30).

Proteins (polymer) are formed from amino acids (monomers), DNA (polymer) from nucleotides (monomers), and starch and cellulose (polymers) from sugar molecules (monomers). A molecule of water is formed each time two monomers join together.

The condensation reaction when two amino acids join to form a dipeptide is shown in Figure 9.31.

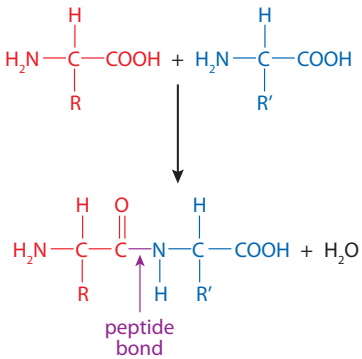

Figure 9.31: Condensation reaction between two amino acids to form a dipeptide and water. R and R′ represent H, CH_3 or other organic groups (the side chain of the amino acid). The word peptide, or dipeptide, tripeptide… polypeptide, is usually used to describe short chains of amino acids.

The dipeptide has a free NH_2 group and a free COOH group, so further condensation reactions can occur to form a polymer chain. A protein could, therefore, be described as a polyamide. The amide linkage in peptides and proteins is usually called a peptide bond.

Biological macromolecules are broken down in hydrolysis reactions

A **hydrolysis** reaction is essentially the reverse of condensation – it involves breaking a covalent bond by the addition of water (Figure 9.32).

The linking bond is broken and the elements of water (H one side and OH the other) are added where the linkage was. Hydrolysis reactions usually occur in the presence of an acid or an alkali, or with enzymes.

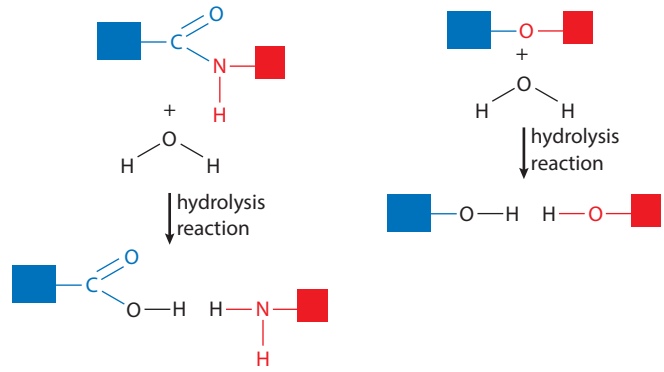

Figure 9.32: Some hydrolysis reactions.

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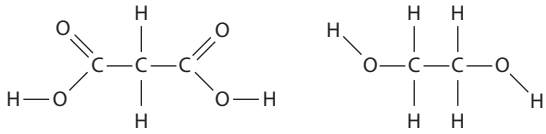
TEST YOUR UNDERSTANDING

7 Draw the repeating unit for the polymer formed when each of the following react, and state whether a polyamide or polyester is formed:

a



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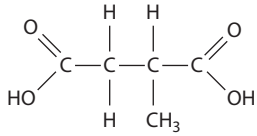
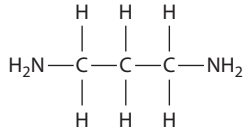
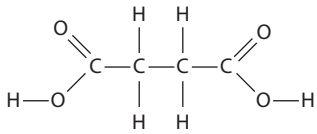
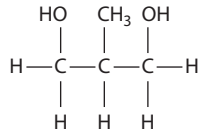




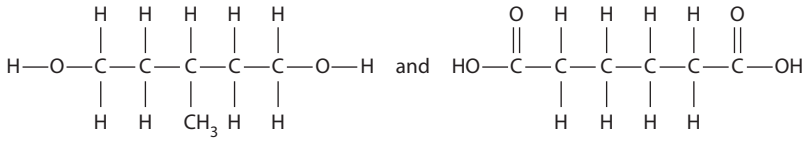
c



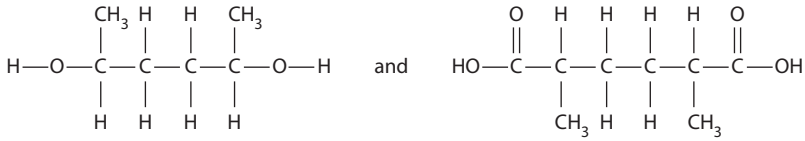


8 Draw two repeating units of the polymers formed when the following pairs of molecules react:

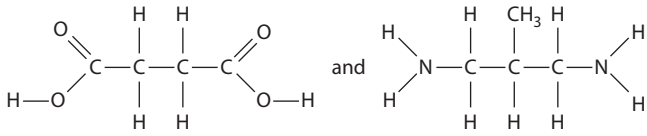
a



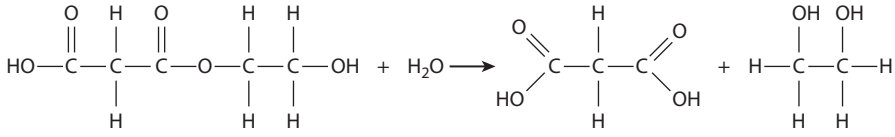
b



9 Write an equation for the formation of a polymer from these monomers:



10 Would the following reaction be described as condensation or hydrolysis?



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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain that there is a continuum between ionic, covalent and metallic bonding	9.1			
use electronegativity values to place substances in a bonding triangle	9.1			
relate the position of a compound in the bonding triangle to its properties.	9.1			
explain the term *alloy*	9.2			
explain the properties of alloys in terms of metallic bonding	9.2			
explain the term *polymer*	9.3			
explain the properties of polymers (plastics) in terms of structure and bonding	9.3			
explain how addition polymers are formed	9.3			
deduce the structure of the repeating unit and equations for the formation of addition polymers	9.3			
explain how condensation polymers are formed	9.3			
deduce the structure of the repeating unit of a condensation polymer	9.3			
explain that biological macromolecules form by condensation polymerisation and break down by hydrolysis	9.3			

REFLECTION

Think about the topics covered in this chapter.

- Which parts are you most confident with?
- Do you need more practice working out the structures of repeating units?
- How confident are you with linking this topic to other topics?
- Would further study on another topic (e.g. Organic Chemistry in Chapter 11) help with the understanding of this topic?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Unit 3

Classification of matter

INTRODUCTION

Chemistry is often divided up into four main branches: inorganic, organic, physical and theoretical chemistry. This unit is about inorganic and organic chemistry. Organic chemistry is the study of carbon compounds. Inorganic chemistry is the study of the reactions, structure and bonding of all other chemical substances. The variation in the structures and properties of inorganic compounds may sometimes seem vast, but the great unifying principle is the periodic table, and by using some of the tools we have already developed, we can understand the trends in the table and rationalise and predict the properties of elements and compounds.

Organic chemistry is an enormous field, and in this unit we will just look at the fundamentals of the subject, concentrating on the structures of organic molecules, and then we will return to it to study some reactions in depth in Unit 6. In Chapter 11 we will only look at relatively simple organic molecules but hopefully you will begin to get some idea of just how complex this branch of chemistry can be. If you are still not convinced, try an internet search for `maitotoxin'.

Some chemists would argue that there are actually five main branches of chemistry, with the fifth being analytical chemistry. In the second part of Chapter 11, we will look at how the structures of organic molecules can be determined. It is one thing carrying out an organic reaction, but how do you know whether you have made what you had hoped to make? Or, faced with a colourless liquid, or some white crystals, how do you work out the structure? Again, we will concentrate on some simple examples, but someone worked out the structure of maitotoxin!

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Chapter 10

The periodic table

LEARNING OBJECTIVES

In this chapter you will:

- describe the structure of the periodic table
- deduce the electron configuration of an element from its position in the periodic table
- explain the trends in the properties of elements down a group and across a period
- describe and explain some reactions of Group 1 and Group 17 elements
- describe the trends in the acid–base behaviour of oxides
- write equations for the reactions with water of the oxides of Group 1 and 2 metals, carbon and sulfur
- explain acid rain and ocean acidification
- deduce oxidation states for elements in molecules and ions and use them to name compounds/ions

- explain the exceptions to the increase in first ionisation energy across a period
- describe and explain the characteristic properties of transition elements
- explain why transition element complexes are coloured

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GUIDING QUESTIONS

- How are the elements arranged in the periodic table?
- What is the connection between an element's position in the periodic table and its properties?
- What are the trends in the periodic table?

Introduction

The periodic table is the grand unifying principle in chemistry, and it could be argued that it *is* chemistry. The periodic table in its current format was first proposed by Mendeleev in 1869 and has been constantly updated since then, as new elements have been discovered. It contains all the elements that are currently known and is arranged in periods and groups, according to the properties of these elements. The position of an element in the periodic table provides instant information to chemists about its characteristics, reactions and compounds.

10.1 The periodic table

The elements in the periodic table are arranged in order of atomic number, starting with hydrogen, which has atomic number 1. The **groups** are the vertical columns in the periodic table, and the **periods** are the horizontal rows (Figure 10.1).

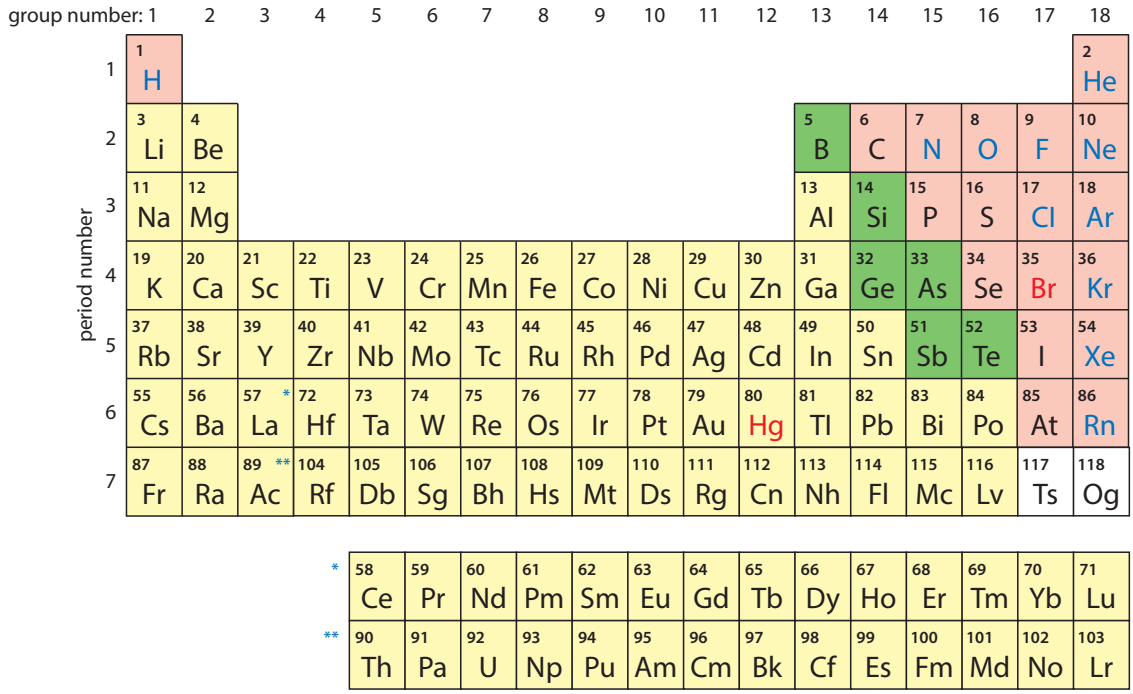

Figure 10.1: The periodic table showing the distribution of metals, metalloids and non-metals. Nothing much is known about the later elements – they are all produced artificially and only a few atoms have been produced that exist for fractions of a second, but their properties can be predicted from the properties of other elements around them. It is uncertain whether Ts and Og will be metals or not, and so, they have been left without a colour.

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KEY POINT

Groups are the vertical columns in the periodic table.

Periods are the horizontal rows in the periodic table.

Most of the elements in the periodic table are metals – these are shown in yellow in Figure 10.1. The elements shown in pink are non-metals. There are some elements, such as Si, Ge (Figure 10.2) and Sb, that have some of the properties of both metals and non-metals or properties that are intermediate between those of a metal and non-metal – these are called **metalloids** and are shaded green. The symbols of the elements that are solid at room temperature and pressure are shown in black in Figure 10.1, whereas those that are gases are in blue and liquids are in red. Og (element 118) will probably be a solid, but this is not really certain.

Figure 10.2: Germanium is a metalloid. The metalloids have some of the properties of metals – germanium is shiny, conducts electricity (although not as well as metals, and conductivity increases as temperature increases) and has a thermal conductivity between that of iron and lead, but it is brittle rather than being malleable/ductile.

NATURE OF SCIENCE

There is some disagreement among chemists about just which elements should be classified as metalloids – polonium and astatine are sometimes included in the list. Why do scientists not always agree? Is it because they have different data available to them, or is it all a matter of interpretation of the data?

INTERNATIONAL MINDEDNESS

There are several elements in the periodic table that are named after places. Sometimes the connection is obvious, for example, francium, germanium and californium, but others are more hidden, for example, gallium (from the Latin name for France), lutetium (the Roman name for Paris), nihonium (from the Japanese word for Japan) and rhenium (from the river Rhein). Four elements are named after the small village of Ytterby in Sweden – yttrium, terbium, erbium and ytterbium – and the names of some other elements that were extracted from minerals found in the quarry in Ytterby also honour this location – scandium (from Scandinavia), holmium (from Stockholm) and thulium (from an ancient name for Scandinavia). Sometimes elements are named after the institutions where they were discovered, for example, berkelium, dubnium and livermorium. Elements are not, of course, always named after places on Earth, and there are many that are names after celestial bodies, e.g. mercury, uranium, selenium (from the Greek word for the moon) and plutonium.

What about the other way round, places named after elements? Probably the most famous example at the moment is Silicon Valley, but others include Argentina (from the Latin word for silver) and there is even Lead, South Dakota, Radium, Kansas, Silver City, New Mexico and Gold Coast Australia, to name but a few.

Some of the groups in the periodic table are given names as well as numbers. Commonly used names are shown in Figure 10.3.

In the periodic table shown in Figure 10.1, it can be seen that the atomic numbers jump from 57 at La (lanthanum) to 72 at Hf (hafnium). This is because, to save space, in most periodic tables, these elements, called the lanthanoid (or lanthanide) elements, are shown below the main part of the table. The actinoid (or actinide) elements, which begin with Ac (actinium), are also usually shown below the main part of the table. Figure 10.3 shows a *long form* of the periodic table, including these elements in their proper places.

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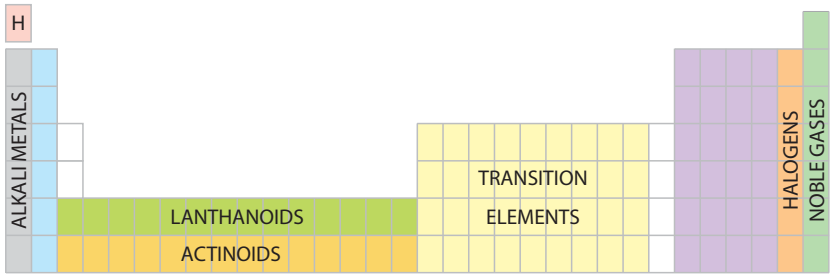

Figure 10.3: The long form of the periodic table, with the names of some of the groups. Hydrogen, though sometimes placed in Group 1, does not count as an alkali metal. The terms 'transition metals' and 'transition elements' are usually used interchangeably. The lanthanoids and actinoids are also often called 'lanthanides' and 'actinides'.

THEORY OF KNOWLEDGE

Mendeleev puzzled over the arrangement of elements in the periodic table, until he had a dream in which he claims to have seen the arrangement. Kekulé also came up with the ring structure of benzene after a dream. Does it matter how a scientist comes up with a hypothesis? What is the difference between a scientific and a non-scientific hypothesis? Is it the origins of the hypothesis, or the fact that it can be tested experimentally (is falsifiable) that makes it scientific?

SCIENCE IN CONTEXT

The rare earth elements are a set of 17 elements, comprising the lanthanoids (La – Lu), Sc and Y. They used to be regarded as curiosities, having some interesting chemistry, but you were unlikely to have even heard of them if you had not done a chemistry degree. However, they have been much more in the news in recent years because of their uses in technology and worries about future supplies. The biggest use of rare earth metals is as catalysts, but up to 16 of the 17 metals are used in mobile phones, and neodymium has probably become the most famous of the rare earth metals because of its use in making powerful magnets. Neodymium magnets, which are the strongest permanent magnets available, are alloys of Nd, Fe and B but often with smaller amounts of other elements, including dysprosium and praseodymium, added. They have a huge number of uses in everyday life, from hard disk drives, speakers and headphones to jewellery clasps, but have also been at the forefront of the fight to reduce global carbon dioxide emissions, through being key parts of most wind turbines (Figure 10.4) and motors in many electric vehicles.

Figure 10.4: Neodymium magnets are a key part of many wind turbines.

Despite their name, the rare earths are not actually that rare and, for example, neodymium is more abundant than lead, cobalt and lithium in the Earth's crust, and even thulium, the least abundant of the rare earths, is still more than 100 times more abundant than gold. Deposits are found throughout the world, with the largest reserves in China, Brazil and Vietnam; however, the rare

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CONTINUED

earths are usually found in low concentrations and separations are difficult. There are also severe environmental concerns about the extraction and refining processes. The world supply is dominated and essentially controlled by China, but, amidst worries in many parts of the world about how future supplies can be maintained, other sources are being developed.

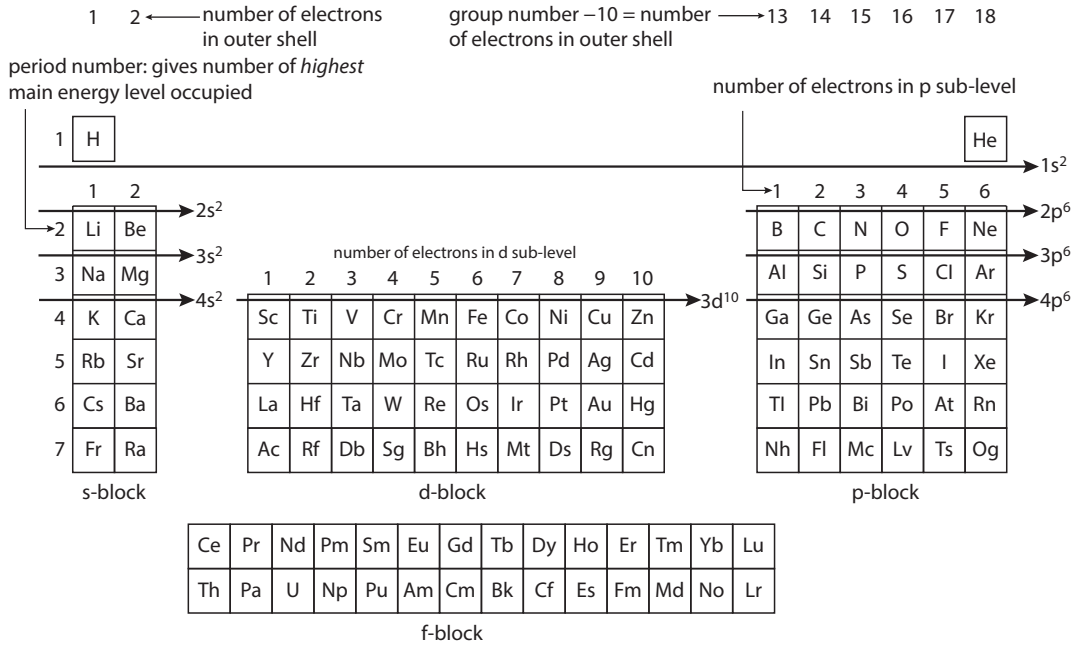

Figure 10.5: Division of the periodic table into blocks. Classification of elements as 'f-block elements' is not straightforward and very often the lanthanoids and actinoids are regarded as f-block elements despite the fact that not all of them have an f subshell as the highest occupied subshell. This is discussed further in the main text and the Theory of Knowledge box.

The periodic table and electron configurations

Link

How to work out electron configurations from the periodic table has already been considered in Chapter 3.

Electrons in the outer shell (the highest main energy level) of an atom are sometimes called valence electrons. The group number of an element is related to the number of valence electrons. All the elements in Group 1 have one valence electron (one electron in their outer shell); all the elements in Group 2 have two valence electrons. For elements in Groups 13–18, the number of valence electrons is given by (group number – 10), so the elements in Group 13 have 13 – 10 = 3 valence electrons and so on.

The period number indicates the number of shells (main energy levels) in the atom, or which shell is the outer shell (highest main energy level). For example, all elements in Period 2 have electrons in the second shell (main energy level) but no electrons in any higher shells.

The periodic table is divided into blocks according to the highest energy subshell (sub-level) occupied by electrons. So, in the s block, all the elements have atoms in which the outer-shell electron configuration is ns^1 or ns^2 (where n is the shell number – principal quantum number), and in the p block, it is the p subshell that is being filled (Figure 10.5).

The noble gases (Group 18) have either two (He) or eight electrons (Ne – Og) in their outer shell. Helium belongs in the s block because its highest energy occupied subshell is 1s, but it is usually put in Group 18 with the other noble gases.

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Although lanthanum is usually regarded as a lanthanoid, its condensed electron configuration is [Xe] $6s^2$ $5d^1$, meaning that it has no f electrons, and its highest occupied subshell is a d subshell. Therefore, lanthanum is better classified as a d-block element rather than an f-block element. It is a similar situation with actinium. There is also a case for classifying lutetium ($4f^{14}$ $5d^1$), thorium ($5f^0$ $6d^2$) and lawrencium ($5f^{14}$ $6d^1$) as d block rather than f block because their highest energy electron is in a d sub-level. These are, however, usually classified as f-block elements.

We can use the block structure to work out electron configurations. Consider sulfur – this element is in Period 3 and Group 16, and so, has three shells (the highest occupied shell is the third) and 16 – 10 = 6 electrons in its outer shell. Its highest energy occupied subshell is a p subshell, therefore, it is in the p block – its condensed electron configuration is [Ne] $3s^2$ $3p^4$ (six valence electrons). The general outer-shell electron configurations for the s- and p-block elements are shown in Table 10.1.

Why are elements put in the same group?

The reactions of an element are determined by the number of electrons in the outer shell (highest main energy level) of their atoms. Because elements in the same group in the periodic table have the same number of electrons in their outer shell, they react in basically the same way – similar chemical properties.

Elements in the same group will form compounds with the same formula, for example, all the Group 1 elements form a chloride with the formula MCl (LiCl, NaCl, etc.), and an oxide with the formula M_2O (Na_2O etc), whereas, for Group 2, the chlorides have the formula MCl_2 and the oxides are MO.

THEORY OF KNOWLEDGE

Is there one definitive periodic table, or is it all a matter of opinion? The positions of elements such as hydrogen, helium, lanthanum and actinium cause disagreement between scientists and are shown differently in different tables. IUPAC has been working on a research project to decide which elements should go in Group 3 – should it be Sc, Y, Lu, and Lr or Sc, Y, La and Ac? If it is Lu and Lr, will that mean that La and Ac are classified as f block elements?

KEY POINT

Elements are put in the same group because they have the same number of outer-shell electrons and, therefore, react in the same way.

1	2	⇦ group number ⇨	13	14	15	16	17	18
ns^1	ns^2		ns^2 np^1	ns^2 np^2	ns^2 np^3	ns^2 np^4	ns^2 np^5	ns^2 np^6
s-block			p-block					

Table 10.1: The outer-shell electron configurations of the s- and p-block elements; '*n*' is the main energy level number or shell number.

TEST YOUR UNDERSTANDING

1 Give the names of the following elements:

- **a** the element in Period 3 and Group 14
- **b** the element in Period 5 and Group 16
- **c** the element in the same group as sulfur but in Period 6
- **d** a halogen in Period 5
- **e** an element in the same period as potassium that has five outer-shell electrons.

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CONTINUED

2 Classify each of the following: Cl Tb Kr W U Os Rb

as: **Alkali metal** **Halogen** **Noble gas** **Transition element** **Lanthanoid** **Actinoid.**

3 Ir Se Ge Ru Ho Si Classify each of these elements, based on their position in the periodic table, as:

Metal **Non-metal** **Metalloid**

4 State whether each of the following elements is in the s, p, d or f block:

Ca, V, Eu, As, Ar, Pu, Fe and K.

10.2 Periodicity

The term periodicity is usually used in chemistry to describe the trends in properties (physical and chemical) that occur across a period and down a group in the periodic table. The trends are very similar down each group and although most of the discussion below about variations across a period will be for Period 3, the same trends are also seen in Period 2.

Atomic radius

The **atomic radius** is basically used to describe the size of an atom. The larger the atomic radius, the larger the atom.

We cannot regard an atom as a hard sphere (like a billiard/pool ball), because of the nature of electrons – there is no well-defined boundary surface, so we have to decide on how we will actually define the atomic radius. The atomic radius is usually taken to be half the internuclear distance in a molecule of the element. Nuclei are far more massive and dense than the electrons, and their positions can be measured by physical techniques. For example, in a diatomic molecule, such as chlorine, where two identical atoms are joined together, the atomic radius would be defined as shown in Figure 10.6.

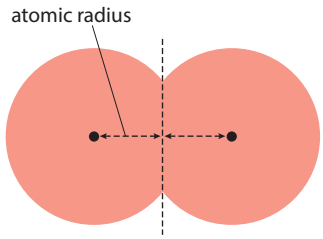

Figure 10.6: The atomic radius of chlorine atoms in a molecule.

From this, we can see that it is not possible to determine the atomic radius for an atom such as argon, because argon does not form covalent bonds.

Atomic radius increases down a group

KEY POINT

Atomic radius increases down a group in the periodic table; the atoms have increasingly more electron shells.

For example, potassium has four shells of electrons, but lithium has only two (Figure 10.7).

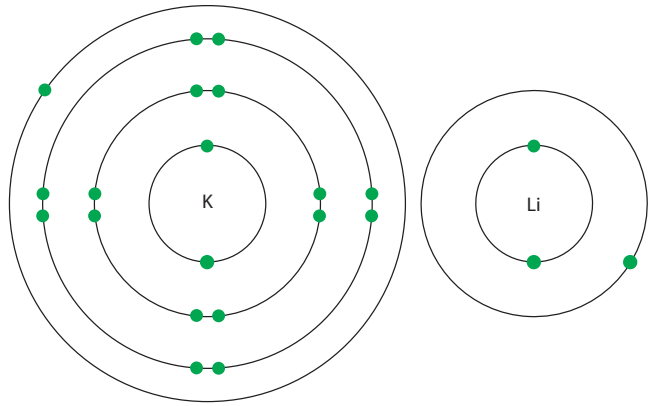

Figure 10.7: Potassium and lithium atoms.

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Although it could be argued that the nuclear charge is higher for K, therefore there is a greater force pulling in the outer electrons, the number of electrons in the inner shells is also greater. The electrons in inner electron shells shield (insulate) the outer electrons from the full attractive force of the nucleus. The number of inner shells that cause shielding increases down the group, and this mostly balances out the increase in nuclear charge.

Link

Shielding is explained in the Higher Level section in Chapter 3.

Atomic radius decreases across a period

Figure 10.8 shows the variation in atomic radius across Period 3 in the periodic table.

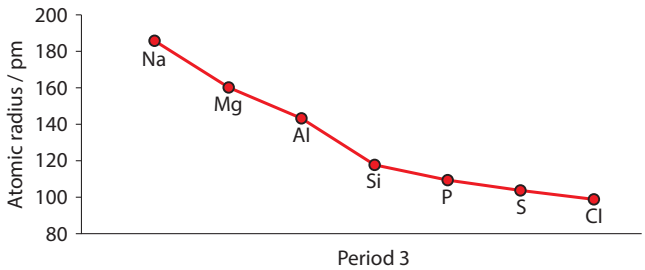

Figure 10.8: The variation in atomic radius across Period 3. No atomic radius is shown for argon because it does not form covalent bonds.

KEY POINT

Atomic radius decreases across a period because nuclear charge increases from left to right across the period, but there is no significant change in shielding because each atom has the same number of inner shells of electrons.

Let's compare sodium and chlorine (Figure 10.9).

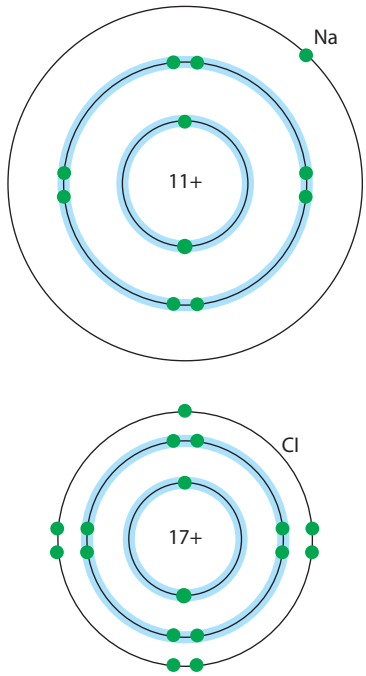

Figure 10.9: Sodium and chlorine atoms. Inner shells, which shield the outer electrons, are highlighted in blue.

Sodium has a nuclear charge (the charge on the nucleus) of 11+ (it has 11 protons in its nucleus), and chlorine has a nuclear charge of 17+. The outer electrons are shielded (screened) from the full attractive forces of the nucleus by the electrons in inner shells (highlighted in blue in Figure 10.8) but not by electrons in the same shell (main energy level). Sodium and chlorine both have two inner shells of electrons and, hence, the amount of shielding is similar. Therefore, because chlorine has a higher nuclear charge, the outer electrons are pulled in more strongly in chlorine than in sodium, and the atomic radius is smaller.

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Ionic radius

The ionic radius is a measure of the size of an ion.

KEY POINT

Ionic radius increases down a group.

The explanation here is the same as for the increase in atomic radius down a group – as we go down a group in the periodic table, the atoms have increasingly more electron shells.

KEY POINT

The ionic radii of positive ions are smaller than their atomic radii.

Figure 10.10 shows a comparison of the atomic and ionic radii (1+ ion) of the alkali metals. Each ion is smaller than the atom from which it is formed (by loss of an electron).

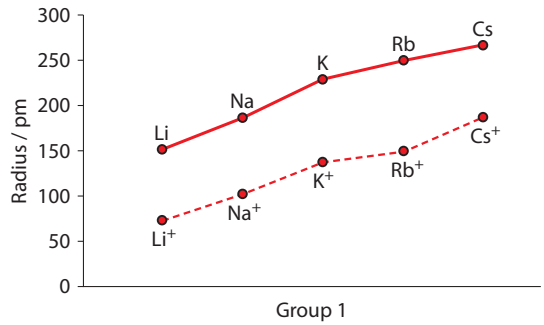

Figure 10.10: Atomic and ionic radii for the alkali metals.

The main reason that Na is larger than Na^+ is because Na has one extra shell of electrons – the electron configuration of Na is 2,8,1, whereas that of Na^+ is 2,8.

Let's consider a more general situation, where both ions have the same numbers of shells, e.g., Fe and Fe^{2+}. They both have the same nuclear charge pulling in the electrons (26+), but there is a greater amount of electron–electron repulsion in Fe because there are 26 electrons compared with only 24 in Fe^{2+}. The electrons are pulled in until the attraction from the nucleus balances with the repulsion between electrons. Therefore, with less repulsion in Fe^{2+}, the electrons can be pulled in closer to the nucleus and the radius is smaller. A representation of the effect of removing one electron from an atom is shown in Figure 10.11.

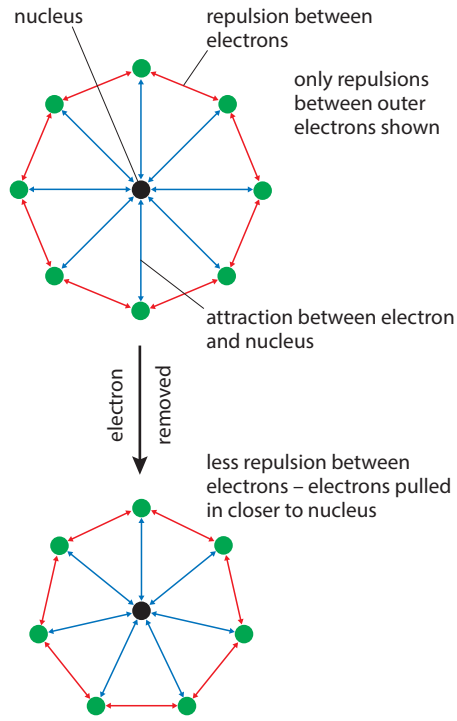

Figure 10.11: When an electron is removed from an atom, the remaining electrons are drawn closer to the nucleus due to reduced repulsion.

KEY POINT

The ionic radii of negative ions are greater than their atomic radii.

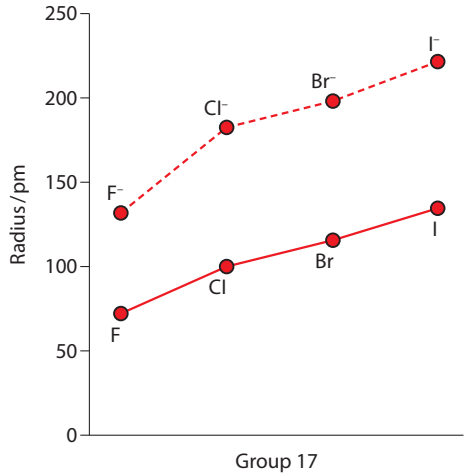

Figure 10.12: A comparison of size between halogen atoms and their ions.

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Figure 10.12 shows how the sizes of halogen atoms compare with that of their ions (1–). Cl^- is larger than Cl because it has more electrons for the same nuclear charge and, therefore, greater repulsion between electrons. Cl has 17 electrons and 17 protons in the nucleus; Cl^- also has 17 protons in the nucleus, but it has 18 electrons. The repulsion between 18 electrons is greater than between 17 electrons, so the electrons cannot be pulled in as closely to the nucleus.

Variation in ionic radius across a period

The variation of ionic radius across a period is not a clear-cut trend, because the type of ion changes going from one side to the other – positive ions are formed on the left-hand side of the period and negative ions on the right-hand side. For positive ions, there is a decrease in ionic radius as the charge on the ion increases, but, for negative ions, the size decreases as the charge decreases (Figure 10.13).

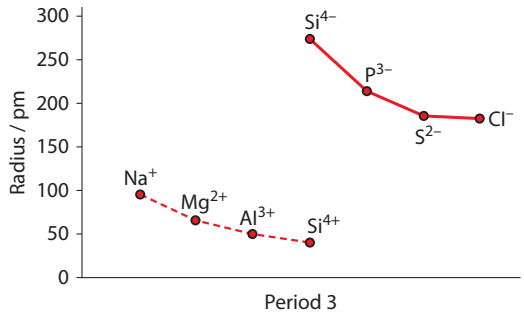

Figure 10.13: Variation of ionic radius of positive and negative ions across Period 3.

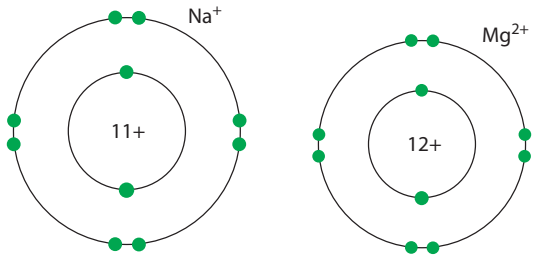

Figure 10.14: Mg^{2+} is smaller than Na^+.

Let us consider Na^+ and Mg^{2+} – the ions are isoelectronic, but Mg^{2+} has one more proton in the nucleus (Figure 10.14). Because there is the same number of electrons in both ions, the electron–electron repulsion is approximately the same; however, the higher nuclear charge in Mg^{2+} means that the electrons are pulled in more closely to the nucleus, and so, the ionic radius is smaller.

Now let us consider P^{3-} and S^{2-}. Both ions have the same number of electrons. The electron–electron repulsion is approximately the same in both ions, but S^{2-} has the higher nuclear charge, so the electrons are pulled in closer to the nucleus in S^{2-} (Figure 10.15).

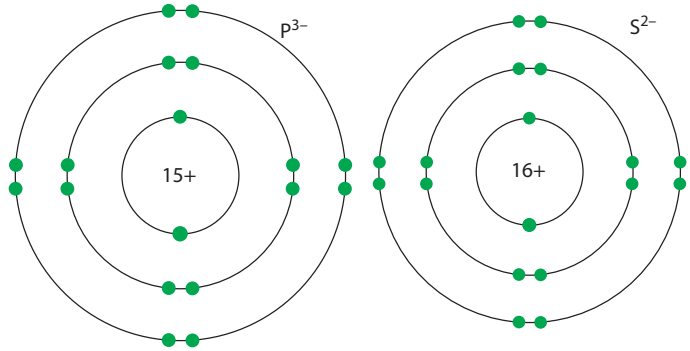

Figure 10.15: S^{2-} is smaller than P^{3-}.

WORKED EXAMPLE 10.1

Arrange Cl^-, K^+ and Ca^{2+} in order of increasing ionic radius.

Answer

These ions all have the same number of electrons (18), and so, the amount of electron–electron repulsion is going to be approximately the same in each of the ions.

The nuclear charges are Cl: 17+, K: 19+, Ca: 20+. Ca^{2+} has the highest nuclear charge; therefore, the electrons will be pulled in closest to the nucleus in Ca^{2+}, so this has the smallest ionic radius.
Cl^- has the lowest nuclear charge, so the electrons will not be pulled in as closely, and Cl^- will have the largest radius.

The order of radii is therefore $Ca^{2+} < K^+ < Cl^-$.

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First ionisation energy

KEY POINT

First ionisation energy decreases down a group.

The first ionisation energy of an element is the energy required to remove the outermost electron from a gaseous atom, that is, the energy for the process:

$M(g) \rightarrow M^+(g) + e^-$

The reason that it is called the *first* ionisation energy is that it is also possible to define a *second* ionisation energy, etc. The second ionisation energy is the energy for the process:

$M^+(g) \rightarrow M^{2+}(g) + e^-$

The decrease in first ionisation energy down Group 1 is shown in Figure 10.16.

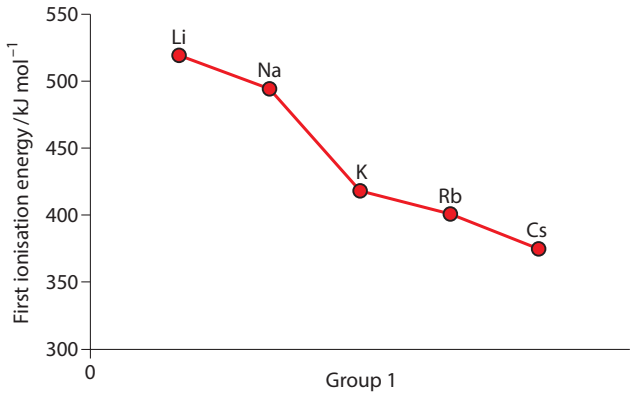

Figure 10.16: First ionisation energy decreases down Group 1.

First ionisation energy decreases down a group because the size of the atoms increases so that the outer electron is further from the nucleus and, therefore, less strongly attracted by the nucleus (Figure 10.17).

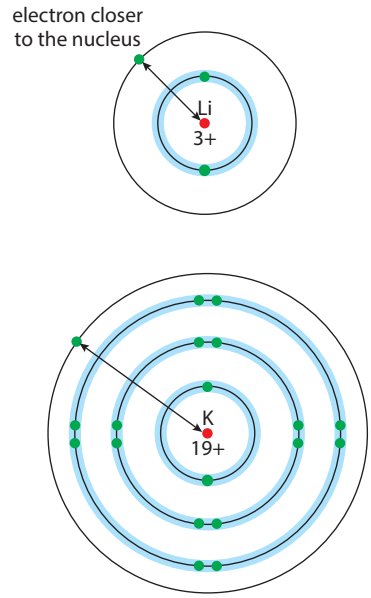

Figure 10.17: Potassium has a lower first ionisation energy than lithium. Electrons that shield the outer electron are highlighted in blue.

Although the nuclear charge also increases down a group, this is largely balanced out by an increase in shielding down the group, as there are more inner shells of electrons. It is the increase in size that governs the change in first ionisation energy.

Variation in first ionisation energy across a period

The general trend is that the first ionisation energy increases from left to right across a period, because there is an increase in nuclear charge with no significant change in shielding (Figure 10.18).

The nuclear charge increases from sodium (11+) to argon (18+) as protons are added to the nucleus (Figure 10.19).

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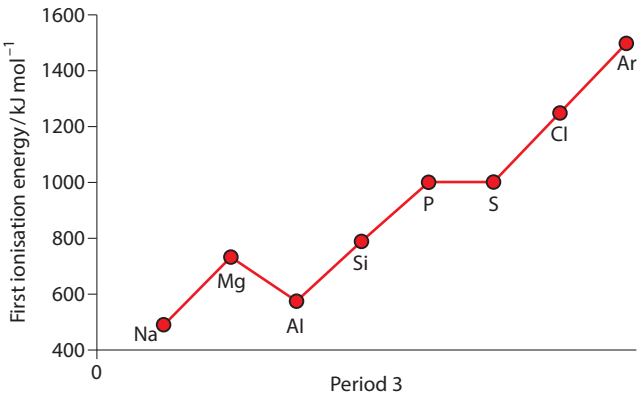

Figure 10.18: The variation in first ionisation energy across Period 3 in the periodic table.

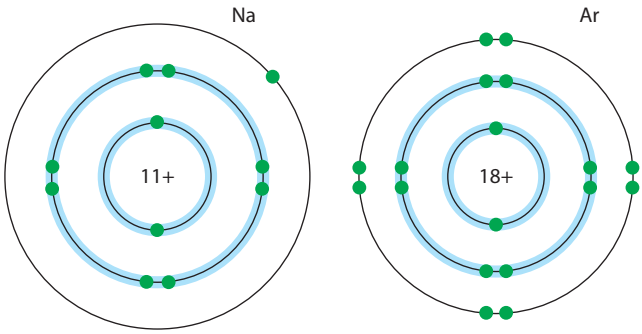

Figure 10.19: Sodium and argon atoms. Shells that shield the outer electrons are shown in blue.

In each case, an electron is removed from the same shell (main energy level) – the number of inner shells that shield the outer electron from the full attractive force of the nucleus is, therefore, the same in each Period 3 atom. The number of electrons in the third shell (main energy level) does increase, but electrons in the same shell do not shield each other very well; so, overall, there is no significant change in shielding. Therefore, the attractive force on the outer electrons increases from left to right across the period because the nuclear charge increases, resulting in the outer electron being most difficult to remove for argon. The argon atom is also smaller (see above) than the sodium atom, and so, the outer electron is closer to the nucleus and more strongly held.

There are two exceptions to the general increase in first ionisation energy across a period – these are only required knowledge for Higher Level students and are discussed in section 10.6.

Metallic properties

The metallic and non-metallic properties of elements can be related to ionisation energies.

A metallic structure consists of a regular lattice of positive ions in a sea of delocalised electrons (Chapter 8, section 8.2).

To form a metallic structure, an element must be able to lose electrons fairly readily to form positive ions. Going across a period, the ionisation energy increases, and so, elements lose electrons less easily. So, metallic structures are formed by elements on the left-hand side of the periodic table, which have lower ionisation energies.

Going down a group in the periodic table, ionisation energy decreases; therefore, elements are much more likely to exhibit metallic behaviour lower down a group. This can be seen especially well in Group 14, going from non-metallic carbon at the top, through the metalloids (Si and Ge), to the metals tin and lead at the bottom.

Electron affinity

The **first electron affinity** is the energy (enthalpy) change when one electron is added to a gaseous atom:

$X(g) + e^- \rightarrow X^-(g)$

It is defined more precisely as the enthalpy change when one electron is added to each atom in one mole of gaseous atoms under standard conditions (see Chapter 13). Electron affinity is difficult to measure experimentally and data are incomplete.

The first electron affinity is exothermic for virtually all elements – it is a favourable process (the energy of the system becomes lower) when an electron is brought from infinity (where it does not feel any attraction from the nucleus) to the outer shell of an atom, where it feels the attractive force of the nucleus. This is analogous to allowing a ball to fall to Earth – potential energy is lower the closer the ball is to the Earth.

An exothermic process corresponds to a negative value for an enthalpy change (see Chapter 12), and so, you have to be careful when comparing electron affinities because the values are all negative. Fluorine has an electron affinity of –328 kJ mol^{-1} and that of chlorine is –349 kJ mol^{-1}, so which one is bigger? Technically, the value for F is closer to zero, and so, it is a larger value, but we are actually only interested in the numerical values of these quantities, so we can either say that the

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value for Cl is more exothermic than the value for F or that the magnitude/numerical value of the electron affinity for Cl is larger.

Variation of electron affnity down a group

KEY POINT

The general trend is that the magnitude of the electron affinity decreases down a group – the values become less exothermic.

It is not, however, a regular trend. Usually, the first member of the group will have a less exothermic electron affinity than the second member, and then the electron affinity becomes less exothermic down the group after that.

A graph of electron affinity down Group 17 is shown in Figure 10.20.

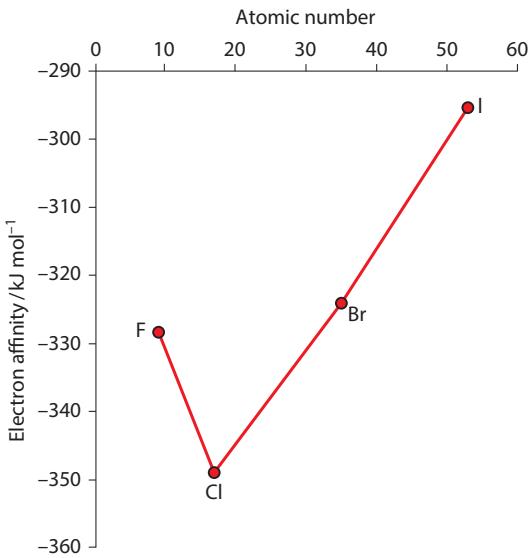

Figure 10.20: Electron affnity values of Group 17 elements.

It can be seen that fluorine has a less exothermic electron affinity than chlorine, but the numerical value of electron affinity decreases down the group from chlorine.

The electron affinity becomes less exothermic from Cl to I as the size of the atom increases. The electron is brought into the outer shell of the atom and, as the atom gets bigger, there is a weaker attraction between the added electron and the nucleus, as it is brought to a position that is further from the nucleus. If there is a weaker attraction, less energy is released. Again, the analogy of a ball falling to Earth can be used: if two balls are moved from the same height, the one which ends up closer to the Earth will have lower potential energy and have lost (released) more energy getting to that point.

Why does the first member of a group often have a less exothermic electron affinity than the second member?

Two opposing factors determine the electron affinity:

- As atoms get larger, the electron is brought into a shell further from the nucleus, and so, is less strongly attracted – this should make the electron affinity less exothermic as we descend a group.
- Electron–electron repulsion between the incoming electron and the electrons already in the atom also affects the electron affinity. As the atoms gets larger, the electrons are, on average, further apart, and there is less electron–electron repulsion. This means that the electron affinity should become more exothermic as a group is descended.

We have to look at experimental data to see which factor is more important. From F to Cl, the decrease in electron–electron repulsion is more significant, but from Cl to I the fact that the electron is further away from the nucleus is more significant. Going from F to Cl, the electron affinity becomes more exothermic because the decrease in electron–electron repulsion outweighs the fact that there is less attraction between the electron and the nucleus.

The electron affinity does actually decrease regularly down Group 1 – Li has the most exothermic electron affinity and Cs the least.

Variation in electron affinity across a period

The trend in electron affinity across Period 3 is shown in Figure 10.21. No value exists for the electron affinity of magnesium.

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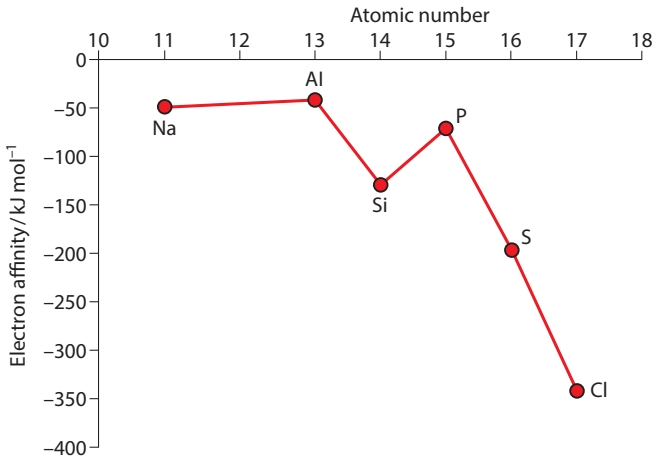

Figure 10.21: Electron affnity values across Period 3.

The general trend is that the electron affinity becomes more exothermic. There is an increase in nuclear charge with no significant change in shielding (because all the atoms have the same number of inner shells) across the period. The increase in nuclear charge also results in a decrease in atomic radius from left to right across the period. Chlorine, therefore, has a higher nuclear charge, approximately the same amount of shielding, and a smaller radius than sulfur, and so, the electron will be more strongly attracted when it is brought towards the outer shell of the chlorine atom. Chlorine, therefore, has a more exothermic electron affinity than sulfur.

Phosphorus has a less exothermic electron affinity than silicon because of its electron configuration. The electron configuration of P is [Ne] $3s^2$ $3p^3$ and that of Si is [Ne] $3s^2$ $3p^2$. When an electron is added to an Si atom, it goes into a p orbital by itself, but P has three unpaired electrons in three separate p orbitals, and so, when one electron is added, this electron must be paired up in the same p orbital as another electron – this introduces an extra repulsion term that is not present in Si. The arguments being used here are very similar to those for the variation of first ionisation energy across a period discussed in Section 10.6.

Aluminium has a less exothermic electron affinity than sodium because an electron is being added to a 3p orbital in aluminium but to a 3s orbital in sodium. The 3p orbital in Al is higher in energy than the 3s orbital in Na; therefore, less energy is released when an electron is added into the 3p orbital in Al.

Electronegativity

KEY POINT

Electronegativity is a measure of the attraction of an atom in a molecule for the electron pair in the covalent bond of which it is a part.

In a covalent bond between two different atoms, the atoms do not attract the electron pair in the bond equally. How strongly the electrons are attracted depends on the size of the individual atoms and their nuclear charge.

KEY POINT

Electronegativity decreases down a group.

Electronegativity decreases down a group because the size of the atoms increases down a group. Consider hydrogen bonded to either F or Cl (Figure 10.22).

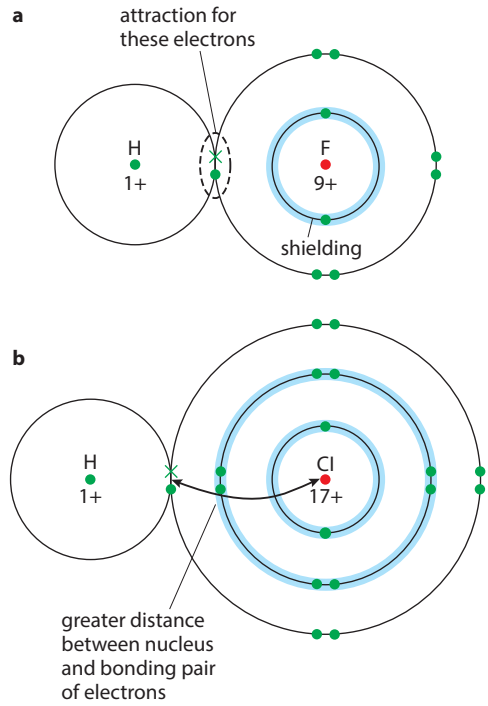

Figure 10.22: Hydrogen bonded to **a** fluorine and **b** chlorine.

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The bonding pair of electrons is closer to the F nucleus in HF than it is to the Cl nucleus in HCl. Therefore, the electron pair is more strongly attracted to the F nucleus in HF, and F has a higher electronegativity than Cl.

Chlorine's higher nuclear charge does not make it more electronegative than fluorine because the shielding from inner shells (shown with blue shading in Figure 10.22) increases from F to Cl, and this balances out the increase in nuclear charge. Chlorine has a nuclear charge that is eight higher than that of F, but it also has eight extra shielding electrons. Another way of saying this is that the *effective* nuclear charge felt by the bonding electrons is approximately the same in each case (+7, if shielding were perfect).

Link

Electronegativity is discussed in more detail in Chapter 7, section 7.6.

KEY POINT

Electronegativity increases across a period.

Electronegativity increases from left to right across a period because there is an increase in nuclear charge with no significant change in shielding. Shielding remains approximately constant because atoms in the same period have the same number of inner shells.

So, if an N—H bond is compared with an F—H bond (Figure 10.23), the electrons in the N—H bond are attracted by the seven protons in the nucleus, but the electrons in the F—H bond are attracted by the nine protons in the F nucleus. In both cases, shielding is approximately the same (because of two inner-shell electrons). The F atom is also smaller than the N atom, and so, the bonding electrons are closer to the nucleus.

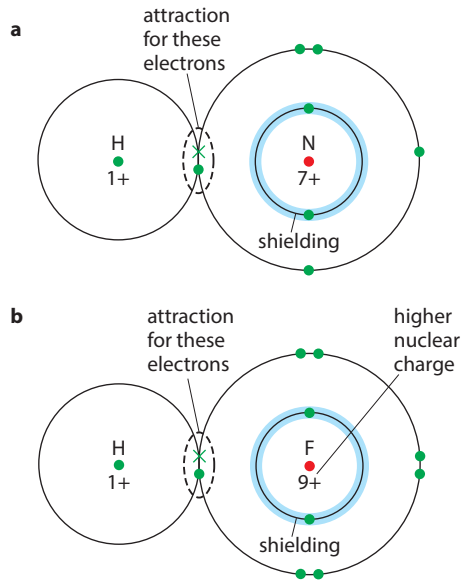

Figure 10.23: Hydrogen bonded to **a** nitrogen and **b** fluorine.

KEY POINT

Trends down a group: these are due to the increase in size of the atoms down a group (more shells of electrons).

Trends across a period: these are due to an increase in nuclear charge with no significant change in shielding because all the atoms have the same number of inner shells.

Summary of periodicity

Table 10.2 shows a summary of the periodicity in the quantities discussed here.

	Atomic radius	Ionic radius	Ionisation energy	Electron affinity	Electronegativity
down a group	increases	increases	decreases	becomes less exothermic*	decreases
across a period	decreases	positive ions get smaller; negative ions get smaller	increases*	becomes more exothermic*	increases

Table 10.2: A summary of trends in the periodic table; – * indicates that the trend is not regular.

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TEST YOUR UNDERSTANDING

5 State whether the following properties increase or decrease across a period:

- **a** electronegativity
- **b** atomic radius.

6 Arrange the following in order of increasing radius (smallest first):

- **a** Ba, Mg, Sr, Ca
- **b** O^{2-}, Na^{+}, F^{-}
- **c** Na, Na^{+}, K, Al^{3+}
- **d** Cl, Te^{2-}, Cl^{-}, S^{2-}

7 Are the following TRUE or FALSE?

- **a** A germanium (Ge) atom is smaller than a silicon (Si) atom, but silicon has a higher first ionisation energy.
- **b** Selenium (Se) has a higher first ionisation energy and electronegativity than sulfur.
- **c** Antimony (Sb) has a higher first ionisation energy and electronegativity than tin (Sn).
- **d** Cl^{-} is bigger than Cl, but Se^{2-} is smaller than Se.
- **e** Iodine has a higher electronegativity than tellurium (Te) but a lower electronegativity than bromine.
- **f** The first electron affinity of F is more exothermic than that of Cl.

10.3 The chemistry of Group 1 and Group 17

Group 1 elements

The elements in Group 1 are known as the **alkali metals**. They are all highly reactive, soft, low-melting-point metals (Table 10.3).

Element	Symbol	Electron configuration	First ionisation energy / kJ mol^{-1}	Melting point/ °C
lithium	Li	[He] $2s^1$	520	181
sodium	Na	[Ne] $3s^1$	496	98
potassium	K	[Ar] $4s^1$	419	64
rubidium	Rb	[Kr] $5s^1$	403	39
caesium	Cs	[Xe] $6s^1$	376	29

Table 10.3: The Group 1 elements.

They are placed together in Group 1 because they all have one electron in their outer shell, and therefore react in very similar ways (similar chemical properties).

The bonding in all these elements is metallic. The solid is held together by electrostatic attraction between the positive ions in the lattice and the delocalised electrons (see Chapter 8, section 8.3).

Melting point decreases down Group 1. The attraction for the delocalised, negatively charged, electrons is due to the nucleus of the positive ion. As the ions get larger as we go down the group, the nucleus becomes further from the delocalised electrons and the attraction becomes weaker (Figure 10.24). This means that less energy is required to break apart the lattice going down Group 1.

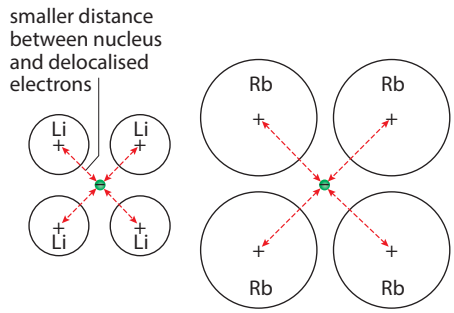

Figure 10.24: The delocalised electrons are attracted more strongly in lithium than in rubidium.

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Metallic character down Group 1

Ionisation energy decreases down Group 1 as the atoms get larger, and we saw before that there was a connection between ionisation energy and metallic character. So, it could be argued that there is an increase in metallic character down Group 1, as the ionisation energy decreases and it becomes easier to form a positive ion.

What does it mean, though, that metallic character increases down Group 1? The Group 1 elements are all metals – they are shiny when freshly cut, malleable, conduct electricity and heat, so how do we quantify how metallic something is? If we look at two of these properties – electrical and thermal conductivity – we find that sodium has the highest electrical and thermal conductivity of all the elements in the group and caesium the lowest, so it could be argued that sodium is the most metallic of the elements in Group 1?

EXAM TIP

The syllabus states that metallic character increases down Group 1, so you should write this in the examination: metallic character increases down Group 1 because the ionisation energy decreases down Group 1, and it becomes easier to form a positive ion.

Reactions of the elements in Group 1

KEY POINT

Reactivity increases down Group 1.

The elements in Group 1 are all reactive metals that react readily with, among other things, oxygen, water and halogens. The atoms all have one electron in their outer shell, and virtually all reactions involve the loss of this outer-shell electron to form a positive ion, M^+. The reactions become more vigorous going down the group because the ionisation energy decreases as the size of the atom increases. This means that, for example, caesium loses its outer electron to form a positive ion much more easily than sodium and will react more vigorously.

Reaction with oxygen

The alkali metals react vigorously with oxygen and all tarnish rapidly in air. The general equation for the reaction is as follows:

$$4M(s) + O_2(g) \rightarrow 2M_2O(s)$$

M_2O is a basic oxide that will dissolve in water to form an alkaline solution, containing M^+ and OH^- ions.

Reaction with water

The alkali metals react rapidly with water. The general equation for the reaction is as follows:

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

An alkaline solution is formed. The alkali metal hydroxides are strong bases and ionise completely in aqueous solution (Chapter 19, Section 19.5).

The following observations could be made when a piece of sodium is put into water:

- the piece of sodium floats – it is less dense than water
- the piece of sodium melts into a ball – the reaction is exothermic, a lot of heat is generated and sodium has a low melting point (98 °C)
- there is fizzing where sodium is in contact with water – hydrogen gas is produced
- the piece of sodium moves around on the surface of water – hydrogen is not produced evenly – sodium is pushed around the surface by hydrogen
- the piece of sodium gets smaller and eventually disappears – it is used up in the reaction.

The reaction with water becomes more vigorous going down the group – lithium does not melt (heat is given off more slowly and it has a higher melting point); potassium bursts into flames (lilac) and caesium explodes as soon as it comes into contact with water.

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Group 17 elements

The elements in Group 17 are known as the halogens. They are all non-metals consisting of diatomic molecules (X_2). Some properties are given in Table 10.4.

Variation of melting and boiling points in Group 17

The melting points and boiling points of the halogens increase going down the group – fluorine and chlorine gas are gases at room temperature and pressure, bromine is a liquid and iodine is a solid. As the relative molecular mass of the X_2 halogen molecules increases, the London forces (Chapter 7, Section 7.7) between molecules get stronger. This means that more energy must be supplied to separate the molecules from each other.

Metallic character increases down Group 17

Metallic character increases down Group 17 as the atoms get larger and ionisation energy decreases so that it becomes easier to form a positive ion. All of the elements, fluorine to bromine, can be quite safely classified as non-metals, but when we get to iodine it does begin to exhibit some metallic properties – the crystals are shiny and look slightly metallic, and the electrical conductivity means that it can be classified as a semiconductor. As you compress iodine (pressures about 200 times atmospheric pressure are required), it does actually change to a metallic form and will exhibit metallic conduction and even superconductivity at low temperatures. There are two more elements in Group 17 below iodine: astatine (element 85) and tennessine (element 117). No one has actually seen or measured the properties of solid samples of these elements, but, based on predicted properties, astatine is often classified as a metalloid (some people believe that it could be classified as a metal) and tennessine could possibly behave as a metal.

Reactions of the elements in Group 17

All the atoms of the elements in Group 17 have seven electrons in their outer shell and react either by gaining an electron to form X^- (halide) ions or by forming covalent compounds. The compounds of the halogens are often called halides, so, for instance, we talk about the *alkali metal halides*, meaning compounds such as sodium chloride or potassium iodide.

Fluorine is the most reactive element known, reacting directly with virtually every other element in the periodic table. Reactivity decreases down the group. The variation in reactivity of the halogens cannot be as easily explained as for the alkali metals. The very high reactivity of fluorine can be explained in terms of an exceptionally weak F—F bond, and the strength of the bonds it forms with other atoms. The reactivity in terms of the formation of X^- ions can be related to a decrease in the magnitude of the electron affinity (energy released when an electron is added to a neutral atom) going down the group from Cl to I as the electron is added to a shell further away from the nucleus, but this is only part of the story and several factors must be considered when explaining the reactivity of the halogens.

KEY POINT

Reactivity decreases down Group 17.

Displacement reactions of halogens

These are reactions between a solution of a halogen and a solution containing halide ions. Potassium chloride, bromide and iodide solutions are all colourless. The colours of chlorine, bromine and iodine solutions are shown in Figure 10.25.

Element	Symbol	Atomic number	Electron configuration	Colour	Melting point / °C	Boiling point / °C	Physical state at room temperature and pressure
fluorine	F	9	[He] $2s^2 2p^5$	pale yellow	–220	–188	gas
chlorine	Cl	17	[Ne] $3s^2 3p^5$	yellow–green	–101	–35	gas
bromine	Br	35	[Ar] $3d^{10} 4s^2 4p^5$	deep red liquid, orange vapour	–7	59	liquid
iodine	I	53	[Kr] $4d^{10} 5s^2 5p^5$	grey shiny solid, purple vapour	114	184	solid

Table 10.4: Properties of halogens.

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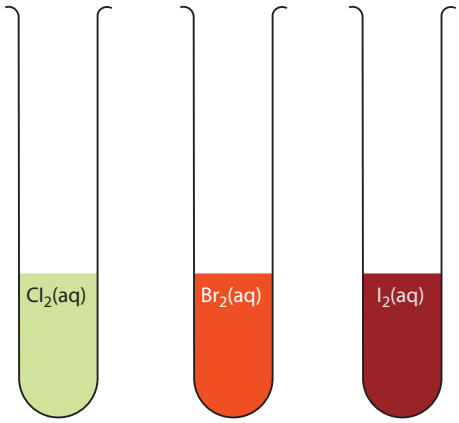

Figure 10.25: Chlorine solution is pale yellow–green (almost colourless if it is dilute), bromine solution is orange (yellow if it is very dilute) and iodine solution is red–brown (orange if it is dilute).

To investigate the displacement reactions, a small amount of a solution of a halogen is added to a small amount of a solution containing a halide ion in a test tube, and any colour changes are observed (see Table 10.5).

The actual colours observed will depend on how concentrated the original solutions were. You cannot actually get a solution of just a halide ion – a positive ion is always required as well, but this plays no role in the reaction, so it would not matter if sodium chloride, bromide or iodide were used instead. Note that, even when no reaction occurs, the final solution will be coloured if you have added a coloured solution.

The reactions that occur are as follows:

$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq)$

$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$

$Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$

We say that the more reactive halogen *displaces* the less reactive halogen from solution. Chlorine is more reactive than bromine and iodine and, therefore, displaces bromine and iodine from solution. Bromine is more reactive than iodine, and so, displaces iodine from solution.

The potassium (K^+) ions play no role in this reaction, and so, we can re-write these equations as ionic equations, which just show the species that actually react:

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

EXAM TIP

Take care with the words that you use when explaining this – use: a more reactive *halogen* displaces a less reactive *halogen*. Do not write: a more reactive halogen displaces a less reactive *halide*.

These reactions are all **redox reactions** (Chapter 20) and involve both **oxidation** and **reduction**. Oxidation can be defined as the loss of electrons and reduction as the gain of electrons. In the first reaction, the Br^- ions lose electrons as they are converted into Br_2, and so we say that Br^- is oxidised to Br_2. The chlorine atoms in Cl_2 gain electrons as they are converted into Cl^-, and so we say that Cl_2 is reduced to Cl^-. Therefore, we can see that a more reactive halogen oxidises the halide ion of a less reactive halogen.

KEY POINT

An oxidising agent is a species that oxidises another species by taking electrons from it, and a reducing agent is a species that reduces another species by giving electrons to it.

In the reaction between chlorine and bromide ions, Cl_2 takes the electrons from Br^-, and thus, oxidises it; therefore, Cl_2 is the **oxidising agent** in this reaction.

	KCl(aq)	KBr(aq)	KI(aq)
$Cl_2(aq)$	no reaction	orange solution (bromine produced)	dark red–brown solution (iodine produced)
$Br_2(aq)$	no reaction	no reaction	dark red–brown solution (iodine produced)
$I_2(aq)$	no reaction	no reaction	no reaction

Table 10.5: Results of reactions between halogen solutions and solutions containing halide ions.

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Br^- ions give electrons to Cl_2 molecules and, therefore, reduces them, so Br^- is the **reducing agent**.

Chlorine oxidises bromide ions to bromine and iodide ions to iodine, but bromine is only able to oxidise iodide ions to iodine; iodine cannot oxidise any other halide ions. Therefore, we can say that chlorine is a stronger oxidising agent than bromine and iodine, and bromine is a stronger oxidising agent than iodine. In terms of electrons, chlorine has the strongest affinity for electrons and will remove electrons from bromide ions and iodide ions.

These reactions will be discussed again in Chapter 20.

10.4 Oxides

Oxides and the variation in metallic properties across a period

Oxides of elements may be classified as basic, acidic or amphoteric. The nature of the oxides changes across a period, and Table 10.6 shows how the oxides change from basic to amphoteric to acidic across Period 3.

In general, metallic oxides are basic and non-metallic oxides are acidic, so the variation in the properties of the oxides is an illustration of how metallic character decreases across a period.

TEST YOUR UNDERSTANDING

8 Write an equation for the reaction of rubidium with water.

9 Arrange Na, Rb, K and Cs in order of reactivity, most reactive first.

10 In each of the following pairs, which has the higher melting point:

a K or Cs

b F_2 or I_2

c Na or Cl_2.

11 Write an ionic equation for the reaction that occurs when chlorine solution is added to potassium iodide solution.

12 State whether each of the following would result in a reaction or not:

a bromine solution + potassium iodide solution

b iodine solution + potassium chloride solution

c chlorine solution + potassium chloride solution.

13 State whether trends down the group in each of the following properties are the same or different when Group 1 and Group 17 are compared:

a electronegativity **b** reactivity

c melting point **d** ionisation energy.

	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulfur	Chlorine
formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2	Cl_2O
					P_4O_{10}	SO_3	Cl_2O_7
nature of element	metal			non-metal			
Structure and bonding	giant ionic			covalent network	covalent molecular		
nature of oxide	basic		amphoteric	acidic			
reaction with water	soluble, reacts	sparingly soluble, some reaction	insoluble		soluble, reacts		
solution formed	alkaline	slightly alkaline	–		acidic		

Table 10.6: The acid–base nature of some Period 3 oxides. There are also other chlorine oxides.

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KEY POINT

Most metal oxides are basic.

A basic oxide is one that will react with an acid to form a salt and water. Some basic oxides are soluble in water and will react to produce an alkaline solution.

Sodium oxide is a basic oxide – it reacts with acids such as sulfuric acid to form salts:

$Na_2O(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

Sodium oxide reacts with water to form sodium hydroxide solution, which is an alkali:

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

All Group 1 oxides react in the same way with water.

KEY POINT

The general equation for a Group 1 oxide reacting with water is:

$M_2O(s) + H_2O(l) \rightarrow 2MOH(aq)$

MgO is another basic oxide. It reacts with hydrochloric acid to form magnesium chloride and water:

$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

Magnesium oxide, because of the relatively high charges on the ions, is not very soluble in water, but it does react to a small extent to form a solution of magnesium hydroxide, which is slightly alkaline:

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$

KEY POINT

The general equation for a Group 2 oxide reacting with water is:

$MO(s) + H_2O(l) \rightarrow M(OH)_2(aq)$

BeO has a high degree of covalent character in its bonding and does not react with water. It is an amphoteric oxide (see below).

CaO is called lime and, when it reacts with water, it forms limewater, which is a solution of calcium hydroxide and is used as a laboratory test for carbon dioxide.

EXAM TIP

The general equations must be learned for examinations.

KEY POINT

Amphoteric oxides react with acids and bases.

Some metals (such as beryllium and aluminium) form **amphoteric** oxides. Amphoteric oxides can react with both acids and bases to form salts, so they have properties of a basic (metal) oxide and an acidic (non-metal) oxide. Metals such as beryllium and aluminium are very good conductors of electricity but also have a significant degree of covalent bonding in their compounds so show both metallic and non-metallic properties.

Aluminium and beryllium oxides do not react with water but do display amphoteric behaviour in that they react with both acids and bases to form salts, e.g.

reaction with acids:
$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
reaction with alkalis/bases:
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

The fact that MgO is a basic oxide but BeO (above Mg in Group 2) and Al_2O_3 are amphoteric oxides, shows the increase in metallic character down a group and the decrease from left to right across a period.

KEY POINT

Most non-metal oxides are acidic.

An acidic oxide is one that reacts with bases/alkalis to form a salt and, if soluble in water, will produce an acidic solution.

SO_2 [sulfur(IV) oxide] and SO_3 [sulfur(VI) oxide] are both acidic oxides. SO_2 reacts with water to form sulfuric(IV) acid, which is otherwise known as sulfurous acid.

KEY POINT

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

The Roman numerals in brackets indicate the **oxidation state** of the sulfur atom; these will be discussed in Section 10.5.

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SO_2 reacts with bases/alkalis to form salts called sulfites, which contain the sulfite [SO_3^{2-}, sulfate(IV)] ion.

SO_3 reacts with water to form sulfuric(VI) acid, which is commonly referred to as 'sulfuric acid'.

KEY POINT

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$

SO_3 reacts with basic oxides to form salts, e.g., with CaO to form $CaSO_4$.

Carbon dioxide is also an acidic oxide. Carbon dioxide dissolves in water to form carbonic acid.

KEY POINT

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

Some non-metals, such as NO and CO, are classified as neutral oxides.

Ocean acidification

Human activity, such as burning fossil fuels and deforestation to create more land for agriculture, is causing carbon dioxide levels in the atmosphere to increase. In the 10 000-year period up to 1750, the CO_2 concentration in the atmosphere remained fairly constant, at around 280 ppm – the current level is around 420 ppm [ppm is *parts per million*: there are 420 cm^3 of CO_2 per million cm^3 (1 m^3) of air].

KEY POINT

Increasing levels of carbon dioxide in the atmosphere resulting from human activity are making the oceans more acidic.

The reactions involved in this section are all reversible and, if you have not met the idea of reversible reactions and position of equilibrium (Chapter 18), it might be better to return to this section later.

Carbon dioxide is slightly soluble in water, and an equilibrium is set up between carbon dioxide in the atmosphere and aqueous carbon dioxide in the oceans:

equilibrium 1: $CO_2(g) \rightleftharpoons CO_2(aq)$

This could also be written as:
$CO_2(atmosphere) \rightleftharpoons CO_2(oceans)$

As the concentration of carbon dioxide in the atmosphere increases, this will shift the position of the above equilibrium to the right – therefore, there will be more carbon dioxide dissolved in the oceans.

Dissolved CO_2 reacts with water to form carbonic acid:

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

Carbonic acid is a weak diprotic acid and can dissociate:

equilibrium 3: $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

equilibrium 4: $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$

As more carbon dioxide dissolves, the position of equilibrium 2 shifts to the right, which increases the concentration of H_2CO_3; this increase causes the position of equilibrium 3 to shift to the right and, therefore, increases the concentration of the $H^+(aq)$ ions and, hence, the acidity of water (see Chapter 19).

Actually, very little dissolved CO_2 is present as H_2CO_3, and equilibrium 3 could be better represented as follows:

$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

KEY POINT

'Ocean acidification' is the reduction of the pH of the oceans over an extended period of time through the increased uptake of carbon dioxide from the atmosphere.

The pH of the ocean is estimated to have decreased by 0.1 units since the industrial revolution, and some scientists believe that it could fall by up to a further 0.4 units by the end of the 21st century.

There are many possible consequences associated with ocean acidification, such as possible effects on the ability of corals, shellfish, phytoplankton, etc. to make calcium carbonate shells and skeletons.

The processes involved in ocean acidification are very complex and another equilibrium involved is the dissolution of $CaCO_3$ (present in rocks/shells, etc.):

equilibrium 5: $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

As acidity (H^+ concentration) rises, equilibrium 4 shifts to the left as extra H^+ reacts with CO_3^{2-}. More $CaCO_3(s)$ dissolves to replace $CO_3^{2-}(aq)$. These equilibria affect the ability of corals/shellfish to make skeletons/shells [$CaCO_3(s)$].

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Acid rain

Rain is naturally acidic because of dissolved carbon dioxide, which dissociates to form H^+ ions:

$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

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

The pH of rainwater is, therefore, about 5.6. This is a natural phenomenon – rain with a pH between 5.6 and 7 is not considered to be '**acid rain**'.

KEY POINT

Acid rain is rain with a pH lower than 5.6.

Sulfur(IV) oxide (sulfur dioxide, SO_2) and nitrogen oxides (NO_x) produced by human activities (and natural processes) can cause the pH of rain to become lower than this, and this is then called acid rain.

Acid deposition is a more general term than acid rain. It refers to any process in which acidic substances (particles, gases and precipitation) leave the atmosphere to be deposited on the surface of the Earth. It can be divided into wet deposition (acid rain, fog and snow) and dry deposition (acidic gases and particles).

Sulfur(IV) oxide can be formed by various natural processes, such as those that occur in volcanoes, but the major source of it in the atmosphere is from the burning of fuels (e.g. coal) that contain sulfur:

$S(s) + O_2(g) \rightarrow SO_2(g)$

SO_2 can dissolve in water to form sulfuric(IV) acid (see equation in Section 10.4), or it can be converted into sulfuric(VI) acid (H_2SO_4) in the atmosphere. The processes involved are complex and do not involve simple oxidation by atmospheric oxygen – interactions with hydroxyl radicals, ozone or hydrogen peroxide are involved. However, the reactions can be summarised as:

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (sulfur(VI) oxide)

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ (sulfuric(VI) acid)

The presence of H_2SO_3 and H_2SO_4 in rain makes it acidic.

Nitrogen oxides also contribute to acid rain. The main anthropogenic (produced by human activities) sources of nitrogen oxides are the internal combustion engine; coal-, gas- and oil-fuelled power stations and heavy-industry power generation. The combustion temperatures of fuels in these processes are very high, and oxidation of atmospheric nitrogen occurs to form NO (nitrogen monoxide, nitric oxide or nitrogen(II) oxide):

$N_2(g) + O_2(g) \rightarrow 2NO(g)$

NO (a neutral oxide) can be oxidised in the atmosphere to NO_2 (an acidic oxide). Again, the exact nature of the process is complex, but the reaction can be summarised as:

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

NO_2 can then react with a hydroxyl radical (HO•) to form nitric(V) acid:

$NO_2(g) + HO\bullet(g) \rightarrow HNO_3(g)$

The following equations are usually given credit in examinations:

$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$

or

$2NO_2(g) + H_2O(l) \rightarrow \underset{\text{nitric(III) acid}}{HNO_2(aq)} + \underset{\text{nitric(V) acid}}{HNO_3(aq)}$

The presence of HNO_2 and HNO_3 in rain makes it acidic.

Note: NO and NO_2 are usually called NO_x when talking about atmospheric pollution.

Link

A radical is a species with an unpaired electron. This is often shown with a dot, as in HO•. NO and NO_2 are also radicals, but we do not usually show the dot as they are molecular species. Radicals are discussed in Chapter 21.

Problems associated with acid rain

- Acid rain can kill trees/plants (Figure 10.26a). It is not necessarily the direct effect of the acid that causes problems but rather an indirect effect. The acid (H^+ ions) can displace metal ions from the soil that are consequently washed away (particularly calcium, magnesium and potassium ions). Mg^{2+} ions are needed to produce chlorophyll, so plants could be prevented from photosynthesising properly. Acid rain also causes aluminium ions to dissolve from rocks, which damages plant roots and limits water uptake. This can cause stunted growth and thinning or yellowing of leaves on trees.
- Acid rain can kill fish. Aquatic life is sensitive to the pH falling below six. Insect larvae, fish and invertebrates, among others, cannot survive below

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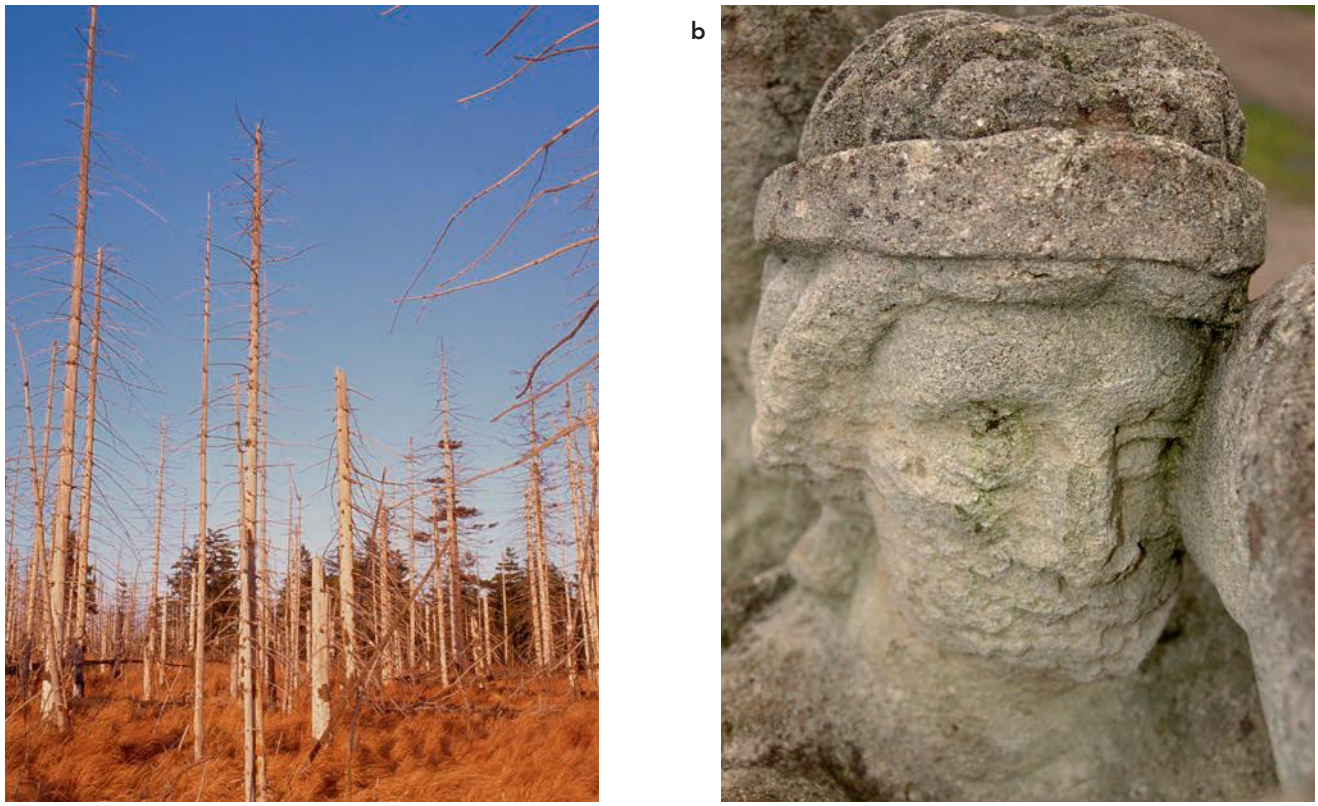

Figure 10.26: Acid rain can **a** kill trees and **b** react with limestone buildings to cause corrosion.

pH 5.2. Below pH 4.0, virtually no life will survive. Acid rain can dissolve hazardous minerals from rocks, which can accumulate in lakes and damage aquatic life; in particular, Al^{3+} ions damage fish gills.

- Acid rain can damage buildings and statues. Limestone and marble are corroded by acid rain (Figure 10.26b). A typical reaction is:

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

- Acid rain can affect human health. Pollutants such as SO_2 and NO_x that lead to acid rain can cause shortness of breath and breathing problems, but the direct effects of acid rain on human health are believed to be small (your skin will not start dissolving if you swim in a lake made more acidic by acid rain!). There are, however, believed to be indirect effects on health from the acidic water dissolving heavy metals, resulting in higher levels of toxic cadmium, lead and aluminium in water supplies and the accumulation of these and mercury in the food chain. Cadmium can cause kidney disease; aluminium has been linked to Alzheimer's disease; lead can impair the mental development of children; mercury can damage the central nervous system and kidneys.

How can ocean acidification and acid rain be stopped/reduced?

Both of these environmental problems stem from the burning of fossil fuels, so the most obvious way to reduce their effect is to use less energy and to generate more of that energy from renewable sources, such as solar or wind energy, rather than from burning fossil fuels. There are things that can be done on a national or international level, but everyone can play their part by, for instance, making greater use of public transport, cutting down on unnecessary journeys, turning off devices when not required, re-using rather than throwing things away, buying less, and thinking about the carbon footprint of things we buy (has it been shipped halfway across the world?).

Other things that can be done to reduce the effects of acid rain include

- removing sulfur before burning fossil fuels or removing SO_2 from the gases produced

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- 'liming' of lakes – calcium oxide or hydroxide neutralises acidity:

  $CaO(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l)$ or
  $Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + 2H_2O(l)$

TEST YOUR UNDERSTANDING

14 Write balanced equations for the following reactions:

a carbon dioxide with water

b sodium oxide with water

c sulfur(VI) oxide with water

d calcium oxide with water.

15 Classify each of the following oxides as acidic or basic or amphoteric:

Na_2O, MgO, Al_2O_3, SiO_2, P_4O_6, P_4O_{10}, SO_2, SO_3, Cl_2O, Cl_2O_7.

16 State whether an acidic or alkaline solution will be formed when each of the following is dissolved in/reacted with water:

a SO_3 **c** Na

b MgO **d** CO_2.

NATURE OF SCIENCE

Science, and the technology that develops from it, has been used to solve many problems – but it can also *cause* them. The development of industrial processes that require large amounts of energy and produce acidic gases led to acid rain and ocean acidification becoming major environmental problems. These problems affect people across the world, and cooperation between scientists and politicians in different countries will be vital in developing methods and policies to solve these problems.

10.5 Oxidation state

So far in this chapter, we have met several compounds and ions, such as nitric(III) acid, sulfur(IV) oxide and the sulfate(IV) ion, where Roman numerals are included in their name. These Roman numerals indicate the *oxidation state* of a particular atom in that compound/ion. Oxidation states are useful because they allow us to keep track of electrons in a type of chemical reaction called a redox reaction, which will be studied in more depth in Chapter 20. They also give us a systematic way of naming compounds, so, for instance, distinguishing between nitrogen(I) oxide (N_2O) and nitrogen(II) oxide (NO).

EXAM TIP

Oxidation state is often called oxidation number – either term may be used in the exam. You can treat them as the same thing.

How to assign oxidation states

To assign oxidation states we treat every bond as ionic and the oxidation state is the charge that each atom would have if electrons were completely transferred.

So, CH_4 is a covalent compound, but we assign oxidation states of –4 for C and +1 for H because we imagine the bonds being formed by each H (the less electronegative atom) transferring 1 electron to the C (the more electronegative atom). Note that the sign comes before the number – this distinguishes an oxidation state from a charge.

EXAM TIP

Oxidation state is written with the sign first, e.g. –2, but a charge is written with the number first, e.g. 2–. This may seem like a trivial point, but, if you get it the wrong way round, you could lose a mark in the exam!

There are some general guidelines for working out oxidation states:

1 If the compound is ionic, the oxidation states are the charges on the ions.

KCl is an ionic compound and the oxidation states are +1 for K and –1 for Cl, which correspond to the charges on the ions (but with the sign before the number).

2 Assume that O has oxidation state –2 and H has oxidation state +1.

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	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17
maximum oxidation state	+1	+2	+3	+4	+5	+6	+7

Table 10.7: The connection between group number and the maximum possible oxidation number. The elements in Groups 1 and 2 virtually always have the group number as their oxidation state.

If the compound contains O and/or H, you can usually assume that the oxidation state of O is –2 and that of H is +1. The only exceptions to this are compounds just containing oxygen and fluorine, peroxides (and superoxides) and metal hydrides, which will be discussed in the Examples section.

3 Assign the most electronegative atom in a molecule/ion a negative oxidation state, according to how many electrons it needs to gain a noble gas electron configuration.

So, in NF_3, F is the more electronegative element and, because a fluorine atom has seven electrons in its outer shell, it needs to gain one electron to have the same number of electrons as Ne (or, the normal charge on F in an ionic compound is 1–); therefore, the oxidation state of F in NF_3 is –1 (and that of N is, therefore, +3).

4 The sum of the oxidation states, taking into account signs and number of each atom, is equal to the overall charge.

In CO_2, C has oxidation state +4 and O has oxidation state –2.

$+4 + 2(-2) = 0$ is the overall charge on the CO_2 molecule.

In CO_3^{2-}, C has oxidation state +4 and O has oxidation state –2.

$+4 + 3(-2) = -2$ is the overall charge on the CO_3^{2-} ion.

5 The oxidation state of atoms in an element is zero.

So, the oxidation state of oxygen in O_2 is zero and that of sodium in sodium metal is zero. The atoms of an element all have the same electronegativity, so we can assume that the electrons are evenly distributed within an element.

6 The maximum possible oxidation state is determined by the number of electrons in the outer shell.

It is not possible to lose more electrons than there are in the outer shell; therefore, the maximum possible oxidation state for an element will be its group number for elements in Groups 1 and 2 and (group number – 10) for elements in Groups 13–17 (see Table 10.7). For example, the maximum possible oxidation state for a Group 16 element is +6 because there are six electrons in the outer shell. For a **transition metal**, the maximum possible oxidation state is given by the sum of the number of electrons in the s and d subshells; therefore, for Mn ([Ar] $4s^2\ 3d^5$), the maximum oxidation state is +7.

Not every atom will exhibit its maximum oxidation state. For instance, the maximum oxidation state shown by F is 0 (and not +7) and that shown by Fe is +6 and not +8.

Examples

SO_2

The compound contains oxygen, which we can assume has an oxidation state of –2. The overall charge on the molecule is zero and, therefore, the oxidation state of sulfur must be +4 to cancel out the total oxidation state of two oxygen atoms (–4) (Figure 10.27).

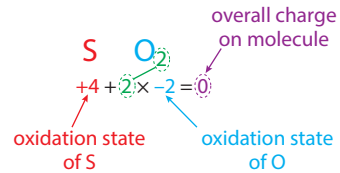

Figure 10.27: Assigning oxidation states in sulfur dioxide.

SO_4^{2-}

Assume that the oxidation state of oxygen is –2. The total oxidation state of four oxygen atoms is 4×-2, or –8. Because the overall charge on the ion is 2–, the oxidation state of sulfur must be +6 to cancel out all but 2 of the total oxidation state of the 4 oxygen atoms (Figure 10.28).

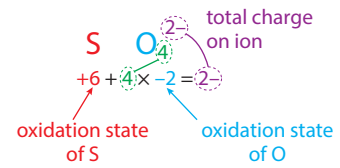

Figure 10.28: Assigning oxidation states in the sulfate (VI) ion.

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N_2H_4

Assume that the oxidation state of H is +1: $4 \times +1 = +4$. Therefore, the 2 N atoms together must have a total oxidation state of −4 to cancel out +4. Therefore, the oxidation state of each N is –2.

$Na_2Cr_2O_7$

There is ionic bonding and covalent bonding here, so it is first split up into its ions: Na^+ and $Cr_2O_7^{2-}$.
The oxidation state of Na is +1, which is its charge. In $Cr_2O_7^{2-}$, we assume that the oxidation state of oxygen is –2. The total oxidation state of 7 oxygen atoms is 7×-2, or –14. Because the overall charge on the ion is 2–, the total oxidation state of 2 chromium atoms together must be +12 to cancel out all but 2 of the total oxidation state of the 7 oxygen atoms. Therefore, the oxidation state of chromium is $\frac{+12}{3}$, or +6 (Figure 10.29).

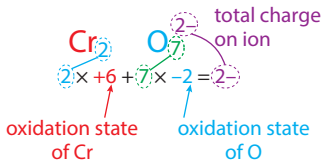

Figure 10.29: Assigning oxidation states in the dichromate (VI) ion.

PCl_3

There is no oxygen or hydrogen, so we must look at which element is more electronegative. Chlorine is more electronegative than phosphorus, so chlorine is assigned an oxidation state according to how many electrons it needs to gain a noble gas electron configuration: one electron. So, the oxidation state of Cl is –1. Another way of thinking about this is that the charge on Cl in an ionic compound is 1–. With 3 Cl atoms with oxidation state –1 and no overall charge, the oxidation state of P must be +3.

Hydrogen peroxide (H_2O_2) and peroxides

H_2O_2 contains both hydrogen and oxygen, however, if we assume that H is +1 and O –2, this does not work, as we get an overall charge of 2–, but the molecule is neutral. If the oxidation state of oxygen is –2, the oxidation state of hydrogen must be +2 to produce no overall charge. This is, however, not possible because hydrogen has only one electron – its maximum oxidation state is +1. This means that the oxidation state of hydrogen in H_2O_2 is +1 and that of oxygen must, therefore, be –1. There are many ionic peroxides, such as Na_2O_2, that contain the O_2^{2-} ion, and the oxidation state of O in all of these will be –1. There are also *superoxides*, such as RbO_2, that contain the O_2^- ion.

Metal hydrides

Hydrogen is less electronegative than virtually all the other non-metals, so we are on fairly safe ground assigning it +1 oxidation state in compounds with non-metals. However, hydrogen also forms hydrides with many metals – for example, NaH and CaH_2. Hydrogen is more electronegative than these metals, and so, its oxidation state will be –1. For many of these compounds, the bonding is mostly ionic, and they can be regarded as containing the H^- ion.

Compounds containing O and F

Oxygen will usually be assigned an oxidation state that is negative because it is the second most electronegative element. However, when it is in compounds with F, it can have a positive oxidation state. For example, OF_2: F is more electronegative, so it is assigned an oxidation state according to the charge it would normally have in an ionic compound: –1. This means that the oxidation state of O must be +2 to give 0 charge overall.

$XeOF_4$

Xenon is less electronegative than fluorine and oxygen, so we assign fluorine –1 and oxygen –2 as oxidation states, and the oxidation state of xenon works out as +6.

Compounds containing a bond between two atoms of an element

We have already met hydrogen peroxide and the unusual oxidation state of oxygen. In general, the oxidation states of atoms will be lower when they are bonded to another atom of the same element. When two atoms of the same element are joined together, the electrons are shared equally, and there is zero contribution to the oxidation state for each atom.

Fractional Oxidation States

There are several compounds/ions where an element appears to have an oxidation state that is not a whole number, e.g. C_3H_8. The oxidation state of C here is $+2\frac{2}{3}$ and is an average value. The C in the middle, which is joined to 2 C atoms (and 2 H atoms) has a lower oxidation state (+2) compared to the end C atoms, which are only joined to one other C atom (and 3 H atoms) and have an oxidation state of +3.

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In the tetrathionate ion, $S_4O_6^{2-}$, the average oxidation state of S is +2.5. Two S atoms are only joined to other S atoms and have an oxidation state of 0 but the other two S atoms are also joined to O atoms and have an oxidation state of +5.

TEST YOUR UNDERSTANDING

17 Determine the oxidation states of all elements in the following species:

P_4, SO_2, SO_3, SO_4^{2-}, SO_3^{2-}, C_2H_5Cl, O_2, CO, C_2H_4, Ba, CrO_4^{2-}, $Cr_2O_7^{2-}$, H_2O_2, BaO_2, CaH_2, $KMnO_4$, $Na_2S_2O_3$, $S_4O_6^{2-}$.

18 Work out oxidation states for nitrogen in the following molecules/ions:

a NF_3 **b** NO

c N_2O **d** N_2O_4

e N_2H_4 **f** NO_2^-.

19 Work out the oxidation state of chlorine in the following species:

a Cl_2O **b** HCl

c ClO_4^- **d** ClF_3

e $HClO_3$.

20 Work out the oxidation state of the species in red in each of the following compounds:

a Na_2O **b** $KBrO_3$

c Na_2SO_3 **d** K_2CrO_4

e NH_4NO_3 **f** KH.

Naming compounds

Binary ionic compounds

We have already seen how to name binary (just containing two elements) ionic compounds in Chapter 6. These are named with the metal first and the negative ion with its name changed by adding the ending 'ide'. Some examples are shown in Table 10.8.

Name	Formula
sodium chloride	NaCl
calcium sulfide	CaS
potassium oxide	K_2O

Table 10.8

Naming compounds using oxidation states

SO_2 and SO_3 are commonly called sulfur dioxide and sulfur trioxide, respectively. They can, however, be named more systematically using the oxidation state of the sulfur atom. So, SO_2 is sulfur(IV) oxide and SO_3 is sulfur(VI) oxide. Strangely enough, no one ever calls carbon dioxide carbon(IV) oxide or carbon monoxide carbon(II) oxide! This naming system is approved by the International Union of Pure and Applied Chemistry (IUPAC). To quote its website: 'The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on chemical nomenclature and terminology'.

KEY POINT

Roman numerals are used for the oxidation states in the names of compounds.

Some names of compounds and ions are shown in Table 10.9.

Compound/ion	IUPAC name
H_2SO_3	sulfuric(IV) acid
H_2SO_4	sulfuric(VI) acid
PCl_3	phosphorus(III) chloride
PCl_5	phosphorus(V) chloride
N_2O	nitrogen(I) oxide
NO_2	nitrogen(IV) oxide
$HClO_3$	chloric(V) acid
$CuSO_4$	copper(II) sulfate
MnO_2	manganese(IV) oxide
Fe_2O_3	iron(III) oxide

Table 10.9: These compounds/ions are named systematically using oxidation states according to the IUPAC system.

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The names of the compounds of transition metals almost always contain the oxidation state – so $FeCl_2$ is called iron(II) chloride and contains the Fe^{2+} ion, whereas $FeCl_3$ is called iron(III) chloride and contains the Fe^{3+} ion.

EXAM TIP

Although you need to know how to name substances using oxidation states, it is still acceptable to use their more common names – like sulfur dioxide for SO_2 and sulfuric acid for H_2SO_4.

EXAM TIP

A question might be phrased as such: 'state the IUPAC name of this compound' or 'name this compound according to IUPAC rules'.

Oxyanions

Oxyanions are negative ions that contain an element and oxygen, such as SO_3^{2-} or NO_2^-. These are best named systematically, but trivial names for these ions are still in general use. Some formulas and names of oxyanions are shown in Table 10.10.

	IUPAC name	Trivial name
SO_4^{2-}	sulfate(VI) ion	sulfate ion
SO_3^{2-}	sulfate(IV) ion	sulfite ion
NO_3^-	nitrate(V) ion	nitrate ion
NO_2^-	nitrate(III) ion	nitrite ion
PO_4^{3-}	phosphate(V) ion	orthophosphate ion
OCl^-	chlorate(I) ion	hypochlorite ion
ClO_3^-	chlorate(V) ion	chlorate ion
ClO_4^-	chlorate(VII) ion	perchlorate ion
$Cr_2O_7^{2-}$	dichromate(VI) ion	dichromate ion
CrO_4^{2-}	chromate(VI) ion	chromate ion
MnO_4^-	manganate(VII) ion	permanganate ion

Table 10.10: Some systematic and trivial (generic) names of some oxyanions. The ones in red are mentioned specifically in the syllabus.

Using this system, $KMnO_4$ would be called potassium manganate(VII) and $Na_2Cr_2O_7$ sodium dichromate(VI).

TEST YOUR UNDERSTANDING

21 Name the following compounds according to IUPAC rules:

a NO **b** Cl_2O_7

c SeO_2 **d** KIO_3

e Cr_2O_3 **f** H_3PO_4

g $NaNO_3$ **h** HOCl

i $NaBrO_3$ **j** NH_4ClO_4.

10.6 Exceptions to the general increase in first ionisation energy across a period

We saw in Section 10.2 that there is a general increase in first ionisation energy across Period 3 (Figure 10.18). The same trend is also seen across Period 2 (Figure 10.30). Two exceptions to the general increase in ionisation energy across a period are shown in each graph.

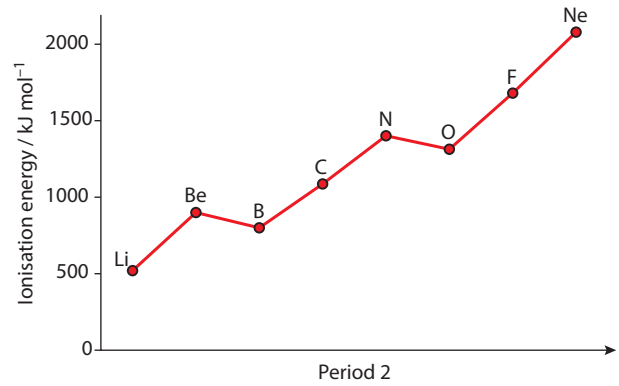

Figure 10.30: The variation in first ionisation energy across Period 2 in the periodic table.

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Even though boron has a higher nuclear charge (more protons in the nucleus) than beryllium, the ionisation energy for boron is lower. The electron configurations of beryllium and boron are:

Be: $1s^2\ 2s^2$ and B: $1s^2\ 2s^2\ 2p^1$.

The major difference is that the electron to be removed from the boron atom is in a 2p sub-level, whereas it is in a 2s sub-level in beryllium. The 2p sub-level in boron is higher in energy than the 2s sub-level in beryllium (Figure 10.31) and, therefore, less energy is required to remove an electron from boron.

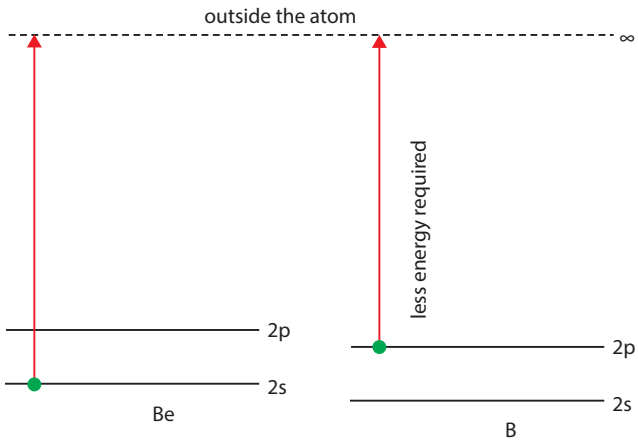

Figure 10.31: The 2p subshell in boron is higher in energy than the 2s subshell in beryllium.

An alternative explanation is that the 2p electron in boron is shielded, to a certain extent, by the 2s electrons, and this increase in shielding from beryllium to boron more than offsets the increase in nuclear charge from beryllium to boron. The 2s electrons shield the 2p electrons because there is a significant probability of the 2s electron being closer to the nucleus and, therefore, getting between the 2p electron and the nucleus.

The second exception is that the first ionisation energy of oxygen is lower than that of nitrogen.

The electron configurations for nitrogen and oxygen are:

N: $1s^2\ 2s^2\ 2p^3$ and O: $1s^2\ 2s^2\ 2p^4$.

The major difference is that oxygen has two electrons paired up in the same p orbital, but nitrogen does not (Figure 10.32).

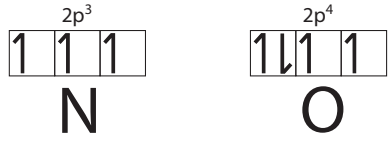

Figure 10.32: Orbital diagrams showing electrons in the 2p sub-levels of nitrogen and oxygen.

An electron in the same p orbital as another electron is easier to remove than one in an orbital by itself because of the repulsion from the other electron.

When two electrons are in the same p orbital, they are closer together than if there is one in each p orbital. If the electrons are closer together, they repel each other more strongly. If there is greater repulsion, an electron is easier to remove.

Across Period 3 there is a general increase in first ionisation energy from Na to Ar, but the first ionisation energy of Al is lower than that of Mg, and the first ionisation energy of S is lower than that of P. All the values for the Period 3 atoms are lower than those of the Period 2 atoms because they are larger atoms, and the outer electron will be further from the nucleus.

TEST YOUR UNDERSTANDING

22 In each case, deduce which species has the higher first ionisation energy.

- **a** Na(g) or K(g)
- **b** C(g) or N(g)
- **c** He(g) or Kr(g)
- **d** Mg(g) or Al(g)
- **e** Cl(g) or Mg(g)
- **f** S(g) or P(g)

23 In each case, deduce which species requires the most energy for removal of the next electron.

- **a** $Na^+(g)$ or $Mg^+(g)$
- **b** $Al^{3+}(g)$ or $Mg^{2+}(g)$
- **c** $O^+(g)$ or $F^+(g)$
- **d** $B^+(g)$ or $C^+(g)$
- **e** $Na^{10+}(g)$ or $Mg^{11+}(g)$

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10.7 The transition elements (d-block)

The first-row d-block elements are as follows:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30

There are also three other rows of d-block elements (Y–Cd, La–Hg, Ac–Cn).

They are called 'd-block' elements because the subshell being filled across this series is the 3d subshell. The electron configurations range from [Ar] $4s^2$ $3d^1$ for scandium to [Ar] $4s^2$ $3d^{10}$ for zinc:

Sc [Ar] $4s^2 3d^1$	Ti [Ar] $4s^2 3d^2$	V [Ar] $4s^2 3d^3$	Cr [Ar] $4s^1 3d^5$	Mn [Ar] $4s^2 3d^5$
Fe [Ar] $4s^2 3d^6$	Co [Ar] $4s^2 3d^7$	Ni [Ar] $4s^2 3d^8$	Cu [Ar] $4s^1 3d^{10}$	Zn [Ar] $4s^2 3d^{10}$

EXAM TIP

Remember, chromium and copper have slightly different electron configurations.

The transition metals or **transition elements** can be defined as different from 'the d-block elements'.

The IUPAC definition of a transition element is 'an element whose atoms have an incomplete (partially filled) d subshell or forms positive ions with an incomplete (partially filled) d subshell.'

According to the IUPAC definition, zinc is not classified as a transition element because the Zn atom does not have a partially filled d subshell and neither does the only ion it forms, the 2+ ion, with electron configuration $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$. Zinc also does not exhibit some of the typical characteristic properties of transition elements detailed in the next section (e.g. it does not form coloured compounds).

KEY POINT

Zinc is not a transition element.

No clear definition of what is meant by a transition element is given in the current IB syllabus. The definition that has been used in previous IB syllabuses is slightly different from the IUPAC definition:

a transition element is an element that forms at least one stable oxidation state (other than zero) with a partially filled d subshell.

According to this definition, zinc is also not counted as a transition element, but whether scandium should be classified as a transition metal is a bit more interesting. In virtually every compound, scandium has an oxidation state of +3 (no d electrons); however, it also forms a couple of compounds (ScH_2 and $CsScCl_3$) with a formal oxidation state of +2, but the bonding in these compounds is more complicated and they do not necessarily contain the 2+ ion.

EXAM TIP

The terms *transition metal* and *transition element* are used interchangeably.

Properties of the transition elements

If we look at the properties of the elements in Period 3 from Na to Ar, we can see that there is a large variation in their properties. They range from sodium, a low melting point, reactive metal, to silicon, a metalloid with a covalent network structure and a high melting point, to chlorine, a reactive diatomic gas, and argon, a highly unreactive monatomic gas. It is not possible to assign any characteristic properties to the elements of Period 3. The transition elements form a set of nine elements across the periodic table, but they are much more similar to each other than the elements across Period 3, and it *is* possible to assign a set of characteristic properties. For instance, they are all metals rather than showing a change from metal to non-metal.

The variation in first ionisation energy and atomic radius of the transition elements and Period 3 elements are compared in Figures 10.30 and 10.31. The variation of ionisation energy and atomic radius across the series of the transition elements is much smaller than across Period 3.

This is because the 3d electrons shield the 4s electrons to a certain extent and increased shielding as more 3d electrons are added largely offsets the increase in nuclear charge from left to right.

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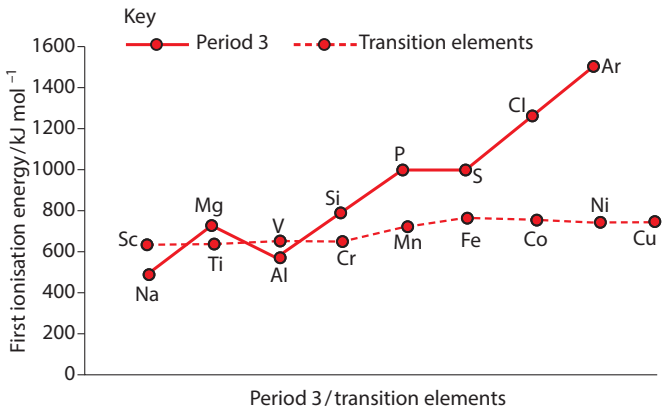

Figure 10.30: A comparison of the variation of first ionisation energy across Period 3 with that across the transition metal series.

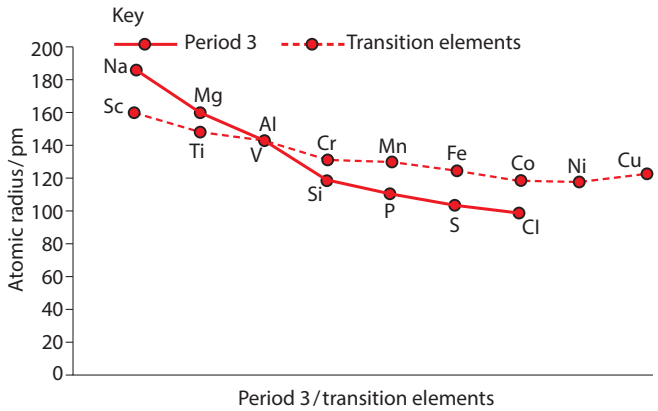

Figure 10.31: A comparison of the variation of atomic radius across Period 3 with that across the transition metal series.

The characteristic properties of transition elements are as follows:

- Transition elements are all typical metals – they have high melting points and densities.
- Transition elements can exhibit more than one oxidation state in compounds/complexes.
- Transition elements form complex ions.
- Transition elements form coloured compounds/complexes.
- Transition elements and their compounds/complexes can act as **catalysts** in many reactions.
- Compounds of transition elements can exhibit magnetic properties.

The metallic properties of transition elements were discussed in Chapter 8; the other properties will be discussed in more detail next.

KEY POINT

The properties of transition elements can be largely related to the presence of partially filled 3d subshells and the involvement of 3d electrons in bonding/reactions.

Ionisation of transition elements

Transition elements form positive ions. The electron configurations of transition element ions were discussed in Chapter 3. It is important to remember the order in which electrons are removed.

KEY POINT

The 4s electrons are always removed before the 3d electrons when an ion is formed.

The electron configurations of some transition metal ions are shown in Table 10.11.

Element	Electron configuration	Ion	Electron configuration
Cr	[Ar] $4s^1$ $3d^5$	Cr^{2+}	[Ar] $3d^4$
		Cr^{3+}	[Ar] $3d^3$
Mn	[Ar] $4s^2$ $3d^5$	Mn^{2+}	[Ar] $3d^5$
Fe	[Ar] $4s^2$ $3d^6$	Fe^{2+}	[Ar] $3d^6$
		Fe^{3+}	[Ar] $3d^5$
Co	[Ar] $4s^2$ $3d^7$	Co^{2+}	[Ar] $3d^7$
Cu	[Ar] $4s^1$ $3d^{10}$	Cu^+	[Ar] $3d^{10}$
		Cu^{2+}	[Ar] $3d^9$

Table 10.11: Electron configurations of transition elements and their ions.

Variable oxidation states

The positive oxidation states exhibited by the transition elements are shown in Figure 10.32. The greatest number of different oxidation states and the highest oxidation states are found in the middle of the series.

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				Mn				
			Cr	+7	Fe			
		V	+6	+6	+6			
	Ti	+5	+5	+5	+5	Co	Ni	Cu
Sc	+4	+4	+4	+4	+4	+4	+4	+4
+3	+3	+3	+3	+3	+3	+3	+3	+3
	+2	+2	+2	+2	+2	+2	+2	+2
	+1	+1	+1	+1	+1	+1	+1	+1
0	0	0	0	0	+0	0	0	0

Figure 10.32: Oxidation states of transition elements in compounds. Not all oxidation states are common – more common oxidation states are highlighted in yellow.

From scandium to manganese, there is an increase in the total number of electrons in the 4s and 3d subshell, so the maximum oxidation state increases. Manganese has the electron configuration [Ar] $4s^2$ $3d^5$ and, therefore, a maximum oxidation state of +7. Iron has 8 electrons in the 4s and 3d subshell and would be expected to have a maximum oxidation state of +8, but as the nuclear charge increases from left to right across the transition element series, and the 3d electrons are more strongly attracted, it becomes more difficult to reach the highest oxidation states towards the right-hand side of the series. The chemistry of copper and nickel is, for this reason, dominated by the lower oxidation states.

KEY POINT

All transition elements (except scandium) show oxidation state +2. In most cases, this is because they have two electrons in the 4s subshell, and removal of these generates an oxidation state of +2.

Why more than one oxidation state?

The 4s and 3d subshell are close in energy, and there are no big jumps in the successive ionisation energies when the 4s and 3d electrons are removed. Therefore, the number of electrons lost will depend on a variety of factors, such as lattice enthalpy, ionisation energy and hydration enthalpy. Electrons are not removed to generate the nearest noble gas electron configuration.

The graph in Figure 10.33 shows a comparison of the first seven ionisation energies of magnesium and manganese.

It can be seen that there is a very large jump between the second and third ionisation energies of magnesium, corresponding to removing the second electron from the 3s subshell but the third electron from the 2p subshell. There is a large energy difference between the 3s and 2p subshells, and Mg only forms a 2+ ion. In manganese, the first two electrons are removed from the 4s subshell, but the third electron is removed from the 3d subshell. The 4s and 3d subshells are very close together in

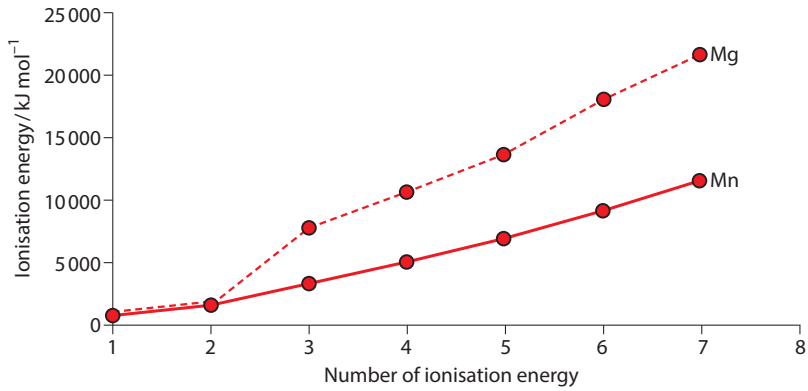

Figure 10.33: Comparison of successive ionisation energies of magnesium and manganese.

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energy, and there are no large jumps in the successive ionisation energies of manganese. This means that manganese can form a variety of oxidation states.

Magnetic properties of transition element compounds

The presence of unpaired d electrons causes some transition element ions/compounds to be **paramagnetic**. The compounds of main group elements do not usually contain unpaired electrons and are said to be **diamagnetic**.

- Paramagnetism is caused by unpaired electrons – paramagnetic substances are attracted by a magnetic field.
- Diamagnetism is caused by paired electrons – diamagnetic substances are repelled slightly by a magnetic field.

All substances have some paired electrons, and so, all substances exhibit diamagnetism. However, the diamagnetic effect is much smaller than the paramagnetic effect, and so, if there are any unpaired electrons present, the paramagnetic effect will dominate, and the substance will be paramagnetic overall and attracted by a magnetic field. The more unpaired electrons, the greater the paramagnetism (magnetic moment).

An example of a main group compound that is paramagnetic is NO_2. If you count up the electrons, you will see that it has an odd number and there will, therefore, be an unpaired electron.

EXAM TIP

You do not need to know the terms paramagnetic and diamagnetic.

Complex ions

Transition element ions form many complexes/complex ions. A **complex ion** consists of a central metal ion surrounded by **ligands**.

KEY POINT

Ligands are negative ions or neutral molecules that have lone pairs of electrons. They use the lone pairs to bond to a metal ion to form a complex ion.

Coordination bonds are formed between the ligand and the transition element ion.

The structure of $[Fe(H_2O)_6]^{2+}$ is shown in Figure 10.34.

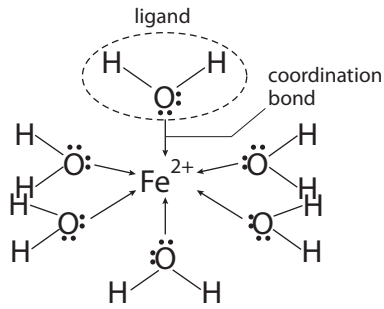

Figure 10.34: A complex ion is formed when ligands bond to a transition element ion. The ligands donate lone pairs into vacant orbitals (3d, 4s or 4p) on the transition element ion.

H_2O is the ligand in this complex ion and each H_2O donates a lone pair of electrons to the Fe^{2+} ion to form a coordination bond.

KEY POINT

A ligand must possess a lone pair of electrons.

The shape of this complex ion is octahedral, and it is called the hexaaquairon(II) ion. The complex ion is usually drawn as shown in Figure 10.35.

Link

A ligand is a Lewis base. When a ligand reacts with a transition metal ion, it donates its lone pair of electrons (acting as a Lewis base) to the transition element ion. The transition element ion accepts the pair of electrons – it is a Lewis acid. This is discussed in more detail in Chapter 22.

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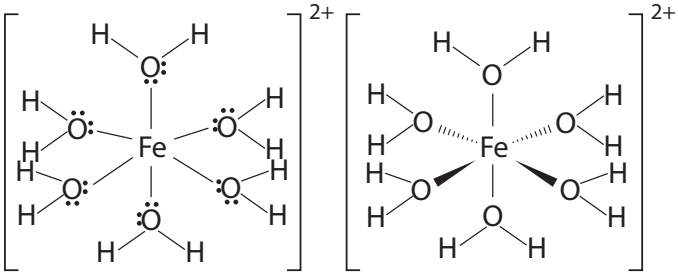
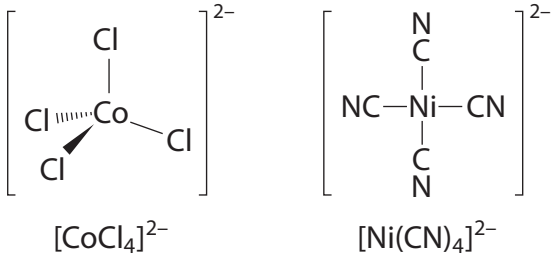


Figure 10.35: How the $[Fe(H_2O)_6]^{2+}$ complex ion is usually drawn. The right-hand diagram shows the octahedral shape more clearly.

All transition elements, with the exception of titanium and scandium, form an octahedral complex ion with the formula $[M(H_2O)_6]^{2+}$ in aqueous solution.

Complex ions can have various shapes, depending on the number of ligands. However, shapes cannot be worked out using the valence shell electron-pair repulsion theory (see Chapter 7, section 7.2) because more subtle factors also govern the overall shape. If a complex ion contains six ligands, it will almost certainly be octahedral, but complexes containing four ligands may be tetrahedral or square planar (Figure 10.36).



$[CoCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$

Figure 10.36: $[CoCl_4]^{2-}$ is tetrahedral, but $[Ni(CN)_4]^{2-}$ is square planar.

EXAM TIP

You should understand the bonding in complex ions and be able to draw an octahedral complex ion, but you do not need to learn the formulas of individual complex ions.

Complex ions can undergo substitution reactions in which, for example, H_2O ligands can be replaced by other ligands. For example, in the addition of concentrated hydrochloric acid to blue copper(II) sulfate solution:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

blue yellow

As the acid is added, the yellow $[CuCl_4]^{2-}$ complex ion is formed. So, the solution changes colour from blue to green (a mixture of blue and yellow). According to Le Chatelier's principle (see Chapter 18), the position of the equilibrium shifts to the right as Cl^- (from hydrochloric acid) is added, to reduce the concentration of Cl^-.

The oxidation state of a transition element in a complex ion

The oxidation state of a transition element in a complex ion can be worked out from the charges on the ligands. Ligands may be either neutral or negatively charged (see Table 10.12).

Neutral ligands	1– ligands
H_2O	Cl^-
NH_3	CN^-
CO	Br^-
	OH^-

Table 10.12: Charges on ligands.

In $[Fe(H_2O)_6]^{2+}$, all the ligands are neutral water molecules. The overall charge on the ion is just due to the iron ion, so the oxidation state of iron must be +2.

In $[Ni(CN)_4]^{2-}$, all the ligands have a 1– charge, so the total charge from all four ligands is 4–. The overall charge on the ion is 2–; so, the oxidation state of nickel must be +2 to cancel out 2– from the 4– charge.

In $[Fe(H_2O)_5(OH)]^{2+}$, five of the ligands are neutral water molecules and one ligand is OH^-. The total charge of the ligands is, therefore, 1–. The overall charge is 2+, so the oxidation state of iron must be +3.

This can be summarised in an equation:

oxidation state of transition metal ion =
charge on complex ion − total charge on ligands

So, in the last example:
oxidation state of Fe = (+2) – (–1) = +3

Looking at these calculations, you can see that a key part is being able to work out whether a ligand is neutral or negatively charged. The ligands that are neutral will usually be molecules that you recognise, such as H_2O, NH_3 and CO. If something does not look like a neutral molecule (e.g. SCN), then it is almost certainly a

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negatively charged ion (SCN^-). There are some ligands that have charges numerically higher than 1–. When O is present in a complex ion, for example, MnO_4^- or $[VO(OH)(H_2O)_4]^+$, it will be covalently bonded to the transition metal ion, usually with a double bond, but, for working out the oxidation state, it will be assumed to have an oxidation state of –2:

$[VO(OH)(H_2O)_4]^+$

total charge on ligands = (2–) + (1–) + (4 × 0) = 3–

oxidation state of transition element ion = charge on complex ion − total charge on ligands

oxidation state of V = (+1) – (–3) = +4

Working out the overall charge on a complex ion

If the oxidation state (charge) of the central transition element ion and the charges on the ligands are known, the overall charge on the complex ion can be worked out. An equation for this can be generated by rearranging the equation from the previous section:

charge on complex ion = oxidation state (charge) of transition element ion + total charge on ligands

WORKED EXAMPLE 10.2

Platinum(II) can form a complex ion with one ammonia and three chloride ligands. What is the overall charge and formula of the complex ion?

Answer

Platinum(II) has a charge of 2+, ammonia is a neutral ligand (NH_3) and chloride has a 1– charge (Cl^-):

total charge on ligands = (0) + (3 × 1–) = 3–

charge on complex ion = oxidation state (charge) of transition metal ion + total charge on ligands

charge on complex ion = (+2) + (3–) = 1–

The formula of the complex ion is $[Pt(NH_3)Cl_3]^-$.

Link

Charges/oxidation states in complex ions are discussed again in Chapter 20.

Catalytic ability

Transition elements and their compounds/complexes can act as catalysts.

KEY POINT

A catalyst is a substance that speeds up a chemical reaction but is unchanged at the end of the reaction.

For example, finely divided iron is the catalyst in the Haber process in the production of ammonia:

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

Iron in this reaction is a heterogeneous catalyst (one that is in a different physical state from the reactants), but transition metal compounds often act as homogeneous catalysts (ones that are in the same phase as the reactants). The ability to act as a catalyst relies on a transition element atom or ion being able to coordinate other molecules/ions to form complex ions and having different oxidation states available so that electrons can be transferred to/from the coordinated groups (ligands).

Coloured complexes

The colours of some complex ions are shown in Table 10.13.

Complex ion	Colour
$[Cu(H_2O)_6]^{2+}$	blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	deep blue/violet
$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
$[Ni(H_2O)_6]^{2+}$	green

Table 10.13: The colours of some complex ions. You do not need to learn these colours.

In this section, we will look at how these colours arise.

In a gaseous transition metal ion, all the 3d orbitals have the same energy – they are degenerate. However, when the ion is surrounded by ligands in a complex ion, these d orbitals split into two groups at different energies. In an octahedral complex ion, $[ML_6]^{2+}$, there are two orbitals in the higher energy group and three orbitals in the lower energy group (Figure 10.37).

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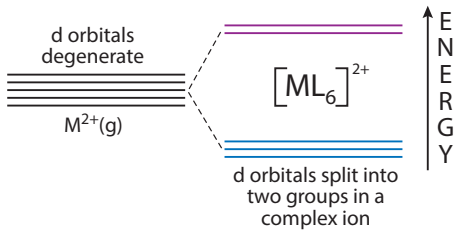

Figure 10.37: The splitting of d orbitals in a complex ion.

Energy, in the form of a certain frequency of visible light, can be absorbed to promote an electron from the lower set of d orbitals to the higher set (Figure 10.38). This is sometimes called a d–d (d to d) transition.

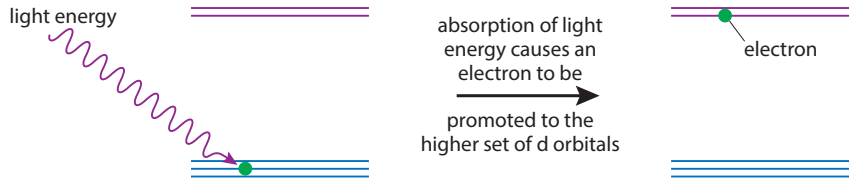

Figure 10.38: Absorption of light by a complex ion.

White light (the light that is all around us) is a mixture of all colours (frequencies) of visible light. The colours that make up white light and their approximate wavelengths are shown in Figure 10.39.

Substances appear coloured because they absorb certain frequencies of visible light. All the other frequencies of light are transmitted/reflected. If some frequencies (the ones absorbed to promote an electron) are removed from white light, it is no longer 'white', so the light transmitted/reflected is coloured.

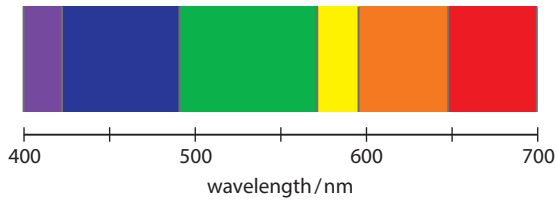

Figure 10.39: The colours that make up white light.

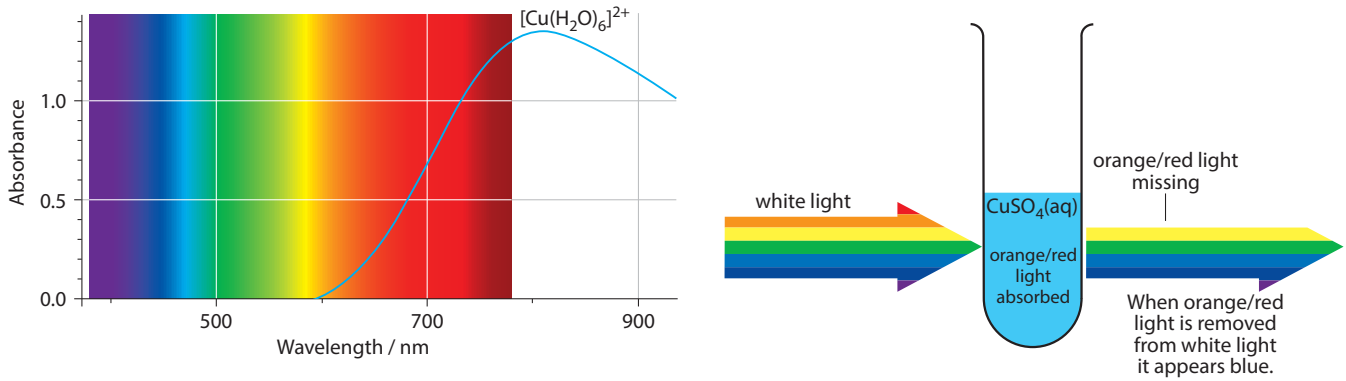

Figure 10.40: Colour and absorption. **a** The absorption spectrum of copper(II) sulfate solution; **b** a diagrammatic representation of the absorption of certain colours of light.

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KEY POINT

For a substance to appear coloured, some frequencies of light in the visible region of the spectrum must be absorbed.

A solution of copper(II) sulfate contains the complex ion, $[Cu(H_2O_6]^{2+}$, which is responsible for the blue colour of the solution. When white light passes through copper sulfate solution (Figure 10.40), orange/red light is absorbed, promoting an electron from the lower set of d orbitals to the higher set. This means that the light that is transmitted (comes out) contains all the colours of the spectrum, except orange/red, and this mixture of colours gives rise to the blue colour of copper(II) sulfate solution.

What colour will a complex ion be?

If a substance only absorbs in the UV or IR region, it will be colourless.

The colour of a substance will appear to an observer as the *complementary* colour to the light that is absorbed. A colour wheel (Figure 10.41) shows which pairs of colours are complementary (opposite each other in the colour wheel).

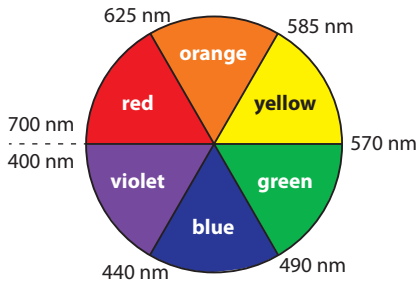

Figure 10.41: A colour wheel – complementary colours are opposite each other in the colour wheel; therefore, blue is complementary to orange and green is complementary to red. The wavelengths are approximate – there is no definitive range for each colour.

If we know the colour of light absorbed, we can work out the colour of the complex ion and vice versa. For example, if a solution absorbs blue light it will appear orange – orange is the complementary colour to blue.

Copper (II) sulfate solution absorbs both orange and red light, and the colour is due to a mixture of blue and green light, sometimes called cyan.

We can also look at the frequencies/wavelengths absorbed/transmitted. For example, copper(II) sulfate solution absorbs in the range from 600 nm upwards (Figure 10.40 a). Light with wavelength in the range 400–600 nm is thus transmitted and this gives rise to the colour that we see.

The equation $c = f\lambda$ This can be used to convert between wavelengths and frequencies.

c is the speed of light (3.00×10^8 ms^{-1}), f is the frequency of light in Hz (s^{-1}), and λ is the wavelength of light in m.

WORKED EXAMPLE 10.3

A transition metal complex ion absorbs light in the range 535–610 THz. Deduce the colour of the complex ion.

Answer

THz stands for terahertz. The conversion between terahertz and hertz is given in the IB data booklet.

$535 \times 10^{12} = 5.35 \times 10^{14}$ Hz

$610 \times 10^{12} = 6.10 \times 10^{14}$ Hz

The colour wheel is labelled in terms of wavelengths in nm, so we need to convert to wavelengths using

$c = f\lambda$

$\lambda = c/f = 3.00 \times 10^8/(5.35 \times 10^{14}) = 5.61 \times 10^{-7}$ m

$\lambda = c/f = 3.00 \times 10^8/(6.10 \times 10^{14}) = 4.92 \times 10^{-7}$ m

Converting these to nm by dividing by 10^{-9} produces the range 492–561 nm.

Looking at the colour wheel in Figure 10.41, we can see that the wavelength range absorbed is in the green part of the spectrum, so green light is absorbed. The colour opposite green in the colour wheel is red, so the complex ion will appear red.

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Some complex ions are colourless

KEY POINT

A partially filled d subshell is required for a complex ion to be coloured.

Sc^{3+} and Ti^{4+} both have no electrons in the 3d subshell and so, are colourless – there are no d electrons to be promoted and therefore, no visible light is absorbed.

The Cu^{+} ion and the Zn^{2+} ion both have ten 3d electrons (Figure 10.42), and, as the higher energy set of d orbitals is full, it is not possible to promote an electron to the higher energy set of orbitals – there is no space for the electron. No light in the visible region of the spectrum is absorbed and these ions are colourless.

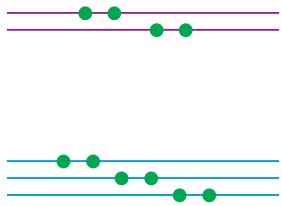

Figure 10.42: A Cu^{+} or Zn^{2+} ion has ten 3d electrons.

EXAM TIP

The following points will be important in an exam answer about why a transition metal complex is coloured:

- d orbitals split into two groups at different energies
- certain frequencies/wavelengths of visible light are absorbed...
- ...to promote an electron from the lower energy set of d orbitals to the higher energy set of d orbitals
- the complementary colour is transmitted/reflected
- a partially filled d subshell is required.

Factors that affect the colour of transition metal complexes

At the simplest level, the colours of transition element complexes can be related to the amount of splitting of the d orbitals. For example, if there is a greater difference in energy between the lower and higher set of d orbitals, then a higher frequency (shorter wavelength) of light will be absorbed and the complementary colour will be different. The following factors all affect the colour of a transition metal complex ion:

- the identity of the metal
- the oxidation state of the metal
- the coordination number (number of coordinated atoms)
- the shape of the complex ion
- the nature of the ligand.

Identity of the metal

Complexes of different metals in the same oxidation state have different colours. For example, $Mn^{2+}(aq)$ ($3d^5$) is very pale pink/colourless, but $Fe^{2+}(aq)$ ($3d^6$) is pale green. Different metal ions have different electron configurations and, because colours are caused by electron transitions, different arrangements of electrons give rise to different colours.

If isoelectronic (same number of electrons) transition metal ion complexes are considered, such as $[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ (both metal ions have five 3d electrons), then there will be a greater amount of splitting of the d orbitals in $[Fe(H_2O)_6]^{3+}$. A higher nuclear charge on the metal ion (26+ for Fe and 25+ for Mn) causes the ligands to be pulled in more closely in an Fe^{3+} complex so that there is greater repulsion between the ligand electrons and the d electrons of the transition metal ion and therefore greater splitting of the d orbitals.

Oxidation state of the metal

The same metal has different colours in different oxidation states. For example: $[Fe(H_2O)_6]^{2+}(aq)$ is pale green and $[Fe(H_2O)_6]^{3+}(aq)$ is pale violet.

There are two reasons for this:

- the electron configurations of the ions are different
- a higher charge on the metal ion causes the ligands to be pulled in more closely so that there is greater

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repulsion between the ligand electrons and the d electrons of the transition metal ion, and therefore, greater splitting of the d orbitals.

KEY POINT

In general, for complex ions containing the same metal and the same ligands, the greater the oxidation state of the transition metal, the greater the splitting of the d orbitals.

Coordination number and shape

The coordination number here refers to the number of ligands attached to the transition metal ion in a complex ion. So, in an octahedral complex ion, the coordination number of the metal is six, because it is bonded to six ligands. With different numbers of ligands and, therefore, different shapes, the set of five d orbitals will be split in different ways (three lower and two higher is only for the octahedral shape), and so, different frequencies of light will be absorbed.

Consider the addition of concentrated hydrochloric acid to blue copper(II) sulfate solution:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

blue — yellow

As the acid is added, the tetrahedral, yellow $[CuCl_4]^{2-}$ complex ion is formed. The solution changes colour from blue to green (a mixture of blue and yellow). The splitting of the d orbitals is much less in a tetrahedral complex than in an octahedral complex and the splitting pattern is also different (two at lower energy and three at higher energy).

Nature of the ligand

The same metal ion can exhibit different colours with different ligands. This is mainly because of the different amount of splitting of the d orbitals caused by different ligands.

Ligands can be arranged into a **spectrochemical series**, according to how much they cause the d orbitals to split:

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CO \approx CN^-$$

So, a chloride ion causes greater splitting of the d orbitals than an iodide ion, and an ammonia molecule causes greater splitting of the d orbitals than a water molecule. $[Cu(NH_3)_4(H_2O)_2]^{2+}$, therefore, has a larger energy gap between the two sets of d orbitals than $[Cu(H_2O)_6]^{2+}$ (Figure 10.43) and absorbs a shorter wavelength (higher frequency/energy) of light. $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is dark blue/violet as it absorbs more in the yellow–green (higher frequency) region of the visible spectrum.

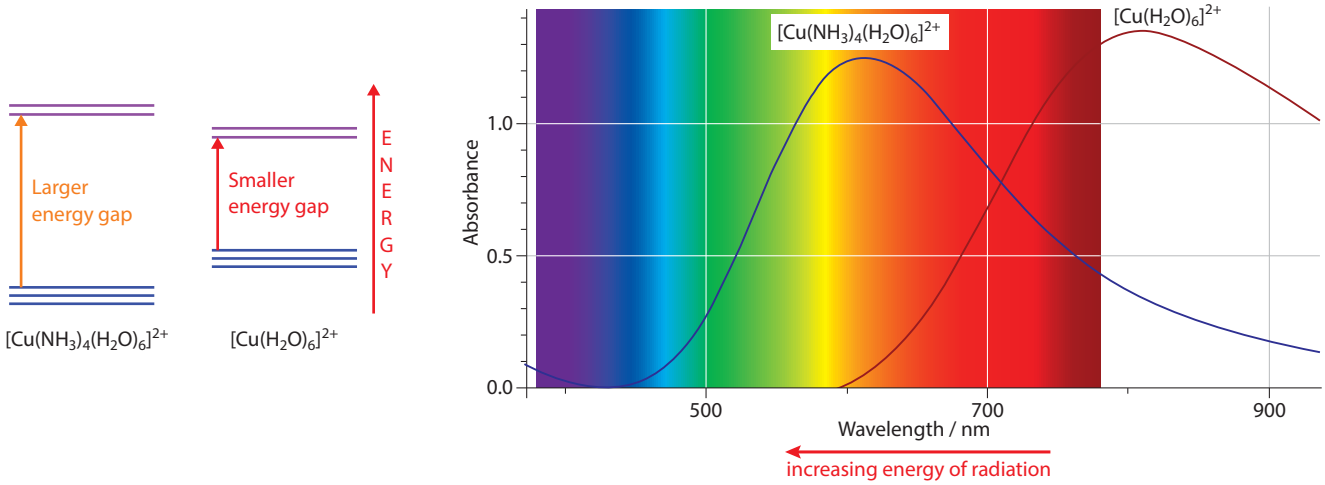

Figure 10.43: $[Cu(H_2O)_6]^{2+}(aq)$ is blue – it has a smaller energy gap between the two sets of d orbitals and absorbs mostly at the red–orange end of the spectrum. $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is dark blue/violet – it has a larger energy gap between the two sets of d orbitals and absorbs more in the yellow–green (shorter wavelength) region of the visible spectrum.

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TEST YOUR UNDERSTANDING

24 State the full electron configuration of the following ions:

a Ni^{2+} **b** Co^{3+}

c V^{3+} **d** Mn^{4+}.

25 Deduce the oxidation state of the transition element in each of these complex ions:

a $[Ni(H_2O)_6]^{2+}$ **b** $[Fe(CN)_6]^{4-}$

c $[MnCl_4]^{2-}$ **d** $[Co(NH_3)_6]^{3+}$

e $[Co(NH_3)_5Br]^{2+}$ **f** $[Co(NH_3)_4Br_2]^{+}$

g $[FeO_4]^{2-}$ **h** $Ni(CO)_4$.

26 State the charge on each of the complex ions:

a $[Fe(CN)_6]^{?}$ contains iron(III)

b $[CuCl_4]^{?}$ contains copper(II)

c $[Ag(NH_3)_2]^{?}$ contains silver(I)

d $[Ti(OH)(H_2O)_5]^{?}$ contains titanium(III).

27 Which of the following compounds/complex ions are likely to be coloured?

TiF_4, VF_5, MnF_3, CoF_2, CuI, $[Zn(H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

28 Which complex ion would be expected to absorb the longer wavelength of light?

$[Fe(H_2O)_6]^{2+}$ or $[Fe(NH_3)_6]^{2+}$

29 A complex ion absorbs light in the range 625 – 660 THz. Deduce the colour of the complex ion.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
describe the structure of the periodic table	10.1			
deduce the electron configuration of an element from its position in the periodic table	10.1			
explain the trends in the properties of elements down a group and across a period	10.2			
describe and explain the reactions of Group 1 elements with water	10.3			
describe and explain the reactions of Group 17 elements with halide ions	10.4			
describe the trends in the acid–base behaviour of oxides	10.4			

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CONTINUED

I can...	Section	Needs more work	Nearly there	Confident to move on
write equations for the reactions of the oxides of Group 1 and 2 metals, and the oxides of carbon and sulfur, with water	10.4			
explain acid rain and ocean acidification	10.4			
deduce oxidation states for elements in molecules and ions	10.5			
name compounds using oxidation states	10.5			
explain the exception to the general increase in first ionisation energy across a period.	10.6			
describe and explain the characteristic properties of transition elements	10.7			
explain why transition element complexes are coloured	10.7			

REFLECTION

To what extent do you feel that your understanding of this topic is active or passive?

Could you explain the trends to someone else? Could you write equations for the reactions that are required on the syllabus?

Can you explain to another student why transition metal complexes are coloured? Does your explanation highlight any gaps in your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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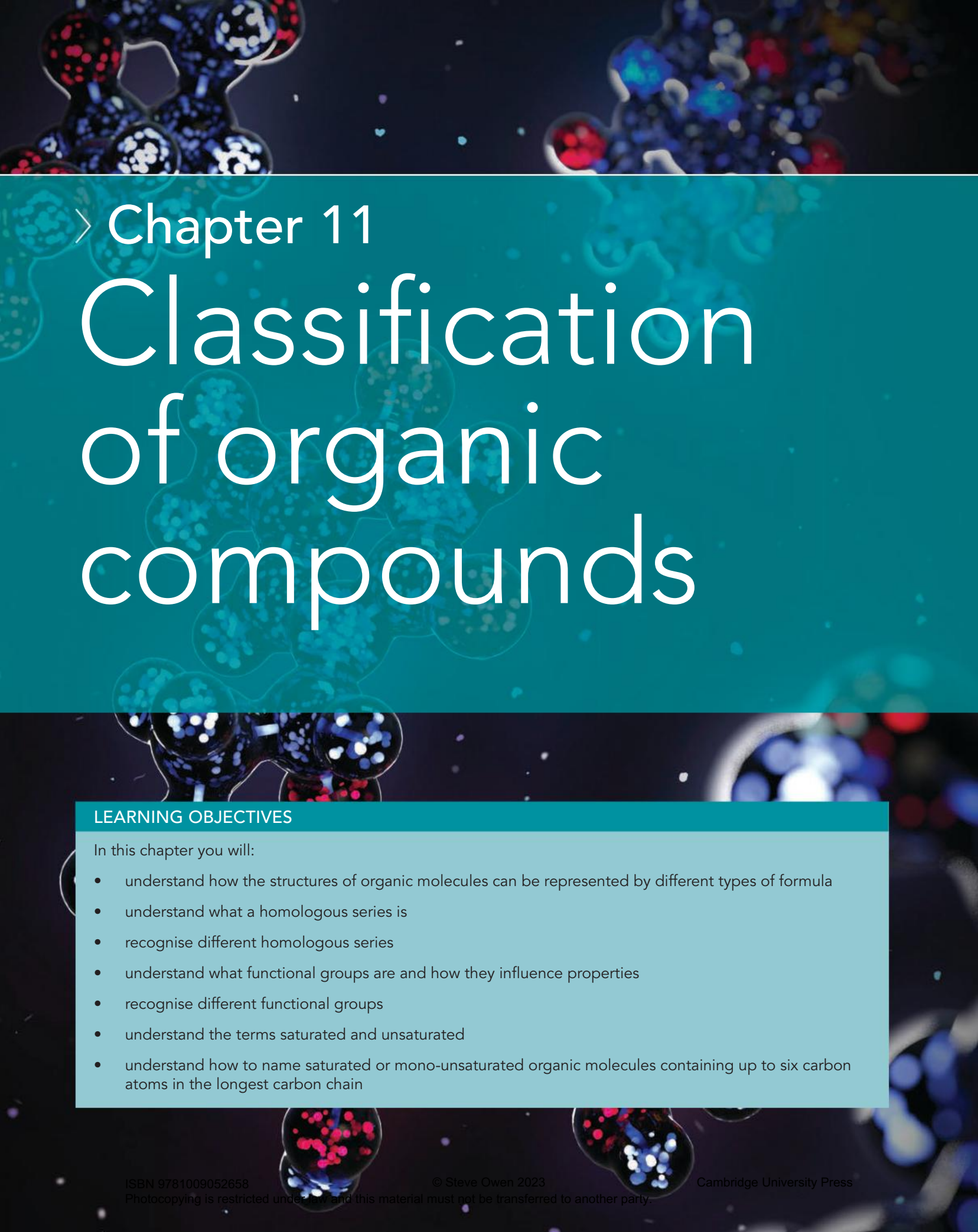

Chapter 11

Classification of organic compounds

LEARNING OBJECTIVES

In this chapter you will:

- understand how the structures of organic molecules can be represented by different types of formula
- understand what a homologous series is
- recognise different homologous series
- understand what functional groups are and how they influence properties
- recognise different functional groups
- understand the terms saturated and unsaturated
- understand how to name saturated or mono-unsaturated organic molecules containing up to six carbon atoms in the longest carbon chain

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CONTINUED

- understand what structural isomers are
- draw structural isomers of compounds
- understand the classification of groups as primary, secondary or tertiary

- understand the term stereoisomerism
- understand *cis–trans* isomerism
- understand what chirality is
- draw enantiomers using stereochemical formulas
- understand how mass spectrometry can be used to provide information about the structure of an organic compound
- understand how infrared (IR) spectroscopy can be used to provide information about the structure of an organic compound
- understand what greenhouse gases are
- learn how ^{1}H nuclear magnetic resonance (NMR) can be used to provide information about the structure of an organic compound
- use spectroscopic data to deduce the structure of an organic compound.

GUIDING QUESTIONS

- What are organic compounds?
- How are organic compounds named?
- What are isomers?
- How do we work out the structures of organic compounds?

Introduction

Organic compounds include methane (the main constituent of natural gas), caffeine, paracetamol, ibuprofen and virtually all the medicines we use, dyes, plastics, proteins, DNA… the list is virtually endless. What they all have in common is that they contain carbon.

Organic chemistry is the study of carbon compounds, and usually refers to compounds containing the C—H bond, although there are also compounds, such as CCl_4, which do not contain H, that are usually classed as organic compounds. Carbon compounds classed as inorganic compounds, rather than organic compounds, include carbon dioxide, carbon monoxide and carbonates.

The chemistry of carbon is more extensive than that of any other element, and there are more organic compounds than all other compounds put together. There are so many organic compounds because carbon atoms can join together to form chains and rings – a property called catenation.

The source of many carbon compounds is crude oil (petroleum), and many substances can be separated from this complex mixture using fractional distillation. These molecules form the basis of organic synthesis reactions, in which ever-more-complex molecules are made to be used as medicines, cosmetics, polymers, etc.

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INTERNATIONAL MINDEDNESS

Most of the world's oil reserves are controlled by just a few countries. It is estimated that more than 80% of the world's oil reserves are controlled by OPEC, an intergovernmental organisation of 13 countries founded in 1960. According to its website,

'OPEC's objective is to co-ordinate and unify petroleum policies among Member Countries, in order to secure fair and stable prices for petroleum producers; an efficient, economic and regular supply of petroleum to consuming nations; and a fair return on capital to those investing in the industry.'

The control of oil has already been the source of conflicts between countries – like the 1990 Gulf War – and is likely to be even more of a political issue in the future as oil reserves dwindle. One of the largest oil-producing countries is the USA. For the first time in history, during the COVID-19 crisis, the price of US crude oil became negative, meaning that oil producers were paying to get rid of oil!

THEORY OF KNOWLEDGE

Is the statement 'there are more organic compounds than all other compounds put together' true? Has someone counted all the compounds, or has this fact been deduced from other knowledge? At what point can we confidently make a statement like this? Can we ever know that it is true? Are there cases where people make statements where they cannot possibly know if they are true or not?

It is actually often quoted that 'there are more carbon compounds than compounds of all other elements put together'. Where did this statement originate? Did one person say it and other people thought it sounded reasonable and then it just gets repeated as a fact? How true is this statement? Well, almost all of these carbon compounds are organic compounds, virtually all of which also contain hydrogen. There are, however, also a large number of inorganic hydrogen compounds, so are there actually more hydrogen-containing compounds than carbon-containing compounds?

11.1 The structures of organic molecules

The structure of butane is shown in Figure 11.1.

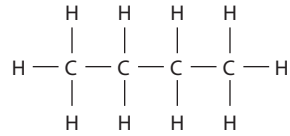

Figure 11.1: The full structural formula of butane.

Every organic molecule can be represented by a molecular formula, which just shows the number of atoms of each element present in a molecule, e.g., the molecular formula of butane is C_4H_{10}. But the molecular formula does not tell us anything about the structure of the molecule, and there is another molecule that also has the molecular formula C_4H_{10} (Figure 11.2).

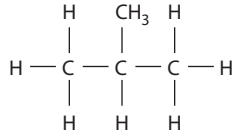

Figure 11.2: 2-methylpropane has the molecular formula C_4H_{10}.

We can distinguish between butane and 2-methylpropane by giving more detail in the formula. The structure of butane can be represented as $CH_3CH_2CH_2CH_3$; this is called a **condensed structural formula** and shows how the atoms are joined together in a molecule but does not show all of the bonds. The condensed structural formula of 2-methylpropane is $(CH_3)_3CH$, which shows three CH_3 (methyl) groups joined to the central carbon.

The clearest way to show the structure of an organic molecule is to use a **full structural formula**, also called a displayed or graphic formula.

KEY POINT

A full structural formula shows all atoms and all bonds in a molecule.

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The full structural formula of butane is shown in Figure 11.1. We often draw molecules using a mixture of full and condensed structures for convenience, and so, the structure of 2-methylpropane (Figure 11.2) shows some bonds and atoms, but has the CH_3 group in a condensed form, because it takes up less space.

EXAM TIP

You must show all bonds when asked to draw a full structural formula. It is important to realise that Figure 11.2 does not show a full structural formula, as not all the bonds are shown.

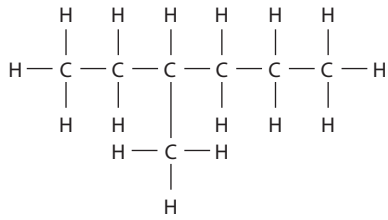
Link

Molecular and empirical formulas were discussed in Chapter 4.

Converting between condensed and full structural formulas

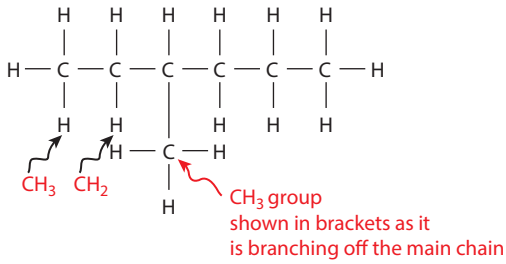
WORKED EXAMPLE 11.1

Deduce the condensed structural formula of the molecule shown.



Answer

We work from left to right (choose which direction makes the process easier) writing each group in condensed form. Any groups attached to the main chain that consist of more than one atom are shown in brackets.



$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$ is the condensed formula.

With long chains, multiple CH_2 groups may be shown in brackets, e.g., $CH_3CH_2CH(CH_3)(CH_2)_2CH_3$.

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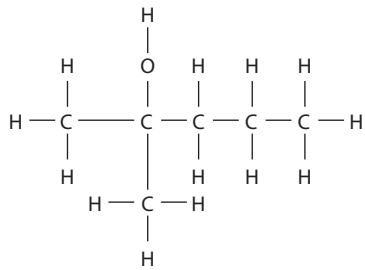
WORKED EXAMPLE 11.2

Write the full structural formula of the molecule with condensed formula $(CH_3)_2C(OH)CH_2CH_2CH_3$.

Answer

$(CH_3)_2$ indicates that there are two CH_3 groups joined to the same carbon. Also attached to that carbon is an OH group. It is probably easiest to start with that carbon and join on the two CH_3 groups and the OH group. The rest of the groups in the chain are then added to produce a full structural formula:

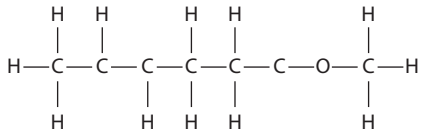


WORKED EXAMPLE 11.3

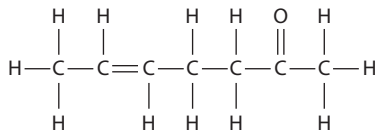
Draw the full structural formula for $CH_3CHCHCH_2CH_2COCH_3$.

Answer

If we work from left to right putting in the bonds, we get



However, this cannot be correct because carbon always forms four bonds. We have used up all the atoms, so now we have to look at putting in some multiple bonds. A C=C bond between carbons 2 and 3 solves one problem, but O can only form two bonds; therefore, we cannot add any other bonds to the structure as it is. So, the only solution is that there must be C=O on the penultimate carbon and not the C—O—C group:



Stereochemical formulas

Although we usually draw the full structurals formulas with 90° bond angles, it must be remembered that, with four electron pairs around each carbon atom, the shape is tetrahedral around each one, and butane should be more correctly drawn as shown in Figure 11.3.

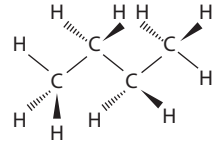


Figure 11.3: The stereochemical formula of butane showing the tetrahedral arrangement around the carbon atoms.

This type of structure is called a **stereochemical formula** and shows the spatial arrangement of the atoms/groups. Remember that a solid wedge represents a bond coming out of the plane of the paper, and a dashed wedge is a bond going into the paper. This type of structure is significantly less convenient to draw, and we only draw them when it is absolutely necessary to show the arrangement of the groups around a certain atom. It is only possible to draw one form of butane, so there is no real need to draw a stereochemical structure, but there are two forms of butan-2-ol and stereochemical structures are essential to distinguish between them (Figure 11.4).

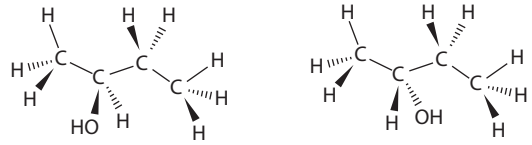


Figure 11.4: The two forms of butan-2-ol drawn using stereochemical formulas.

If you look carefully at the two molecules in Figure 11.4, you will see that it is not possible to put one on top of the other so that all atoms match up – they are different molecules.

We generally only, however, show the stereochemistry where it is absolutely necessary, and a more common representation of one of the forms of butan-2-ol is shown in Figure 11.5.

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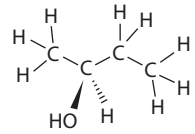


Figure 11.5: The stereochemistry is generally only shown around key atoms in structures.

Skeletal formulas

These are the simplest structures to draw and are commonly used by organic chemists, but they are probably also the most difficult to interpret until you get used to them. A **skeletal formula** is a representation of the structure of a molecule that shows just the bonds in the carbon skeleton and any groups joined to the carbon skeleton. Carbon atoms are not shown explicitly nor are hydrogen atoms joined to carbon atoms. A skeletal formula and the full structural formula for the same molecule are shown in Figure 11.6.

In a skeletal formula, each point or vertex in the structure represents a C atom with the appropriate number of H atoms. Hydrogen atoms are only generally shown when they are part of a group, such as OH, or are required to show the stereochemistry.

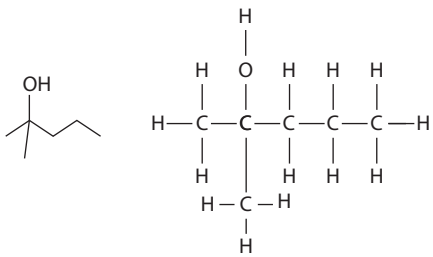
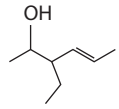


Figure 11.6: A skeletal formula and a full structural formula for 2-methylpentan-2-ol.

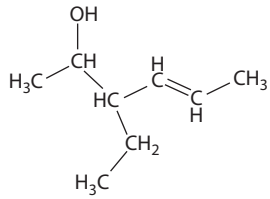
WORKED EXAMPLE 11.4

Deduce the molecular formula of the molecule shown:



Answer

Put a C at each vertex and add in the appropriate number of H atoms, remembering that C always forms four bonds:



Count up the total number of each atom to give the molecular formula: $C_8H_{16}O$

Models of organic structures

Models made with a molecular model kit or generated by a computer program can provide a useful way of visualising the structures of molecules. Some computer-generated models of butane (C_4H_{10}) are shown in Figure 11.7 and a photograph of a model of butane in Figure 11.8.

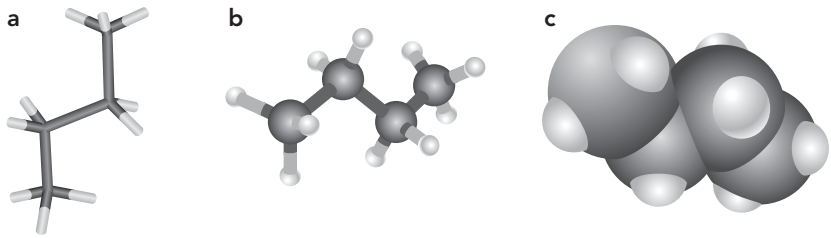


Figure 11.7: Computer-generated images of the structure of C_4H_{10}: **a** a stick model, **b** a ball and stick model and **c** a space-filling model.

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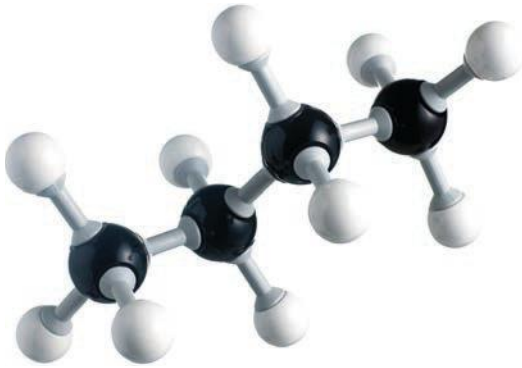


Figure 11.8: A model of the structure of C_4H_{10}.

Compounds containing a phenyl group

Benzene has the molecular formula C_6H_6, and its molecules have a planar, hexagonal ring of six carbon atoms with one hydrogen atom joined to each carbon. It is usually represented by the skeletal formula shown in Figure 11.9.

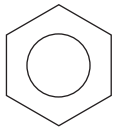


Figure 11.9: The usual representation of a molecule of benzene.

Benzene rings are common structural units in many organic compounds. In this case, they will have lost one or more hydrogen atoms to allow them to join onto other atoms and are referred to as *phenyl groups*.

When determining molecular formulas or condensed structural formulas for compounds that contain phenyl groups, it must be remembered that there is a carbon atom and, if there is nothing else attached, a hydrogen atom at each vertex. So, for example, methylbenzene has the molecular formula C_7H_8 and can be represented in different ways (Figure 11.10). The condensed structural formula of methylbenzene can be written as $C_6H_5CH_3$.

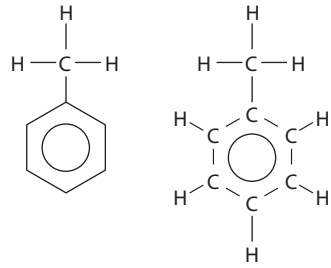


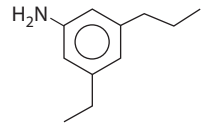
Figure 11.10: Representations of methylbenzene.

KEY POINT

Compounds that contain a phenyl group are described as aromatic. Organic compounds without phenyl groups are called **aliphatic**.

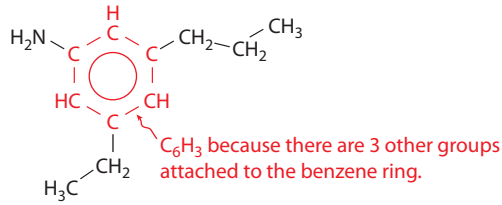
WORKED EXAMPLE 11.5

Deduce the molecular formula of the molecule shown:



Answer

Add in all the C atoms and then the H atoms. Remember that each C only forms three bonds in the phenyl group (the fourth bond is represented by the ring):



Count up the total number of each atom present in the molecule to give the molecular formula: $C_{11}H_{17}N$.

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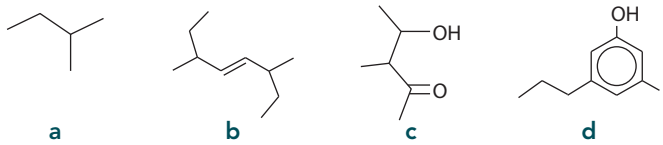
TEST YOUR UNDERSTANDING

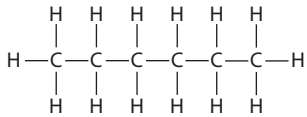
1 Determine the molecular formula of each molecule from the skeletal formula:



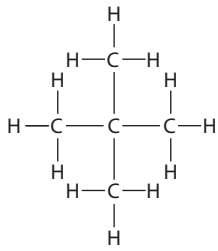
a b c d

2 Write condensed structural formulas for each of the following:

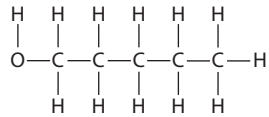
a



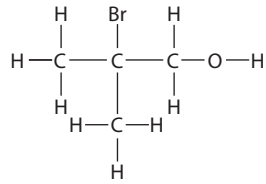
b



c



d



3 Draw full structural formulas for the following:

a $CH_3CH_2CH(CH_3)_2$

b $(CH_3)_3COH$

c $CH_3CH_2CHCH_2$

d $(CH_3)_2CO$

e $CH_3(CH_2)_3CH_2COCH_3$.

4 Draw a stereochemical formula for $CH_3CHBrCH_3$.

11.2 Homologous series and functional groups

KEY POINTS

A homologous series is a series of compounds that have the same functional group. Each member differs from the next by a common structural unit (usually —CH_2—).

A functional group is the atom or group of atoms in a molecule that gives it its characteristic chemical properties – this is the reactive part of a molecule. A functional group also influences the physical properties of a compound.

The straight-chain alkanes are a **homologous series**. The first six members are shown in Table 11.1.

The molecular formula of the members of a homologous series can be described by a general molecular formula, which can be used to determine the molecular formula of any member of the series.

For example, the molecular formula of all alkanes can be represented by the general formula C_nH_{2n+2}, and it can be deduced that, for example, eicosane, the alkane with 20 carbon atoms, has $(20 \times 2) + 2$, i.e., 42 hydrogen atoms and its molecular formula is $C_{20}H_{42}$.

The features of a homologous series are as follows:

- they can usually be described by a general molecular formula, e.g., C_nH_{2n+2} for alkanes (non-cyclic) and C_nH_{2n} for alkenes

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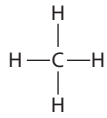
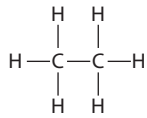
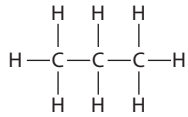
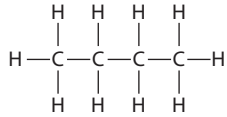
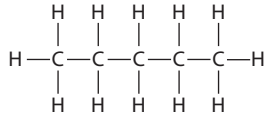
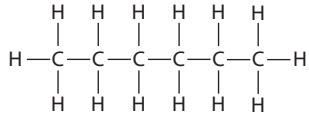
Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
methane	CH_4	CH_4	CH_4	
ethane	C_2H_6	CH_3	CH_3CH_3	
propane	C_3H_8	C_3H_8	$CH_3CH_2CH_3$	
butane	C_4H_{10}	C_2H_5	$CH_3CH_2CH_2CH_3$	
pentane	C_5H_{12}	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	
hexane	C_6H_{14}	C_3H_7	$CH_3CH_2CH_2CH_2CH_2CH_3$	

Table 11.1: The first six straight-chain alkanes.

- members of the series have the same functional group and, therefore, similar chemical properties
- members of the series show a gradation in physical properties, such as boiling point.

Although there is not really a functional group in alkanes, because only single C—C and C—H bonds are present, alkanes all react in the same way, for instance, they all undergo substitution reactions when reacted with chlorine in the presence of UV light (see Chapter 22, section 22.1).

The first five members of the homologous series of straight-chain alkenes with C=C between carbon 1 and 2 are shown in Table 11.2. Here the general formula is C_nH_{2n}. The functional group of alkenes is the C=C group. This group gives alkenes a set of characteristic chemical properties, for instance, they will react with bromine water to decolorise it (see Chapter 22, section 22.2).

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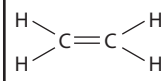
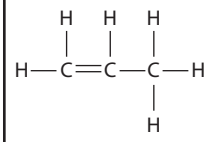
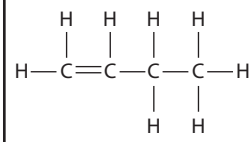
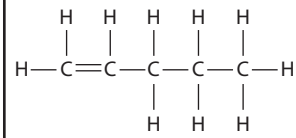
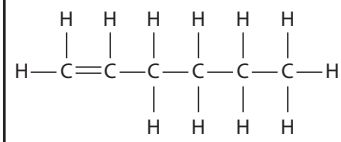
Name	Molecular formula	Empirical formula	Structural formula	
			Condensed	Full
ethene	C_2H_4	CH_2	CH_2CH_2	
prop-1-ene	C_3H_6	CH_2	CH_2CHCH_3	
but-1-ene	C_4H_8	CH_2	$CH_2CHCH_2CH_3$	
pent-1-ene	C_5H_{10}	CH_2	$CH_2CHCH_2CH_2CH_3$	
hex-1-ene	C_6H_{12}	CH_2	$CH_2CHCH_2CH_2CH_2CH_3$	

Table 11.2: The first five members of the alkene homologous series.

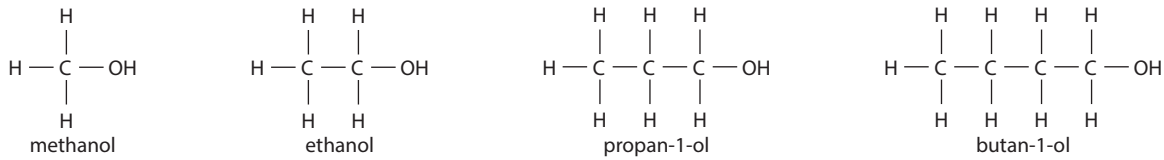


Figure 11.11: The first four members of the alcohol series.

The first four members of the homologous series of primary (see the section on classification of groups as primary, secondary and tertiary) straight-chain alcohols are shown in Figure 11.11.

Note that the diagrams in Figure 11.11 do not show the full structural formulas because the O—H bonds are not shown. However, it is a structural formula type that is often drawn to represent molecules.

Here, the general molecular formula is $C_nH_{2n+2}O$, which could also be written as $C_nH_{2n+1}OH$, to show that all the molecules contain an OH group.

The functional group of alcohols is the OH (hydroxyl) group. Because alcohols contain a different functional group to alkanes and alkenes, they react in a completely different way. The OH group also means that the alcohols have hydrogen bonding between molecules and, therefore, higher boiling points than alkanes and alkenes with a similar relative formula mass. Therefore, the functional group also influences physical properties.

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Hydrocarbons

Alkanes and alkenes are both classified as **hydrocarbons**.

KEY POINT

A hydrocarbon is a compound containing *only* carbon and hydrogen.

Alcohols are *not* hydrocarbons because they also contain oxygen.

Functional groups

As discussed previously, a functional group is the atom or group of atoms in a molecule that gives an organic molecule its characteristic chemical properties and influences the physical properties of the molecule.

Organic chemistry is mostly the chemistry of the transformation of functional groups. Most of an organic molecule will usually be just a hydrocarbon chain consisting of CH_2 and CH_3 groups – this is unreactive – the functional group is the *reactive* part of an organic molecule. The functional group generally reacts in the same way whatever molecule it is in or wherever it is in a molecule (although, see the section on classification of groups as primary, secondary and tertiary). For example, all alkenes react in the same way because it is just the C=C group that reacts, so it does not really matter how large or how small the molecule as a whole is; the rest of the molecule is unreactive. The reactions of a particular functional group will also, usually, be independent of other functional groups in a molecule. Therefore, the C=C group will react in the same way no matter what other functional groups are present in the molecule.

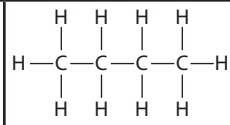
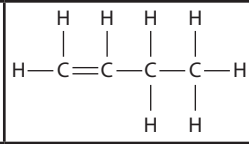
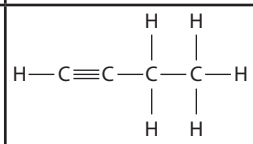
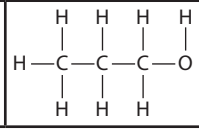
Classes of compounds, homologous series and functional groups

Table 11.3 shows some classes of compounds (homologous series) and functional groups.

The names used in Table 11.3 are those used in the IB syllabus.

Some notes on the names of functional groups:

- The functional group in an alkene is a carbon–carbon double bond.
- The functional group in an alkyne is a carbon–carbon triple bond.
- The halogeno functional group is more usually called a *halo* group.
- Technically, the names 'hydroxyl' and 'carboxyl' refer to **radicals**, so a hydroxyl radical is HO•, and more properly these groups in organic compounds should be referred to as *hydroxy* or *carboxy* groups, but they are virtually always called hydroxyl and carboxyl groups.

Homologous series/class name	Functional group	Functional group name	Example	General name	Example name
alkane				alkane	butane
alkene	C=C			alk-*x*-ene (or *x*-alkene)	but-1-ene (or 1-butene)
alkyne	C≡C			alk-x-yne (or x-alkyne)	but-1-yne (or 1-butyne)
alcohol	—OH	hydroxyl		alkan-*x*-ol (or *x*-alkanol)	propan-1-ol (or 1-propanol)

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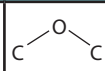
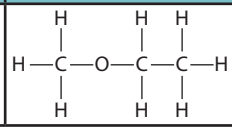
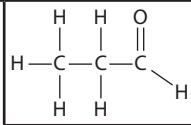
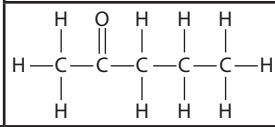
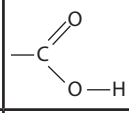
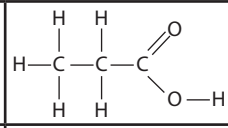
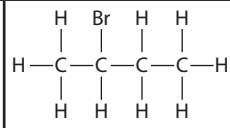
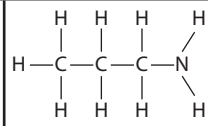
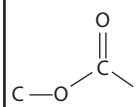
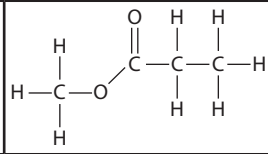
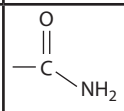
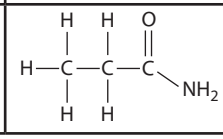
Homologous series/class name	Functional group	Functional group name	Example	General name	Example name
ether		alkoxy		alkoxyalkane	methoxyethane
aldehyde		carbonyl		alkanal	propanal
ketone				alkan-*x*-one (or *x*-alkanone)	pentan-2-one (or 2-pentanone)
carboxylic acid		carboxyl		alkanoic acid	propanoic acid
halogenoalkane	—X X = F/Cl/ Br/I	halogeno (fluoro/ chloro/ bromo/iodo)		*x*-haloalkane	2-bromobutane
amine	—NH_2 —NHR —NR_2	amino		alkylamine or *x*-aminoalkane or alkan-*x*-amine or *x*-alkanamine	propylamine or 1-aminopropane or propan-1-amine or 1-propanamine
ester		ester		alkyl alkanoate	methyl propanoate
amide		amido		alkanamide	propanamide

Table 11.3: Functional groups that you are likely to meet. The names used for functional groups are those used on the IB syllabus. 'R' can be used to represent an alkyl group – so a general carboxylic acid may be represented as RCOOH and an aldehyde as RCHO. R is sometimes also used to represent a phenyl group (—C_6H_5) or H. An amide could also have the H atoms on N replaced by R groups to give, e.g., —$CONR_2$.

- Usually, the term 'carbonyl group' is just used to refer to C=O present in aldehydes and ketones, which are called carbonyl compounds, although, of course, it appears in other compounds (it can, more generally, be called an *oxo* group).
- The amides we meet here are technically *carboxamides* because they are derived from a carboxylic acid (there are other types of amides).

It is important to note that the name of the functional group is not always the same as the name of the homologous series (class name), for example, the functional group in an alcohol is the hydroxyl (—OH) group.

EXAM TIP

When asked to name functional groups in an organic molecule, it is important to use the functional group name and not the class/ homologous series name.

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The phenyl group

The phenyl group is the functional group found in all **aromatic** compounds. Technically, the term refers to a C_6H_5 group, but it is used more widely to refer to any multiply-substituted groups derived from a benzene ring present in organic compounds. Therefore, a phenyl group is present in all the molecules shown in Figure 11.12.

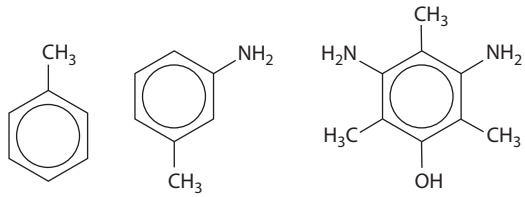


Figure 11.12: Some compounds containing a phenyl group.

Homologous series and physical properties

The members of a homologous series are often described as showing a *gradation in physical properties*, that is, the physical properties change in a gradual and generally predictable way as the length of the hydrocarbon chain gets longer.

Boiling points increase as the carbon chain gets longer

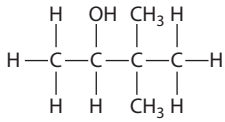
As the number of carbon atoms in a molecule in any homologous series increases, the boiling point increases.

The boiling point of straight-chain alkanes increases when a methylene (—CH_2—) group is added, because the strength of the London forces between molecules

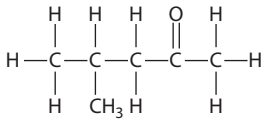
TEST YOUR UNDERSTANDING

5 Name the class of compound (homologous series) to which each of the following molecules belongs:

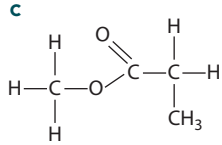
a



b

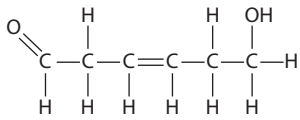


c

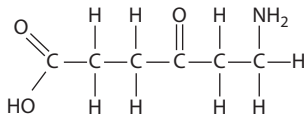


6 Name the functional groups present in the following molecules:

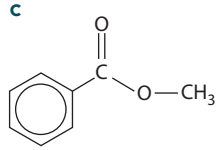
a



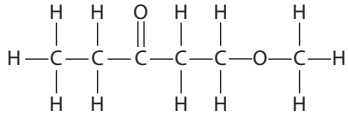
b



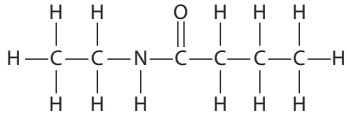
c



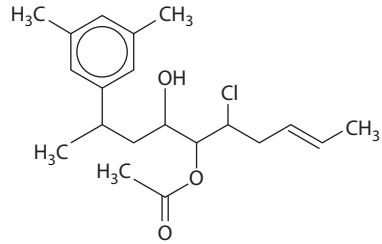
d



e



f



7 Draw the structures of the following:

a the ester with molecular formula $C_2H_4O_2$

b the amide with molecular formula CH_3NO

c the ether with molecular formula C_3H_8O

d the two amines with molecular formula C_2H_7N.

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increases as the relative molecular mass (number of electrons in the molecule) of the alkane increases. A similar trend is seen in the boiling points of other homologous series. Figure 11.13 compares the boiling points of alcohols (with the —OH group on the first carbon atom), aldehydes and alkanes. All three series show the same trend – the boiling point increases as the number of carbon atoms increases.

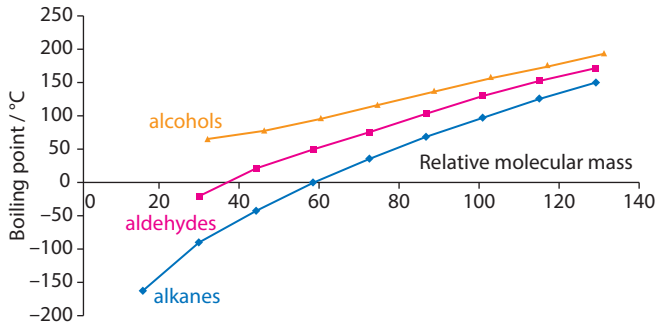

Figure 11.13: The boiling points of some alkanes, aldehydes and alcohols.

The graph also illustrates that comparisons based on relative molecular mass (and hence, strength of London forces) can be made within a particular homologous series but not between homologous series – the alcohol with $M_r = 32.05$ has a higher boiling point than the alkane with $M_r = 72.17$. This can be explained in terms of the nature of the intermolecular forces.

The structures of an alcohol, an aldehyde and an alkane with approximately the same relative molecular masses are shown in Figure 11.14.

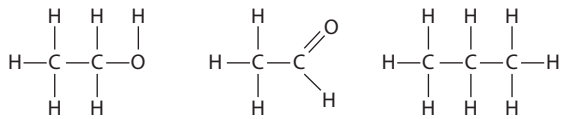

Figure 11.14: These compounds all have very similar relative molecular masses but very different boiling points.

Propane has the lowest boiling point because it is non-polar and only has London forces between molecules. Ethanal has a higher boiling point because it is polar (O is more electronegative than C and H and the dipoles do not cancel) and so also has dipole–dipole forces between molecules. Ethanol has the highest boiling point because, as well as being polar, it also has hydrogen bonding between molecules (due to the —OH group) and so, overall, has the strongest intermolecular forces.

The differences between the boiling points of the three types of compounds get smaller as the M_r increases. So, for instance, the boiling point of heptadecan-1-ol ($C_{17}H_{35}OH$, $M_r = 256.53$) is only 8 °C higher than that of octadecane ($C_{18}H_{38}$, $M_r = 254.56$) – as the molecules get larger, a greater proportion of the molecule is the hydrocarbon chain, which is the same for both molecules and the functional group has a smaller influence on the physical properties.

Solubility and chain length

Alkanes are insoluble in water because the energy to disrupt hydrogen bonding between water molecules would not be paid back by the weak London forces (and dipole-induced dipole forces) formed between the non-polar hydrocarbon chain and water molecules. Ethanol is, however, soluble in water in all proportions – this is because the —OH group allows it to hydrogen bond with water. The solubility of alcohols decreases as the length of the non-polar hydrocarbon chain increases (see Chapter 7, section 7.9) and the —OH functional group has less of an influence on the overall physical properties. Therefore, pentan-1-ol and hexan-1-ol are only sparingly soluble in water.

NATURE OF SCIENCE

There are certain areas of scientific research that are more controversial and involve significant ethical implications. Organic chemists make a large range of substances and amongst these are pesticides, drugs and food additives. These are all substances that are almost certainly being produced because a need exists and there is the potential to make money, but they could also have an adverse effect on the environment and human health. Scientists, however, also have to earn a living and, if working for a large company (which is likely to be driven solely by the desire to make money), may not have the choice to follow their own interests and conscience when selecting projects. Regulatory authorities have to consider the risks and benefits of new substances before licensing them for use.

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11.3 Naming organic molecules

IUPAC nomenclature

Organic molecules are named according to the International Union of Pure and Applied Chemistry (IUPAC) system. Although older non-systematic names are still in use in some situations, molecules should, wherever possible, be named according to the set of systematic rules laid out in the sections that follow.

Naming alkanes and halogenoalkanes

We have already seen the names of the straight-chain alkanes in Table 11.1. In this section, we will learn how to name branched-chain alkanes and halogenoalkanes. Halogenoalkanes have a halogen atom (halogeno/halo group) as the functional group.

The following set of rules should be applied to name alkanes and halogenoalkanes:

1 Find the longest continuous carbon chain in the molecule.

2 Choose the prefix from Table 11.4 corresponding to the number of carbon atoms in the longest continuous carbon chain and add the ending '-ane' to indicate that there are only C—C single bonds.

No. of carbon atoms	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-

Table 11.4: Prefixes indicating the number of carbon atoms in the longest continuous carbon chain.

3 Look for substituent groups (alkyl groups or halogen atoms) – the names for these are shown in Table 11.5.

4 Number the positions of the substituent groups using the combination that has the lowest individual numbers (not the sum).

5 Where two different substituents would have the same numbers when numbering from different directions, the one that comes first in the alphabet is assigned the lower number.

6 Choose a prefix from Table 11.6 to indicate the number of each substituent present.

7 Arrange the names of the substituent groups in alphabetical order (ignoring the prefix used in step 6).

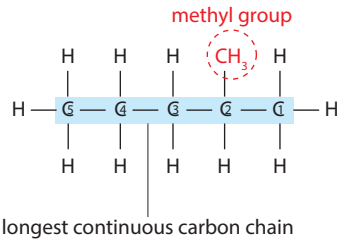
Substituent group	Name	Substituent group	Name
$-CH_3$	methyl	—F	fluoro
$-C_2H_5$	ethyl	—Cl	chloro
$-C_3H_7$	propyl	—Br	bromo
		—I	iodo

Table 11.5: The names of substituent groups.

No. of identical substituents	Prefix
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-

Table 11.6: Prefixes indicating the number of identical substituents.

Example: 2-methylpentane



The longest continuous carbon chain has five carbon atoms, and this gives the basic name 'pentane'. A methyl (CH_3) group is present in the molecule, and this is on carbon number 2 if we start numbering from the right-hand carbon atom. This adds '2-methyl' to the name.

If we had started numbering from the left-hand carbon atom, we would have a methyl group on carbon 4, and the name 4-methylpentane. The name with the lower number is chosen, so the molecule is called 2-methylpentane. Note: there is no gap between methyl and pentane; this is all one word.

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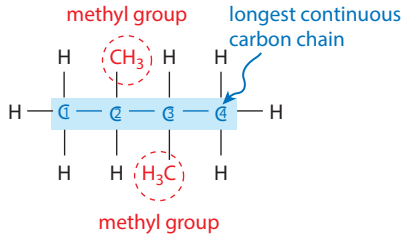
KEY POINTS

When naming molecules, we use commas between numbers and dashes between numbers and letters.

All substituents must be numbered from the same direction.

Example: 2,3-dimethylbutane

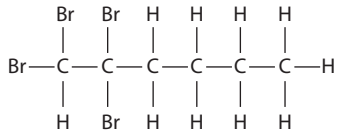


The longest continuous carbon chain is four carbon atoms, and this gives rise to the 'butane' part of the name. There are two methyl groups, so we use 'dimethyl'. These methyl groups are on carbon 2 and carbon 3, so we have '2,3-dimethyl'. Do not be tempted to number the methyl groups from two different directions to give 2,2-dimethyl – all substituents must be numbered from the same direction. Note that methyl groups can be shown in structures as CH_3 or H_3C.

KEY POINT

Every substituent must have a number to indicate its position on the carbon chain.

Example: 1,1,2,2-tetrabromohexane



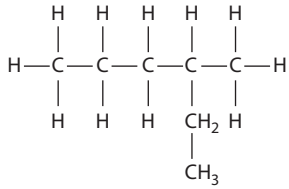
The longest continuous carbon chain is of six carbon atoms, and this gives rise to the 'hexane' part of the name. There are four bromine atoms, so we use 'tetrabromo'. Each bromine atom must have a number, and so, we have '1,1,2,2-tetrabromo'.

KEY POINT

The longest continuous carbon chain may not always be shown as a horizontal, straight line of carbon atoms.

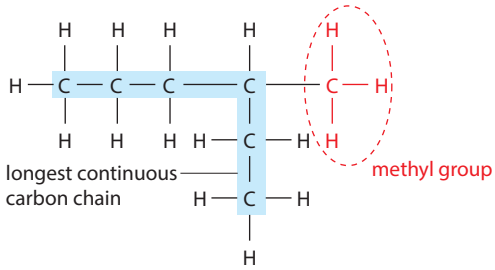
WORKED EXAMPLE 11.6

Deduce the IUPAC name of the molecule shown:



Answer

It might be tempting to name this molecule 2-ethylpentane, but, if we trace out the longest continuous chain, we see that it contains six C atoms and not five. The molecule is, therefore, called 3-methylhexane.



KEY POINT

Substituent groups should be arranged in alphabetical order.

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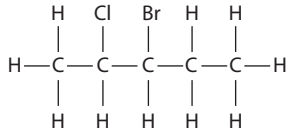
WORKED EXAMPLE 11.7

Name the molecule shown according to IUPAC rules:



Answer

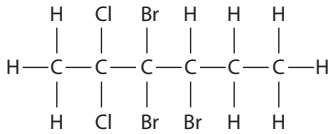
The longest continuous carbon chain has five C atoms and, therefore, we have pentane. The lowest possible numbers are obtained by numbering from the left-hand side, which gives 2-chloro and 3-bromo, rather than 3-bromo and 4-chloro. Bromo comes before chloro in the alphabet; therefore, the name is 3-bromo-2-chloropentane.

KEY POINT

Ignore 'di', 'tri', etc. when putting substituent groups in alphabetical order.

WORKED EXAMPLE 11.8

Name the molecule shown using IUPAC rules:



Answer

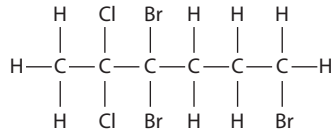
The longest continuous carbon chain has six C atoms, and so, we have hexane. The lowest individual numbers are obtained by numbering from the left. This gives 2,2-dichloro and 3,3,4-tribromo. We ignore the 'di' and 'tri' when putting these in alphabetical order; therefore, we get 3,3,4-tribromo-2,2-dichlorohexane.

KEY POINT

Use the name that gives the lowest individual number not the lowest sum of numbers.

WORKED EXAMPLE 11.9

Name the molecule shown using IUPAC rules:



Answer

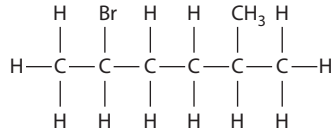
The longest continuous carbon chain has six C atoms, and so, we have hexane. If we number from the left, we get 2,2-dichloro and 3,3,6-tribromo. If we number from the right, we get 1,4,4-tribromo and 5,5-dichloro; although this gives a higher total number (19 compared to 16), we use this combination because it contains the lowest individual number (1 compared to 2); therefore, the name of the molecule is 1,4,4-tribromo-5,5-dichlorohexane.

KEY POINT

Where two or more substituents would have the same numbers when numbering from either side, the one that comes first in the alphabet (ignoring di-, tri-, etc.) is allocated the lowest position number.

WORKED EXAMPLE 11.10

Deduce the IUPAC name of the molecule shown:



Answer

The longest continuous carbon chain has six C atoms, and so, we have hexane. There are two substituents on the chain – a bromo group and a methyl group. Numbering from the left, we get 2-bromo-5-methylhexane. Numbering from the right, we get 5-bromo-2-methylhexane. Both names contain the same numbers, and so, the name is chosen according to position in the alphabet. 'Bromo' comes before 'methyl' in the alphabet, and so, the numbering is chosen to give the lower number to 'bromo'. The name of the molecule is 2-bromo-5-methylhexane.

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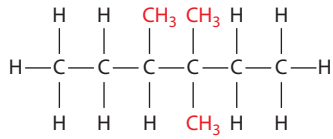
KEY POINT

If all the groups are the same and the first number is the same numbering from both directions, look at the second number and choose the name that has the lower second number.

WORKED EXAMPLE 11.11

Name the molecule shown using IUPAC rules:



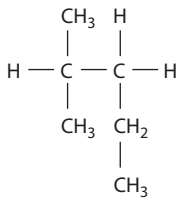
Answer

The longest continuous carbon chain has six C atoms, and so, we have hexane. If we number from the left, we get 3,4,4-trimethylhexane. If we number from the right, we get 3,3,4-trimethylhexane. Both names start with 3, but they differ at the second digit, and so, the name 3,3,4-trimethylhexane is chosen because it gives the lower number at the second position.

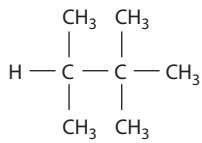
TEST YOUR UNDERSTANDING

8 Name the following molecules:

a

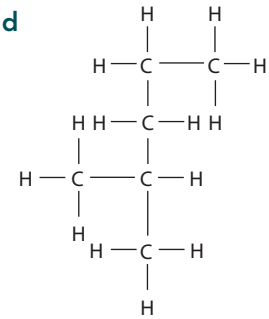


b



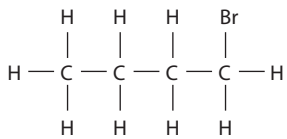
c $CH_3(CH_2)_2C(CH_3)_3$

d

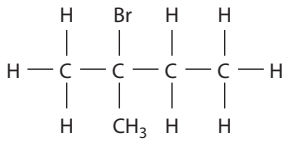


9 Name the following molecules:

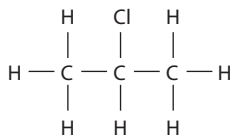
a



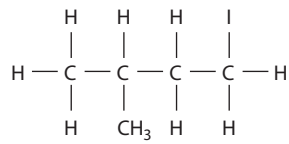
b



c



d



10 Draw the following molecules:

a 3-methylhexane

b 2-bromobutane

c 2,2,3-trimethylpentane

d 1,2,2-tribromo-3-chlorobutane

e 2,4-dimethylhexane.

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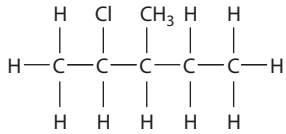
CONTINUED

11 Name the following molecules:

a



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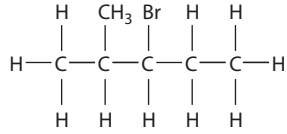
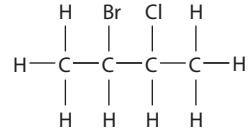


c



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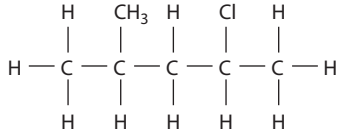
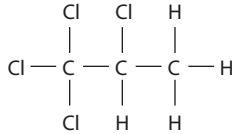


e



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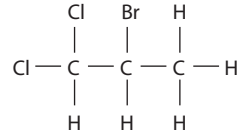
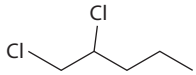


12 Give the correct name for each of the following:

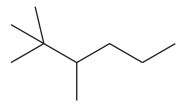
a 1,2-dimethylbutane **b** 1,2,3-trimethylpropane **c** 1-methyl-2,2-dimethylpropane.

13 Name the following molecules:

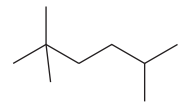
a



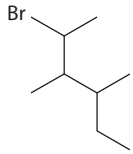
b



c



d



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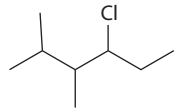

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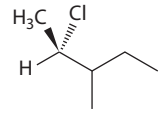
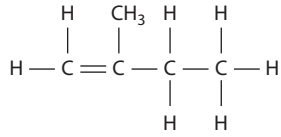


Naming alkenes

Alkenes are hydrocarbons containing C=C. All alkenes (with just one C=C) contain twice as many H atoms as C atoms and, therefore, all have the same empirical formula: CH_2. The names of alkenes are of the form *alk-x-ene* (*x*-alkene is also acceptable). The number, *x*, indicates the position of the double bond. If there is a double bond between carbon 1 and carbon 2, the lower number is taken to generate a '-1-ene'. If there are alkyl groups present in the molecule, the numbering is chosen to give the double bond the lowest possible number, rather than the alkyl groups.

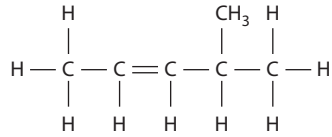
Alkynes contain a C≡C and are named in the same way, except the suffix -yne is used.

Example: 2-methylbut-1-ene



The molecule has four carbon atoms in the longest continuous carbon chain; therefore, we have the stem 'but-'. There is a C=C double bond in the molecule, so we add the ending 'ene' rather than 'ane'. The double bond is between carbon 1 and carbon 2, so we choose the lower of these two numbers to give '-1-ene' . The methyl group on carbon 2 produces '2-methyl' and the overall name 2-methylbut-1-ene.

Example: 4-methylpent-2-ene



The molecule has five carbon atoms in the longest continuous carbon chain; therefore, we have the stem 'pent-'. There is a C=C, so we have pentene. If we number from the left, we get 4-methylpent-2-ene. If we number from the right, we get 2-methylpent-3-ene. Although the second name contains lower numbers, the molecule is called 4-methylpent-2-ene to give the lowest possible number to the C=C group.

In general, a **functional group** that appears at the end of a name (e.g. -ene) always has priority, with regard to

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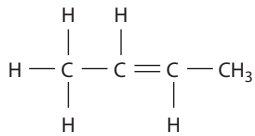
numbering, over a substituent (e.g. methyl, chloro) that appears at the beginning of a name.

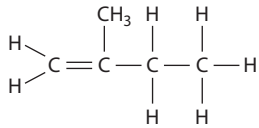
TEST YOUR UNDERSTANDING

14 Name the following molecules:

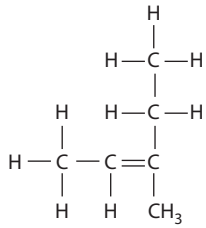
a



b



c



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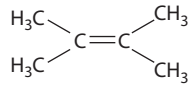
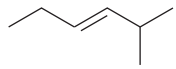


e



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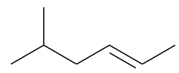


15 Draw the following molecules:

a pent-2-ene

b 2,3-dimethylbut-1-ene

c 4-methylhex-1-ene

d 5,5-dimethylhex-2-ene.

Naming organic compounds containing oxygen

Naming alcohols

All alcohols contain the —OH (hydroxyl) functional group. Alcohols are named as *alkan-x-ol* (*x*-alkanol is also acceptable). Carbon atoms are numbered to give the lowest possible value for *x*.

Table 11.7 lists the first four straight-chain alcohols that have the OH group on the end C atom.

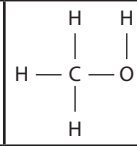
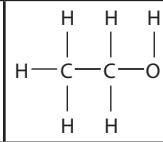
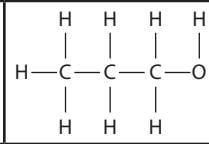
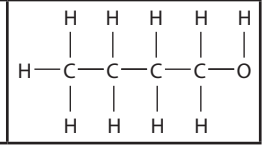
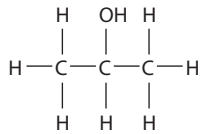
Name	Structural formula	
	Condensed	Full
methanol	CH_3OH	
ethanol	CH_3CH_2OH	
propan-1-ol	$CH_3CH_2CH_2OH$	
butan-1-ol	$CH_3(CH_2)_2CH_2OH$	

Table 11.7: The first four members of the alcohol homologous series.

Example: propan-2-ol



There are three C atoms in the longest continuous chain and there are only C—C single bonds, so we have the name propane. However, we drop the 'e' at the end because the next letter (if there were no number) would be a vowel, and so, have 'propan'. The OH group is on carbon 2; therefore, we have propan-2-ol.

KEY POINT

When the chain is branched, the name is chosen to give the lowest number to the OH group, rather than to alkyl groups.

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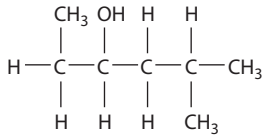
WORKED EXAMPLE 11.12

Name the molecule shown according to IUPAC rules.



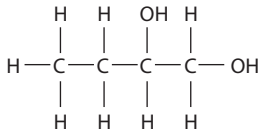
Answer

The longest continuous carbon chain has six C atoms (be careful, it goes around the corner!), and there are only C—C single bonds; therefore, we have hexane. Because it is an alcohol, we drop the 'e' to give us 'hexan'. Numbering from the left, we get 5-methylhexan-3-ol. Numbering from the right, we get 2-methylhexan-4-ol. The number is chosen to give the lowest possible number to the OH group, and so, the molecule is called 5-methylhexan-3-ol, despite the fact that this gives higher numbers overall.

KEY POINT

When more than one OH group is present we retain the 'e'.

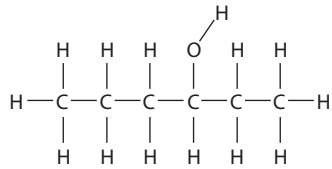
When two —OH groups are present in a molecule, we have a 'diol', and so, the 'e' in the name of the hydrocarbon chain is retained because diol starts with a consonant rather than a vowel. The name of the molecule shown is, therefore, butane-1,2-diol:



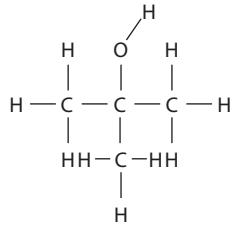
TEST YOUR UNDERSTANDING

16 Name the following molecules:

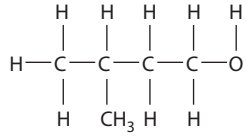
a



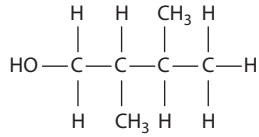
b



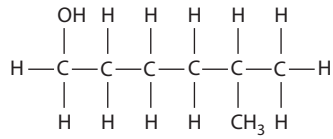
c



d



e



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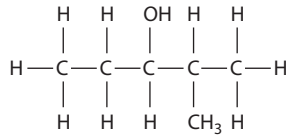
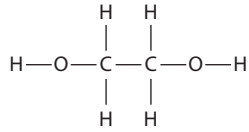


g



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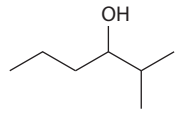
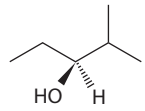


i



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Aldehydes, ketones and carboxylic acids

Aldehydes and ketones are two classes of compounds containing the *carbonyl* (C=O) functional group. Collectively, they are, therefore, called *carbonyl compounds*. Aldehydes have the C=O group at the end of a chain, so that the C of the C=O is bonded to an H. Aldehydes, therefore, contain the CHO group. Ketones have the C=O in the middle of a chain, so the C of the C=O is bonded to a C atom on both sides (Figure 11.15).

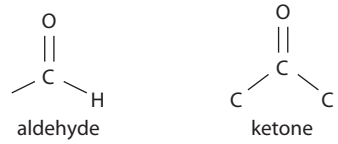


Figure 11.15: The carbonyl group in aldehydes and ketones.

The simplest aldehyde is methanal, but the simplest ketone is propanone (Figure 11.16).

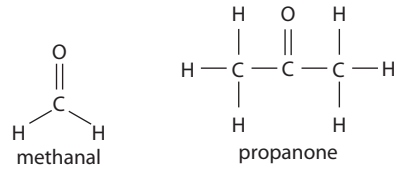


Figure 11.16: The simplest aldehyde and simplest ketone.

The structures of some other aldehydes, ketones and carboxylic acids are shown in Table 11.8.

Condensed structural formulas for aldehydes can be written using the CHO group – so ethanal can be written as CH_3CHO and butanal as $CH_3CH_2CH_2CHO$.

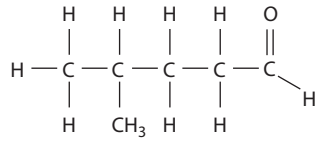
The condensed structural formulas for ketones can be written using the CO group – so propanone can be written as CH_3COCH_3 or $(CH_3)_2CO$ and pentan-2-one as $CH_3COCH_2CH_2CH_3$.

- *Al*dehydes are named based upon alkan*al*.
- Ket*one*s are named as alkan-*x*-*one* (*x*-alkanone is also acceptable).

In aldehydes, the carbon of the CHO group is numbered carbon 1 and everything else is numbered relative to that. For ketones, the numbering scheme is chosen to give the C=O group the lowest possible number.

WORKED EXAMPLE 11.13

Name the molecule shown using IUPAC rules:



Answer

The C=O group is at the end of a carbon chain (a CHO group is present) and, therefore, the molecule is an aldehyde. This gives us an 'al' ending. The longest continuous carbon chain is five atoms (including the C of the C=O) and there are only C—C single bonds; therefore, we have pentane. The 'e' is dropped because the 'al' part of the name starts with a vowel, and so, we have pentanal. We start numbering from the CHO group, so the methyl group is on carbon number 4 and the name is 4-methylpentanal.

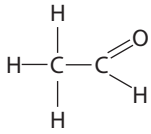
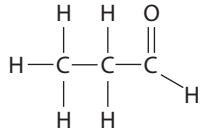
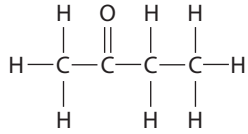
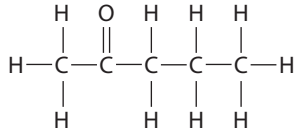
Aldehydes		Ketones	
			
ethanal	propanal	butanone	pentan-2-one

Table 11.8: Some aldehydes and ketones.

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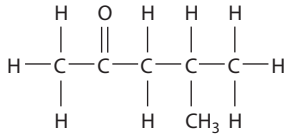
WORKED EXAMPLE 11.14

Name the molecule shown using IUPAC rules:



Answer

The C=O group is in the middle of the chain (C—CO—C group present) and, therefore, the molecule is a ketone. This gives us an 'one' ending. The longest continuous carbon chain is five atoms and there are only C—C single bonds; therefore, we have pentane. The 'e' is dropped because the 'one' part of the name starts with a vowel, and so, we have pentanone. If we start numbering from the left, we get 4-methylpentan-2-one, and if we number from the right, we get 2-methylpentan-4-one. The name is chosen to give the lowest possible number to the C=O group and, therefore, 4-methylpentan-2-one is preferred.

Carboxylic acids

Carboxylic acids are a class of compounds containing the carboxyl (COOH) functional group. The carboxyl group is shown as COOH or CO_2H in condensed structural formulas and is drawn out fully in Figure 11.17.

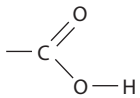


Figure 11.17: The carboxyl group.

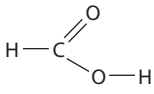
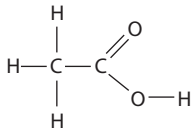
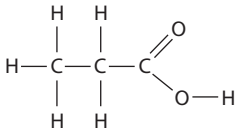
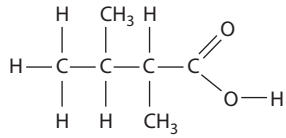
	
methanoic acid	ethanoic acid
	
propanoic acid	

Table 11.9: The first three carboxylic acids.

WORKED EXAMPLE 11.15

Deduce the IUPAC name of the molecule shown:

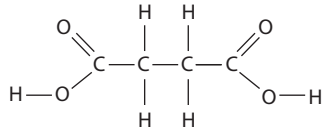


Answer

The presence of a COOH group means that this is a carboxylic acid and gives us an 'oic acid' ending. The longest continuous carbon chain is four atoms (including the C of the COOH) and there are only C—C single bonds; therefore, we have butane. The 'e' is dropped because the 'oic acid' part of the name starts with a vowel, and so, we have butanoic acid. We start numbering from the COOH group, so the methyl groups are on carbon numbers 2 and 3, and the name is 2,3-dimethylbutanoic acid.

WORKED EXAMPLE 11.16

Name the molecule shown using IUPAC rules:



Answer

The presence of two COOH groups means that we get a 'dioic acid' ending.

The longest continuous carbon chain is four atoms and there are only C—C single bonds; therefore, we have butane. The molecule is, therefore, called butanedioic acid. We do not drop the 'e' of butane because 'dioic' starts with a consonant.

The first three carboxylic acids are shown in Table 11.9.

Carboxylic acids have names based on *alkanoic acid*. The carbon of the COOH group is numbered carbon 1 and everything else is numbered relative to that.

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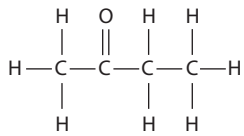
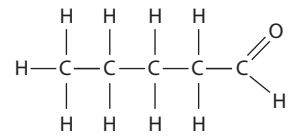
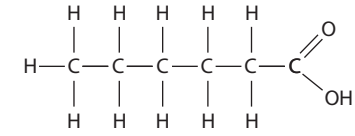
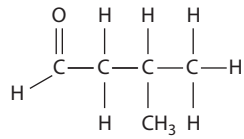
TEST YOUR UNDERSTANDING

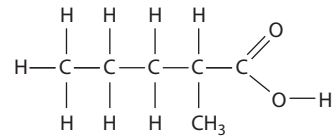
17 Name the following compounds according to IUPAC rules:

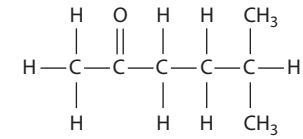
a 

b 

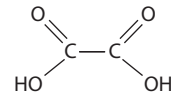
c 

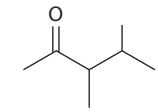
d 

e 

f 

g $(CH_3)_2CHCH_2COOH$

h 

i 

18 Draw the structures of each of the following molecules:

a butanal **b** 2-methylpentanal **c** pentan-3-one

d 3-methylpentanoic acid **e** 5-methylhexan-2-one.

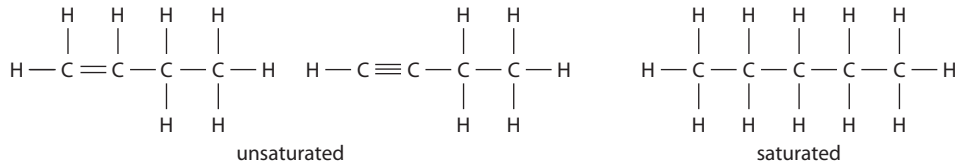


Figure 11.18: Saturated and unsaturated hydrocarbons.

Saturated and unsaturated compounds

Compounds containing C=C or C≡C are described as **unsaturated**. Therefore, alkenes and alkynes are unsaturated compounds. Alkanes and other compounds that only contain single bonds between C atoms are described as **saturated** (Figure 11.18).

KEY POINTS

Unsaturated compounds are compounds that have at least one double (C=C) or triple (C≡C) bond between carbon atoms in the molecule.

Saturated compounds have only single bonds between carbon atoms.

All the aldehydes, ketones and carboxylic acids shown in the previous section are usually described as saturated – although they contain a double bond, it is not between two C atoms.

Naming mono-unsaturated compounds containing other groups

So far, we have only named compounds containing one functional group. In this section, we will name compounds that contain one C=C (mono-unsaturated) as well as another group.

When the molecule contains a halogen atom or an alkyl group as well as C=C we can name it fairly easily using the rules we have studied previously. The C=C always takes priority over halogen atoms or alkyl groups and is assigned the lowest possible number.

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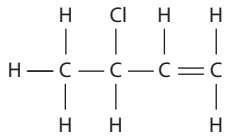
Example: 3-chlorobut-1-ene



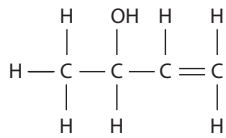
This molecule has four C atoms in the longest continuous carbon chain and contains C═C; therefore, we use the name butene. The name is chosen to give the lowest number to the C═C group, and so, we have but-1-ene. The Cl atom is then on carbon 3 and the molecule is 3-chlorobut-1-ene.

KEY POINT

When hydroxyl (OH), carbonyl (C═O) or carboxyl (COOH) groups are also present in a molecule, these have priority over the C═C group and get the lowest possible number.

WORKED EXAMPLE 11.17

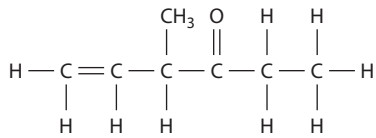
Name the molecule shown using IUPAC rules:



The molecule shown has four C atoms in the longest continuous carbon chain and contains C═C; therefore, we use the name butene. The molecule also contains OH, so we have an 'ol' in the name. The 'e' of butene is dropped because it would be followed by a vowel, and so, we get butenol. The name is chosen to give the lowest number to the OH group, and so, we number from the left and have '2-ol'. Numbering from the left, C═C is between carbon 3 and carbon 4 – the lower number is chosen. The name of the molecule is, therefore, but-3-en-2-ol.

WORKED EXAMPLE 11.18

Name the molecule shown using IUPAC rules:



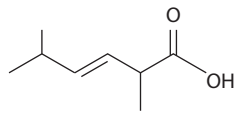
CONTINUED

Answer

The molecule has six atoms in the longest continuous carbon chain and contains C═C; therefore, we use the name hexene. The molecule also contains a C═O group (C—CO—C) in the chain, so it is a ketone, and we have an 'one' in the name. The 'e' of hexene is dropped, and so, we get hexenone. The name is chosen to give the lowest number to the C═O group, and so we number from the right and have '3-one'. Numbering from the right, there is a methyl group on carbon 4 and C═C between carbon 5 and carbon 6. The name of the molecule is, therefore, 4-methylhex-5-en-3-one.

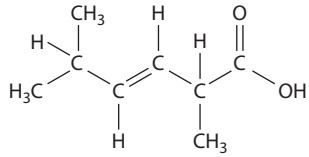
WORKED EXAMPLE 11.19

Deduce the name of the molecule shown:



Answer

It is probably easiest to draw the molecule out showing all the C and H atoms.



The molecule has six atoms in the longest continuous carbon chain and contains C═C; therefore, we use the name hexene. The molecule also contains a COOH (carboxyl) group, and so, we have an 'oic acid' in the name. The 'e' of hexene is dropped, and so, we get hexenoic acid. The COOH is assigned position 1 in the chain. Numbering from the right, then there are methyl groups on carbons 2 and 5 and C═C between carbons 3 and 4. The name of the molecule is, therefore, 2,5-dimethylhex-3-enoic acid.

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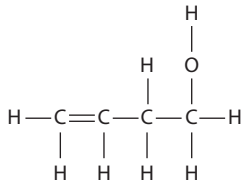
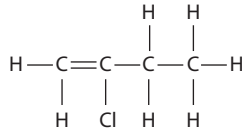
TEST YOUR UNDERSTANDING

19 Name the following molecules:

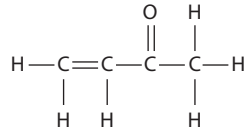
a



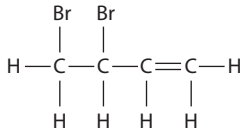
b



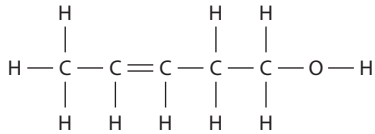
c



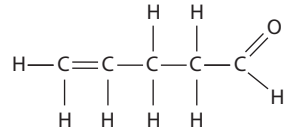
d



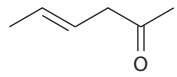
e



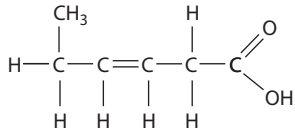
f



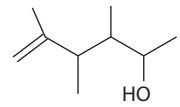
g



h



i



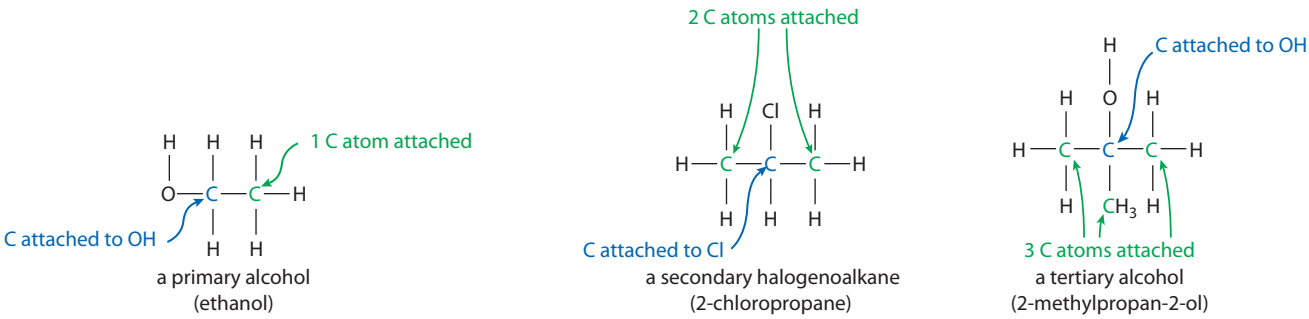


Figure 11.19: Alcohols and halogenoalkanes can be classified as primary, secondary or tertiary.

Primary, secondary and tertiary organic compounds

Primary, secondary and tertiary alcohols and halogenoalkanes

Alcohols and halogenoalkanes are described as *primary*, *secondary* or *tertiary*, depending on the number of carbon atoms attached to the carbon with the —OH group or halogen atom (Figure 11.19).

KEY POINT

A primary alcohol/halogenoalkane has one C atom attached to the C that is bonded to the halogeno/hydroxyl group; a secondary alcohol/halogenoalkane has two C atoms attached to the C that is bonded to the halogeno/hydroxyl group; a tertiary alcohol/halogenoalkane has three C atoms attached to the C that is bonded to the halogeno/hydroxyl group.

A more complete way of describing these groups is to say:

- a primary alcohol/halogenoalkane has at least two H atoms on the C attached to the halogeno/

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hydroxyl group. That is, it contains a —CH_2X group (where X is a halogen atom or an OH group)

- a secondary alcohol/halogenoalkane has only one H atom on C attached to the halogeno/hydroxyl group
- a tertiary alcohol/halogenoalkane has no H atoms on the C attached to the halogeno/hydroxyl group.

Ethanol is a primary alcohol because it has one carbon atom attached to the C with the —OH group – it contains the —CH_2OH group.

2-chloropropane is a secondary halogenoalkane because it has two carbon atoms attached to the C with Cl – there is only one H atom on the C attached to Cl.

2-methylpropan-2-ol is a tertiary alcohol because it has three C atoms attached to the C with the —OH group – there are no H atoms on the C attached to the OH group.

Methanol is a primary alcohol and chloromethane is a primary halogenoalkane. Even though there are no other carbon atoms attached to the C with the —OH/Cl group, they both contain the —CH_2X group (Figure 11.20), and so, are primary.

Figure 11.20: Methanol and chloromethane are both primary.

Primary, secondary and tertiary amines

Amines are also classified as primary, secondary or tertiary but using slightly different reasoning. The focus here is on the nitrogen atom in the amino functional group. If the nitrogen atom is attached to one carbon atom and two hydrogen atoms, then it is a primary amine; if nitrogen is attached to two carbon atoms and one hydrogen atom, it is a secondary amine; and if nitrogen is attached to three carbon atoms and has no hydrogen atoms, it is a tertiary amine. This means that

- primary amines contain the —NH_2 functional group
- secondary amines contain —NHR (where 'R' represents an alkyl group)
- tertiary amines contain —NR_2 (see Figure 11.21).

R could also be an aryl group (a phenyl group).

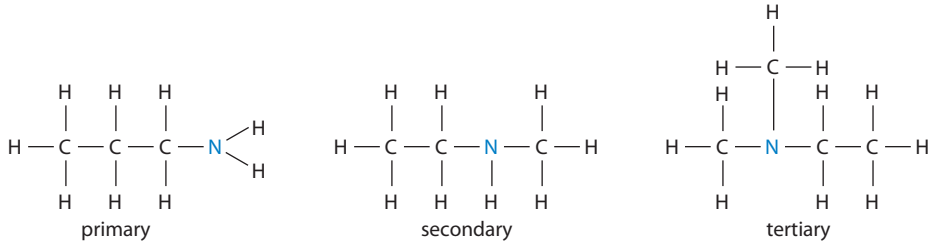
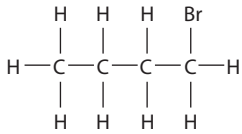


Figure 11.21: Primary, secondary and tertiary amines.

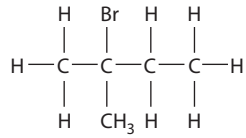
TEST YOUR UNDERSTANDING

20 Classify each of the following molecules as primary, secondary or tertiary and name the halogenoalkanes and alcohols:

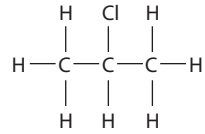
a



b



c



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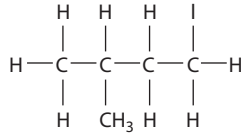

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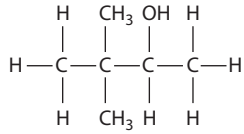

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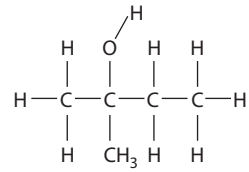

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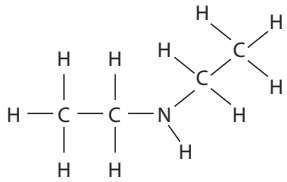

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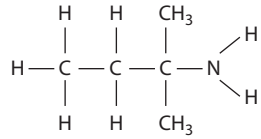


11.4 Isomers

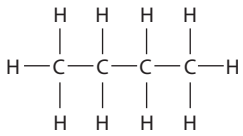
There are various forms of isomerism – the simplest is *structural isomerism*.

Structural isomerism

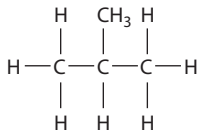
KEY POINT

Structural isomers are two or more compounds that have the same molecular formula but different structural formulas – the atoms are joined together in different ways (they have different connectivities).

The two **structural isomers** with molecular formula C_4H_{10} are



butane



2-methylpropane.

The carbon atoms are joined together differently in the two structures and they have different names.

The structural isomers of C_5H_{12} are shown in Figure 11.22.

It is important to note that the structures shown in Figure 11.23 are *not* separate isomers of C_5H_{12} but are identical to each other. In a molecule in which only C—C single bonds are present, there is fairly free rotation about the single bond. Therefore, although we can show molecules bent into various conformations, if the atoms are joined together in the same way (same connectivity), the molecules are *not structural* isomers.

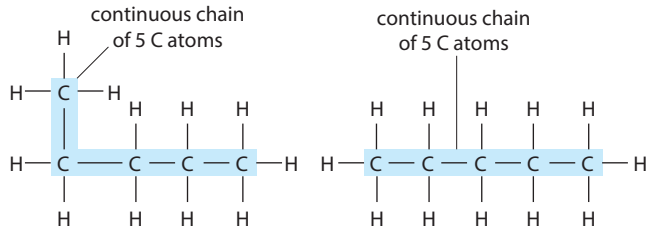


Figure 11.23: These two structures are drawn slightly differently. Careful examination reveals that all the atoms are joined together in exactly the same way and that there is a continuous chain of five carbon atoms in both structures. They are 'both' called pentane.

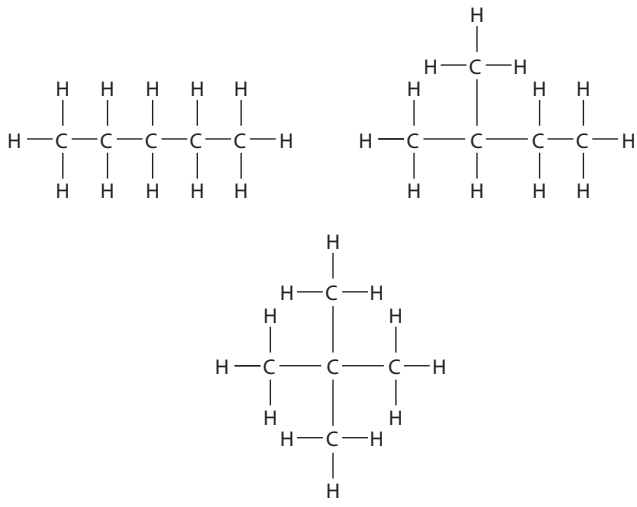


Figure 11.22: The isomers of C_5H_{12}.

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Chain isomers

All the isomers shown previously can be called *chain isomers* because the carbon atoms are joined together differently – they have different *carbon skeletons*. Some isomers of C_6H_{14} are shown in Table 11.9. These are also all chain isomers. The isomer that has a single continuous chain of C atoms is called a *straight-chain isomer*, and those with alkyl groups (CH_3 in this case) attached to the chain are called *branched-chain isomers*.

In general, branched-chain isomers have lower boiling points than straight-chain isomers. This is because the branches prevent the main chains from getting as close together, and there are fewer points of contact between the molecules, so the London forces between the branched molecules are weaker.

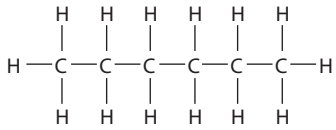
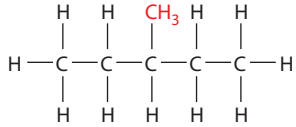
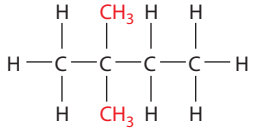
Longest carbon chain in the molecule	Isomer
chain of six C atoms	
chain of five C atoms	
chain of four C atoms	

Table 11.9: Some chain isomers of C_6H_{14}.

Position isomers

Position isomers are another type of structural isomer. These have the same carbon skeleton but differ in the position of functional groups on the carbon skeleton. Two position isomers with the formula C_6H_{12} are shown in Figure 11.24.

Propan-1-ol and propan-2-ol (Figure 11.25) are also position isomers.

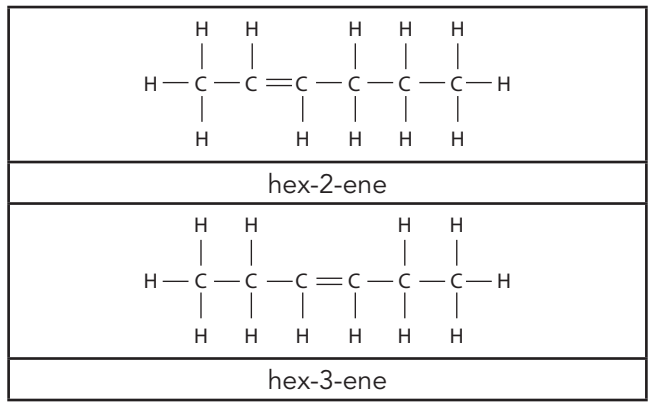


Figure 11.24: Hex-2-ene and hex-3-ene are position isomers – they both have a chain of six C atoms but differ in the position of C=C.

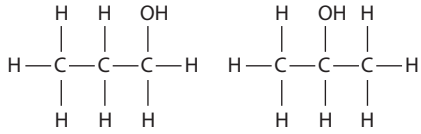


Figure 11.25: Propan-1-ol and propan-2-ol are also position isomers – they both have a chain of three C atoms but differ in the position of the OH group.

Position isomers in aromatic compounds

The groups around a phenyl group can also be in different positions relative to each other. Position isomers of $C_6H_4Cl_2$ are shown in Figure 11.26.

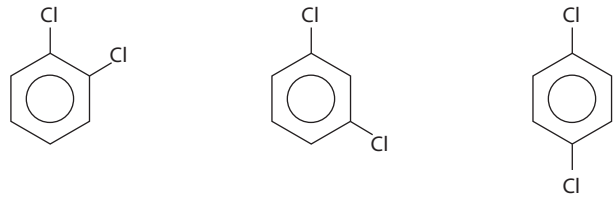


Figure 11.26: There are three position isomers of $C_6H_4Cl_2$ that contain a phenyl group.

Link

In Chapter 7, section 7.16, when we were looking at the structure of benzene, we used the fact that there were only three isomers of $C_6H_4Cl_2$ as evidence for a delocalised structure.

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Functional group isomers

Isomers may have different functional groups. Figure 11.27 shows another isomer of C_6H_{12} that is not an alkene but contains a ring of four carbon atoms. This is called a cycloalkane.

Some functional group isomers are shown in Table 11.10.

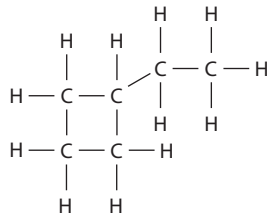


Figure 11.27: Ethylcyclobutane.

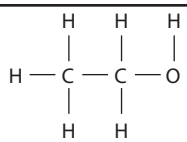
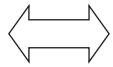
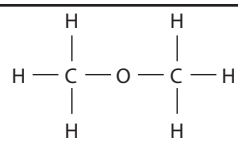
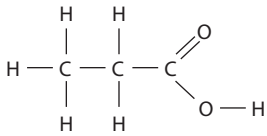
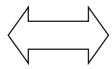
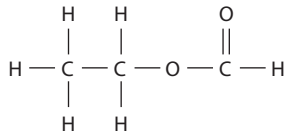
		
an alcohol: hydroxyl functional group	functional group isomers	an ether: alkoxy functional group
		
a carboxylic acid: carboxyl functional group	functional group isomers	an ester: ester functional group

Table 11.10: Two pairs of functional group isomers.

TEST YOUR UNDERSTANDING

21 Draw and name all the structural isomers of C_4H_8 that are alkenes.

22 Draw all the structural isomers of C_5H_{10}.

23 **a** Draw all the structural isomers of $C_4H_{10}O$.

b Name all the isomers from part **a** that are alcohols.

c Classify three pairs of isomers from part **a** as chain isomers, position isomers or functional group isomers.

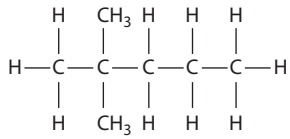
24 Draw all the esters that are isomeric with these carboxylic acids:

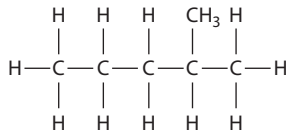
a butanoic acid **b** pentanoic acid.

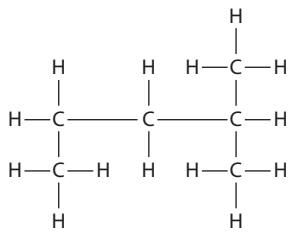
25 One isomer of $C_4H_8Br_2$ is 1,1-dibromobutane. Draw and name the other isomers and classify them as chain or position isomers of 1,1-dibromobutane.

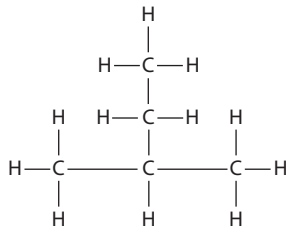
26 Draw all isomers of $C_5H_{10}O$ that contain a ring of 5 atoms.

27 Identify the two compounds that are identical:

A 

B 

C 

D 

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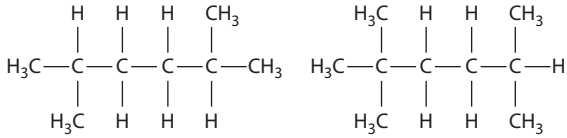
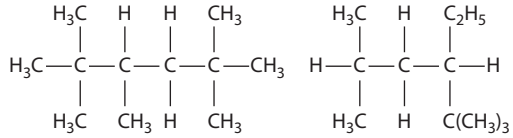
28 In each case identify whether each pair of compounds are isomers, identical or neither:

a



b



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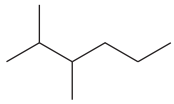
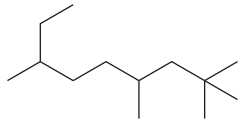


$(CH_3)_2CHCH(CH_3)CH_2CH_2CH_3$

d



$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)C(CH_3)_3$

Stereoisomerism

We have already seen structural isomerism, in which molecules have the same molecular formula but the atoms are joined together differently.

KEY POINT

Stereoisomers have the same structural formula (the atoms are joined together in the same way – same connectivity and same bond multiplicities), but the atoms are arranged differently in space.

Because **stereoisomers** have the same connectivities, they have the same names, except for an extra descriptor to indicate the spatial arrangement of the groups. Therefore, *cis*-but-2-ene and *trans*-but-2-ene are stereoisomers, but *cis*-but-2-ene and but-1-ene are structural isomers – they have different names.

There are two different types of stereoisomerism that we will look at: ***cis–trans* isomerism** and **optical isomerism**.

cis–trans isomerism

We find this type of isomerism in alkenes and in cyclic (ring) compounds.

KEY POINT

In *cis–trans* isomerism, two compounds have the same structural formula, but the groups are arranged differently in space around a double bond or a ring.

Figure 11.28 shows the *cis–trans* isomers of 1,2-dichloroethene. The chlorine atoms are arranged either on opposite sides of the double bond, forming the *trans* isomer, or on the same side of the double bond, forming the *cis* isomer.

trans -1,2-dichloroethene *cis* -1,2-dichloroethene

Figure 11.28: Stereoisomers of 1,2-dichloroethene.

KEY POINT

cis: same side

trans: opposite sides

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How do *cis–trans* isomers arise?

To understand how *cis–trans* isomerism arises in alkenes, we must remind ourselves about the nature of the C—C single bond and a C═C double bond. A single bond is a sigma bond, and a double bond consists of a sigma and a pi bond (Figure 11.29).

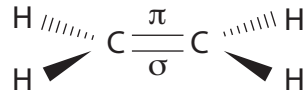

Figure 11.29: A double bond is composed of σ and π components.

Fairly free rotation about a C—C single bond is possible because the nature of the sigma bond does not restrict rotation. However, with C═C, the π component of the bond prevents the groups on either side of it from rotating relative to each other (Figure 11.30).

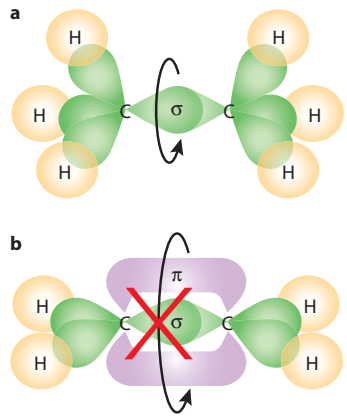

Figure 11.30: a Free rotation of groups around a C—C bond. **b** Restricted rotation of groups about a C═C bond.

The π bond would have to be broken to allow rotation to occur: this takes a lot of energy and does not occur under normal circumstances.

KEY POINT

cis–trans isomerism arises in alkenes because the π component of the C═C bond restricts rotation of groups around the bond.

From this discussion, we can see that the structures shown in Figure 11.31 do not represent *cis–trans* isomers because there is a single bond between the two C atoms and the CH_2Cl groups can rotate relative to each other. These diagrams represent the same molecule just shown in different conformations.

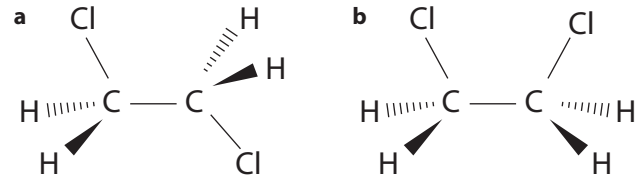

Figure 11.31: Both diagrams show the same molecule – 1,2-dichloroethane – they are not isomers in the sense that we saw them above – the individual forms cannot be isolated – but they are sometimes called *conformational isomers* or *conformers*.

KEY POINT

cis–trans isomerism requires two different groups on *both* sides of the double bond.

It can be the same two groups on both carbons of the C═C, but the key point is the groups must be different on *each* carbon. Figure 11.32 shows that *cis–trans* isomers exist for but-2-ene.

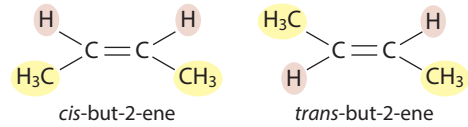

Figure 11.32: But-2-ene has 2 different groups on each C of the C═C.

If we look at the structure of but-1-ene (Figure 11.33), however, we can see that there are two groups the same (two H atoms) on one side of the C═C and, therefore, but-1-ene does not exhibit *cis–trans* isomerism.

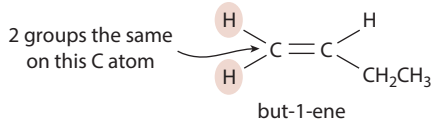

Figure 11.33: But-1-ene does not exhibit *cis–trans* isomerism.

If we try to draw out two different forms of but-1-ene (Figure 11.34), we can see that both structures are identical – the second is simply the first turned upside down.

Other examples of molecules that do and do not exhibit *cis–trans* isomerism are shown in Table 11.11.

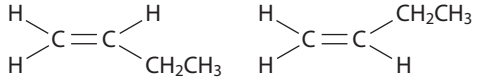

Figure 11.34: These two structures are identical.

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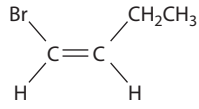
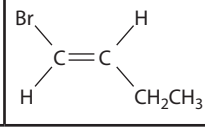
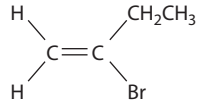
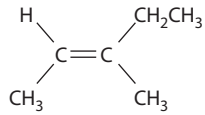
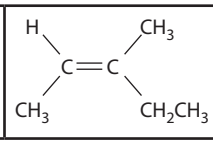
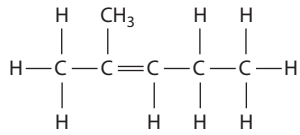
Compound	*cis–trans* isomers?	*cis* isomer	*trans* isomer
1-bromobut-1-ene	yes		
2-bromobut-1-ene	no		
3-methylpent-2-ene	yes		
2-methylpent-2-ene	no		

Table 11.11: Examples of molecules that do and do not exhibit *cis–trans* isomerism.

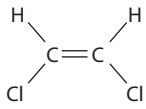
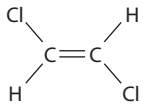
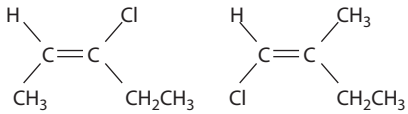
		
	***cis*-1,2-dichloroethene**	***trans*-1,2-dichloroethene**
M_r	96.94	96.94
boiling point (°C)	60.5	48.7

Table 11.12: *cis–trans* isomers have different physical properties.

cis–trans isomers must have the same connectivity

Consider the two molecules:



These molecules look as if they could be *cis–trans* isomers of each other – they both have the same molecular formula and two different groups on both sides of C=C. They are, however, structural isomers and not *cis–trans* isomers. We can spot this because the atoms are joined together differently. In the left-hand structure, there is a chain of five C atoms, but in the right-hand structure there is only a chain of four C atoms. This means that they have different names – the left-hand molecule is 3-chloropent-2-ene and the right-hand one is 1-chloro-2-methylbut-1-ene. The *cis–trans* isomers of both molecules do exist, but they are not shown here.

Properties of *cis–trans* isomers

Table 11.12 shows that *cis–trans* isomers have different physical properties.

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The structures of *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene differ in the orientation of their chlorine atoms around the C=C bond. This leads to the *cis* form being polar and the *trans* form being non-polar (Figure 11.35).

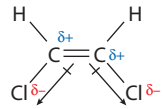

Figure 11.35: *cis*-1,2-dichloroethene is polar – the dipoles do not cancel.

The *trans* form is non-polar because the orientation of the chlorine atoms around the double bond means that the dipoles cancel (Figure 11.36).

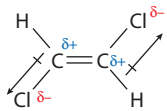

Figure 11.36: *trans*-1,2-dichloroethene is non-polar – the dipoles cancel.

So, there are permanent dipole–dipole interactions between molecules of *cis*-1,2-dichloroethene but not between molecules of the *trans* form. Both molecules have the same relative molecular mass (and hence, very similar London forces), so the difference between boiling points is due to the permanent dipole–dipole interactions between the *cis* molecules. *cis–trans* isomers may also have different chemical properties.

Cycloalkanes

A cycloalkane is a ring (cyclic) compound containing only single C—C single bonds (and hydrogen). The simplest members of the homologous series are cyclopropane (C_3H_6) and cyclobutane (C_4H_8). Cycloalkanes are structural (functional group) isomers of the corresponding alkene.

Two different ways of drawing these molecules are shown in Figure 11.37, and a computer-generated model of cyclobutane is shown in Figure 11.38.

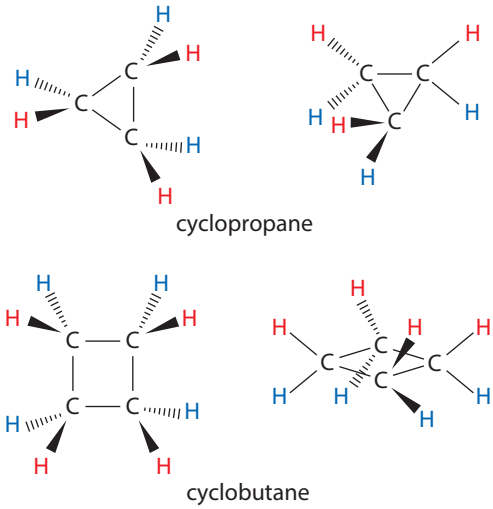

Figure 11.37: Two ways of drawing cyclopropane and cyclobutane. Hydrogen atoms above the plane of the ring are red and those below are blue. A ring containing three atoms, such as in cyclopropane, is called a three-membered ring; that in cyclobutane is a four-membered ring.

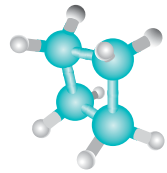

Figure 11.38: A computer-generated model of cyclobutane.

KEY POINT

If a cycloalkane has at least two carbon atoms that have two different groups attached, it will exhibit *cis–trans* isomerism.

cis–trans isomerism in substituted cycloalkanes

The *cis* and *trans* forms of 1,2-dimethylcyclobutane are shown in Table 11.14.

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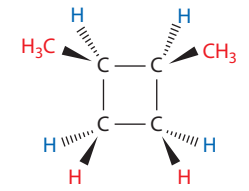
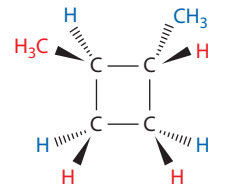
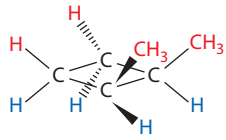

cis-1,2-dimethylcyclobutane


trans-1,2-dimethylcyclobutane



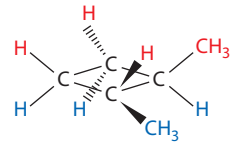
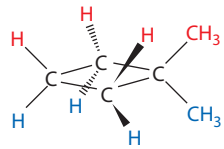


Table 11.14: Different ways of showing the isomers of 1,2-dimethylcyclobutane.

In the *cis* form, the two methyl groups are on the same side of the ring, and in the *trans* form, they are on opposite sides of the ring. The ring structure prevents rotation of a group from above the plane of the ring to below the ring. Groups cannot be rotated from above to below the ring without breaking a C—C bond in the ring structure – this would require a lot of energy.

Note:



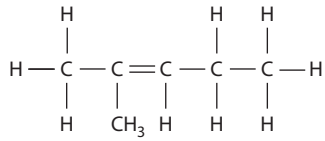
Is not a stereoisomer of 1,2-dimethylcyclobutane but a structural isomer. The atoms are joined together differently with two methyl groups on the same carbon atom, so it has a different name, 1,1-dimethylcyclobutane. This molecule does not show *cis–trans* isomerism.

1,3-dimethylcylobutane is another structural isomer of 1,1-dimethylcyclobutane and 1,2-dimethylcyclobutane, and does exhibit *cis–trans* isomerism.

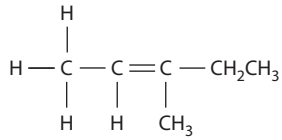
TEST YOUR UNDERSTANDING

29 Which of the following will exhibit *cis–trans* isomerism? If the molecule exhibits *cis–trans* isomerism, draw the *cis* and *trans* forms.

a



b



c 2,3-dimethylpent-2-ene

d 3,4-dimethylpent-2-ene

e 1,2,3-trimethylcyclopropane

f 1,3-dimethylcyclobutane

Chirality

KEY POINT

Molecules are described as chiral if mirror images of the molecule are *non-superimposable*.

Butan-2-ol (Figure 11.39) is a **chiral** molecule.

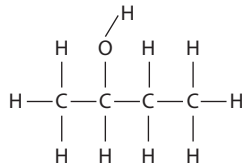


Figure 11.39: The full structural formula of butan-2-ol.

It is possible to draw two separate structures for butan-2-ol that are mirror images of each other. The two mirror images of butan-2-ol are shown, using stereochemical formulas, in Figure 11.40.

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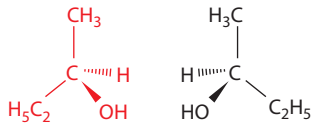


Figure 11.40: The two forms of butan-2-ol are mirror images of each other.

Although they look identical, if we try to put one molecule 'on top' of the other (Figure 11.41), it can be seen that only two of the groups can be made to correspond – the other two groups are arranged differently around the central carbon atom.

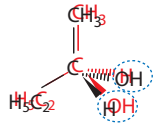


Figure 11.41: The mirror images of butan-2-ol are non-superimposable, so they are not identical.

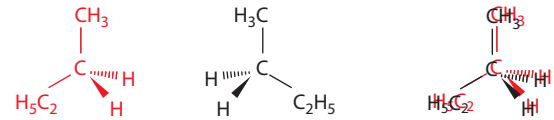
Therefore, the molecules are not identical but isomers of each other – the two isomers are *non-superimposable* (the term *non-superposable* is also used) – they cannot be placed on top of each other so that all groups match up. The word 'chiral' is derived from the Greek word for hand – your hands are non-superimposable mirror images of each other – although they look identical, if you try to put your right hand on top of your left hand, the thumb of your right hand will be on top of the little finger of your left hand. The non-superimposable mirror images of a chiral molecule are called **enantiomers**. So, Figure 11.40 shows the two enantiomers of butan-2-ol.

To exhibit this property of chirality – that the mirror images are not superimposable – there must be an *asymmetric carbon atom* – a carbon atom with *four different* groups attached. This carbon atom with four different groups attached is called a **chirality centre** (chiral centre).

KEY POINT

Chiral molecules contain an asymmetric carbon atom, a carbon atom with 4 different groups attached. This carbon atom is called the chirality centre (chiral centre).

If you look at butane (Figure 11.42), you can see that it has a maximum of only three different groups attached to any one carbon atom and, therefore, the mirror images *are* superimposable. Butane does not exhibit chirality and is described as an *achiral* molecule.



a **b**

Figure 11.42: There is only one form of butane: **a** these two mirror images are identical; **b** the mirror images are superimposable, so butane is achiral.

Link

We can talk about the *configuration* of the chirality centre, that is the spatial arrangement of the groups at the chirality centre, and will look at reactions that involve an inversion of the configuration in Chapter 22.

Some chiral molecules are shown in Table 11.15.

Some achiral molecules are shown in Table 11.16.

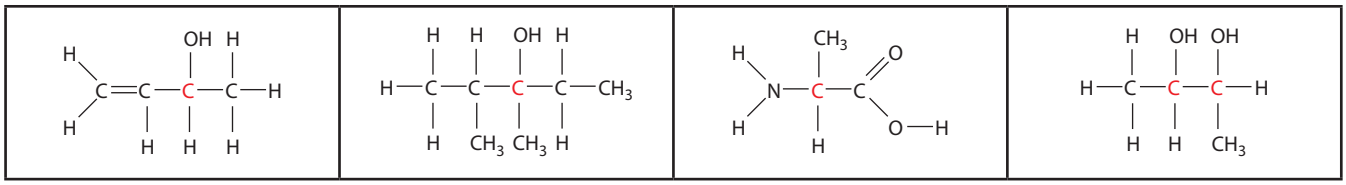


Table 11.15: Chiral molecules – the chirality centres (chiral centres) are shown in red.

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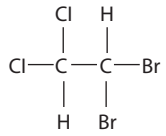
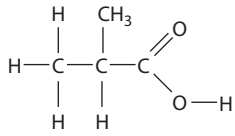
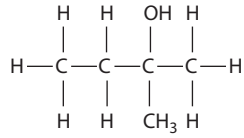
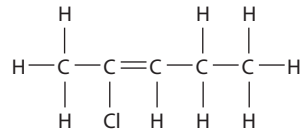
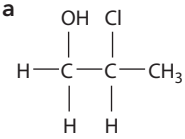
			

Table 11.16: Some achiral molecules – they do not contain a C atom with four different groups attached. Take care with CH_3 groups shown either in condensed form or with all C—H bonds.

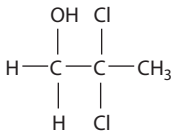
WORKED EXAMPLE 11.19

Identify which of the two molecules shown is chiral and draw clear 3D diagrams (stereochemical formulas) to show the enantiomers of the chiral molecule.

a

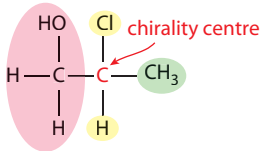


b



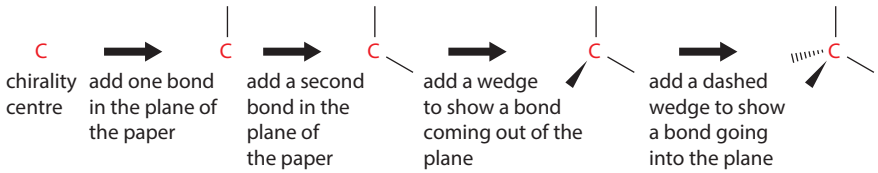
Answer

The first thing to look for is a chirality centre – a C atom with four different groups attached. Only A has a carbon atom with four different groups attached; therefore, it is the chiral molecule.



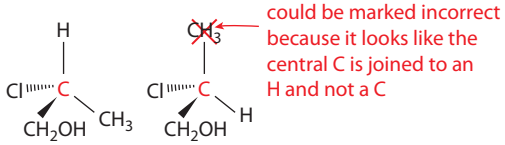
It is important to remember that the chirality centre must have four different *groups* attached and not 4 different *atoms*. The C highlighted here has two C atoms attached but one is part of a CH_3 group and the other is part of a CH_2OH group, so they are different.

To draw the stereochemical formula, start with the chirality centre and draw four bonds in a tetrahedral shape around this. This is most easily done as follows:



Now arrange the four groups around the chirality centre. There is no right or wrong way of doing this – just put them in anywhere.

Do, however, be careful that you show bonds to the correct atoms:



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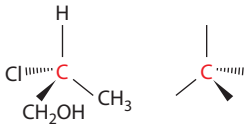
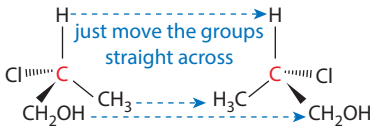
CONTINUED

Now draw the mirror-image tetrahedron:



The groups stay in the same position in the mirror image, e.g., CH_2OH, which was attached to a solid wedge coming out of the paper in the original molecule, is attached to the same type of bond in the mirror image.

Note: there is no need to draw CH_2OH as a mirror image, that is, as HOH_2C (it is not a chiral group):



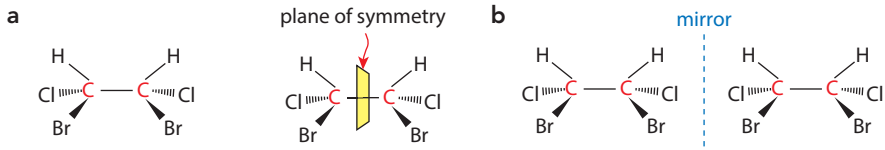


Figure 11.43: Molecules with a plane of symmetry are achiral. The mirror images the molecule in **a** are shown in **b** The structures in **b** are identical and therefore superimposable.

Not everything with an asymmetric carbon atom is chiral

If a molecule has a plane of symmetry, it will be achiral even if it contains a C atom with four different groups attached. This is because the symmetry will mean that the mirror images are superimposable. The molecule shown in Figure 11.43 is achiral, even though it has two C atoms with four different groups attached. The mirror image (Figure 11.43**c**) is identical to the original molecule and, therefore, superimposable.

cis- and *trans*-1,2-dichlorocyclopropane (Figure 11.44), both contain two asymmetric carbon atoms.

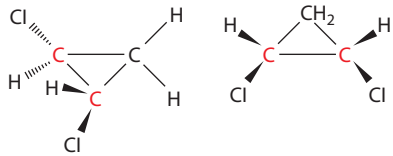


Figure 11.44: *trans*-1,2-dichlorocyclopropane and *cis*-1,2-dichlorocyclopropane both contain asymmetric carbon atoms, shown in red.

The carbon atoms shown in red are asymmetric carbon atoms because the C atoms have four different groups attached: —H, —Cl, a —CH_2 group going one way around the ring, and a —CHCl group going the other way around the ring. This is shown in Figure 11.45.

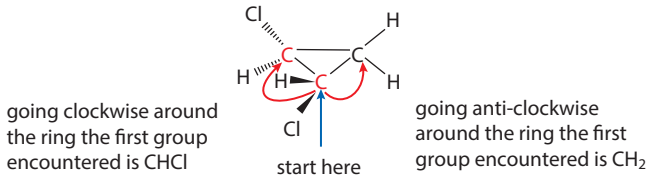


Figure 11.45: In addition to H and Cl directly attached to the C indicated with the blue arrow, if we go clockwise around the ring, the group attached to this C is —CHCl, but in the anticlockwise direction it is a —CH_2 group.

Only *trans*-1,2-dichlorocyclopropane is chiral because *cis*-1,2-dichlorocyclopropane has a plane of symmetry (Figure 11.46).

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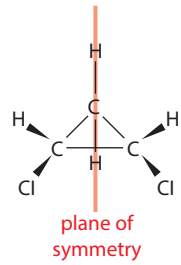

Figure 11.46: *cis*-1,2-dichlorocyclopropane has a plane of symmetry and is, therefore, achiral – it can be superimposed on its mirror image.

Chiral molecules show optical activity

The two enantiomers of chiral compounds have the property that they rotate **plane-polarised light** in opposite directions. Or, more precisely, they rotate the plane of polarisation of plane-polarised light in opposite directions. This property is called optical activity and each enantiomer can be said to be **optically active**.

Normal, non-polarised, light vibrates in all planes (Figure 11.47).

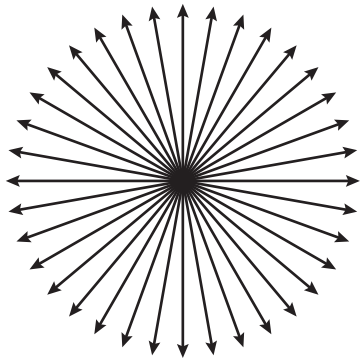

Figure 11.47: If we imagine being able to look at the vibrations in a beam of non-polarised light coming towards us, then it could be represented as shown here.

If non-polarised light is passed through a polarising filter, plane-polarised light is produced (Figure 11.48). Plane-polarised light vibrates in one plane only.

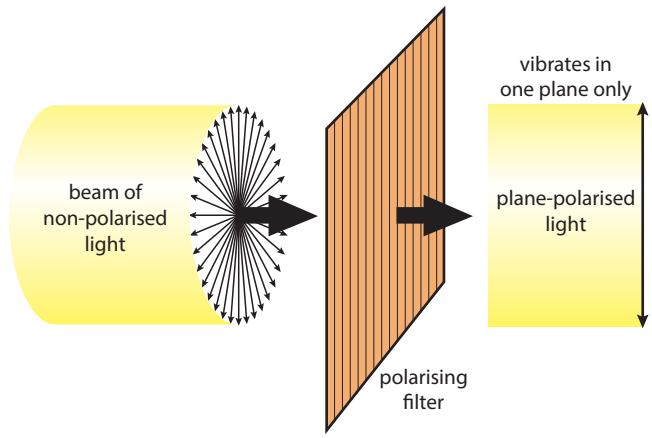

Figure 11.48: Plane-polarised light is light that vibrates in one plane only.

The two enantiomers of butan-2-ol are optically active. If plane-polarised light is passed through separate samples of the two enantiomers of butan-2-ol (Figure 11.49), we find that one of the enantiomers rotates the plane of the plane-polarised light to the right (clockwise), and the other enantiomer rotates the plane of the plane-polarised light to the left (anticlockwise). The two enantiomers rotate the plane of the plane-polarised light by equal amounts (if the light is passed through samples containing equal numbers of moles).

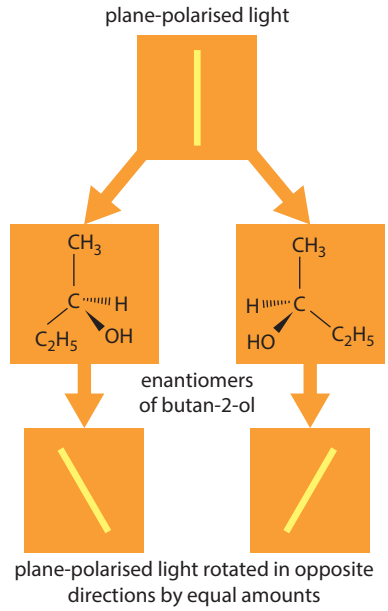

Figure 11.49: The two enantiomers of butan-2-ol rotate plane-polarised light in opposite directions by equal amounts.

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A polarimeter can be used to distinguish between enantiomers

A simple polarimeter consists of a source of light (usually a sodium lamp producing one specific wavelength), two polarising filters, a sample tube and a scale to measure the degree of rotation of the plane-polarised light (Figure 11.50).

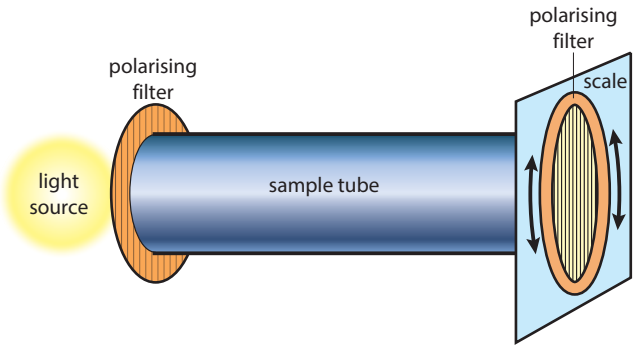

Figure 11.50: A simple polarimeter.

The solvent in which the test substance is to be dissolved is placed in the sample tube, and the second polarising filter is rotated until no light can be seen. At this point, the polarising filters are exactly crossed (at 90° to each other) (Figure 11.51).

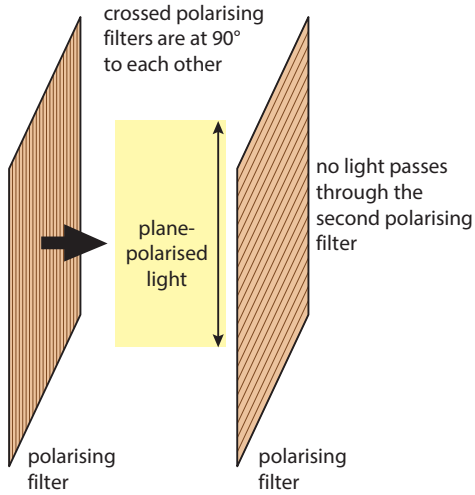

Figure 11.51: When polarising filters are crossed, no light can pass through, unless it has been rotated by an optically active sample between the first and second filters.

The solvent is then replaced by the sample dissolved in the solvent and the polarising filter rotated again until no light can be seen. The angle through which light is rotated by the sample is the difference between the readings with and without the sample.

Enantiomers of a particular substance can be distinguished using a polarimeter because one enantiomer rotates the plane-polarised light clockwise and the other rotates it in the opposite direction.

KEY POINT

The enantiomers of chiral substance rotate plane-polarised light in opposite directions (by equal amounts), and so can be distinguished using a polarimeter.

Racemic mixtures

KEY POINT

A **racemic mixture (racemate)** is an equimolar (same number of moles) mixture of the two enantiomers of a chiral compound.

A **racemic mixture (racemate)** has no effect on plane-polarised light – it is not optically active. This is because the rotation effects of the two enantiomers cancel each other out.

Because the enantiomers are equally stable, reactions that produce molecules containing a chiral carbon atom will usually produce a racemic mixture – the resulting reaction mixture will have no effect on plane-polarised light.

EXAM TIP

If the product of a reaction has a chirality centre and you are asked why it is not optically active – the answer is usually 'because a racemic mixture is formed'.

Properties of enantiomers

- Enantiomers have identical physical properties (e.g. melting point, boiling point and solubility), except they rotate the plane of plane-polarised light in opposite directions (by equal amounts).
- Enantiomers have identical chemical properties when they react with substances that are not chiral.
- They may react differently when reacted with something that is chiral. For example, the active site of an enzyme could be chiral and so the enzyme may only catalyse the reaction of one of the enantiomers.

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SCIENCE IN CONTEXT

The sedative thalidomide was introduced in the late 1950s and was used in various countries throughout the world. It was thought to be safe with very few side-effects. As well as being a sedative, it was also effective at relieving nausea, and so, was widely given to pregnant women in the first three months of pregnancy to alleviate morning sickness. The result was devastating, with thousands of children being born with missing or malformed limbs, and a number dying in infancy. This tragedy could have been avoided if the drug had been evaluated for teratogenicity (toxicity to the foetus) before it was marketed.

Thalidomide was given as a mixture of enantiomers (racemic mixture), but one of the enantiomers (the *S*-enantiomer) was responsible for producing a teratogenic effect and caused limb deformities in the foetus (Figure 11.52).

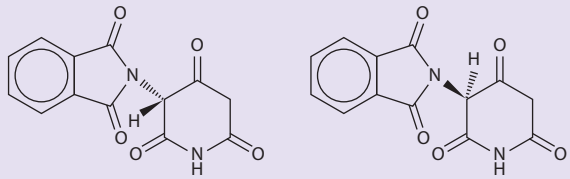


Figure 11.52: Enantiomers of thalidomide.

Administering just one enantiomer would not have helped in the case of thalidomide because the enantiomers interconvert in the body, producing the racemic mixture. Nowadays, if a new drug is going to be marketed as the racemic mixture, testing must be carried out on each enantiomer separately and on the racemic mixture.

Thalidomide is actually still used nowadays – marketed as Thalomid® – it is used to treat leprosy and certain cancers. One of the top-10 drugs, in terms of value of sales, lenalidomide (marketed as Revlimid®) has a structure very similar to that of thalidomide (Figure 11.53) and is administered as a racemic mixture; it is used in the treatment of cancer.

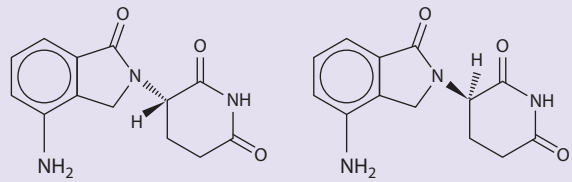


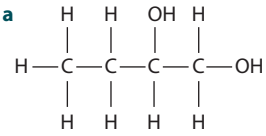
Figure 11.53: The enantiomers of lenalidomide

It is believed that lenalidomide also has teratogenic effects. Why do you think that these drugs are used despite the consequences of disastrous side-effects and what precautions must be taken when prescribing them?

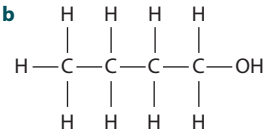
TEST YOUR UNDERSTANDING

30 Which of the following molecules are chiral? For those that are, identify the chirality centre (chiral centre) and draw three-dimensional diagrams showing the enantiomers.

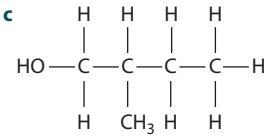
a



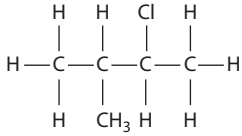
b



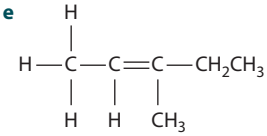
c



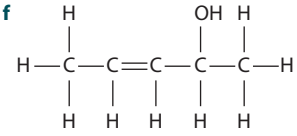
d



e



f



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CONTINUED

31 Which of the following are chiral?

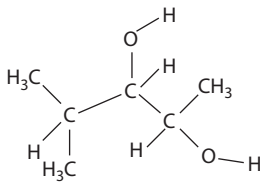
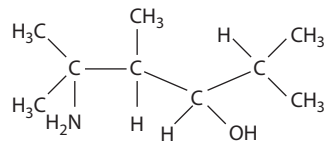
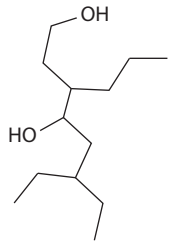
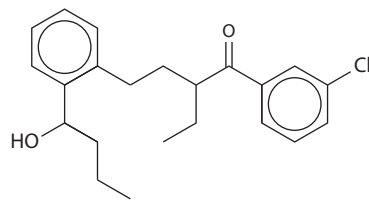
a 1-bromobutane

b 2-bromobutane

c $CH_3CH_2CH(OH)COOH$

d $(CH_3)_2CHCHClCH(CH_3)_2$

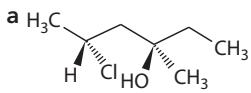
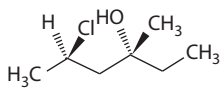
32 Identify chirality centres in each of the following by putting a * next to any chirality (chiral) centres:

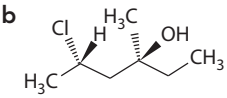
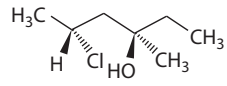
33 For each of the following pairs state whether they are

structural isomers, enantiomers, identical, not isomers:

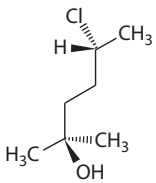
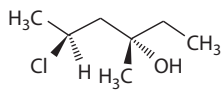
a

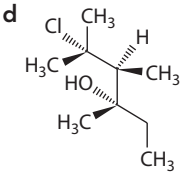
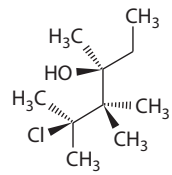
b

c

d

11.5 Spectroscopic identification of organic compounds

So far in this chapter, we have seen the structures of many organic compounds, but how exactly do we work out these structures? If a chemist is presented with a white crystalline substance or a colourless liquid, what steps do they take to identify it? This is especially important in synthetic organic chemistry (making organic molecules) – organic chemists use their knowledge of existing organic reactions, which is usually to do with functional group interconversions, to plan synthetic routes to their target compound. They then carry out these chemical reactions, but how do they know that they have made what they expected to make?

The structures of organic molecules may be worked out using a variety of spectroscopic techniques. Additional information may also come from elemental analysis of the composition of a compound to generate the empirical formula.

The three main spectroscopic techniques are

- IR spectroscopy
- NMR spectroscopy
- mass spectrometry.

Each technique provides different data.
The information from any one of these techniques is normally not sufficient to work out the structure of an organic molecule completely, and all three are usually used together.

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Infrared (IR) spectroscopy

IR spectroscopy can be used to identify the bonds/functional groups present in a molecule. Molecules absorb IR radiation because the atoms that make up the bonds are vibrating relative to each other – each bond has a characteristic vibrational frequency: the stretching frequency.

In an IR spectrometer, electromagnetic radiation in the range 400–4000 cm^{-1} is passed through a sample. The printout of the spectrum then shows which frequencies (wavenumbers) are absorbed by the sample. More detail about the theory of absorption of IR radiation is given in the section on greenhouse gases.

The unit used in IR spectroscopy is the wavenumber (cm^{-1}). This represents the number of wavelengths per cm and is proportional to frequency and to energy. We usually, however, talk about the 'frequency' of IR radiation absorbed, rather than the 'wavenumber' of radiation absorbed.

IR spectra are always looked at with the baseline (representing 100% transmittance, zero absorbance of IR radiation) at the top. The troughs (usually called 'bands') represent frequencies (in wavenumbers) at which radiation is absorbed (Figure 11.54).

The spectrum is usually divided up into two regions, above and below 1500 cm^{-1}. The segment of the spectrum below 1500 cm^{-1} is called the *fingerprint region* and is characteristic of the molecule as a whole. The region above 1500 cm^{-1} is where we usually look to identify the bonds present in a molecule.

The bonds which are present in a molecule can be determined by looking at the frequencies of IR radiation absorbed. For instance, in the IR spectrum of propanone, there are two bands in the region above 1500 cm^{-1}, corresponding to absorptions by the C—H bond and the C═O bond.

A comparison of the fingerprint region of a spectrum with IR spectra in databases can be used to identify molecules. For example, butanone (Figure 11.55) and propanone (Figure 11.55) both show very similar bands in the region above 1500 cm^{-1}, because they have the same bonds and same functional group (C═O), but they can be distinguished using their fingerprint regions, which are very different.

The frequencies (in wavenumbers) at which some bonds absorb are shown in Table 11.13.

We interpret IR spectra to identify the bonds present in molecules and, for instance, using Table 11.13 we can distinguish between an absorption band indicating the presence of C═C and one indicating the presence of C═O. We cannot always, however, distinguish between functional groups, and Table 11.17 does not allow us to distinguish between C═O in a ketone and in an ester.

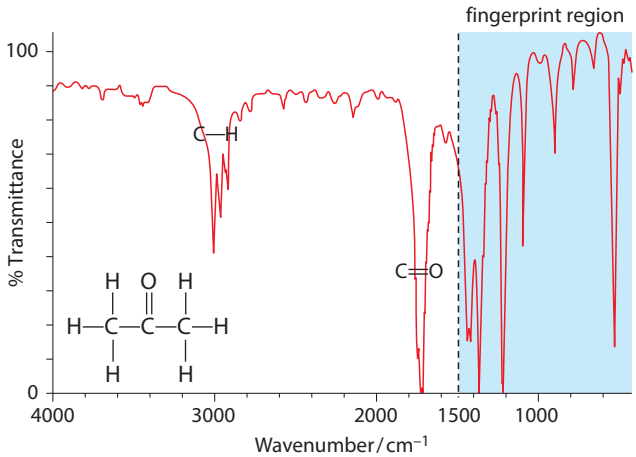

Figure 11.54: The IR spectrum of propanone, CH_3COCH_3.

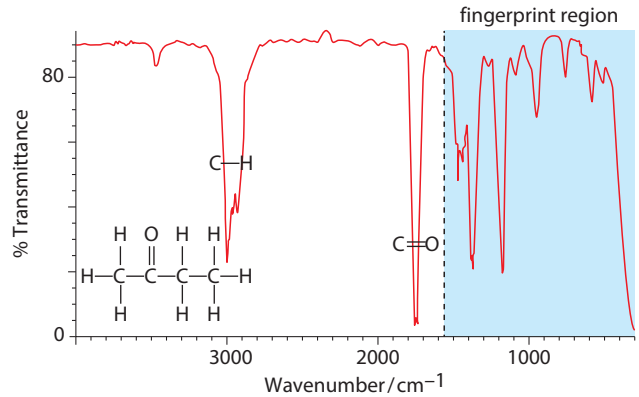

Figure 11.55: Butanone has a very similar IR spectrum to propanone in the region above 1500 cm^{-1} because it contains the same bonds, but the fingerprint region is different.

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Bond	Class of compound	Characteristic range of wavenumber / cm^{-1}
C—Cl	chloroalkane	600–800
C—O	alcohol, ether, ester, carboxylic acid	1000–1300
C=C	alkene	1610–1680
C=O	aldehyde, ketone, carboxylic acid, ester	1700–1750
C≡C	alkyne	2100–2260
O—H	hydrogen bonded in carboxylic acids	2400–3400
C—H	alkane, alkene, arene	2840–3100
O—H	hydrogen bonded in alcohols, phenols	3200–3600
N—H	primary amine	3300–3500

Table 11.13: The characteristic ranges of wavenumbers at which some bonds vibrate.

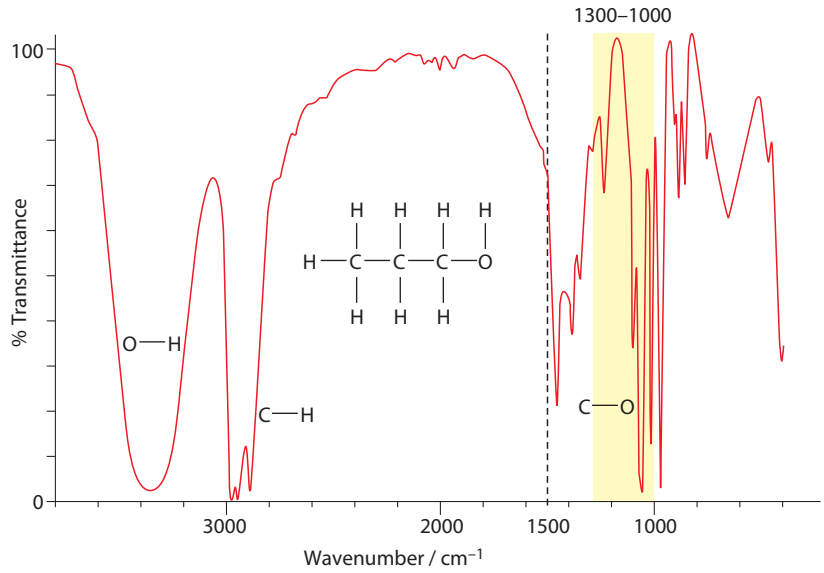

Figure 11.56: The IR spectrum and full structural formula of propan-1-ol.

EXAM TIP

A table of IR absorption frequencies is given in the IB chemistry data booklet. The values in that table differ slightly from those given here – you will need to use the values in the data booklet for the examination.

Interpreting IR spectra

Propan-1-ol

The IR spectrum and full structural formula of propan-1-ol are shown in Figure 11.56.

By comparison of the bands with the values in Table 11.17, we can identify an O—H absorption (about 3350 cm^{-1}) and a C—H absorption (about 2900–3000 cm^{-1}). We can see from the structure that propan-1-ol contains C—O, so we need to check the 1000–1300 cm^{-1} to make sure that there is an absorption in this region, which there is.

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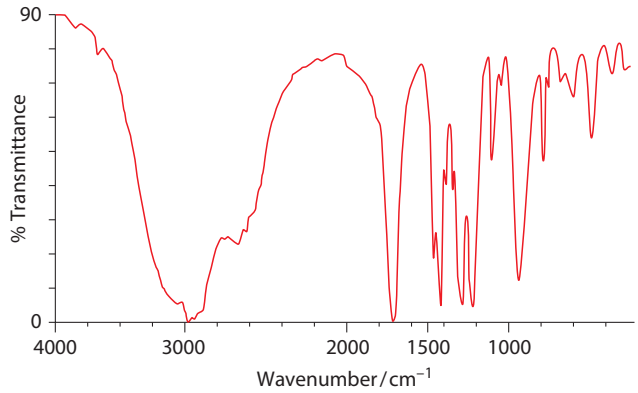
WORKED EXAMPLE 11.20

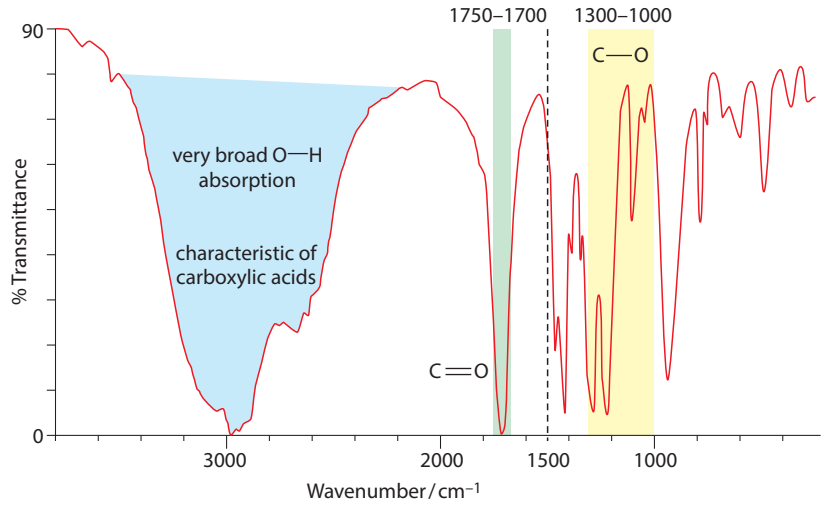
The IR spectrum shown is for a molecule containing carbon, hydrogen and oxygen. There is one functional group in the molecule. Identify two bonds present in the molecule and suggest the identity of the functional group.



Answer

First look at the region above 1500 cm^{-1}. Match up the frequencies of bands in the spectrum with the frequencies given in Table 11.17. The presence of an absorption band in the 1700–1750 cm^{-1} region suggests that there is a C═O bond in the molecule. The very broad absorption band between about 2400 and 3400 cm^{-1} is due to an O—H bond – a very broad band in this region is characteristic of carboxylic acids. The C—H stretch also occurs in the region around 3000 cm^{-1}, but this is usually significantly obscured by the broad O—H absorption of a carboxylic acid. This information suggests that the molecule is a carboxylic acid, containing the carboxyl functional group, —COOH.

The functional group of a carboxylic acid has a C—O bond as well as a C═O bond, and so, we should now look in the fingerprint region to confirm the presence of an absorption in the region 1000–1300 cm^{-1}, which is indeed the case. If there were no band in this region, we would have to review our hypothesis that the molecule is a carboxylic acid. The annotated IR spectrum is



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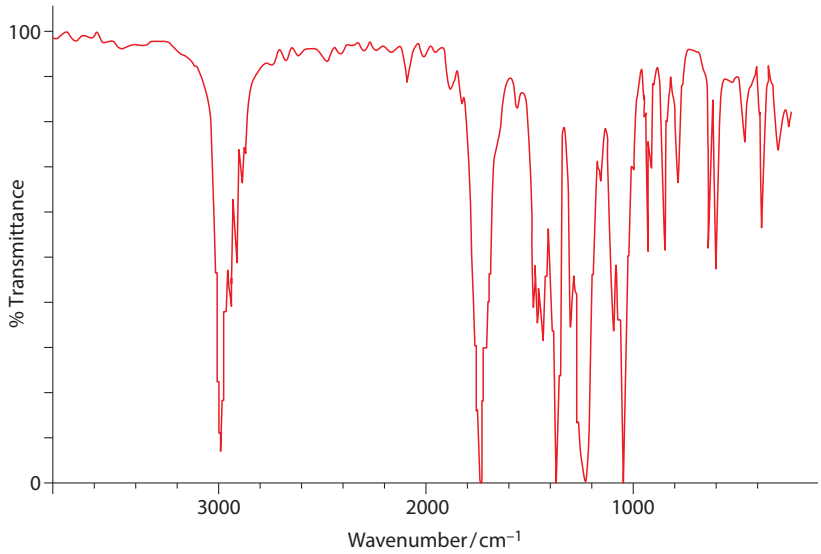
Only use the fingerprint region to confirm the presence of bonds

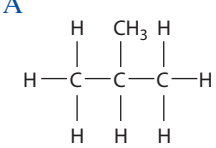
The region below 1500 cm^{-1} contains many absorptions, due to C—C bonds and C—H bonds, and is difficult to interpret. We usually only look at the fingerprint region to *confirm* the presence of a particular bond, once we have a good idea of the structure of the molecule. For example, a band in the 1000–1300 cm^{-1} region does not mean that there is necessarily a C—O bond in a molecule – but the absence of a band in this region means that a C—O bond is not present. For example, in the IR spectrum of propanone (Figure 11.54), there are bands in the 1000–1300 cm^{-1} region but no C—O bond. Similarly, all the spectra that we have seen so far contain bands in the 600–800 cm^{-1} region, but none of the molecules contain a C—Cl bond (see Table 11.17). We would only look for an absorption in that region to confirm the presence of a C—Cl bond if other information suggested that there was a Cl atom in the molecule.

WORKED EXAMPLE 11.21

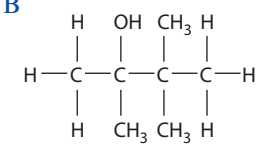
The IR spectrum shown is for one of the compounds below. Identify the compound and explain how you arrive at your choice.



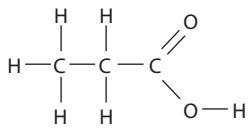
A



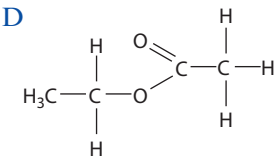
B



C



D



Answer

Looking in the region above 1500 cm^{-1}, we can identify an absorption band around 2840–3100 cm^{-1} that is due to a C—H bond, and an absorption in the region 1700–1750 cm^{-1} that is due to a C=O bond. This eliminates molecules A and B because neither contains a C=O bond.

Molecule C is a carboxylic acid, which would be expected to have a broad O—H absorption band in the region 2400–3400 cm^{-1}. There is no absorption in this region, except the C—H absorption, so the spectrum cannot be that of molecule C.

This means that we are left with molecule D. Molecule D contains C—H bonds and C=O bonds and should give rise to a band in the region 1000–1300 cm^{-1} because it contains a C—O bond – the spectrum shows that there is an absorption in this region.

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TEST YOUR UNDERSTANDING

Use Table 11.17 to answer the following questions.

34 Which of the following compounds will have an IR absorption band in the 1700–1750 cm^{-1} region?

A but-2-ene

B propanal

C CH_3COCH_3

D $CH_3CH_2CH_2CH_2Cl$

E CH_3COOCH_3

F $CH_3CH_2CH(OH)CH_3$

G CH_3CH_2COOH

35 Predict the IR absorption bands and the bonds responsible for them in the region above 1500 cm^{-1} for the following:

a propane **b** propan-2-ol

c propene **d** propanoic acid.

The greenhouse effect

The greenhouse effect is a natural phenomenon and an important mechanism for maintaining the Earth's temperature at a reasonable level. Without some sort of greenhouse effect, the Earth would be too cold to maintain life as we know it.

Some of the short-wavelength solar radiation (UV and visible light) from the sun that reaches the Earth is reflected back into space, and the rest passes through the atmosphere to reach the Earth's surface. The surface absorbs some of this radiation and heats up. The warmed surface radiates longer-wavelength IR radiation. Part of this radiation is absorbed by the greenhouse gases, such as carbon dioxide, in the atmosphere. The energy absorbed by greenhouse gases is then transferred to surrounding molecules when they collide, increasing the (translational) kinetic energy of the surrounding molecules and, hence, the temperature of the atmosphere.

The overall effect is that heat is 'trapped' by the gases in the atmosphere (Figure 11.57).

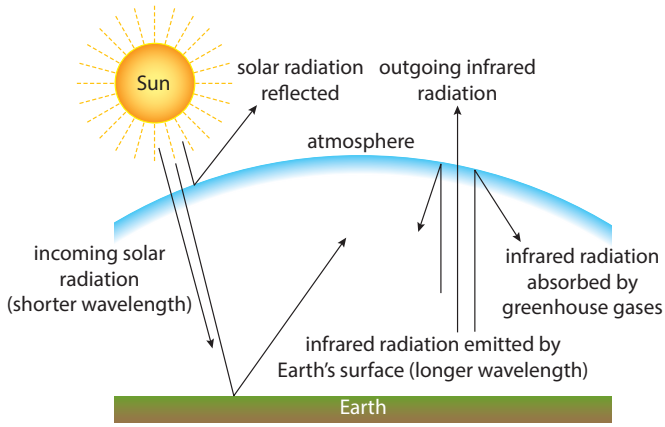

Figure 11.57: The greenhouse effect.

The natural equilibrium between incoming and outgoing radiation maintains the Earth's mean temperature at about 15 °C. If the amount of greenhouse gases in the atmosphere increases, then more IR radiation will be absorbed and the global temperature should increase.

KEY POINT

Certain gases in the atmosphere, known as greenhouse gases, absorb infrared radiation.

Which gases are greenhouse gases?

KEY POINT

For a molecule to be able to absorb IR radiation, there must be a change in dipole moment when it vibrates.

The dipole moment is a measure of the polarity of a molecule. The size of the dipole moment depends on the magnitude of the partial charges (δ+/δ−) and on the distance between them. The bigger the partial charges or the bigger the distance between them, the larger the dipole moment. All polar molecules have a dipole moment, but non-polar molecules have a dipole moment of zero.

Even at absolute zero, molecules are vibrating. Any polar molecule will be a greenhouse gas because, as the molecule vibrates the atoms get closer together or further apart, so the dipole moment changes and the molecule can absorb IR radiation. Thus, H_2O and CF_2Cl_2 are greenhouse gases.

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Homonuclear (two atoms the same) diatomic molecules have a zero dipole moment, and this cannot change as they vibrate, because both atoms attract the electrons in the bond equally. Therefore, homonuclear diatomic molecules cannot absorb IR radiation – they are *IR inactive*. This is essential for the existence of life on Earth because it means that the main gases in the atmosphere, O_2 (21%) and N_2 (78%), cannot absorb IR radiation and, therefore, do not contribute to the greenhouse effect.

Carbon dioxide is a greenhouse gas

Although carbon dioxide and methane are both non-polar, they are both greenhouse gases because they can vibrate in certain ways that cause the dipole moment to change, so they can absorb IR radiation (Figure 11.58).

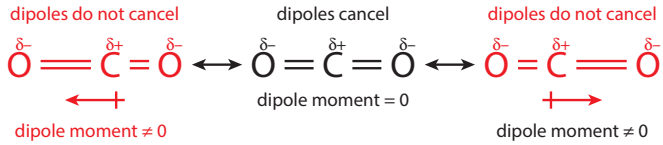

Figure 11.58: The CO_2 molecule can vibrate in different ways. This vibrational mode is called the asymmetric stretch and causes the dipole moment (polarity) of the molecule to change.

TEST YOUR UNDERSTANDING

36 Which of the following molecules will absorb IR radiation and be greenhouse gases?

O_2, HCN, HF, H_2, CO, CO_2, H_2S, N_2, $CFCl_3$, N_2O

SCIENCE IN CONTEXT

Greenhouse gases

In the 100 years up to 2005, global temperatures increased by about 0.7 °C, and in the past 30 years, temperatures are estimated to have increased by about 0.2 °C per decade. Most scientists believe that the main reason for this is an enhanced greenhouse effect, which has been caused by an increase in anthropogenic (caused by human activity) greenhouse gases – for example, carbon dioxide produced by burning fossil fuels or methane from agriculture. The effects of global warming and climate change linked to this enhanced greenhouse effect are already being seen, and many people believe that the consequences for the world over the next century could be catastrophic if nothing is done to reduce the rate at which greenhouse gases are being added to the atmosphere.

Carbon dioxide, methane and water vapour are the three most important greenhouse gases in the Earth's atmosphere. The contribution of a particular greenhouse gas to global warming depends on several factors: its ability to absorb IR radiation; its abundance in the atmosphere; its atmospheric lifetime; and the wavelength range in which it absorbs IR radiation.

The potential for a particular gas to cause global warming can be described in terms of its global-warming potential (GWP), which is the potential for 1 kg of a gas to cause global warming over a particular time period (e.g. 20 years or 100 years) compared to that of 1 kg of CO_2. Methane has a much higher (about 20–30 times) global-warming potential than that of carbon dioxide but is produced in much smaller amounts. However, scientists have become extremely worried about the effects of increased levels of methane in the atmosphere; these have increased by about 10% in the last 30 years and are now about 2.5 times higher than pre-industrial levels. Anthropogenic sources of methane include the fossil fuel industry and agriculture, with some estimates suggesting that livestock contribute about 15% to annual emissions of greenhouse gases.

ISBN 9781009052658

Structure determination using mass spectrometry

Mass spectrometry can be used to determine the relative molecular mass of a molecule (from the molecular ion) and identify groups present (from the fragmentation pattern).

A sample of the organic compound to be investigated is injected into a mass spectrometer, where it is vaporised. It is then bombarded with high-energy electrons to produce positive ions. These pass on through the mass spectrometer where they are separated according to mass (actually the mass-to-charge ratio) and detected. It is important to remember that only positive ions can be detected in a mass spectrometer.

The mass spectrometer sorts molecules according to their mass-to-charge ratio (*m*/*z* or *m*/*e*). We assume here that only 1+ ions are formed so that the mass-to-charge ratio is equal to the mass.

The molecular ion

The ion produced when just one electron is removed from a molecule is called the *molecular ion*, M^+.

For example, when a sample of propane (C_3H_8) is introduced into a mass spectrometer and is bombarded with electrons, the $C_3H_8^+$ ion is produced:

$$C_3H_8(g) + e^- \rightarrow C_3H_8^+(g) + 2e^-$$

KEY POINT

The peak in the spectrum at the highest mass (*m*/*z*) value corresponds to the molecular ion and indicates the relative molecular mass of the molecule.

The mass spectrum of propane is shown in Figure 11.59.

We can therefore deduce from Figure 11.59 that the relative molecular mass of propane is 44. It is important to note that the molecular ion peak is not necessarily the biggest peak (highest peak) in terms of abundance, but it has the highest *m*/*z* value (furthest to the right). Remember, the mass of an electron is negligible, so the mass of the molecular ion is essentially the same as that of the molecule.

A mass spectrum may also show a peak with a mass one unit higher than the molecular ion – an $(M + 1)^+$ peak. This would be a small peak at $m/z = 45$ in the mass spectrum of propane and is caused by the presence of an atom of ^{13}C in some molecules. ^{13}C is an isotope of carbon – its natural abundance is low at 1.1%.

The fragmentation pattern

It can be seen from the mass spectrum of propane in Figure 11.59 that there are lots of peaks other than the molecular ion peak. These peaks form the **fragmentation pattern** and arise because, once an electron has been

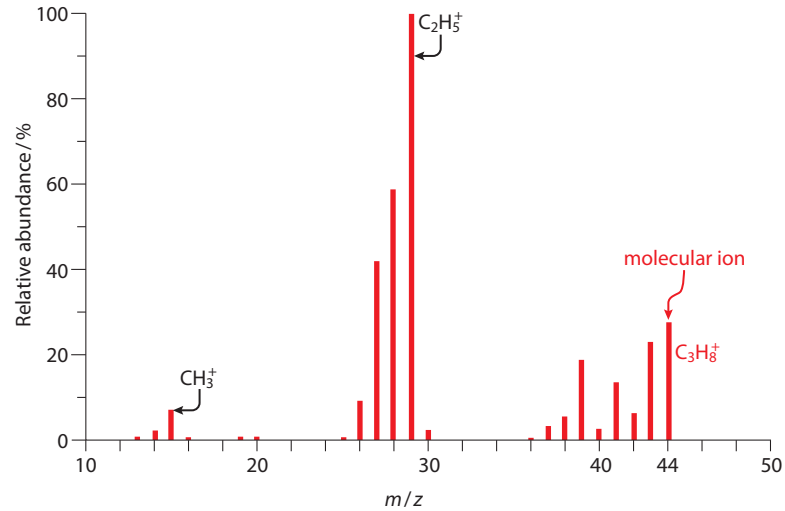

Figure 11.59: The mass spectrum of propane: $CH_3CH_2CH_3$.

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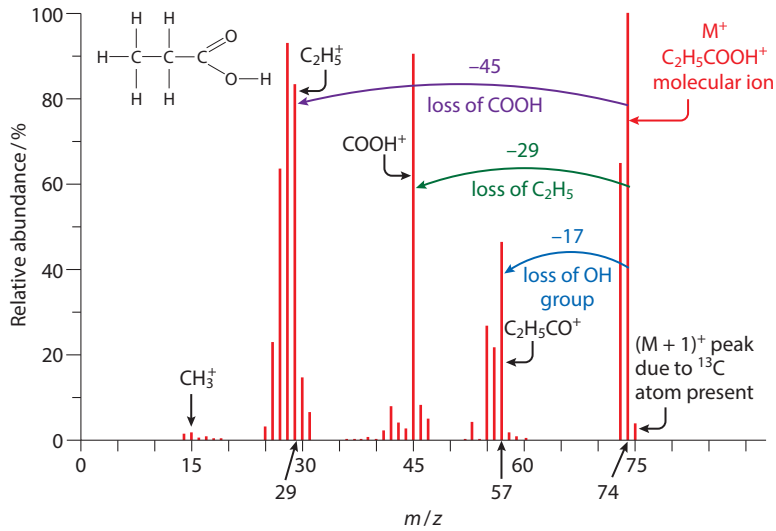

Figure 11.60: The mass spectrum of propanoic acid, CH_3CH_2COOH.

knocked out of a molecule, the ions produced are unstable and some fall apart, for example:

$C_3H_8^+ \rightarrow C_2H_5^+ + CH_3$

Of the many millions of molecular ions produced in the mass spectrometer, some will arrive at the detector intact, but others will break apart in different ways.

For example, some will fragment to produce $C_2H_5^+$ and CH_3, whereas others will fragment to CH_3^+ and C_2H_5:

$C_3H_8^+ \rightarrow C_2H_5 + CH_3^+$

CH_3 and C_2H_5 are called radicals – they are species with an unpaired electron. There are also many other ways that the molecules can break apart.

Any positive ions formed in the fragmentation process will produce a peak in the mass spectrum. The peak at *m*/*z* 29 in the mass spectrum of propane is due to the $C_2H_5^+$ ion. Only positive ions can pass through a mass spectrometer, so the CH_3 radical produced in the first fragmentation process does not give rise to a peak. However, there is a peak at *m*/*z* 15 due to CH_3^+, produced in the second fragmentation process.

Interpreting fragmentation patterns

We can think of fragmentation in two ways – we can look at

- the ion formed when a molecular ion breaks apart
- the group lost from a molecular ion.

Look at the mass spectrum of propanoic acid in Figure 11.60.

The molecular ion peak occurs at *m*/*z* 74, so the relative molecular mass is 74.

There is a peak in the spectrum at *m*/*z* 57, which corresponds to the loss of OH (mass 17) from the molecular ion. So, the fragment responsible for the peak at *m*/*z* 57 is ($C_2H_5COOH^+ - OH$), that is, $C_2H_5CO^+$.

The peak at *m*/*z* 45 corresponds to the loss of 29 mass units from the molecular ion. C_2H_5 is a group with mass 29, and so, we can deduce that C_2H_5 is lost from $C_2H_5COOH^+$ to form the $COOH^+$ ion, which is what gives rise to the peak at *m*/*z* 45.

The peak at *m*/*z* 29 is due to the $C_2H_5^+$ ion, which is formed by loss of COOH from $C_2H_5COOH^+$.

The formulas of some common fragment ions are shown in Table 11.14.

Peaks can also be thought of as being formed when fragments are lost from a molecule, so another way of giving some of this information is shown in Table 11.15. In this case the *m*/*z* value of a peak will be the relative molecular mass (M_r) minus the mass of the fragment lost. Groups lost from a molecular ion do not need a positive charge.

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Fragment	Mass of fragment ion	Possible inference
CH_3^+	15	
OH^+	17	alcohol/carboxylic acid
$C_2H_5^+/CHO^+$	29	ethyl group/aldehyde
CH_3O^+/CH_2OH^+	31	methyl ester/ether/primary alcohol
CH_3CO^+	43	ketone with C=O on second C
$COOH^+$	45	carboxylic acid
$C_6H_5^+$	77	arene/phenyl group

Table 11.14: Formulas of some common fragment ions.

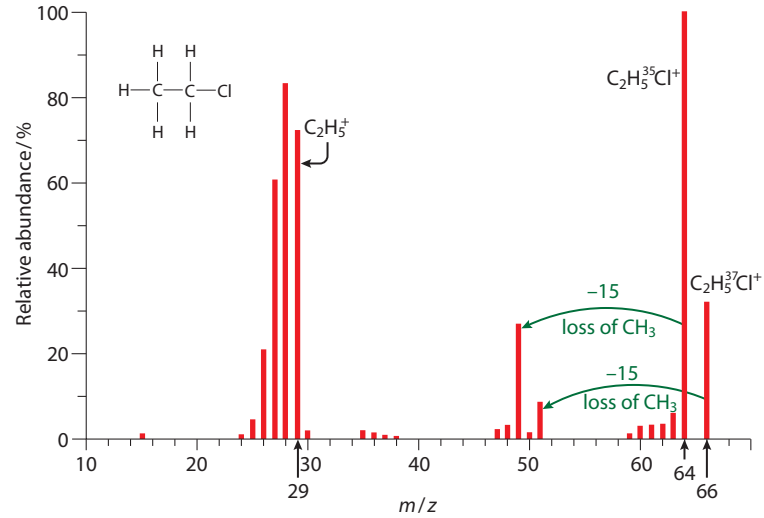

Figure 11.61: The mass spectrum of chloroethane: CH_3CH_2Cl.

Fragment lost	Mass lost
$.CH_3$	15
$.CH_3CH_2/.CHO$	29

Table 11.15: Another way of presenting the information in Table 11.18. The fragments are shown with a . in the IB data booklet to indicate that they are radicals (see Chapter 21).

EXAM TIP

Only positive ions give peaks in a mass spectrum. So, if you are asked to identify the species responsible for the peak at a certain *m/z* value, you must not forget the + charge.

The fragmentation pattern in a mass spectrum can be very complicated, and you should not try to identify every single peak. Molecules can undergo fragmentation in many different ways – they can also undergo rearrangement as they fragment.

Isotopes give rise to separate peaks

The mass spectrum of chloroethane is shown in Figure 11.61.

The relative molecular mass of chloroethane can be calculated to be 64.5 (to one decimal place), but it can be seen that there is no peak at 64.5. The relative atomic mass of chlorine, 35.45, is an average value and arises because chlorine has two isotopes, ^{35}Cl and ^{37}Cl, with an abundance ratio of approximately 3:1.

There are no chlorine atoms with a mass of 35.45, only chlorine atoms with a mass of 35 or with a mass of 37. Therefore, some chloroethane molecules contain a ^{35}Cl atom and others have a ^{37}Cl atom, and we get molecular ion peaks at *m/z* 64 ($C_2H_5^{35}Cl^+$) and *m/z* 66 ($C_2H_5^{37}Cl^+$).

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WORKED EXAMPLE 11.22

The mass spectrum of a hydrocarbon. with molecular formula C_8H_{10}, contains peaks at $m/z = 106$, 91, 77 and 15.

a Suggest identities for these peaks.

b Suggest the identity of the fragment lost to form the peak at $m/z = 77$.

c Suggest the identity of the molecule.

Answer

a If we add up the relative atomic masses using 12 for C and 1 for H, we get 106 as the relative molecular mass. Therefore, the peak at $m/z = 106$ corresponds to the molecular ion peak,$C_8H_{10}^+$.

We know the molecule just contains C and H, so we can see that the peak at $m/z = 15$ must correspond to CH_3^+ because $12 + 3 \times 1 = 15$.

Next, we can look at which combinations of C and H will give 77. It could be

$6 \times 12 + 5 \times 1$

$5 \times 12 + 17 \times 1$

$4 \times 12 + 29 \times 1$, etc.

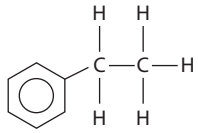
However, the maximum number of H for 5 C atoms is 12 ($2n + 2$ for an alkane); therefore, C_5H_{17}, C_4H_{29}, etc. are not possible. The only possible combination of C and H that produces a mass of 77 is C_6H_5. Therefore, the peak at 77 is due to the $C_6H_5^+$ ion. This is most likely to be a phenyl group.

91 is 14 more than 77. 14 is $12 + 2 \times 1$, so there will be an additional CH_2 group on C_6H_5, and the peak in the mass spectrum at 91 is due to $C_7H_7^+$, which is likely to be $C_6H_5CH_2^+$.

b $106 - 77 = 29$, so we know a mass of 29 is lost from the molecular ion to form the peak at 77. The only combination of C and H that adds up to 29 is C_2H_5; therefore, this is the identity of the fragment lost. Note that a + charge is not required here because this is a fragment *lost* – it is not forming a peak in the spectrum.

If the molecule had also contained oxygen, then another possible fragment of mass 29 is CHO – you may have to look at other information provided to decide between the various possibilities in an examination question.

c Using all the information we deduced in **a** and putting together C_6H_5 and C_2H_5 fragments, suggests that the molecule is $C_6H_5CH_2CH_3$, that is, ethylbenzene:



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WORKED EXAMPLE 11.23

The molecular ion peak for a compound containing C, H and O only occurred at $m/z = 74$ in the mass spectrum. Deduce possible molecular formulas for the compound.

Answer

To do this, we have to add up possible combinations of C, H and O to make 74. Let's first of all try some combinations with one O atom.
Taking away 16 from 74 gives us 58, but $5 \times 12 = 60$, so there must be fewer than 5 C atoms in the molecule, so let's start with 4 and work our way down.

$58 - 4 \times 12 = 10$, which gives us C_4H_{10}

$58 - 3 \times 12 = 22$, which gives us C_3H_{22}

The maximum number of H atoms for n C atoms is $2n + 2$; therefore, C_3H_{22} is not possible. Therefore, we can work out that one possible molecular formula is $C_4H_{10}O$.

Now let's try 2 O atoms: $74 - 2 \times 16 = 42$.

If we follow the same procedure, we get

$42 - 3 \times 12 = 6$, which gives us C_3H_6

$42 - 2 \times 12 = 18$, which gives us C_2H_{18}, which is not possible.

So, another possible molecular formula is $C_3H_6O_2$.

Let's try three O atoms. $74 - 3 \times 16 = 26$, and we can work out that the only possibility is $C_2H_2O_3$.

If we try four O atoms, then we get $74 - 4 \times 16 = 10$, which is not enough for a C atom, so there are no possibilities.

There are thus three possible molecular formulas for a compound with this molecular ion: $C_4H_{10}O$, $C_3H_6O_2$ and $C_2H_2O_3$. Further information from the fragmentation pattern, elemental analysis or other spectroscopic techniques would be required to distinguish between these possibilities.

TEST YOUR UNDERSTANDING

37 The molecular ion peaks for a series of compounds that all contain carbon, hydrogen and oxygen and no other elements occur at the values shown. Suggest possible molecular formulas for the compounds.

a 44 **b** 60

c 72 **d** 88

38 The following peaks occur in the mass spectra of compounds containing carbon, hydrogen and oxygen only. Suggest possible identities for the fragments responsible.

a 15 **b** 28

c 29 **d** 31

e 43 **f** 45

g 59 **h** 77

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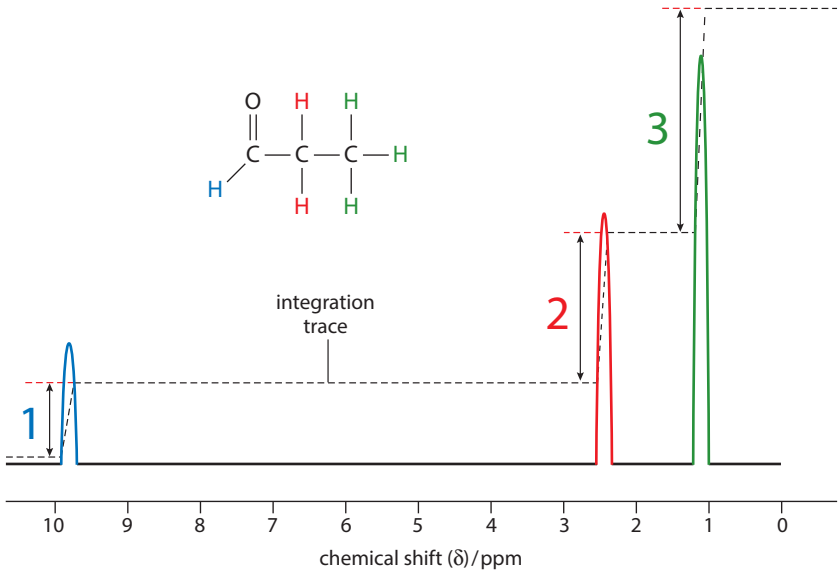

Figure 11.62: The low-resolution NMR spectrum of propanal: CH_3CH_2CHO. The integration trace allows us to work out the ratio of the numbers of protons in each environment.

Proton NMR spectroscopy

Proton NMR (or ^{1}H NMR) is one of the most powerful techniques for deducing the structure of an organic molecule.

A hydrogen nucleus (proton) has a property called spin. The spin of the nucleus makes it act like a tiny bar magnet. This bar magnet can either align itself with (lower energy) or against (higher energy) an externally applied magnetic field. Energy in the radiofrequency range of the electromagnetic spectrum can be used to cause a hydrogen nucleus to change its orientation relative to the applied magnetic field. It is these changes in energy state that are exploited in NMR spectra.

KEY POINT

Proton NMR looks at the H atoms in a molecule.

In analysing NMR spectra, we are looking at absorptions due to ^{1}H nuclei (usually just called protons) – this technique provides information about the environments of H atoms in molecules. In discussions of NMR, the terms proton, H atom and ^{1}H nucleus are used fairly interchangeably, however, it is always the nucleus of a hydrogen (^{1}H) atom that gives rise to the signal in the NMR spectrum.

The low-resolution NMR spectrum of propanal is shown in Figure 11.62.

KEY POINT

Signals/peaks in an NMR spectrum correspond to groups of protons (hydrogen atoms) in different chemical environments.

There are three signals in the NMR spectrum of propanal – these correspond to groups of protons (H atoms) in three different chemical environments in one molecule of propanal. The protons in the different environments are coloured differently in Figure 11.62. Hydrogen atoms joined to the same carbon atom are said to be *chemically equivalent* (or just 'equivalent').

KEY POINT

The area under a signal/peak in an NMR spectrum corresponds to the number of protons in a particular environment.

Figure 11.62 shows that the signals have different sizes. The area underneath a signal is proportional to the number of hydrogen atoms in that environment. So, the area under the red signal is twice (two H in this environment) the area under the blue signal (one H in this environment); and the area under the green signal (three H in this environment) is three times that under the blue signal.

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KEY POINT

The integration trace tells us the ratio between the number of protons (H atoms) in each environment.

An NMR spectrometer can work out the area under each signal to produce an integration trace on the spectrum – this is the dashed line in Figure 11.62. The vertical heights of the steps in the integration trace are proportional to the number of hydrogen atoms in each environment. To determine the ratio between the number of hydrogen atoms (protons) in each environment, measure the vertical height of each step in the integration trace using a ruler and find the ratio between the heights – this is the same as the ratio between the numbers of H atoms in each environment.

So, in Figure 11.62, the steps that we measure are marked with a double-headed arrow. The heights of the steps are as follows:

blue signal = 10 mm, red signal = 20 mm,
green signal = 30 mm

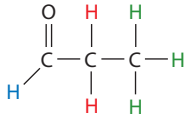
So, it can be seen that the ratio between the number of H atoms in each environment is 1:2:3. In this molecule, we have 6 H atoms, and so, this ratio also gives us the number of H atoms in each environment, but if there were 12 H atoms in the molecule, there would be 2, 4 and 6 H atoms in each environment, respectively.

KEY POINT

The **chemical shift** gives us information about the environment a particular proton is in.

The horizontal scale on an NMR spectrum is the **chemical shift**, which is given the symbol δ and is expressed in parts per million (ppm). Chemical shift data provide information about the environments that protons (hydrogen atoms) are in – protons in different chemical environments have different chemical shifts.

For instance, if we look at propanal again, the H atom coloured blue is joined to a C=O group, whereas those coloured red are just part of a CH_2 group, so they are in different environments. The H atoms coloured green are in a different environment again – they are part of a CH_3 group that is next to a CH_2 group.

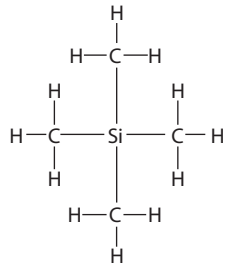


The chemical shift scale may seem strange, having units of ppm, but this is because it is a ratio. The resonant frequency of a particular proton depends on the magnetic field strength of the instrument used, therefore the scale is designed as a ratio that is independent of this so that comparisons can be made.

KEY POINT

Chemical shifts are measured relative to TMS.

Chemical shift values are measured relative to an internal standard, tetramethylsilane (TMS):



In any NMR experiment, a small amount of TMS is added to the sample to produce a signal in the spectrum. The protons in TMS are assigned an arbitrary chemical shift of 0.00 ppm, and all chemical shifts are measured relative to this.

TMS was chosen as the standard because

- It has 12 protons all in the same environment, and so gives a strong signal when only a small amount is added.
- The chemical shift of the protons in TMS is at a lower value than the protons in virtually all organic molecules, therefore, TMS fixes the lower end of the chemical shift scale.
- The position of the chemical shift is such that it is well away from the chemical shifts of protons in nearly all organic molecules, so the TMS signal does not overlap with the protons signals in which we are interested.
- It is non-toxic.
- It is inert, so it will not react with the sample.
- It is volatile and easy to remove from the sample.

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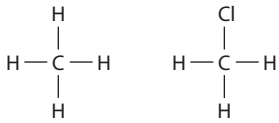
How to work out the number of different chemical environments in a molecule

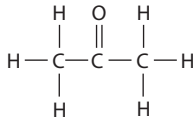
Hydrogen atoms attached to the same carbon atom are in the same environment and will produce one signal. So, there will be one signal (peak) in the NMR spectrum of each of methane and chloromethane.



KEY POINT

If the molecule is symmetrical, H atoms may be in the same chemical environment.

The structure of propanone is shown below:



The molecule is symmetrical, and so, all six H atoms are in the same chemical environment and, therefore, there will be just one signal in the NMR spectrum.

Pentanone (Figure 11.63) is also symmetrical, so this time the four H atoms marked in red are equivalent to each other and produce one signal in the NMR spectrum. The six H atoms marked in green are also equivalent to each other, so produce one signal in the NMR spectrum, but the environment of the protons in green is different to those in red, and so, the chemical shifts of the two groups of protons are different and there are two signals (not counting TMS) in the NMR spectrum.

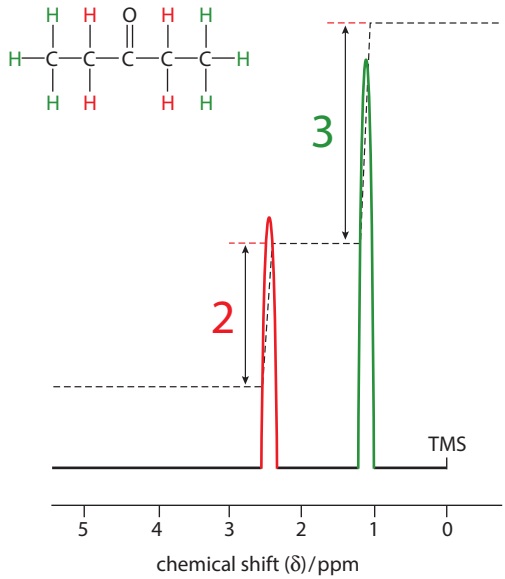
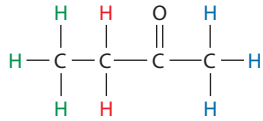


Figure 11.63: The low-resolution NMR spectrum of $CH_3CH_2COCH_2CH_3$ has two signals.

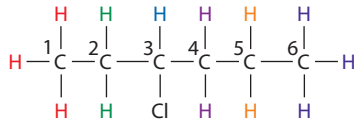
KEY POINT

If the molecule is not symmetrical, the H atoms on each C could be in different environments.

Butanone below is not symmetrical and has protons in three different chemical environments:



3-chlorohexane is also not symmetrical:



There are H atoms in six different chemical environments and, therefore, six separate signals in the NMR spectrum. It may seem that there is little difference between the H atoms on carbon 1 and carbon 6, they are both part of a $—CH_3$ group and both next to a $—CH_2$ group, but the H atoms on carbon 1 are closer to the C with the Cl atom, and this is enough to make them non-equivalent. In reality, the chemical shifts for the H atoms on carbon 1 and carbon 6 will be virtually identical, and the signals will overlap in the spectrum.

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KEY POINT

Hydrogen atoms in methyl groups attached to the same carbon atom are in the same chemical environment.

Propan-2-ol (Figure 11.64 a) has two methyl ($—CH_3$) groups attached to the central C – all six H atoms in these methyl groups are in the same environment. 2-Methylpropan-2-ol (Figure 11.64b) has three methyl groups attached to the same C atom – nine H atoms all in the same chemical environment.

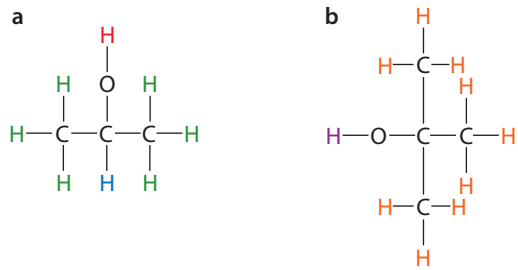


Figure 11.64: Proton environments of **a** propan-2-ol, **b** 2-methylpropan-2-ol.

KEY POINT

Hydrogen atoms attached to atoms such as nitrogen and oxygen also produce signals in the spectrum.

Therefore, there are three signals in the NMR spectrum of ethanol and four signals in the NMR spectrum of propan-1-amine (Figure 11.65).

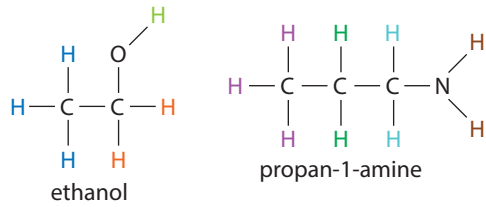
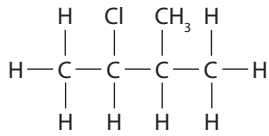


Figure 11.65: The structures of ethanol and propan-1-amine.

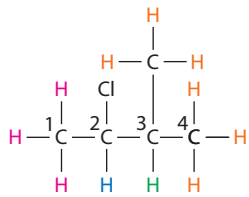
WORKED EXAMPLE 11.24

Deduce the number of different chemical environments for H atoms and the ratio of the number of H atoms in each environment in the molecule shown here:



Answer

First, let's draw this out as a full structural formula:



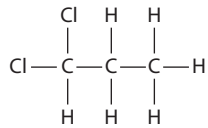
The molecule is not symmetrical, but there are two methyl groups attached to carbon 3 – these six H atoms are all in the same environment. Overall, there are four different chemical environments for H.

The ratio between the number of H atoms in each environment is just given by counting the number of H atoms in each environment; in this case, 3:1:1:6. The order you put these in does not matter.

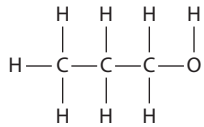
TEST YOUR UNDERSTANDING

39 Suggest the numbers of signals and the ratio between the areas under the signals in the NMR spectrum of each of the following:

a



b



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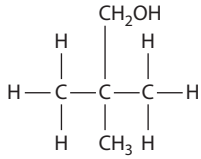
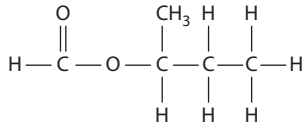
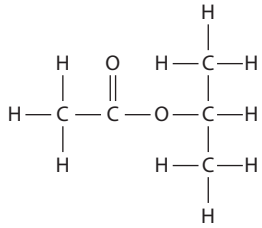
c



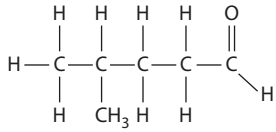
d



e



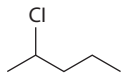
f



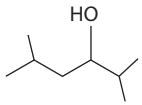
g $CH_3CH_2CH_2CHClCH_3$

h $(CH_3)_3CCH_2C(CH_3)_3$

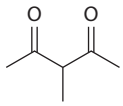
i



j



k



Matching chemical shift values to those in a table of data

Some typical values for the chemical shifts of protons in different environments are given in Table 11.16.
The values in Table 11.16 are approximate and can vary depending on other groups attached.

EXAM TIP

The representation of groups and chemical shifts here is different from those in the IB Chemistry data booklet. You should practise using those as well.

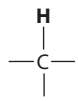
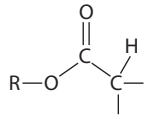
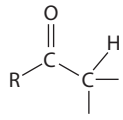
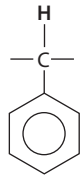
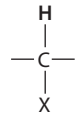
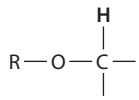
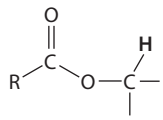
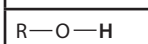
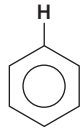
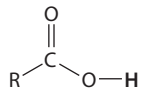
Type of proton	Chemical shift /ppm	Comments
	0.9–1.7	H on a carbon chain but not next to any other functional groups
	2.0–2.5	H on a C next to C=O of an ester
	2.1–2.7	H on a C next to C=O of an aldehyde or ketone
	2.3–3.0	H on a C attached to a benzene ring
 X is a halogen	3.2–4.4	H attached to a C that also has a halogen atom attached
	3.3–3.7	H attached to a C that has an O attached
	3.7–4.8	H on a C next to C—O of an ester
	0.5–5.0	H attached to O in an alcohol
	6.7–8.2	H attached to a benzene ring
	9.4–10.0	H attached to C=O of an aldehyde
	9.0–13.0	H on an O in a carboxylic acid

Table 11.16: Chemical shifts for protons in different environments.

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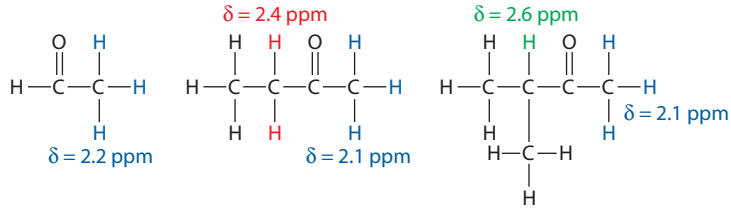

Figure 11.66: Chemical shifts are influenced by the number of hydrogen atoms on a particular carbon atom, but the ranges in Table 11.22 include all possibilities.

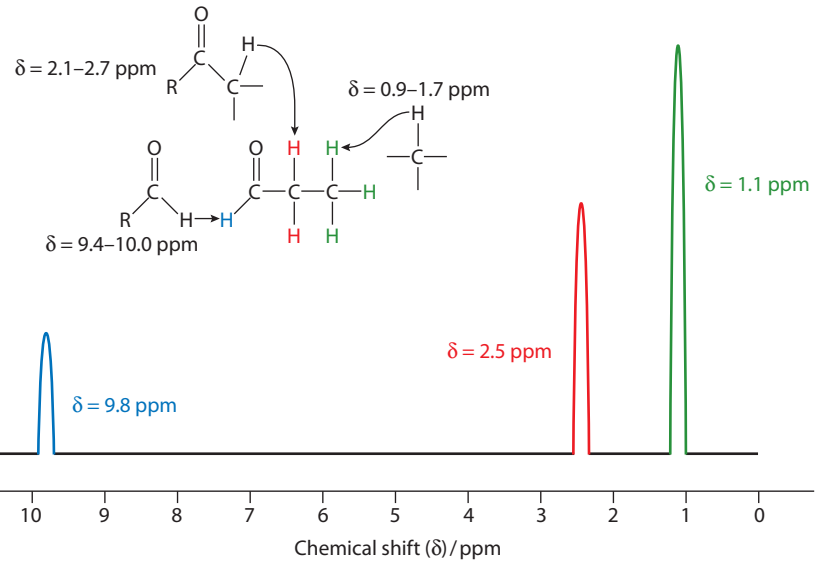

Figure 11.67: The NMR spectrum of propanal: CH_3CH_2CHO.

When predicting a chemical shift, do not worry about the number of H atoms

It does make a difference how many other hydrogen atoms are attached to the carbon atom to which the hydrogen of interest is attached. However, when using tables such as Table 11.20, you can assume that the ranges given in the table include all possibilities, and just look at the *environment* of the hydrogen atom rather than the *number* of hydrogen atoms in that environment.

So, if we look at the molecules shown in Figure 11.66, the H atoms highlighted could all be described as 'an H atom on a carbon next to the C═O group of an aldehyde or ketone'. In some cases, there is one H in the environment we are looking at, in others two and in others three. The chemical shift of these protons all come in the range 2.1–2.7 ppm – this is the range stated in Table 11.20.

EXAM TIP

The IB data booklet includes separate chemical shift ranges for protons that are part of $–CH_3$, $–CH_2R$ and $–CHR_2$ groups. These, however, only refer to protons that are part of an alkyl group that is not next to any other functional groups. For all other groups, ignore the number of H atoms in that environment – the chemical shift range given will include all possible numbers of H atoms.

Try to find the best match possible

When using a table of chemical shift values, you must try to find the best match to the proton environments in the molecule you are analysing.

In the spectrum of propanal (Figure 11.67), the H (blue) attached directly to the C═O group would be expected

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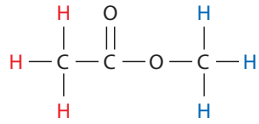
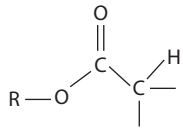
WORKED EXAMPLE 11.25

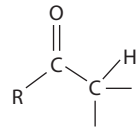
Predict chemical shift values for the protons highlighted in red and in blue in the molecule shown.



Answer

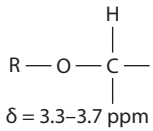
If we look at the H atoms in red, these are on a C which is next to a C=O group, so we have two possibilities:

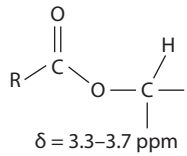




We need to therefore look beyond just the C=O group and see what is next to it. In the molecule we are looking at, there is a singly bonded O atom the other side of the C=O, and so, we have an ester group. The chemical environment of the H atoms in red, therefore, matches better to the left-hand structural element, and we can quote a range of 2.0–2.5 ppm for the chemical shift. It does not matter that there are three H atoms in this environment in the molecule we have, but only one H atom shown in our data table – we assume that the range covers all possibilities.

If we look at the H atoms in blue, we have H atoms on a C that is also singly bonded to an O atom. There are again two possibilities in our table:





Again, if we look at the next atom, the right-hand unit provides the better match, and so, we predict a chemical shift in the range 3.7–4.8 ppm for the H atoms in blue.

to have a chemical shift in the range 9.4–10.0 ppm (actual chemical shift: 9.8 ppm).

The H in red is an H attached to a C next to the C=O of an aldehyde/ketone and will have a chemical shift in the range 2.1–2.7 ppm (actual value 2.5 ppm).

The best match for the H atoms in the CH_3 group is the group shown in Table 11.20 as an H joined to a C with no other functional groups attached in the range 0.9–1.7 ppm (actual value 1.1 ppm).

High-resolution NMR spectra

So far, we have looked at low-resolution NMR spectra, where every signal representing H atoms in a particular chemical environment just appears as a single signal. Here, we will look at high-resolution NMR spectra, where some of the signals are split. The low- and high-resolution NMR spectra of 1,1,2-trichloroethane are shown in Figure 11.68.

There are two signals in the low-resolution spectrum because there are two different chemical environments for protons (hydrogen atoms). However, in the high-resolution spectrum, each of these signals is split. The splitting is due to the hydrogen atoms on *adjacent* (carbon) atom(s). How the signal is split depends on the number of H atoms on the adjacent atom. In this case, the signal due to H_1 is split into three (a triplet), because there are two H atoms on the adjacent carbon atom. The signal due to H_2 and H_3 is split into two (a doublet), because there is one H on the adjacent carbon atom. This splitting is called spin–spin splitting or spin–spin coupling.

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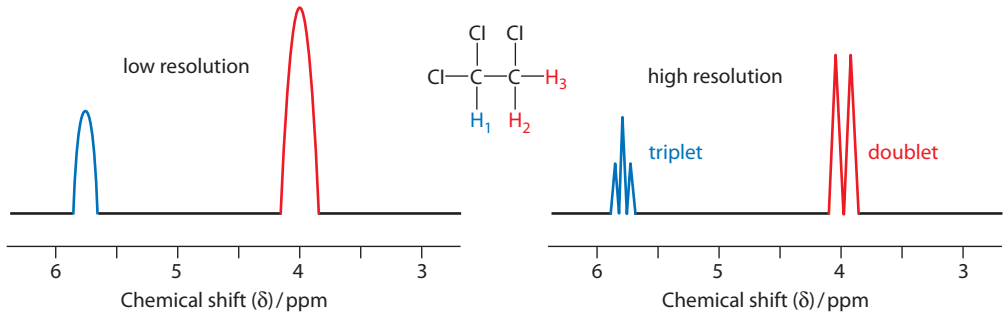

Figure 11.68: The low- and high-resolution NMR spectra of 1,1,2-trichloroethane.

				
	singlet	1 : 1 doublet	1 : 2 : 1 triplet	1 : 3 : 3 : 1 quartet
Multiplicity	1	2	3	4
No. of equivalent protons on adjacent atoms	0	1	2	3

Table 11.17: Different types of splitting patterns.

The different types of splitting patterns and the $n + 1$ rule

You will encounter singlets, doublets, triplets and quartets in NMR spectra. We sometimes talk about the *multiplicity* of a signal, the number of smaller signals/peaks it is split into. The multiplicity of a triplet is three and that of a doublet is two.

There is a simple connection between the multiplicity of a signal and the number of hydrogen atoms on the adjacent atom.

KEY POINT

If there are n protons (hydrogen atoms) on an adjacent atom, the signal for a particular proton will be split into $(n + 1)$ peaks/signals.

This can also be stated the opposite way.

KEY POINT

If the multiplicity of a signal is x, then the number of hydrogen atoms on the adjacent atom is $x - 1$.

A summary of the different types of splitting patterns that you will encounter is given in Table 11.17.

The intensities of the lines in a splitting pattern are given by Pascal's triangle (Figure 11.69). So, we talk about a 1 : 1 doublet (the areas under the peaks are equal) or a 1 : 2 : 1 triplet, etc.

		1		singlet
	1		1	doublet
1		2		1 triplet
1	3	3	1	quartet

Figure 11.69: Pascal's triangle.

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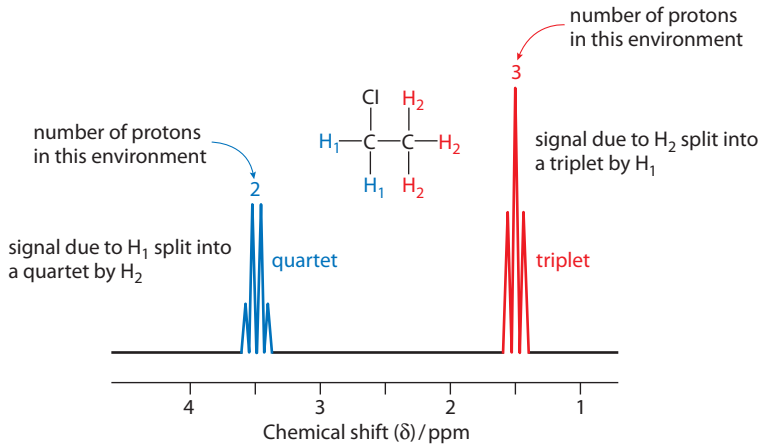


Figure 11.70: The NMR spectrum of chloroethane.

Interpreting high-resolution NMR spectra

The NMR spectrum of chloroethane is shown in Figure 11.70.

There are two sets of signals in the NMR spectrum of chloroethane because there are two different chemical environments for protons (hydrogen atoms). The number above each set of peaks in the spectrum indicates the number of protons in that environment and is obtained from the integration trace.

The signal at δ = 3.5 ppm is due to the 2 H atoms coloured blue in the structure of chloroethane. This signal is split into a quartet – a quartet consists of four peaks and, therefore, has a multiplicity of four. Since 4 − 1 = 3, we can deduce that there are 3 hydrogen atoms on the adjacent carbon atom (the H atoms in red).

It is important to realise that the signal at δ = 3.5 ppm is due to the 2 protons highlighted in blue, but the splitting is giving us information about the H atoms in red – the H atoms on the adjacent C.

The signal at δ = 1.5 ppm is due to the 3 H atoms coloured red in the structure of chloroethane. This signal is split into a triplet (multiplicity = 3). We take 1 away from the multiplicity: 3 − 1 = 2 and, therefore, we can deduce that there must be 2 hydrogen atoms on the adjacent carbon atom (the H atoms in blue).

KEY POINT

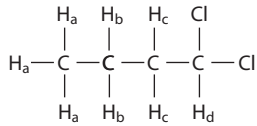
Splitting of the signal of a group of protons is due to the protons on *adjacent* (carbon) atoms.

EXAM TIP

When a signal due to two hydrogen atoms is split into a quartet and the signal due to three hydrogen atoms is split into a triplet, this indicates the presence of an ethyl group (CH_3CH_2) in a molecule – well worth remembering!

'Rules' for spin–spin coupling

- Protons on the same atom (e.g. CH_3, CH_2) do not split each other – they are chemically equivalent.
- Splitting generally only occurs with protons on adjacent atoms:



  H_a protons couple only with H_b protons – H_c and H_d are too far away.
- Protons attached to oxygen or nitrogen atoms do not usually show or cause splitting – this is because the protons exchange with each other and with the solvent and experience an 'average' environment.

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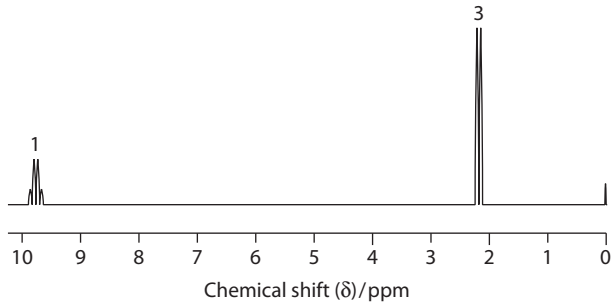
Working out structures from NMR spectra

WORKED EXAMPLE 11.26

The NMR spectrum for a molecule with molecular formula C_2H_4O is shown below. Deduce the full structural formula of the molecule.



Answer

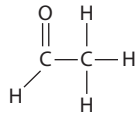
There are two groups of signals, indicating two different environments for H in this molecule. Remember, the signal at δ = 0 is due to TMS (the reference standard).

The numbers above the signals indicate the number of H atoms (protons) in each environment. There are therefore 3 protons with a signal centred on δ = 2.2 ppm and 1 proton with a signal centred on 9.8 ppm.

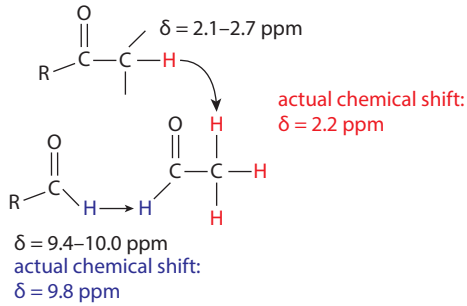
Remember: multiplicity − 1 = number of hydrogen atoms on adjacent carbon atom.

The signal at δ = 2.2 is split into a doublet (multiplicity 2) and, since 2 − 1 = 1, this indicates that there is 1 H on the adjacent C atom. The signal at δ = 9.8 is split into a quartet (multiplicity 4) and, since 4 − 1 = 3, there are 3 H atoms on the adjacent C atom.

The only structure that fits in with this is:



We can check the assignment of the protons by looking at Table 11.20. We can see that the chemical shifts we would suggest from our structure fit in with the chemical shifts of the signals in the spectrum.



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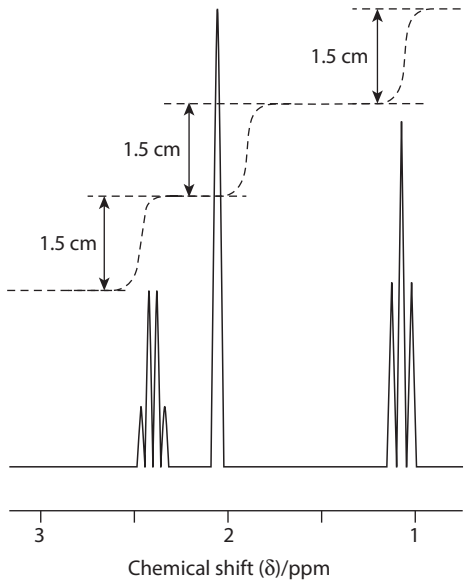
WORKED EXAMPLE 11.27

The NMR spectrum for a compound with molecular formula C_4H_8O is shown below. Deduce the structure of the compound.



Answer

There are three groups of signals, so there must be three different chemical environments for H in this molecule.

Next, we measure the vertical heights of the steps in the integration trace – these are 1 cm, 1.5 cm and 1.5 cm. Multiplying by 2 to get whole numbers, we get 2, 3, 3 – this gives us the ratio of the number of protons (hydrogen atoms) in the different environments. Because there is a total of eight hydrogen atoms in the molecule, we also know the actual number of hydrogen atoms in each environment.

Chemical shift /ppm	2.4	2.1	1.1
No. of protons in environment	2	3	3

The signal at $\delta = 2.4$ ppm is split into a quartet (multiplicity 4). Now $4 - 1 = 3$, so we know that there must be 3 hydrogen atoms on the adjacent C atom. Analysing all the signals in the spectrum gives the following data:

Chemical shift /ppm	2.4	2.1	1.1
No. of protons in environment	2	3	3
Splitting	quartet	singlet	triplet
Multiplicity	4	1	3
No. of protons on adjacent C atom	3	0	2

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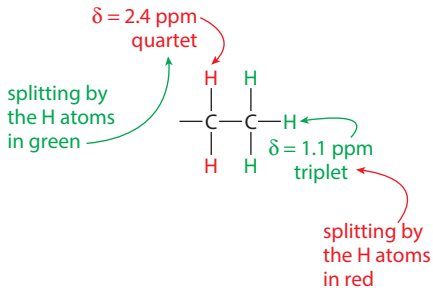
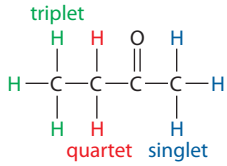
CONTINUED

The signals at δ = 2.4 ppm and 1.1 ppm are caused by an ethyl group – the signal due to 2 H atoms is split by 3 H atoms on the adjacent C, and the signal due to 3 H atoms is split by 2 H atoms on the adjacent C.

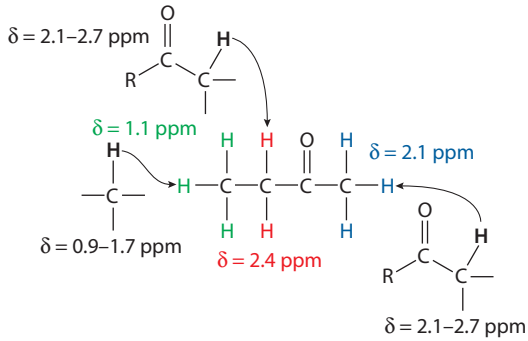


We know that there are four C atoms in the molecule but only three sets of signals. There are also three H atoms that have no H atoms on the adjacent C. These two pieces of information together suggest that there is a carbon atom with no hydrogen atoms attached.

The only structure that fits with all this information is



As a final check, we should try to match up the chemical shifts of the protons with the values given in Table 11.20.



All protons have chemical shifts in the expected ranges

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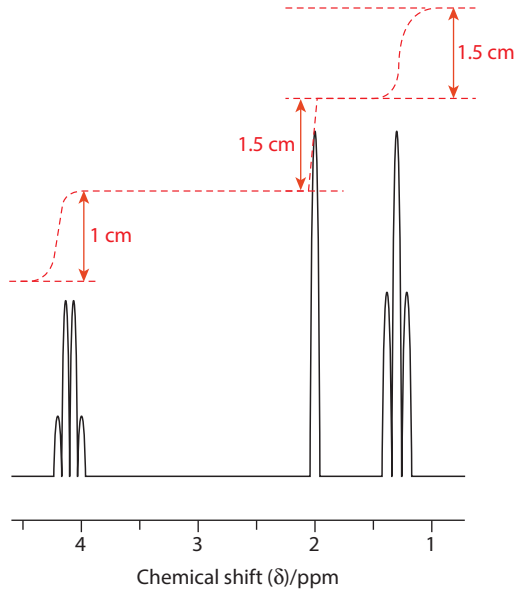
WORKED EXAMPLE 11.28

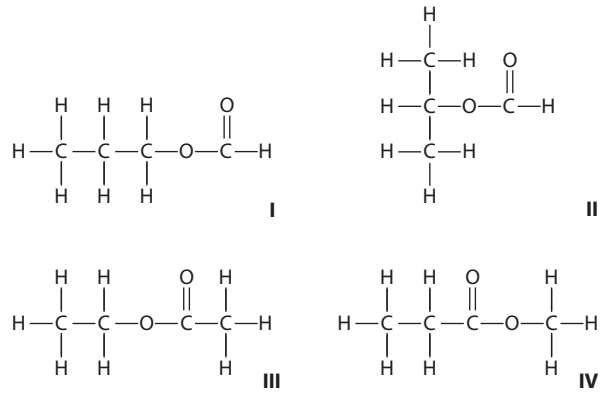
The NMR spectrum for an ester with molecular formula $C_4H_8O_2$ is shown.



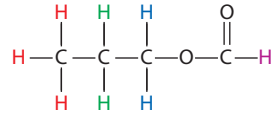
Deduce the structure of the compound.

Answer

We know the molecular formula and that the compound is an ester, so one place to start would be to draw out all the esters with this molecular formula – there are four:



There are three groups of signals, and so, there are three different environments for H. This means that we can eliminate structure I because this has four different chemical environments for H:



All the others have three different chemical environments for H.

The next piece of information we can look at is the integration trace. If we measure the vertical height of the steps, they are 1.0 cm, 1.5 cm and 1.5 cm, working from left to right, which gives

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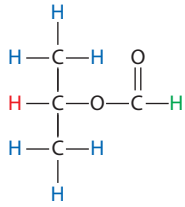
us the ratio 2 : 3 : 3 for the number of H atoms in each environment. This allows us to eliminate structure II, as this would have the ratio 6 : 1: 1.

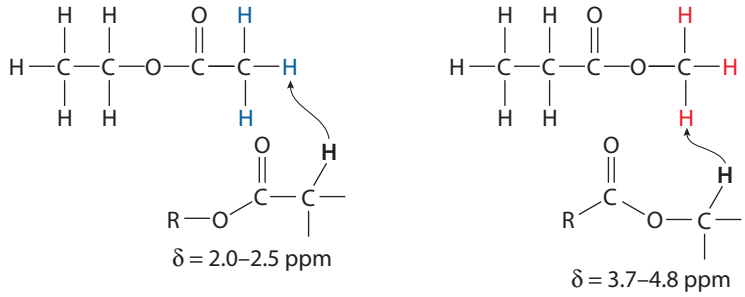


Next we need to look at the splitting pattern:

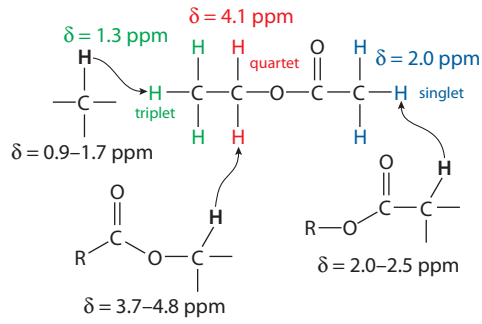
Chemical shift /ppm	4.1	2.0	1.3
No. of protons in environment	2	3	3
Splitting	quartet	singlet	triplet
Multiplicity	4	1	3
No. of protons on adjacent C atom	3	0	2

As in the previous example, there is an ethyl group present – the signal due to 2 H atoms at $\delta = 4.1$ ppm is split by 3 H atoms on the adjacent C, and the signal due to 3 H atoms at $\delta = 1.3$ ppm is split by 2 H atoms on the adjacent C. There is also a group of three hydrogen atoms with no hydrogens on the adjacent carbon. Both ester III and ester IV have this pattern of H atoms, so we cannot use the splitting pattern to distinguish between them.

The only way we can distinguish between these two molecules is to use the chemical shift values. If we consider the singlets, we can use the values in Table 11.20 to predict the chemical shifts for these protons:



The singlet in the spectrum occurs at $\delta = 2.0$ ppm, so this molecule is the one on the left in the diagram above – ester III – ethyl ethanoate:



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Notes on NMR spectra

When there are groups of equivalent protons on adjacent atoms, these all cause splitting of the signal. Therefore, in the NMR spectrum of the molecule shown in Figure 11.71, the signal due to the H highlighted in red is split into a triplet by the two equivalent protons on the adjacent C atoms.

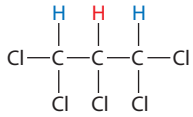


Figure 11.71: The signal of the H in red is split by both the H atoms in blue.

When a molecule is non-symmetrical and there are non-equivalent protons on each side of a particular group, the spectrum becomes complex. Figure 11.72 shows the structural formula of propan-1-ol.

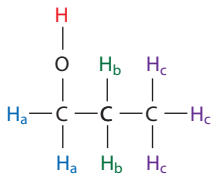


Figure 11.72: Propan-1-ol.

In the NMR spectrum of this compound, the H_b signal is split by H_a and H_c. Depending on the strength of coupling to each set of protons, the signal for H_b could either be described as a quartet of triplets or a triplet of quartets. This signal is therefore very complicated, and it would be difficult to see the exact nature of the splitting. One way of describing this signal is as a *complex multiplet*.

For a molecule such as methylbenzene (Figure 11.73), the protons on the ring are not all equivalent, but, because they are in very similar environments, they are likely to show up as just one signal in the NMR spectrum, unless a very high-resolution spectrum is generated.

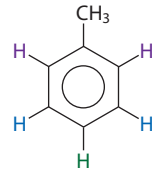
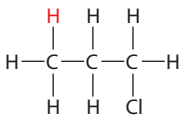


Figure 11.73: Methylbenzene.

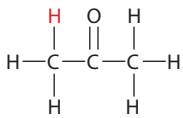
TEST YOUR UNDERSTANDING

40 State the multiplicity of the signal of the H highlighted in red in each structure.

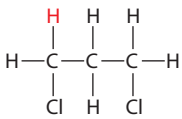
a



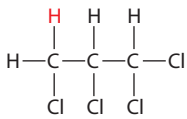
b



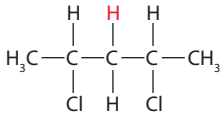
c



d



e



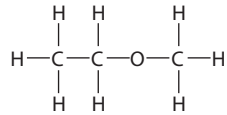
41 Suggest the splitting pattern for each of the following:

a 1,1-dibromo-2,2-dichloroethane

b 1,1,3,3-tetrachloropropane

c propanoic acid

d



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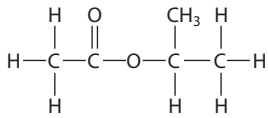
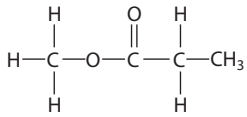
42 The NMR spectrum of each of the following contains a singlet. Use Table 11.20 to suggest the chemical shift range for the singlet.

a propan-2-ol

b



c



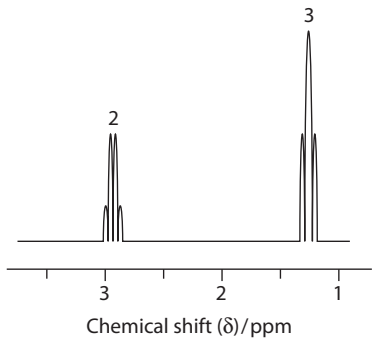
d pentan-2-one

e 2,2-dimethylpropanal (2 singlets)

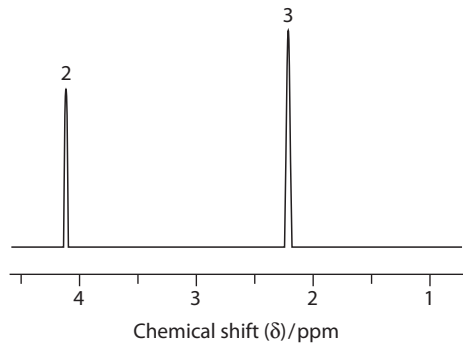
f butanoic acid

43 The NMR spectra below are for two compounds with molecular formula C_3H_5OCl. Determine the structural formula of each compound.

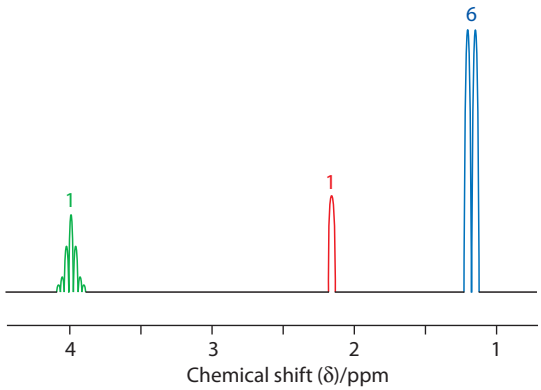
a



b



44 The NMR spectrum shown below is of an alcohol. Work out the structure of the alcohol and state the multiplicity of the signal at $\delta = 4.0$ ppm.



Using combined spectroscopic techniques to determine the structure of a molecule

In practice, information from more than one spectroscopic technique is usually required to determine the structure of a molecule. This is best illustrated using some worked examples.

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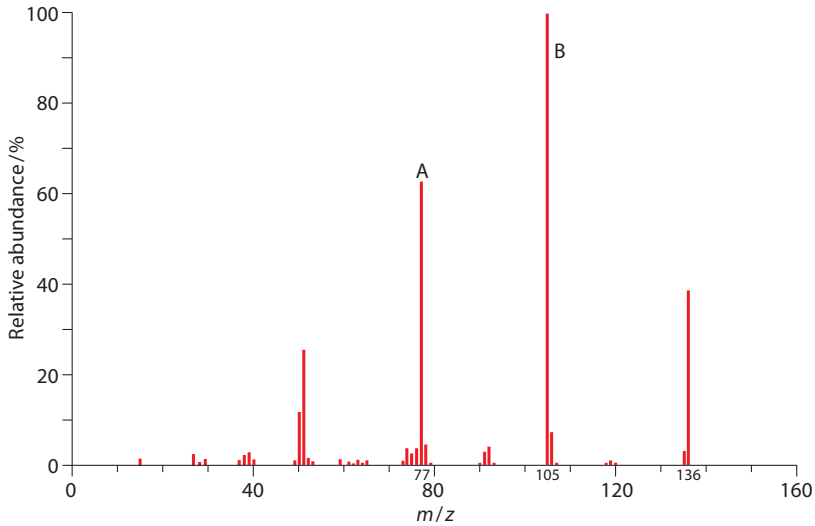
WORKED EXAMPLE 11.29

The mass spectrum below is for a compound, X, that contains carbon, hydrogen and oxygen.
The IR spectrum of X has an absorption band at 1725 cm^{-1}.
The NMR spectrum consists of signals in the range $\delta = 7.2 - 8.1$ ppm and a singlet at 3.9 ppm.



a What is the relative molecular mass of X?

b Given that X contains two oxygen atoms, suggest the molecular formula for X.

c Identify which group is lost from the molecular ion to form the peak marked B.

d Suggest the identity of the species responsible for the peak marked A.

e Deduce the structural formula of X.

Answer

a Using the mass spectrum, the peak at highest *m*/*z* value represents the molecular ion – so the relative molecular mass is 136.

b Two oxygen atoms have a combined mass of 32 and, if we subtract this from 136, we get 104. The only other elements in the molecule are carbon and hydrogen, so we must make 104 from a combination of the masses of these. Seven carbon atoms give a combined mass of $7 \times 12 = 84$, which would require there to be $104 - 84 = 20$ hydrogen atoms in the molecule. However, the alkane with 7 carbon atoms has only 16 hydrogen atoms; therefore, $C_7H_{20}O_2$ is not possible.
9 carbon atoms have a mass of 108, so this also does not work.

Therefore, the only possible molecular formula containing two oxygen atoms that adds up to 136 is $C_8H_8O_2$.

c Peak B occurs at *m*/*z* 105. Now, $136 - 105 = 31$. So, we must think of combinations of C, H and O that add up to 31. The only possible combination is CH_3O, so this group is lost from the molecular ion to produce peak B. (Note that C_2H_7 also adds up to 31, but the maximum number of hydrogen atoms for 2 carbon atoms is 6.)

d Peak A occurs at *m*/*z* 77. The fragment responsible for this is $C_6H_5^+$.

e The peak at *m*/*z* 77 indicates that the compound contains a phenyl group. This is further confirmed by the NMR signals in the range 7.2–8.1 ppm, which is the range for H attached to a benzene ring (Table 11.20).

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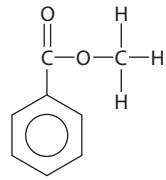
The loss of 31 mass units from the group suggests that it contains the —OCH_3 group. This is also suggested by the singlet in the NMR signal at δ = 3.9 ppm. It is a singlet because there are no H atoms on the adjacent atom (O). The chemical shift of this signal is in the range for an H on a C next to the singly bonded O of an ester group (δ = 3.7–4.8 ppm in Table 11.20).

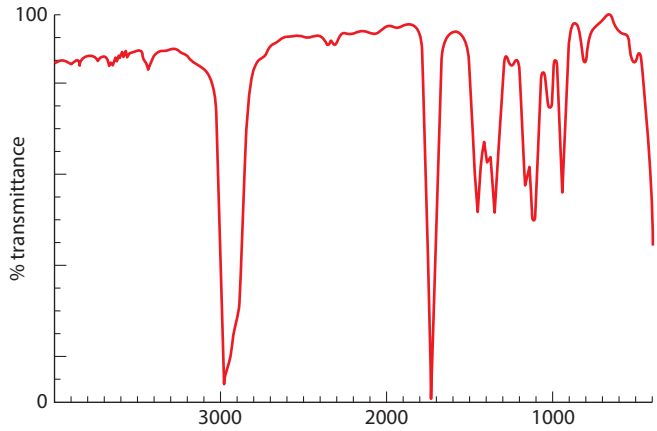


The presence of an absorption band at 1725 cm^{-1} in the IR spectrum suggests (using Table 11.17) that the molecule contains a C═O group. This would also fit in with an ester group being present. The only possible molecule that contains all these elements is:

WORKED EXAMPLE 11.30

An organic compound, Y, is shown by elemental analysis to contain 69.7% carbon, 11.7% hydrogen and 18.6% oxygen by mass. The following information about the structure of Y is available:

- mass spectrum: the molecular ion peak occurs at *m*/*z* 86
- IR spectrum:



- NMR spectrum: only two signals – one quartet (δ = 2.4 ppm) and one triplet (δ = 1.1 ppm).

Determine the structure of the molecule from these data.

Answer

First of all, we need to determine the empirical formula (see Chapter 4):

	C	H	O
percentage	69.7	11.7	18.6
calculate no. of moles	69.7 ÷ 12.01	11.7 ÷ 1.01	18.6 ÷ 16.00
amount in mol / mol	5.80	11.6	1.16
divide by smallest to get ratio	5.80 ÷ 1.16	11.6 ÷ 1.16	1.16 ÷ 1.16
ratio of atoms present	5	10	1

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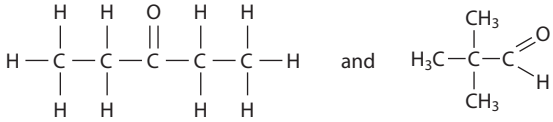
Therefore, the empirical formula is $C_5H_{10}O$. From the mass spectrum, we know that the molecular ion occurs at $m/z = 86$. The empirical formula mass (to the nearest whole number) is also 86, so the empirical formula and molecular formula are the same, and the molecular formula is thus $C_5H_{10}O$.

The IR spectrum has an absorption band in the range 1700–1750 cm^{-1}, indicating a C=O group in an aldehyde, ketone, carboxylic acid or ester. Because there is only one oxygen atom in the molecule, we can rule out esters and carboxylic acids because they both have two oxygen atoms in the functional group. Therefore, the compound must be an aldehyde or a ketone.

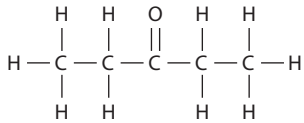
The NMR spectrum indicates that there are only two different chemical environments for the hydrogen atoms in the molecule. There are several different isomers that can be drawn for a compound with molecular formula $C_5H_{10}O$ containing a C=O group, but only the two below have just two different chemical environments for protons:


and

The splitting pattern from the NMR data can be used to distinguish between these two structures:

- a quartet indicates the presence of hydrogen atoms adjacent to a C atom with three H atoms attached
- a triplet indicates the presence of hydrogen atoms adjacent to a C atom with two H atoms attached.

These two signals together indicate the presence of an ethyl group. This group is present in only the left-hand structure, so we can conclude that Y is the left-hand structure, pentan-3-one:



The NMR spectrum of the right-hand molecule would consist of two singlets because all the hydrogen atoms have no hydrogen atoms on the adjacent carbon.

As a final check, you should use Table 11.20 to compare the chemical shift values given with what you would expect for pentan-3-one.

EXAM TIP

When deducing structures from multiples pieces of information, it is important to use all the data given in your answer to score full marks.

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Not yet	Nearly there	Ready to move on
convert between different types of formula for organic molecules	11.1			
explain what a homologous series is	11.2			
recognise different homologous series	11.2			
explain the term functional group	11.2			
recognise different functional groups	11.2			
explain the terms saturated and unsaturated	11.2			
name saturated or mono-unsaturated organic molecules containing up to six carbon atoms in the longest carbon chain	11.3			
explain what structural isomers are	11.4			
draw structural isomers of compounds	11.4			
classify groups as primary, secondary or tertiary	11.4			
explain the term stereoisomerism	11.4			
explain *cis–trans* isomerism and recognise and draw *cis–trans* isomers	11.4			
explain what chirality is	11.4			
draw enantiomers using stereochemical formulas	11.4			
deduce information about the structure of an organic compound from a mass spectrum	11.5			
deduce information about the structure of an organic compound from IR spectra	11.5			
explain what greenhouse gases are	11.5			
deduce information about the structure of an organic compound from ^{1}H NMR spectra	11.5			
use spectroscopic data to deduce the structure of an organic compound.	11.5			

REFLECTION

To what extent would you assess your understanding of naming organic compounds as active or passive? It is very different understanding the rules from being able to use them. Do you need more practice on this? Programs are available that allow you to draw molecules and name them, or get together with a fellow student and test each other by drawing compounds and naming them.

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Unit 4

What drives chemical reactions?

INTRODUCTION

In this unit, we will begin our in-depth study of physical chemistry. We have already looked at some chemical reactions in terms of the rearrangements of electrons that occur during them, but chemical reactions are also accompanied by energy changes. Can you think of reactions you are familiar with that give out heat (exothermic reactions)? This should be a relatively easy task, as we are all familiar with combustion (burning) because, despite the rise of renewable energy, our modern world is powered by combustion reactions. You may, however, find it more difficult to think of a chemical reaction where heat is taken in (endothermic reaction)? These reactions are, however, also important in modern life; the production of concrete and steel, the most widely used construction materials in the world, both involve the endothermic decomposition of calcium carbonate. We are also surrounded by physical processes that are endothermic: just put an ice cube onto your hand – melting is a process that requires the input of energy – energy from your hand is transferred to the ice cube to overcome the forces between water molecules. But why should an ice cube melt when the temperature is +5 °C and not when it is –5 °C? In Unit 2, we explained this in terms of the strength of the forces between the molecules, but here we will look at the role of entropy.

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Chapter 12

Measuring enthalpy changes

LEARNING OBJECTIVES

In this chapter you will:

- understand the difference between heat and temperature
- understand the difference between exothermic and endothermic reactions
- understand what is meant by the term stability
- sketch and interpret energy profiles
- understand the term standard enthalpy change for a reaction
- calculate standard enthalpy changes from experimental data.

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GUIDING QUESTIONS

- What are exothermic and endothermic reactions?
- How do we measure the quantity of heat given out or taken in by reactions?
- What are the limitations of measurements of enthalpy changes?

Introduction

Virtually every chemical reaction will be accompanied by a temperature change, and knowledge of these temperature changes allows us to work out how much energy is transferred in the reaction. Some reactions give out huge amounts of energy; for example, nitroglycerine gives out almost 7000 kJ per kg when it explodes, but other reactions give out/take in very little energy. For example, you probably would not even notice a temperature change if you added a teaspoon of table salt to a saucepan of water, but there would be one (the temperature would go down by less than 0.1 °C if you dissolved 5 g of salt in 1 litre of water). Energy changes play an important part in determining whether a reaction will occur or not, so accurate determination of values for the heat energy taken in or given out in a reaction is essential to an understanding of chemical reactions.

12.1 Heat and temperature

Heat and **temperature** are very different things that often get confused.

KEY POINTS

Heat is the energy that flows from something at a higher temperature to something at a lower temperature because of the temperature difference between them.

Temperature is a measure of the average kinetic energy of particles.

Internal energy (sometimes called chemical energy) is the name given to the total amount of energy (kinetic and potential) in a sample of a substance.

Heat is something that *flows* between objects rather than something that an object has. If a 100 g block of iron at 100 °C is placed in contact with a 50 g block of iron at 50 °C, heat will flow from the hotter block to the colder one, until they are at the same temperature. When they are at the same temperature, the 100 g block of iron will have higher internal energy simply because there is more of it, but the average kinetic energy of the particles in the two blocks will be the same because they are at the same temperature.

Heat, as a flow of energy, has the units joules (J) or kilojoules (kJ). Temperature has units of kelvin (K) or degrees centigrade (°C).

12.2 Exothermic and endothermic reactions

The system and the surroundings

We often use the words 'system' and 'surroundings' to describe what is happening in terms of energy flow in chemical reactions.

The 'system' is the chemical reaction we are studying and the 'surroundings' is everything else in the universe (Figure 12.1).

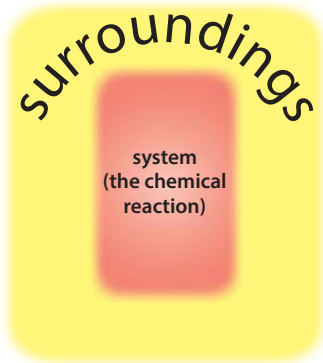

Figure 12.1: The Universe! We can divide the universe up into the chemical reaction (the system) and everything else (the surroundings).

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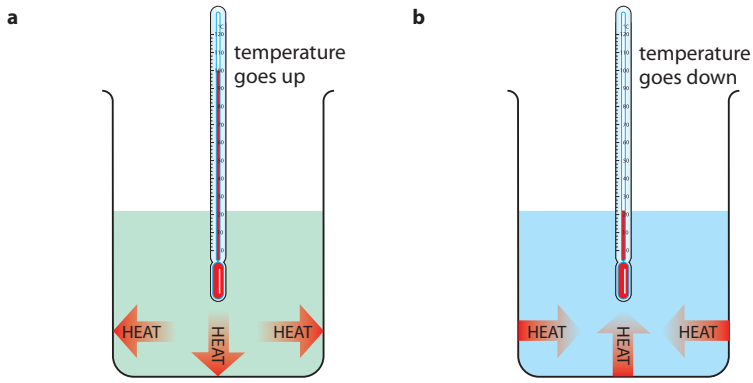

Figure 12.2: a The heat energy released in an exothermic reaction comes from the decrease in internal energy (the total energy) of the system. **b** An endothermic reaction can be regarded as involving a conversion of heat to chemical energy (internal energy) as energy flows from the surroundings.

So, if we carried out the reaction between hydrogen gas and chlorine gas to make gaseous hydrogen chloride in a sealed container:

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

the system would be hydrogen, chlorine and hydrogen chloride. The container and everything outside it would be the surroundings. If a reaction occurs in solution, at this level, we can regard the chemicals involved in the reaction as the system and the water of the solution as part of the surroundings (although the distinction is not as clearcut here).

What are exothermic and endothermic reactions?

Chemical reactions may be classified as either **exothermic** or **endothermic**.

It is important to remember that these reactions involve an energy transfer. In simple terms, we can look at these as reactions involving an interchange between chemical energy and heat energy.

An exothermic reaction can be regarded as involving a conversion of chemical energy into heat energy. There is a decrease in chemical energy (internal energy) of the system, as the reactants are converted into products. There is, thus, a flow of heat from the system to the surroundings, and the energy of the surroundings increases (Figure 12.2**a**). All combustion (burning) reactions are exothermic, and other exothermic reactions you will come across include the neutralisation reaction between an acid, such as hydrochloric acid, and an alkali, such as sodium hydroxide.

An endothermic reaction involves a conversion of heat energy into chemical energy. Energy is transferred from the surroundings, as heat, to the system (Figure 12.2**b**). The surroundings, thus, have lower energy, and the chemical (internal) energy of the system has increased. The energy is not present in the system as heat but is 'stored' in chemical bonds. The dissolving of ammonium nitrate in water is an endothermic process.

KEY POINTS

In an exothermic reaction, heat energy is transferred from a system (chemical reaction) to the surroundings – the surroundings get hotter.

In an endothermic reaction, a system (chemical reaction) takes in heat energy from the surroundings – the surroundings get colder.

Enthalpy changes

The quantity of heat energy given out or taken in by a chemical reaction depends on whether it is done in a sealed container (constant volume) or in an open container (constant pressure) and, in order to be clear about which we are referring to, we define a quantity called the *enthalpy change of a system*. The **enthalpy change** is the heat energy exchanged with the surroundings at constant *pressure*. All the reactions we

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will encounter at this level will be done in vessels open to the atmosphere, so they are at constant pressure. The enthalpy change is then basically the quantity of heat energy taken in/given out in a chemical reaction.

Enthalpy is given the symbol H and enthalpy change is ΔH. It is not possible to measure the enthalpy (H) of a system (related to the total energy of all the particles making up a substance), but only the enthalpy change (ΔH), when the system moves from an initial state to some final state, and so, we will always talk about the enthalpy *change* of a reaction as this is what we can measure.

Note that Δ means a change in a quantity.

ΔH values are usually quoted under standard conditions. This is discussed in more detail in Section 12.3.

In this section, the terms enthalpy and energy will be used fairly interchangeably. At this level, the enthalpy of a system can be regarded as essentially the total energy stored in a substance – i.e., basically the same as the internal energy. This is not strictly true, but it is sufficient for a good understanding of the concepts.

Enthalpy changes in exothermic reactions

KEY POINT

ΔH for an exothermic reaction is negative.

Consider a reaction such as methane burning in oxygen:

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

$$\Delta H = -891 \text{ kJ mol}^{-1}$$

ΔH is negative, which indicates that this reaction is exothermic – heat is given out to the surroundings. If you held your hand near some burning methane (e.g. a Bunsen burner), your hand would get hot – heat is being transferred to it!

Figure 12.3 shows an enthalpy level diagram for the combustion of methane.

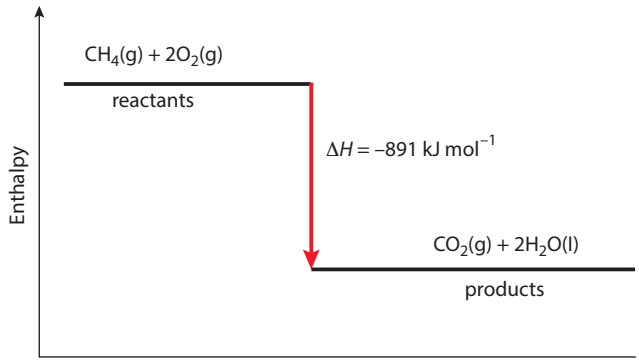

Figure 12.3: An enthalpy level diagram for the combustion of methane, an exothermic reaction. No scale is shown on the vertical axis because we cannot measure the initial enthalpy or final enthalpy of the system.

The reactants (CH_4 and O_2) have more energy than the products and, as the reactants are converted into the products, this energy must be given out – it is transferred to the surroundings as heat. The enthalpy change of the reaction is the amount of heat given out – this is shown by the red arrow. The energy of the system (the chemicals we are looking at in the reaction) has decreased, and so, we show this with the negative sign for ΔH.

Stability and exothermic reactions

The term **stability** is usually used to describe the relative energies of reactants and products in a chemical reaction. In an exothermic reaction, the products are at a lower energy (enthalpy) level than the reactants, and we say that the products are more stable than the reactants.

Total energy is conserved in a chemical reaction

Energy cannot be created or destroyed, it can only be converted from one form to another (this is known as the first law of thermodynamics).

Figure 12.3, shows that, for an exothermic reaction:

total enthalpy of the reactants
= total enthalpy of the products + heat given out

or ΔH = enthalpy of products – enthalpy of reactants

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Enthalpy changes in endothermic reactions

KEY POINT

ΔH for an endothermic reaction is positive.

The reaction between nitrogen and oxygen to form nitrogen(II) oxide (nitric oxide) is endothermic:

$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = +181 \text{ kJ mol}^{-1}$

Figure 12.4 shows that the products have higher energy than the reactants.

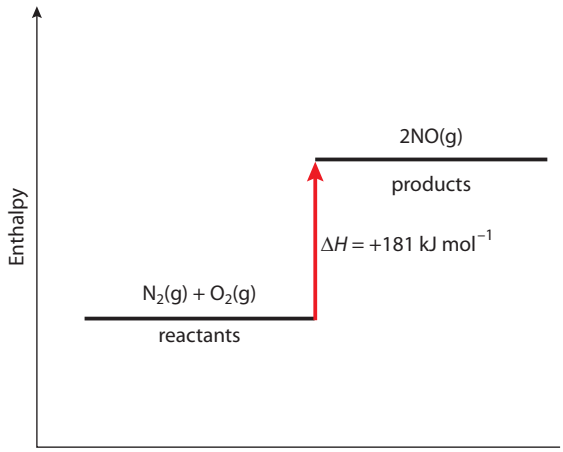

Figure 12.4: An enthalpy level diagram for an endothermic reaction.

Energy (heat) must flow from the surroundings into the system as the reactants are converted to the products. Remember that the 'extra' energy is not present in the products as heat – heat is converted into internal energy, so the internal energy (chemical energy) of the products is greater than that of the reactants – the products do not contain more heat than the reactants. If you were holding a tube in which this reaction was occurring, your hand would feel colder – heat is being transferred from your hand to the system. The amount of heat transferred is the enthalpy change, as shown by the red arrow in Figure 12.4. Because energy is transferred into the system and the energy of the system increases, the sign of ΔH is positive.

Link

The reaction between nitrogen and oxygen here looks like a combustion reaction because it is a reaction with oxygen gas. We would normally say that all combustion reactions are exothermic, but this reaction is endothermic. What exactly is a combustion reaction? Does a reaction have to be exothermic to be a combustion reaction; does there need to be a flame? Combustion reactions are discussed in Chapter 14. Why this reaction is endothermic can be understood from a discussion of bond energies (Chapter 13) – the triple bond between the N atoms is very strong and requires a lot of energy to break.

Endothermic reactions and stability

The products of an endothermic reaction have higher energy (enthalpy) than the reactants and are, therefore, less stable than the reactants.

Total energy is conserved

Endothermic reactions involve an increase in enthalpy as the reactants are converted into products:

total enthalpy of products
= total enthalpy of reactants + heat taken in

or, as above,
ΔH = enthalpy of products – enthalpy of reactants

Energy profiles and stability

An energy profile, also called a potential energy profile or potential energy diagram, can be used to show the energy changes occurring during a chemical reaction. The energy profiles for exothermic and endothermic reactions are shown in Figure 12.5.

Link

Energy profiles are used more often in discussions about rate of reaction and will be discussed in Chapter 17, section 17.3.

A reaction coordinate represents the progress of a reaction from reactants to products. As reactant particles approach each other, repulsion between the particles and the partial breaking of bonds causes the potential energy of the system to increase.

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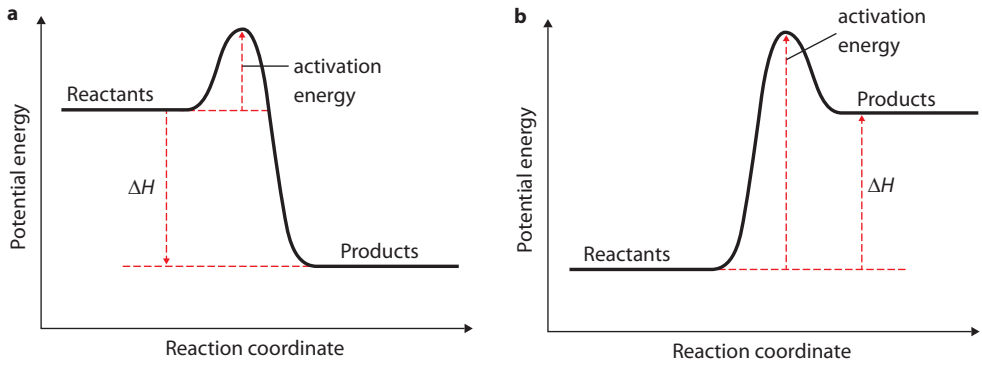

Figure 12.5: a Energy profile for an exothermic reaction; **b** energy profile for an endothermic reaction.

The activation energy is the minimum energy that colliding particles must have before a collision results in a chemical reaction – this will be considered in more detail in Chapter 17, section 17.3.

In an exothermic reaction, the products are at lower energy than the reactants and are more stable than the reactants. For an endothermic reaction, the products are at higher energy and are less stable than the reactants.

TEST YOUR UNDERSTANDING

1 The enthalpy changes when 1 mol of a substance is dissolved in water are shown below. In each case, state whether the process is exothermic or endothermic and whether the temperature goes up or down when the substance is added to water.

   a $NaOH(s) \rightarrow NaOH(aq)$ $\Delta H = -45$ kJ mol^{-1}

   b $NH_4Cl(s) \rightarrow NH_4Cl(aq)$ $\Delta H = +15$ kJ mol^{-1}

   c $HCl(g) \rightarrow HCl(aq)$ $\Delta H = -75$ kJ mol^{-1}

2 In each case, state whether the products are more or less stable than the reactants and draw a potential energy profile for the reaction:

   a $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -394$ kJ mol^{-1}

   b $I_2(s) + H_2(g) \rightarrow 2HI(g)$ $\Delta H = 53$ kJ mol^{-1}

12.3 Enthalpy changes and standard conditions

Enthalpy changes have different values, depending on the conditions under which they are measured. To make them transferable, they are all quoted for the same set of conditions, which are called **standard conditions**.

An enthalpy change under standard conditions is called a standard enthalpy change and has the symbol $\Delta H^{\ominus}$, where the symbol $\ominus$ means 'under standard conditions'.

There is no mention of temperature in the definition of standard conditions, and a temperature should always be specified for a standard enthalpy change. This can then be written as $\Delta H^{\ominus}(298.15\ K)$. Where no temperature is stated, we will assume that the temperature is 298.15 K.

By defining a **standard state**, we are able to use an arbitrary reference point for thermodynamic quantities – see enthalpy of formation in Chapter 13.

KEY POINTS

Standard conditions:

- pressure = 100 kPa (1.00×10^5 Pa)
- substances in standard states

Standard state refers to the pure substance at 100 kPa and a specified temperature (assume 298.15 K, unless another temperature is specified). For solutions, it refers to a concentration of 1 mol dm^{-3}.

If an enthalpy change is not measured under standard conditions, its value can be corrected to that under standard conditions.

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Standard enthalpy change of reaction ($\Delta H_r^\ominus$)

KEY POINT

Standard enthalpy change of reaction is the enthalpy change (heat given out or taken in) when molar amounts of reactants, as shown in the stoichiometric equation, react together under standard conditions.

For example, for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, the standard enthalpy change of reaction is –92 kJ mol^{-1}.

This means that 92 kJ of heat energy is given out when 1 mol N_2 reacts with 3 mol H_2 to form 2 mol NH_3.

If the equation is written as follows:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \quad \Delta H_r^\ominus = -46 \text{ kJ mol}^{-1}$$

then the enthalpy change of reaction is for 0.5 mol N_2 reacting, and the enthalpy change is half as much.

The 'r' subscript is often omitted, and the standard enthalpy change for a reaction just written as $\Delta H^\ominus$.

12.4 Measuring enthalpy changes

In this section, we will consider some experimental methods for measuring enthalpy changes of chemical reactions. The process of measuring enthalpy changes experimentally is called **calorimetry**. To be able to calculate enthalpy changes, we must first understand the concept of specific heat capacity.

Specific heat capacity

KEY POINT

The **specific heat capacity**, (c), of a substance is the energy required to raise the temperature of 1 g of substance by 1 K (1 °C).

It can also be defined as the energy to raise the temperature of 1 kg of substance by 1 K.

Specific heat capacity has units of J g^{-1} K^{-1} or J g^{-1} °C^{-1}. Units that are also encountered are kJ kg^{-1} K^{-1} or J kg^{-1} K^{-1}.

The specific heat capacity of aluminium is 0.90 J g^{-1} °C. Therefore, if 0.90 J of heat energy is transferred to 1 g of aluminium, the temperature is raised by 1 °C (Figure 12.6).

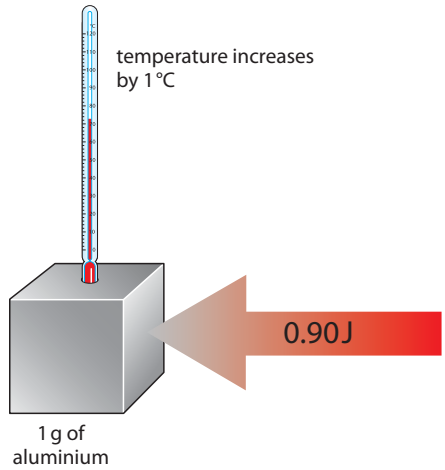

Figure 12.6: The specific heat capacity of aluminium is 0.90 J g^{-1} °C^{-1}.

If 1.80 J of heat energy were put into this block of aluminium, the temperature would go up by 2 °C.

If the 1 g block of aluminium were replaced by a 2 g block of aluminium, then 1.80 J would be required to raise the temperature by 1 °C, because 0.90 J is required to raise the temperature of each 1 g by 1 °C. The quantity of heat energy required is, therefore, proportional to the mass and temperature change. An equation can be derived for how much heat energy (Q) must be supplied to raise the temperature of mass m by ΔT °C:

KEY POINT

$Q = mc\Delta T$

Note:

- the quantity of heat energy may be given the symbol Q or q
- 1 K is the same as 1 °C when temperature changes are being considered.

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Specific heat capacity indicates how much energy is required to heat up a substance; therefore, substances with higher specific heat capacities are more difficult to heat up than substances with lower specific heat capacities. For example, the specific heat capacity of iron is roughly half that of aluminium. Therefore, if the same quantity of heat energy is supplied to 10 g of each metal, the temperature of the iron will go up by twice as much.

The specific heat capacity can also be used to work out the heat energy given out when a substance cools. For instance, when 1 g of aluminium cools from 21 to 20 °C, 0.90 J of energy is given out.

Standard enthalpy change of combustion ($\Delta H_c^\ominus$)

KEY POINT

The **standard enthalpy change of combustion** is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

A **standard enthalpy change of combustion** is always negative because combustion is always an exothermic process. For example:

$CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_c^\ominus = -891$ kJ mol^{-1}

Measuring an enthalpy change of combustion

The basic idea is that the heat given out in a combustion reaction is used to heat another substance of known specific heat capacity, such as water. The equation $Q = mc\Delta T$ can be used to calculate the quantity of heat given out.

The experimental set-up shown in Figure 12.7 can be used to determine the enthalpy change when one mole of a liquid substance is burnt (the enthalpy change of combustion). The mass and temperature change of the water must be measured, as well as the mass change of the alcohol.

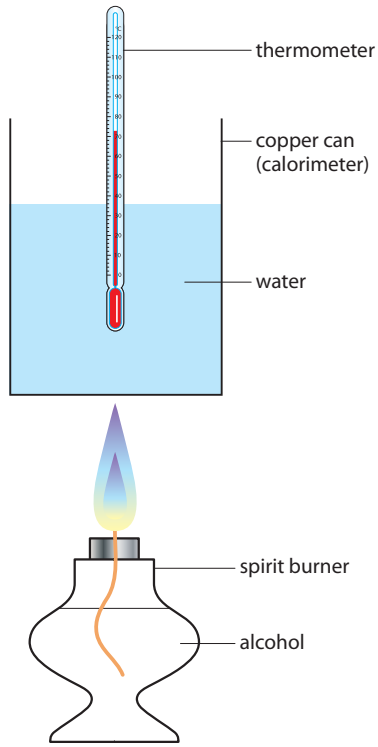

Figure 12.7: An experiment to work out the enthalpy change of combustion of an alcohol.

WORKED EXAMPLE 12.1

Use the following experimental data to determine the enthalpy change of combustion of ethanol (C_2H_5OH) given that the specific heat capacity of water is 4.18 J g^{-1} °C^{-1}.

mass of water = 150.00 g

initial temperature of water = 19.5 °C

maximum temperature of water = 45.7 °C

initial mass of spirit burner = 121.67 g

final mass of spirit burner = 120.62 g

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Answer

the temperature change of the water = 45.7 – 19.5 = 26.2 °C

The heat energy supplied to the water is given by

$Q = mc\Delta T$

$Q = 150.00 \times 4.18 \times 26.2 = 16\,400$ J

This heat energy is supplied by the burning of the ethanol.

mass of ethanol burnt = 121.67 – 120.62 = 1.05 g

The amount in mol of ethanol burnt is given by

$$\text{amount } (n) = \frac{\text{mass}}{\text{molar mass}}$$

The molar mass of ethanol is 46.08 g mol^{-1}.

Therefore:

$$\text{amount of ethanol burnt } (n) = \frac{1.05}{46.08} = 0.0226 \text{ mol}$$

When 0.0228 mol ethanol is burnt, 16 400 J of heat energy are produced.

Therefore, the energy released when one mole is burnt is given by

$$\text{energy} = \frac{16\,400}{0.0228} = 721\,000 \text{ J mol}^{-1}$$

The enthalpy change of combustion of ethanol is therefore:

$\Delta H_c^{\ominus} = -721$ kJ mol^{-1}

A negative sign has been inserted here to show that the reaction is exothermic – combustion reactions are always exothermic. More than three significant figures were carried through on the calculator to give this final answer.

The last stages of the calculation are summarised in the equation: $\Delta H = -\frac{Q}{n}$

EXAM TIP

Note: the mass of water and not the mass of ethanol is used here – it is the water that is being heated.

Problems with the experimental method

The accepted literature value for the enthalpy change of combustion of ethanol is –1371 kJ mol^{-1}, so this experiment does not give a very accurate answer. There are several major flaws (systematic errors) in the experimental set-up. The main systematic errors are

- heat loss to the surroundings
- incomplete combustion of ethanol

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- evaporation of water
- evaporation of ethanol.

The biggest problem is that of heat loss to the surroundings. Of the heat energy released when ethanol burns, only some of it goes into heating water – the rest goes into heating the copper can and the surrounding air. This will make the experimental value less exothermic than 'expected'. Improvements that could be made to the experimental procedure to reduce the effect of this systematic error are as follows:

- determining the specific heat capacity and temperature change of the can and taking this into account when doing the calculation
- insulating the can, so that less heat is lost through the can to the surroundings
- using some sort of draught shield to reduce convection currents around the experiment, etc.

Link

A systematic error is an error introduced into an experiment by the apparatus or the procedure. To reduce the effect of systematic errors, the experimental procedure and/or apparatus must be modified in some way. Repeating exactly the same experiment will not reduce the systematic errors.

Accuracy refers to how close an experimental value is to the accepted value. Systematic errors result in lack of accuracy.

Another major problem with the experiment is incomplete combustion of the ethanol. When ethanol undergoes complete combustion, the equation for the reaction is as follows:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

However, if there is not a sufficient supply of oxygen to the flame, some of the ethanol can burn to produce carbon monoxide and soot (carbon) as well as water. This is called incomplete combustion and gives out less heat than complete combustion, so, again, making our experimental value less exothermic than 'expected'.

Incomplete combustion causes the flame to be yellow/orange, rather than blue, because of the presence of soot particles, and soot can also be seen on the bottom of the copper can. It is difficult to come up with a realistic improvement to reduce incomplete combustion when working in a normal school laboratory.
More sophisticated experiments use apparatus such as a bomb calorimeter, which is a heavily insulated piece of apparatus in which the substance is ignited electronically in a plentiful supply of oxygen.

When the fastest moving water molecules escape from the surface of water in the copper can, they cause a decrease in the average kinetic energy of the remaining particles; in other words, evaporation causes the water to cool down. This will, therefore, also contribute to the experimental value for the enthalpy change of combustion being less exothermic than the literature value. The fact that, with less water present, less energy has to be supplied to raise its temperature reduces this effect very little (the energy to vaporise 1 g of water is about 100 times greater than the energy required to raise its temperature by 20 °C).

Evaporation of water can be reduced by putting a lid on the copper can.

Evaporation of ethanol will cause the measured mass change to be greater than it should have been. So, in the final stage of the calculation, we are dividing by a larger number of moles (n is larger) and, therefore, the answer will come out as less exothermic. Evaporation of ethanol can be reduced by putting a lid on the spirit burner any time when it is not being used to heat water.

NATURE OF SCIENCE

When we carry out experiments to measure enthalpy changes, we often get unexpected values. What criteria do we use when carrying out these experiments, to decide whether there are flaws in the experiment or flaws in the theory? How do we decide whether results are anomalous?

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TEST YOUR UNDERSTANDING

The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.

3 Work out the specific heat capacities of each metal from data given:

- **a** Gold: the temperature of 2.00 g of gold is raised by 11.7 °C when 3.00 J of energy is supplied.
- **b** Silver: the temperature of 100.0 g of silver is raised by 2.12 °C when 50.0 J of energy is supplied.

4 Calculate the temperature change of the water in each case:

- **a** 10 000 J of heat is supplied to 100 g of water
- **b** 40 kJ of heat is supplied to 250 g of water
- **c** 1000 kJ of heat is supplied to 10.0 kg of water.

5 Calculate the enthalpy change, in kJ mol^{-1}, when 1.00 mol is burnt in each case (the molar volume of a gas at STP is 22.7 dm^3 mol^{-1}):

- **a** 105 000 J is given out when 0.100 mol of A is burnt
- **b** 84 000 J is given out when 0.042 mol of B is burnt
- **c** 11 000 J is given out when 0.500 g of CH_3OH is burnt
- **d** 6000 J is given out when 0.150 g of C_6H_6 is burnt
- **e** 13 000 J is given out when 200 cm^3 (measured at STP) of $C_2H_6(g)$ is burnt.

6 **a** When 1.20 g of hexane (C_6H_{14}) is burnt, the temperature of 250.0 g of water is raised by 56.0 °C. Calculate the enthalpy change when one mole of hexane is burnt.

b When 0.870 g of pentan-1-ol ($C_5H_{11}OH$) is burnt, the temperature of 180.0 g of water is raised by 38.0 °C. Calculate the enthalpy change when one mole of pentan-1-ol is burnt.

c When 0.521 g of benzene (C_6H_6) is burnt, the temperature of 320.0 g of water is raised by 12.2 °C. Calculate the enthalpy change when one mole of benzene is burnt.

d When 2.00 kg of octane (C_8H_{18}) is burnt, the temperature of 500 kg of water is raised by 46.0 °C. Calculate the enthalpy change when one mole of octane is burnt.

7 A student uses an experimental set-up similar to that shown in Figure 12.7 to determine the enthalpy change of combustion of propan-1-ol (C_3H_7OH).

a Determine the enthalpy change of combustion of propan-1-ol using the student's experimental data:

mass of water = 200.00 g

initial temperature of water = 18.2 °C

maximum temperature of water = 38.6 °C

initial mass of spirit burner = 185.51 g

final mass of spirit burner = 184.56 g

b The actual value for the enthalpy change when one mole of propan-1-ol is burnt is –2010 kJ mol^{-1}. Account for any differences between this value and the one calculated from the experimental data in question **7a**.

8 Use the following experimental data to determine the enthalpy change of combustion of methanol (CH_3OH):

mass of water = 150.00 g

initial temperature of water = 19.5 °C

maximum temperature of water = 37.7 °C

initial mass of spirit burner = 154.23 g

final mass of spirit burner = 153.42 g

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Enthalpy changes in solution

A general method for measuring enthalpy changes involving solutions in the laboratory is as follows:

1 measure out known quantities of reagents
2 record the initial temperatures of the reagents that are solutions
3 mix together the reagents in a polystyrene cup (good insulator)
4 record the maximum/minimum temperature observed.

The specific heat capacity of the final solution is assumed to be the same as for water.

Determining the enthalpy change of neutralisation

The **standard enthalpy change of neutralisation** ($\Delta H_n^{\ominus}$) is the enthalpy change when one mole of water molecules is formed when an acid (H^+) reacts with an alkali (OH^-) under standard conditions:

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

The enthalpy change of neutralisation is always exothermic.

SCIENCE IN CONTEXT

If you look at the packaging of most foodstuffs, they have energy values printed on them and we usually talk about how many calories there are in, say, a bar of chocolate. But what is a calorie? One calorie is the energy required to raise the temperature of 1 g of water by 1 °C, so it is equivalent to 4.18 J. The values printed on labels are not, however, actually in 'calories' but rather kcal, where 1 kcal is the energy required to raise the temperature of 1 kg or 1 litre of water by 1 °C. The calorific values of foods were originally worked out from experiments using a bomb calorimeter, where the food would be ignited in a plentiful supply of oxygen and the amount of heat energy given out when it was completely combusted determined. Therefore, when we say that a 100 g bar of chocolate contains 560 calories, what we actually mean is that, when the chocolate is completely combusted, 560 000 calories (about 2340 kJ) of energy (heat) would be transferred, which is the amount of energy that would raise the temperature of 10 litres of water by 56 °C.

Calorific values from food are, however, not generally determined experimentally, but rather by calculations based on the composition of the food using the Atwater system. In this system, carbohydrates contribute 4 kcal per gram, fats 9 kcal per gram and proteins 4 kcal per gram to the total calorific value of the food; these are average values from calorimetry experiments (alcohol, by the way, is taken to supply 7 kcal per gram). So, when it states on a label that a bar of chocolate has an energy value of 560 kcal, this number has been worked out from the mass of carbohydrate, fat and protein in the bar and not by burning the chocolate bar. Average values are used in the calculation, which will affect the accuracy of the value, and it is also important to realise that the value may not be the same as the metabolisable energy – not all the energy from these foods is necessarily available to your body.

WORKED EXAMPLE 12.2

Consider the following experiment:

- 100.0 cm^3 of 1.00 mol dm^{-3} potassium hydroxide solution was measured out and poured into a polystyrene cup
- the temperature of the potassium hydroxide solution was measured
- 120.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was measured out and the initial temperature was measured
- the hydrochloric acid was poured into the polystyrene cup and the mixture stirred rapidly
- the maximum temperature was recorded.

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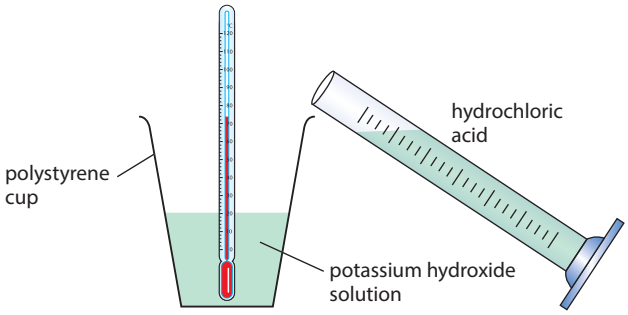

The results of this experiment are as follows:

initial temperature of potassium hydroxide solution = 19.7 °C

initial temperature of hydrochloric acid = 19.7 °C

maximum temperature reached = 25.9 °C

Use these data to determine the enthalpy change of neutralisation.

Answer

temperature change of the mixture: 25.9 – 19.7 = 6.2 °C

total volume of the reaction mixture: 100.0 + 120.0 = 220.0 cm^3

We will make two assumptions when carrying out the calculation:

Assumption 1: the density of the potassium hydroxide and hydrochloric acid solutions are the same as water, so 1 cm^3 of solution has a mass of 1 g.

Therefore, the mass of 220.0 cm^3 of solution is 220.0 g.

Assumption 2: the specific heat capacity of the mixture is the same as that of water.

Both assumptions are fairly reasonable because the solutions are mostly water.

We can work out how much heat (Q) has been released in this reaction by using the temperature change of the mixture:

$Q = mc\Delta T = 220 \times 4.18 \times 6.2 = 5700$ J

To work out the enthalpy change of neutralisation, we need to know how many moles of water have been formed. The equation for the reaction is

$KOH + HCl \rightarrow KCl + H_2O$

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amount in mol of KOH = concentration × volume in dm^3

amount in mol of KOH = 1.00 × (100 ÷ 1000) = 0.100 mol

amount in mol of HCl = 1.00 × (120 ÷ 1000) = 0.120 mol

The chemical equation indicates that 0.100 mol of HCl is required to react with 0.100 mol KOH (the mole ratio is 1 : 1 for HCl and KOH).

In experiments such as these, it is usually good practice to add an excess of one reagent to reduce effects due to **random errors** (uncertainties in measurements) and **systematic errors** (if concentrations are not exactly as stated on the bottle). Excess (more than enough to react) hydrochloric acid was therefore added – this ensured that all the potassium hydroxide reacted.

The HCl is in excess, so the amount in mol of water produced (n) is 0.100 mol. Therefore, 5700 J of energy is released when 0.100 mol water is formed.

The definition of enthalpy change of neutralisation is the enthalpy change when *one mole* of water is produced. Therefore, for one mole of water formed:

$$\Delta H = -\frac{-Q}{n} = \frac{-5700}{0.100} = -57\,000 \text{ J mol}^{-1}$$

Therefore, the enthalpy change of neutralisation is $\Delta H_n^{\ominus} = -57.0$ kJ mol^{-1}. This is negative because the reaction is exothermic.

The accepted literature value for the enthalpy of neutralisation of KOH with HCl is –57.2 kJ mol^{-1}.

Possible errors in this experiment are heat loss to the surroundings and the assumptions that have been made about the specific heat capacities and the density of the solutions. The heat capacity of the calorimeter (polystyrene cup) was also not taken into account – some of the heat energy given out from the reaction was used to heat up the cup.

Why use excess HCl?

When we do the experiment in a laboratory, although it may say on the bottles that the concentrations of the KOH and HCl are both 1.00 mol dm^{-3}, unless you have made up the solutions yourself, how do you really know that? In this reaction, we reduce the number of possible systematic errors by adding excess HCl. If we add 100 cm^3 of both HCl and KOH then, if *either* solution is not the stated concentration, this will affect the final value that is obtained. However, it is (hopefully) highly unlikely that the concentration on the bottle of HCl is so wrong that 120 cm^3 will not provide enough HCl to react with all the KOH; therefore, only inaccuracies in the concentration of KOH will affect the final value obtained.

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WORKED EXAMPLE 12.3

a 100.0 cm^3 of 1.00 mol dm^{-3} potassium hydroxide solution was reacted with 100.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid. The temperature rise was 6.82 °C. Calculate the enthalpy change of neutralisation.

b The experiment in part **a** was repeated with 50.0 cm^3 of 1.00 mol dm^{-3} potassium hydroxide solution and 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid. Calculate the temperature change of the reaction mixture.

Answer

a We can use the method from the previous example to calculate the enthalpy change of neutralisation:

$Q = mc\Delta T = 200 \times 4.18 \times 6.82 = 5700$ J

The amount in mol of KOH and HCl in this case are the same, both 0.100 mol. Therefore, 0.100 mol water is formed.

$$\Delta H = -\frac{-Q}{n} = -\frac{-5700}{0.100} = -57\,000 \text{ J mol}^{-1}$$

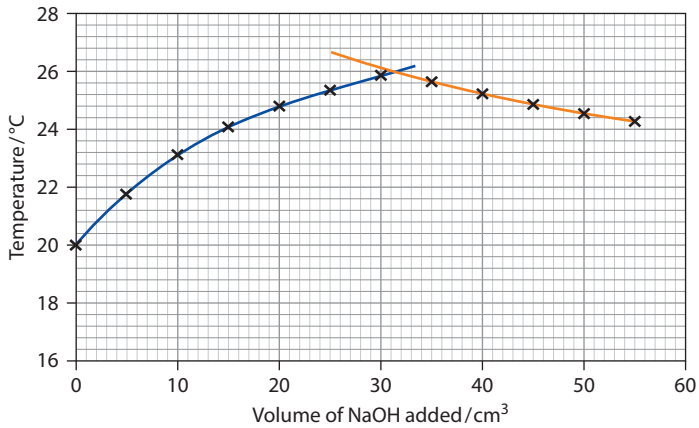
Therefore, the enthalpy change of neutralisation is $\Delta H_n^{\ominus} = -57.0$ kJ mol^{-1}

b We *could* do all the calculations again, but a shortcut is to use the answer from part **a** and think about how the volumes and concentrations used in part **b** compare with those in part **a**.

The volume of each solution is half that in part **a**, but the concentrations are the same. Therefore, we can deduce that the number of moles of water formed will be half as much as in part **a**. This means that half as much heat energy will be given out in the neutralisation reaction. However, the total volume of reaction mixture that is being heated is half the original volume, therefore, only half as much heat energy will be required to heat it to the same temperature. So, the temperature change in this experiment is the same as in part **a**, i.e., 6.82 °C.

WORKED EXAMPLE 12.4

The graph shows data from an experiment in which sodium hydroxide solution was added to 25.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid. The temperature of the reaction mixture was recorded after the addition of each 5.00 cm^3 portion of sodium hydroxide and two lines of best fit drawn through the data. The hydrochloric acid and sodium hydroxide were originally at the same temperature. Use the graph to determine the enthalpy change of neutralisation for this reaction.



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CONTINUED

Answer

We can see from the graph that the initial temperature of the hydrochloric acid is 20.0 °C.

The temperature initially increases because, when the sodium hydroxide solution is added, a neutralisation reaction occurs and this is exothermic. However, once sufficient sodium hydroxide has been added to react with all the hydrochloric acid, no more reaction occurs and adding colder sodium hydroxide (20 °C) to the reaction mixture, which is now hotter than 20 °C, will cause the overall temperature to decrease (the temperature will also decrease as heat is lost to the surroundings). We thus have two separate curves – one where the temperature increases as the neutralisation reaction occurs and one where the temperature decreases once there is no more neutralisation. The curves are continued on (extrapolated) to determine the point at which they cross. The point at which the curves cross represents the volume of sodium hydroxide needed for exact neutralisation and the maximum temperature reached in this reaction.

From the graphs, we can estimate that the maximum temperature is 26.0 °C, and this occurs at a volume of 31.2 cm^3.

The temperature change in the neutralisation reaction is 26.0 – 20.0 = 6.0 °C

The total volume of the reaction mixture at the neutralisation point is 25.0 + 31.2 = 56.2 cm^3

$Q = mc\Delta T = 56.2 \times 4.18 \times 6.0 = 1409$ J

$$\text{amount in mol of HCl} = 1.00 \times \frac{25.0}{1000} = 0.0250 \text{ mol}$$

All the HCl reacts, so the amount of water formed is also 0.0250 mol:

$$\Delta H = -\frac{-Q}{n} = \frac{-1409}{0.0250} = -56400 \text{ J mol}^{-1}$$

Therefore, the enthalpy change of neutralisation from this experiment is

$\Delta H_n^{\ominus} = -56.4$ kJ mol^{-1}

Determining the enthalpy change of solution

The **standard enthalpy change of solution** ($\Delta H_{sol}^{\ominus}$) is the enthalpy change when one mole of solute is dissolved in excess solvent to form a solution of 'infinite dilution' under standard conditions, e.g.:

$$NH_4NO_3(s) \xrightarrow{\text{excess } H_2O} NH_4^+(aq) + NO_3^-(aq)$$

$\Delta H_{sol}^{\ominus} = +25.7$ kJ mol^{-1}

'Infinite dilution' means that any further dilution of the solution produces no further enthalpy change, i.e., the solute particles are assumed not to interact with each other in the solution.

The enthalpy change of solution may be exothermic or endothermic.

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WORKED EXAMPLE 12.5

Consider the following experiment:

- 100.0 cm^3 of water was measured out and poured into a polystyrene cup
- the temperature of the water was measured
- 5.20 g of ammonium chloride was measured out
- the ammonium chloride was added to the water
- the solution was stirred vigorously until all the ammonium chloride had dissolved
- the minimum temperature was recorded.

The results of this experiment are as follows:

initial temperature of water = 18.3 °C

minimum temperature = 15.1 °C

Use the experimental data to determine the enthalpy change of solution of ammonium chloride.

Answer

Temperature change of the mixture: 15.1 – 18.3 = –3.2 °C

The temperature change is negative because the temperature has gone down.

We will assume that the density of the solution is the same as that of water, and so,100.0 cm^3 of solution has a mass of 100.0 g. We can work out how much heat has been absorbed in this reaction by using the temperature change of the mixture:

$Q = mc\Delta T = 100.0 \times 4.18 \times -3.2 = -1340$ J

Assumption: the specific heat capacity of the solution is the same as that of water.

To work out the enthalpy change of solution, we need to know how many moles of ammonium chloride dissolved:

$$\text{amount in mol of } NH_4Cl = \frac{\text{mass}}{\text{molar mass}}$$

Therefore, the amount in mol (n) of NH_4Cl that dissolves = (5.20 ÷ 53.50) = 0.0972 mol

Therefore, 1340 J of energy is absorbed when 0.0972 mol NH_4Cl dissolve.

The definition of enthalpy change of solution is the enthalpy change when one mole of substance dissolves. Therefore, for one mole of NH_4Cl dissolving:

$$\Delta H = -\frac{-Q}{n} = \frac{-(-1340)}{0.097} = 13800 \text{ J mol}^{-1}$$

There are two negative signs; therefore, the value is positive.

Therefore, the enthalpy change of solution is $\Delta H^{\ominus}_{sol} = +13.8$ kJ mol^{-1}. This value is positive because the reaction is endothermic.

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CONTINUED

The accepted value for the enthalpy change of solution of ammonium chloride is 15.2 kJ mol^{-1}. Errors in this experiment include the absorption of heat from the surroundings and the assumption about the specific heat capacity of the solution being the same as that of water. The mass of the ammonium chloride was also not taken into account when working out the heat energy released in the experiment (i.e. it was not included in the mass of the solution) – we do not know the specific heat capacity of ammonium chloride solution, so we are assuming that the reaction (system) is affecting the temperature of the water (surroundings).

The results from this experiment are greatly improved by vigorous stirring of the solution, because ammonium chloride does not dissolve instantaneously. If it is allowed to dissolve slowly, there is more time for heat to be absorbed from the surroundings and the temperature drop is not as large as expected. This effect can be reduced by using the technique of the next experiment.

Extrapolation can be used to estimate a temperature change

WORKED EXAMPLE 12.6

The following experiment may be used to determine the enthalpy change of reaction for

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

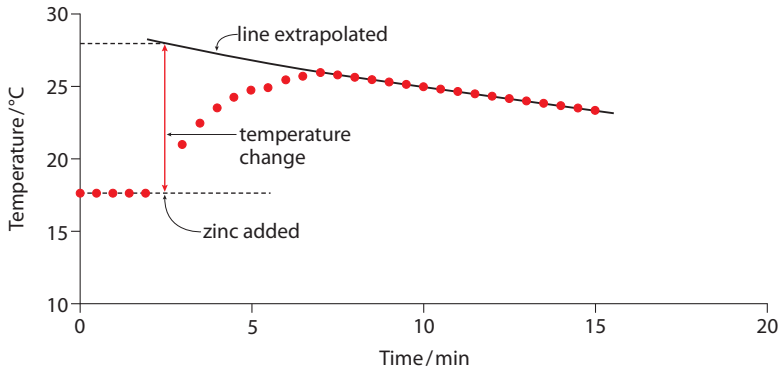
50.0 cm^3 of 0.200 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene cup.

The temperature was recorded every 30 s for 2 min.

At 2 min 30 s, 1.20 g of powdered zinc was added; this is an excess.

The mixture was stirred vigorously and the temperature recorded every half minute for several minutes.

The results obtained were then plotted to give the graph shown:



Use these data to determine the enthalpy change for this reaction.

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CONTINUED

Answer

The problem with this reaction is that it does not occur instantaneously, and so, although heat is being given out in the reaction, at the same time, the reaction mixture is also cooling down by losing heat to the surroundings. From the graph, there is an initial rise in temperature, where heat being given out by the reaction is the major factor, but, after that, overall, the reaction mixture cools. By extrapolating the line back from this cooling part of the curve, we can estimate the temperature from which the mixture appears to be cooling. If we look at the value of the temperature on this curve at 2 min 30 s, the point at which the zinc was added, we should get an estimate of the temperature rise if the reaction had occurred instantaneously. It can be seen that this temperature rise is greater than the temperature rise actually measured in the experiment.

From the graph, we estimate the temperature change as 10.3 °C.

The heat given out in the reaction is given by

$Q = mc\Delta T = 50.0 \times 4.18 \times 10.3 = 2150$ J

Assumption: the density of copper(II) sulfate solution is the same as that of water.

To work out the enthalpy change of reaction, we need to know how many moles of copper(II) sulfate reacted (zinc was in excess – more than enough to react with all the copper(II) sulfate).

amount in mol of $CuSO_4$ = concentration × volume in dm^3

amount in mol of $CuSO_4 = 0.200 \times (50.0 \div 1000) = 0.0100$ mol

Therefore, 2150 J of energy is released when 0.0100 mol copper(II) sulfate reacts.

For the reaction of one mole of copper sulfate:

$$\Delta H = -\frac{-Q}{n} = \frac{-2150}{0.0100} = -21\,5000 \text{ J mol}^{-1}$$

Therefore, the enthalpy change of reaction = –215 kJ mol^{-1}.

The extrapolation of the line is very much a matter of judgement and is a source of random error in the experiment.

Link

This is a redox reaction, which is often called a displacement reaction or a single replacement reaction – zinc is more reactive than copper and displaces it from solution. Zinc is the reducing agent in this reaction and copper(II) sulfate is the oxidising agent – see Chapter 20.

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TEST YOUR UNDERSTANDING

9 In each case, work out the enthalpy change of solution:

a 2.00 g of $NaNO_3$ is dissolved in 25.0 cm^3 of water and the temperature goes down by 4.20 °C

b 1.20 g of $KClO_4$ is dissolved in 50.0 cm^3 of water and the temperature goes up by 1.80 °C

c 2.50 g of $NaBr•2H_2O$ is dissolved in 30.0 cm^3 of water and the temperature goes down by 2.10 °C.

10 **a** 200.0 cm^3 of 0.150 mol dm^{-3} hydrochloric acid is mixed with 100.0 cm^3 of 0.300 mol dm^{-3} sodium hydroxide solution. The temperature rises by 1.36 °C. If both solutions were originally at the same temperature, calculate the enthalpy change of neutralisation.

b Predict the temperature rise if the experiment in part **a** is repeated using:

i 400.0 cm^3 of 0.150 mol dm^{-3} hydrochloric acid and 200.0 cm^3 of 0.300 mol dm^{-3} sodium hydroxide solution

ii 200.0 cm^3 of 0.300 mol dm^{-3} hydrochloric acid and 100.0 cm^3 of 0.600 mol dm^{-3} sodium hydroxide solution

iii 50.0 cm^3 of 0.300 mol dm^{-3} hydrochloric acid and 25.0 cm^3 of 0.600 mol dm^{-3} sodium hydroxide solution.

11 **a** When 1.00 g of magnesium chloride is dissolved in 50.0 cm^3 of water, the temperature goes up from 21.5 to 29.1 °C. Calculate the enthalpy change of solution of magnesium chloride.

b Predict the temperature change when 2.00 g of magnesium chloride is dissolved in 100 cm^3 of water.

c Predict the temperature change when 2.00 g of magnesium chloride is dissolved in 50.0 cm^3 of water.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the difference between heat and temperature	12.1			
explain the difference between exothermic and endothermic reactions	12.2			
explain the term stability	12.2			
draw energy profiles for exothermic and endothermic reactions	12.2			
explain the term standard enthalpy change for a reaction	12.3			
calculate standard enthalpy changes from experimental data.	12.4			

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REFLECTION

- How much experience do you have of practical work? To what extent do you feel that carrying out practical work would help you understand the concepts in this chapter better?
- Try to explain specific heat capacity and enthalpy change of solution to another student.

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 13

Energy cycles in reactions

LEARNING OBJECTIVES

In this chapter you will:

- understand the term average bond enthalpy
- calculate enthalpy changes using bond enthalpies
- uses Hess's law to calculate enthalpy changes

- calculate enthalpy changes using standard enthalpy changes of combustion
- understand the term standard enthalpy change of formation
- calculate enthalpy changes using standard enthalpy changes of formation
- use a Born–Haber cycle to calculate enthalpy changes for ionic compounds.

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GUIDING QUESTIONS

- How can we work out enthalpy changes for reactions involving covalent substances?
- How can we work out enthalpy changes for reactions involving ionic substances?

Introduction

In the previous chapter, we looked at how to measure enthalpy changes experimentally; however, it is not possible to determine all enthalpy changes experimentally, and here, we will look at how to calculate enthalpy changes for reactions we do not know using known quantities. We will be mostly using the ideas of Hess's law. Germain Henri Hess was a Swiss–Russian chemist who published a paper in 1840, putting forward the idea that the amount of heat energy given out/taken in when substances combined did not depend on whether they combined directly or indirectly.

13.1 Bond enthalpies

Enthalpy changes for reactions in the gas phase can be worked out if we know the quantity of energy required/released when bonds are broken/made. To be able to do this, we must first consider the definition of **bond enthalpy** (also just called *bond energy*).

KEY POINT

Bond enthalpy is the enthalpy change when one mole of covalent bonds, in gaseous molecules, are broken under standard conditions.

The quantity defined here is also called the bond dissociation enthalpy – it refers to breaking a specific bond in a gaseous molecule (compare with *average* bond enthalpy below).

For example, the H—H bond enthalpy is 436 kJ mol^{-1}, which can be represented by the equation:

$H_2(g) \rightarrow 2H(g) \qquad \Delta H^{\ominus} = +436 \text{ kJ mol}^{-1}$

One mole of H_2 molecules is broken apart to give two moles of gaseous hydrogen atoms.

The H—Cl bond enthalpy is 431 kJ mol^{-1}, which is represented by

$HCl(g) \rightarrow H(g) + Cl(g) \qquad \Delta H^{\ominus} = +431 \text{ kJ mol}^{-1}$

EXAM TIP

$HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

does *not* represent the bond enthalpy of HCl. $\frac{1}{2}H_2(g)$ represents half a mole of H_2 molecules and is not the same as H(g), which is one mole of gaseous H atoms. The process shown here would involve breaking the bond in HCl but also making bonds in H_2 and Cl_2.

KEY POINTS

Bond breaking requires energy (endothermic): ΔH positive.

Bond making releases energy (exothermic): ΔH negative.

Energy must be supplied to break apart two atoms in a molecule against the attractive force holding them together. Bond breaking is, therefore, an endothermic process: ΔH is positive. Energy is released when two atoms come together to form a bond – bond making is an exothermic process: ΔH is negative.

Bond enthalpy values are usually quoted as positive values, for the bond-breaking process. The same amount of energy is released when a bond is formed as is required to break it; therefore, 431 kJ is released when 1 mol of H—Cl bonds are formed:

$H(g) + Cl(g) \rightarrow HCl(g) \qquad \Delta H^{\ominus} = -431 \text{ kJ mol}^{-1}$

Average bond enthalpy

There can only be one value for the bond enthalpy for the H—H bond – this is the amount of energy to break apart the H_2 molecule in the gaseous state. However, the strength of the bonds between different atoms varies within compounds and from compound to compound.

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For example, for methane, the energy to break the first C—H bond is very different from that required to break the last bond:

$CH_4(g) \rightarrow CH_3(g) + H(g)$ $\Delta H = 439$ kJ mol^{-1}

$CH_3(g) \rightarrow CH_2(g) + H(g)$ $\Delta H = 463$ kJ mol^{-1}

$CH_2(g) \rightarrow CH(g) + H(g)$ $\Delta H = 423$ kJ mol^{-1}

$CH(g) \rightarrow C(g) + H(g)$ $\Delta H = 339$ kJ mol^{-1}

Overall, then, we can work out the enthalpy change for breaking all the C—H bonds in methane:

$CH_4(g) \rightarrow C(g) + 4H(g)$ $\Delta H = 1664$ kJ mol^{-1}

We could then calculate an average C—H bond enthalpy for methane by dividing this value by 4 to give a value of 416 kJ mol^{-1}. This would be useful for bond enthalpy calculations involving methane; however, the energy to break the first C—H bond in ethane (C_2H_6) is 422 kJ mol^{-1}, and the energies to break that bond in ethene (C_2H_4) and ethyne (C_2H_2) are 462 and 558 kJ mol^{-1} respectively. So, to use bond enthalpies in calculations, technically we should have tables of all the bond dissociation enthalpies in each separate compound. This would not only be time-consuming and cumbersome to determine but would limit the number of compounds for which we could do calculations (compounds for which data exists). Therefore, we use instead **average bond enthalpies**.

Some average bond enthalpies are shown in Table 13.1.

KEY POINT

Average bond enthalpy is the average amount of energy required to break one mole of covalent bonds, in gaseous molecules under standard conditions. 'Average' refers to the fact that the bond enthalpy is different in different molecules and, therefore, the value quoted is the average amount of energy to break a particular bond in a range of typical molecules containing that bond.

EXAM TIP

When defining 'average bond enthalpy', it is important to define 'bond enthalpy' and explain 'average'.

Link

The connections between bond enthalpies, bond order and bond length are discussed in Chapter 7. The C≡O in CO is stronger than the N≡N in N_2, but the bond lengths are very similar. Can the difference be explained in terms of the polarity of the C—O bond compared to the N—N bond?

The connection between the carbon–halogen bond enthalpies and the rate of nucleophilic substitution is discussed in Chapter 22.

Bond	Bond enthalpy/ kJ mol^{-1}	Bond	Bond enthalpy/ kJ mol^{-1}	Bond	Bond enthalpy/ kJ mol^{-1}	Bond	Bond enthalpy/ kJ mol^{-1}
H—H	436	C—H	414	O—O	144	C—O	358
C—C	346	Si—H	323	O=O	498	C=O	804
C=C	614	N—H	391	Si—O	466	C≡O	1070
C≡C	839	P—H	322	F—F	159	C—N	286
Si—Si	226	O—H	463	Cl—Cl	242	C=N	615
N—N	158	S—H	364	Br—Br	193	C≡N	890
N=N	470	F—H	567	I—I	151	C—F	492
N≡N	945	Cl—H	431	N—Cl	192	C—Cl	324
P—P	198	Br—H	366	Si—F	597	C—Br	285
S—S	266	I—H	298	N—F	278	C—I	228

Table 13.1: Average bond enthalpies.

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KEY POINT

Bond energy calculations may be inaccurate.

Because we use *average* bond enthalpies in the calculations below, the values we obtain for the overall enthalpy changes will often be different from, and less reliable than, calculations using enthalpy values that are specific to a particular compound (for example, enthalpy changes of formation and combustion) or experimental values.

For example, if we use the bond enthalpies in Table 13.1 to calculate the enthalpy change for the following reaction:

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

we get the value –808 kJ mol^{-1} (see Worked Example 13.1 for how to do this calculation). If, however, we calculate the value using enthalpy changes that are specific to these compounds, we get the value –803 kJ mol^{-1}. The difference arises because we are not using the actual bond energies in CH_4, CO_2 and H_2O but rather average values.

KEY POINT

Bond enthalpies are only applicable to reactions occurring in the gaseous state.

If a substance is in the solid or liquid state, then energy must also be supplied to break intermolecular forces as well as breaking the covalent bonds between atoms.

If we consider the process:

$Br_2(l) \rightarrow 2Br(g) \qquad \Delta H^{\ominus} = +224 \text{ kJ mol}^{-1}$

This does not represent the Br—Br bond enthalpy. This equation can be broken down into two separate processes:

$Br_2(l) \rightarrow Br_2(g) \qquad \Delta H^{\ominus} = +31 \text{ kJ mol}^{-1}$

$Br_2(g) \rightarrow 2Br(g) \qquad \Delta H^{\ominus} = +193 \text{ kJ mol}^{-1}$

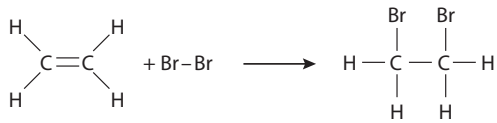
The first process is called the enthalpy change of vaporisation – energy is required to break the London forces between the Br_2 molecules – no covalent bonds are broken in this process. The second equation represents the bond enthalpy for breaking the Br–Br bond. The overall enthalpy change for $Br_2(l) \rightarrow 2Br(g)$ is the sum of these two enthalpy changes (see the section on Hess's law).

Using bond enthalpies to calculate enthalpy changes

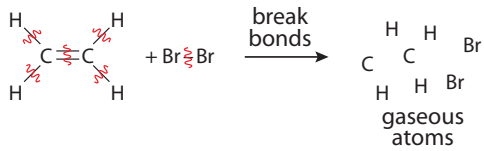
Let's look at the basic principles of how to use bond enthalpies to calculate the enthalpy change for a reaction. Consider the reaction between ethene and bromine to produce 1,2-dibromoethane:

$C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$

If the species are drawn as full structural formulas, then all the bonds can be seen clearly:



We imagine the reaction happening with all the bonds in the reactants being broken:



The reaction does not actually happen like this, it is just a way of working out the enthalpy change.

The total enthalpy change when all the bonds are broken can be calculated (Table 13.2):

Bond broken	Bond enthalpy /kJ mol^{-1}	Number of bonds	Total energy /kJ mol^{-1}
C—H	414	4	1656
C=C	614	1	614
Br—Br	193	1	193
Total enthalpy change to break all bonds			2463

Table 13.2: Enthalpy change for bond breaking.

The total enthalpy change when all the bonds are broken is +2463 kJ mol^{-1}. This value is positive because breaking bonds is an endothermic process.

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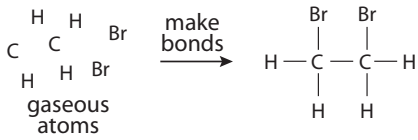
Then new bonds form to make the products:



The total enthalpy released when all the bonds are made can be calculated (Table 13.3):

Bond made	Bond enthalpy /kJ mol^{-1}	Number of bonds	Total energy /kJ mol^{-1}
C—H	414	4	1656
C—C	346	1	346
C—Br	285	2	570
Total enthalpy released when bonds made			2572

Table 13.3: Enthalpy change for bond making.

Making bonds is an exothermic process, so the total enthalpy change when all the bonds are made is –2572 kJ mol^{-1}.

If we add up these enthalpy changes for breaking and making bonds, we get the overall enthalpy change for the reaction:

$\Delta H^{\ominus} = 2463 - 2572 = -109$ kJ mol^{-1}

Note that bromine and 1,2-dibromoethane are both liquids at 298.15 K. The equation here is for the reaction in the gas phase, and the enthalpy change will not be the same as for the reaction involving liquid bromine to form $C_2H_4Br_2(l)$.

The process of calculating enthalpy changes using bond enthalpies can be simplified by using an equation.

KEY POINT

$\Delta H^{\ominus} = \Sigma$(bond enthalpies for bonds broken) $- \Sigma$(bond enthalpies for bonds made)

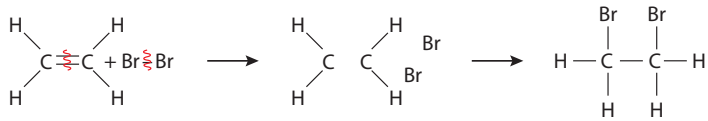
Or, just $\Delta H^{\ominus} = \Sigma$(bonds broken) $- \Sigma$(bonds made)

Or, in words: 'the enthalpy change of reaction is the sum of all the bonds broken minus the sum of all the bonds made', where the bond enthalpies are taken directly from Table 13.1 and no signs changed, i.e., all values are put in as positive.

This approach would give

$\Delta H^{\ominus} = [(4 \times 412) + (1 \times 612) + (1 \times 193)] - [(4 \times 412) + (1 \times 348) + (2 \times 276)] = -109$ kJ mol^{-1}

A shortcut for doing this calculation would be to realise that there are four C—H bonds in ethene and four C—H bonds in 1,2-dibromoethane and, therefore, there is no need to make or break these bonds:



The experimental value for the enthalpy change for the reaction of $C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$ is –121 kJ mol^{-1}, which is significantly different from the value of –109 kJ mol^{-1} obtained using bond enthalpy calculations. This is because the bond enthalpy values are average values and not specific to these compounds.

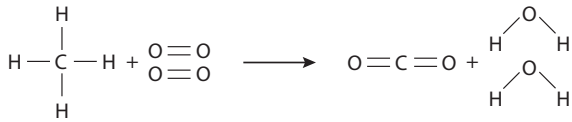
WORKED EXAMPLE 13.1

Using the bond enthalpies given in Table 13.1, calculate the enthalpy change for the reaction:

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

Answer

It is important to draw out the reaction showing full structural formulas to make sure that you identify the number and type of bonds that are present:



Σ(bonds broken) = 4 × C—H + 2 × O=O
= 4 × 414 + 2 × 498 = 2652 kJ mol^{-1}

Σ(bonds made) = 2 × C=O + 4 × O—H
= 2 × 804 + 4 × 463 = 3460 kJ mol^{-1}

$\Delta H = \Sigma$(bonds broken) $- \Sigma$(bonds made)

$\Delta H = 2652 - 3460 = -808$ kJ mol^{-1}

A reaction in the gas phase will be exothermic if more energy is released when bonds are formed (exothermic) than is required to break bonds (endothermic). This could be the case if stronger/more bonds are formed than broken.

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Working out a bond enthalpy from an enthalpy change of reaction

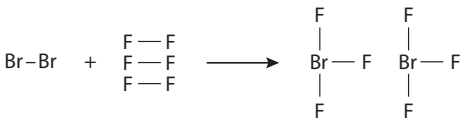
WORKED EXAMPLE 13.2

Using the bond enthalpies for the F—F and Br—Br bonds and the enthalpy change of reaction given, calculate the mean Br—F bond energy in BrF_3:

$Br_2(g) + 3F_2(g) \rightarrow 2BrF_3(g) \qquad \Delta H^{\ominus} = -545 \text{ kJ mol}^{-1}$

Answer

Again, we draw out the reaction with full structural formulas:



$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$

$-545 = [193 + (3 \times 159)] - [6 \times \text{Br—F}]$

Rearranging this, we get:

$6 \times \text{Br—F} = 193 + (3 \times 159) + 545$

$6 \times \text{Br—F} = 1215$

Therefore, the Br—F bond enthalpy is $1215 \div 6$, i.e., 203 kJ mol^{-1}.

SCIENCE IN CONTEXT

The air around us is made up of about 78% nitrogen gas, N_2. There is a very strong triple bond (bond energy 945 kJ mol^{-1}) between the nitrogen atoms, which makes nitrogen very unreactive, and so it is used, for instance, as an inert atmosphere in packets of crisps (Figure 13.1) to reduce oxidation of the fats (which would occur if oxygen were present) and increase the shelf life. So, when you look at a packet of crisps, and think this packet seems to contain more air than crisps, it is not air, but nitrogen, and it is there for a very good reason.

The triple bond between nitrogen atoms also has a huge influence on the properties of other substances for exactly the opposite reason. A lot of energy is needed to break the triple bond between nitrogen atoms but that also means that a lot of energy is released when the triple bond is formed, which is why nitrogen is the basis of most explosives.

Figure 13.1: Crisp packets are filled with nitrogen.

Probably the most famous high explosive, and still one of the most widely employed for commercial and military purposes, is TNT (trinitrotoluene or 2-methyl-1,3,5-trinitrobenzene):

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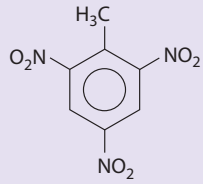


When this compound explodes, it decomposes rapidly to form, amongst other things, nitrogen gas. The formation of the triple bonds between nitrogen atoms means that a great deal of heat is given out (the enthalpy change is about 4000 kJ per kg), but nitrogen is also a gas, so you also have a rapidly expanding gas (the explosion of 1 kg of TNT produces over 700 dm^3 of gas) – an explosion.

The energy of bomb explosions is usually compared to that of TNT, so, for instance, the nuclear bomb, nicknamed 'Little Boy', that was dropped on Hiroshima is described as an approximately 15 kiloton bomb, which means that the energy released was equivalent to 15 000 tonnes of TNT.

Other nitrogen-containing explosives include nitroglycerine, $[(CH_2ONO_2)_2CHONO_2]$, which, when mixed with kieselguhr produces dynamite. Inventing dynamite was the basis of Alfred Nobel's fortune and provided the funds for the Nobel Prize, which recognises the achievements of those people who have, in the words of his will, 'conferred the greatest benefit to humankind'.

TEST YOUR UNDERSTANDING

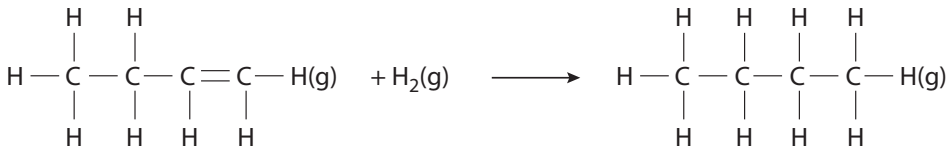
1 Write equations to represent the bond enthalpy of

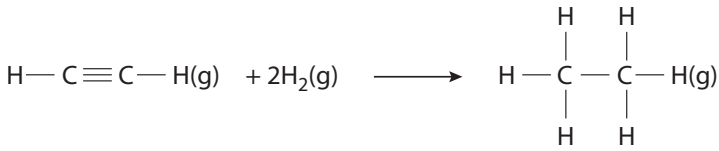
a Cl_2 **b** HBr.

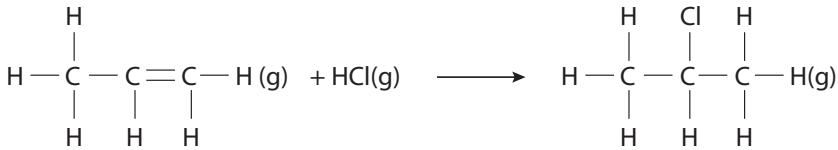
2 Use the bond enthalpies in Table 13.1 to work out the enthalpy changes for the following reactions:

a $2H-H(g) + O=O(g) \longrightarrow 2\,H-O-H(g)$

b $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

c 

d 

e 

f $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$.

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3 Use the bond enthalpies in Table 13.1 to work out the enthalpy changes for the following combustion reactions:

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

b $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

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

d $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

e $2C_2H_2(g) + 3O_2(g) \rightarrow 4CO(g) + 2H_2O(g)$

f $CH_3CH_2CH_2OH(g) + 4\frac{1}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$.

4 Calculate the mean Cl—F bond enthalpy, given the following data:

$Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g)$ $\quad \Delta H^{\ominus} = -164$ kJ mol^{-1}

and the Cl—Cl and F—F bond enthalpies in Table 13.1.

5 Calculate the mean Cl—F bond enthalpy, given the following data:

$ClF_3(g) + F_2(g) \rightarrow ClF_5(g)$ $\quad \Delta H = -91$ kJ mol^{-1}

and the F—F bond enthalpy in Table 13.1.

Hint: Both ClF_3 and ClF_5 just contain single bonds between Cl and F.

13.2 Hess's law

It is not always possible to design experiments to measure certain enthalpy changes, and so, we often have to use data from reactions in which the enthalpy change can be measured to work out the enthalpy change for a particular reaction in which it cannot be measured directly. In order to do this, we use **Hess's law**.

KEY POINT

Hess's law states the enthalpy change accompanying a chemical reaction is independent of the pathway between the initial and final states.

What this basically means is that, if we consider the conversion of A into B (Figure 13.2), the enthalpy change for the reaction is the same if we go directly from A to B or indirectly via other reactions and substance C.

Using this cycle, if we know the value for ΔH_1 (for the conversion of A to C) and ΔH_2 (for the conversion of C to B), we can work out the value of the enthalpy change ΔH_r for the conversion of A into B. Therefore, in this case:

$\Delta H_r = \Delta H_1 + \Delta H_2$

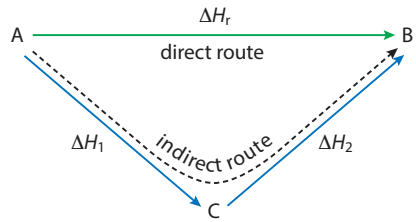

Figure 13.2: The enthalpy change does not depend on the route between A and B.

Let us consider a slightly different situation in which the enthalpy changes we know are

$A \rightarrow C = \Delta H_1$ $\quad B \rightarrow C = \Delta H_2$

This produces a slightly different cycle, in which the arrow for ΔH_2 is the other way around, because the reaction we know is from B to C (Figure 13.3).

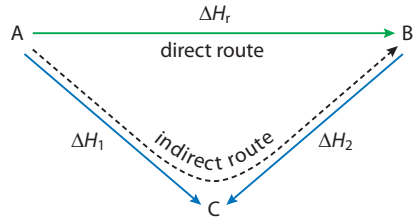

Figure 13.3: If we know the enthalpy change for the conversion B → C, rather than C → B, the arrow between B and C is the other way around.

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Now the enthalpy change from A to B is given by $\Delta H_r = \Delta H_1 - \Delta H_2$. We have $-\Delta H_2$ in this case, because the conversion C → B along the indirect route (A → C → B) goes in the opposite direction to the arrow we have drawn for ΔH_2.

Why Hess's law works

The reason Hess's law works can be understood from Figure 13.4.

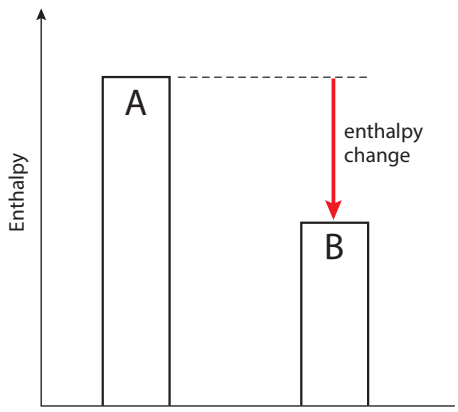


Figure 13.4: A and B have a certain amount of enthalpy, so the enthalpy change for the conversion of A into B is always the same.

Enthalpy is basically a property of a substance under a certain set of conditions. This means that the enthalpy depends on the substance and the conditions. So, A has a certain amount of enthalpy, B has a certain amount of enthalpy, and these are fixed for a particular set of conditions. The route that is taken between A and B cannot affect the amount of enthalpy A or B has and, therefore, the difference in enthalpy between A and B is constant.

This is a bit like saying that the distance between Kuala Lumpur and Berlin is 9614 km – it does not matter what route you take between these two places, they remain the same distance apart.

Working out enthalpy changes

Hess's law can be used to work out unknown enthalpy changes from ones that are known.

For, example, we can use these two known enthalpy changes:

reaction 1: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\ \Delta H_1 = -286\ \text{kJ mol}^{-1}$

reaction 2: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)\ \Delta H_2 = -242\ \text{kJ mol}^{-1}$

to calculate the enthalpy change for the process $H_2O(l) \rightarrow H_2O(g)$.

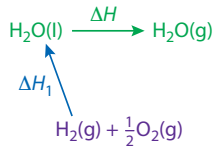
We will consider two different ways of doing this.

Method A (enthalpy cycle)

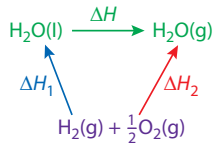
We will use the enthalpy changes we have been given to construct a cycle.

The enthalpy change that we have to find is put at the top of the cycle:

We can then add in the reactions we know. First reaction 1:

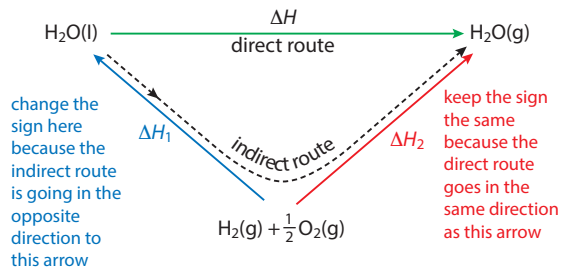


And then reaction 2, to complete the cycle:



The reaction for which we are trying to find the enthalpy change is $H_2O(l)$ to $H_2O(g)$.

From Hess's law, the enthalpy change for the direct route [$H_2O(l) \rightarrow H_2O(g)$] is the same as that for the indirect route going from $H_2O(l)$ to $H_2(g) + \frac{1}{2}O_2(g)$ then to $H_2O(g)$:



The indirect route goes in the opposite direction to the ΔH_1 arrow, so that sign is changed, but in the same direction as the ΔH_2 arrow, so that sign remains the same. We therefore have

$\Delta H = -\Delta H_1 + \Delta H_2$

Substituting values, we get

$\Delta H = -(-286) + (-242) = +44\ \text{kJ mol}^{-1}$

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EXAM TIP

It is always worth thinking – does my answer make sense? Would you expect the enthalpy change for the conversion of $H_2O(l)$ to $H_2O(g)$, the vaporisation of water, to be exothermic or endothermic?

Method B (manipulating equations)

In this method, we rearrange the equations for the data given to produce the equation for the reaction corresponding to the enthalpy change we have to find:

target reaction: $H_2O(l) \rightarrow H_2O(g)$

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

reaction 2: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242$ kJ mol^{-1}

In our target reaction, $H_2O(l)$ (highlighted in red) is on the left, but in reaction 1, it is on the right. We therefore reverse reaction 1 so that $H_2O(l)$ is on the left-hand side, as in the target equation:

$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\Delta H = +286$ kJ mo1^{-1}

This also changes the sign: if the enthalpy change is –286 kJ mol^{-1} in one direction, it must be +286 kJ mol^{-1} in the other direction.

$H_2O(g)$ is on the right in the target reaction and on the right in reaction 2; therefore, we do not need to do anything to reaction 2.

We now have $H_2O(l)$ and $H_2O(g)$ on the correct sides and can add the two equations and the two enthalpy changes together:

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

$\cancel{H_2(g)} + \cancel{\frac{1}{2}O_2(g)} \rightarrow H_2O(g)$ $\Delta H = -242$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = +44$ kJ mol^{-1}

The terms that are the same on both sides cancel out to produce the overall, target, equation.

This is very similar to methods for solving simultaneous linear equations in mathematics.

The relationship between the various enthalpy changes in the previous example can be seen in an enthalpy level diagram (Figure 13.5). Downward arrows represent exothermic processes.

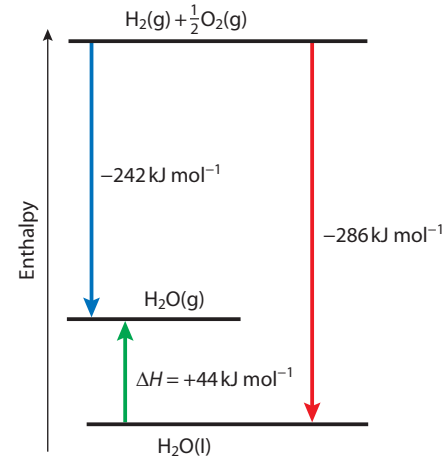

Figure 13.5: An enthalpy level diagram. Exothermic processes are shown as downwards arrows, and endothermic reactions as upwards arrows.

WORKED EXAMPLE 13.3

Given these enthalpy changes

$2C(s) + O_2(g) \rightarrow 2CO(g)$ $\Delta H_1 = -222$ kJ mol^{-1} reaction 1

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_2 = -394$ kJ mol^{-1} reaction 2

calculate the enthalpy change for the reaction: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Answer

We will, again, look at two methods for solving this problem.

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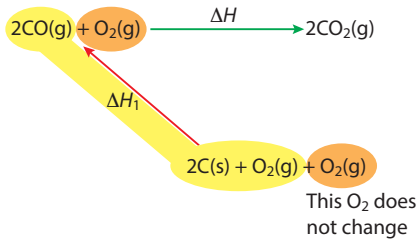
Method A (using a cycle)

The enthalpy change that we have to find is put at the top of the cycle and then, adding in reaction 1, we get:



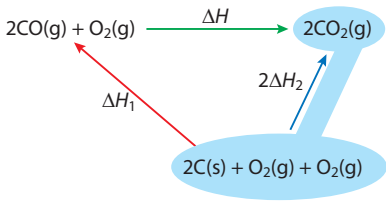
Reaction 1 is highlighted in yellow and shows the reaction of two C and one O_2 to form two CO. The other O_2, highlighted in orange, remains unchanged, and the enthalpy change for this process [converting $O_2(g)$ to $O_2(g)$] is zero. This means that the total enthalpy change along the red arrow is ΔH_1.

The target reaction involves the formation of 2 mol $CO_2(g)$, but reaction 2 gives us the enthalpy change for the formation of 1 mol $CO_2(g)$.

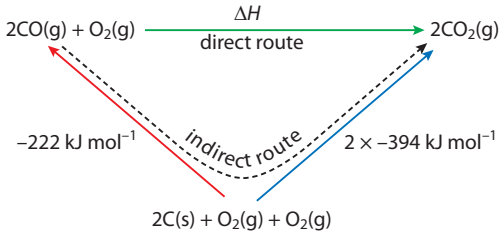
Therefore, before reaction 2 is added to the cycle, it must be multiplied by 2, because we need to form 2 mol CO_2. The enthalpy change must also be multiplied by two, hence we get

$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$ $\qquad 2\Delta H_2 = 2 \times -394 = -788 \text{ kJ mol}^{-1}$

This reaction is highlighted in blue in the cycle:



The values can now be put into the cycle:



Because the direction of the indirect route arrow is opposite to that of the red arrow, the sign of the quantity on the red arrow is reversed. The overall enthalpy change is thus given by

$\Delta H = -\Delta H_1 + 2\Delta H_2$

$\Delta H = -(-222) + (2 \times -394) = -566 \text{ kJ mol}^{-1}$

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Method B (manipulating the equations)

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$		target reaction
$2C(s) + O_2(g) \rightarrow 2CO(g)$	$\Delta H_1 = -222$ kJ mol^{-1}	reaction 1
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_2 = -394$ kJ mol^{-1}	reaction 2

The differences between the target reaction and the reactions we have been given are highlighted.

First, reaction 1 is reversed to give two CO on the left-hand side, as in the target reaction:

$2CO(g) \rightarrow 2C(s) + O_2(g)$ $\Delta H = +222$ kJ mol^{-1} sign changed.

Now reaction 2 is multiplied by 2 to give $2CO_2$ on the right-hand side, as in the target reaction:

$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$ $\Delta H = -788$ kJ mol^{-1} (enthalpy change multiplied by two)

We now have two CO(g) on the left-hand side and two $CO_2(g)$ on the right-hand side, as in the target equation. The two equations and their enthalpy changes are now added together, and common terms cancelled to produce the target equation and its enthalpy change:

$$\begin{array}{lcll} 2CO(g) & \rightarrow & \cancel{2C(s)} + \cancel{O_2(g)} & \Delta H = +222 \text{ kJ mol}^{-1} \\ \cancel{2C(s)} + \cancel{2}O_2(g) & \rightarrow & 2CO_2(g) & \Delta H = -788 \text{ kJ mol}^{-1} \\ \hline 2CO(g) + O_2(g) & \rightarrow & 2CO_2(g) & \Delta H = -566 \text{ kJ mol}^{-1} \end{array}$$

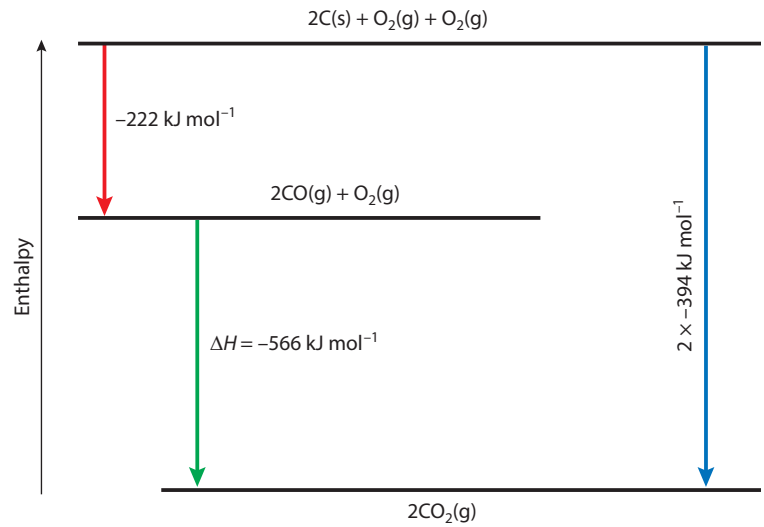

Figure 13.6: An enthalpy level diagram. Exothermic processes are shown as downward arrows – endothermic processes would be shown as upward arrows.

The relationship between the various enthalpy changes in Worked Example 13.3 can be seen in an enthalpy level diagram (Figure 13.6).

EXAM TIP

Only one of these methods needs to be understood.

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WORKED EXAMPLE 13.4

The enthalpy changes for two reactions are as follows:

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -297$ kJ mol^{-1}

$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$ $\Delta H = -396$ kJ mol^{-1}

Calculate the enthalpy change for the reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$.

Answer

Here we will just use the method which involves manipulating the equation.

Let's highlight the differences:

target reaction: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

reaction 1: $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -297$ kJ mol^{-1}

reaction 2: $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$ $\Delta H = -396$ kJ mol^{-1}

There are 2 mol $SO_2(g)$ on the *left*-hand side in the target reaction, but reaction 1 has 1 mol $SO_2(g)$ on the *right*-hand side. We must therefore multiply reaction 1 by 2:

$2S(s) + 2O_2(g) \rightarrow 2SO_2(g)$ $\Delta H = -594$ kJ mol^{-1}

and then reverse it:

$2SO_2(g) \rightarrow 2S(s) + 2O_2(g)$ $\Delta H = +594$ kJ mol^{-1}

This now gives us 2 mol $SO_2(g)$ on the left-hand side, as in our target reaction.

There are 2 mol $SO_3(g)$ on the right-hand side in our target reaction, but reaction 2 has only 1 mol $SO_3(g)$ on the right-hand side. We must therefore multiply reaction 2 by 2:

$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -792$ kJ mol^{-1}

This now gives us $2SO_3(g)$ on the right-hand side, as in our target reaction.

We can now add these equations and enthalpy changes together, cancelling out like terms that are the same on both sides:

$2SO_2(g) \rightarrow 2S(s) + 2O_2(g)$ $\Delta H = +594$ kJ mol^{-1}

$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -792$ kJ mol^{-1}

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -198$ kJ mol^{-1}

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WORKED EXAMPLE 13.5

A more difficult example, involving three equations

Use the information given below to calculate the enthalpy change for the reaction:

$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$

$H_2O(l) \rightarrow H_2O(g)$	$\Delta H_1 = +44$ kJ mol $^{-1}$	reaction 1
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	$\Delta H_2 = -1371$ kJ mol^{-1}	reaction 2
$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$	$\Delta H_3 = -1409$ kJ mol^{-1}	reaction 3

Answer

An energy cycle could be drawn but the question is most easily solved by manipulating the equations.

target reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$

reaction 1: $H_2O(l) \rightarrow H_2O(g)$ $\Delta H_1 = +44$ kJ mol^{-1}

reaction 2: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H_2 = -1371$ kJ mol^{-1}

reaction 3: $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H_3 = -1409$ kJ mol^{-1}

The differences have been highlighted.

Our target equation has $H_2O(g)$ on the left-hand side. Reaction 1 has the correct number of $H_2O(g)$, but on the wrong side, so reaction 1 must be reversed:

$H_2O(g) \rightarrow H_2O(l)$ $\Delta H = -44$ kJ mol^{-1}

The target equation has $C_2H_5OH(l)$ on the right. Reaction 2 has the correct number of $C_2H_5OH(l)$, but on the wrong side, so Reaction 2 must also be reversed:

$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2(g)$ $\Delta H = +1371$ kJ mol^{-1}

Reaction 3 has the correct numbers of $C_2H_4(g)$ on the correct side, so it is left unchanged.

All the species are now on the correct sides, as in the target reaction. These equations are now added and common species cancelled:

$H_2O(g) \rightarrow \cancel{H_2O(l)}$ $\Delta H = -44$kJ mol^{-1}

$\cancel{2CO_2(g) + 3H_2O(l)} \rightarrow C_2H_5OH(l) + \cancel{3O_2(g)}$ $\Delta H = +1371$ kJ mol^{-1}

$C_2H_4(g) + \cancel{3O_2(g)} \rightarrow \cancel{2CO_2(g) + 2H_2O(l)}$ $\Delta H = -1409$ kJ mol^{-1}

$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$ $\Delta H = -82$ kJ mol^{-1}

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TEST YOUR UNDERSTANDING

6 a Use the data here to calculate the enthalpy change for the process:
$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1371$ kJ mol^{-1}

$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1415$ kJ mol^{-1}

b Use the data here to calculate the enthalpy change for the process:
$C_6H_6(l) \rightarrow C_6H_6(g)$

$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$
$\Delta H = -6544$ kJ mol^{-1}

$2C_6H_6(g) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$
$\Delta H = -6606$ kJ mol^{-1}

7 a Use the data here to calculate the enthalpy change for the following reaction:

$BrF(g) + 2F_2(g) \rightarrow BrF_5(l)$

$BrF(g) + F_2(g) \rightarrow BrF_3(l)$ $\Delta H = -242$ kJ mol^{-1}

$BrF_3(l) + F_2(g) \rightarrow BrF_5(l)$ $\Delta H = -158$ kJ mol^{-1}

b Use the data here to calculate the enthalpy change for the following reaction:
$ClF_3(g) + F_2(g) \rightarrow ClF_5(g)$

$Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g)$ $\Delta H = -328$ kJ mol^{-1}

$Cl_2(g) + 5F_2(g) \rightarrow 2ClF_5(g)$ $\Delta H = -510$ kJ mol^{-1}

8 a Use the data below to calculate the enthalpy change for the following process:

$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	$\Delta H = -92$ kJ mol^{-1}
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$	$\Delta H = -484$ kJ mol^{-1}

b Use the data below to calculate the enthalpy change for the following process:

$3Mn_3O_4(s) + 8Al(s) \rightarrow 9Mn(s) + 4Al_2O_3(s)$

$3Mn(s) + 2O_2(g) \rightarrow Mn_3O_4(s)$	$\Delta H = -1387$ kJ mol^{-1}
$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$	$\Delta H = -1669$ kJ mol^{-1}

c Use the data below to calculate the enthalpy change for the following process:

$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(l)$

$S(s) + O_2(g) \rightarrow SO_2(g)$	$\Delta H = -297$ kJ mol^{-1}
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$\Delta H = -196$ kJ mol^{-1}
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$	$\Delta H = -130$ kJ mol^{-1}

9 Use the data below to work out an enthalpy change for the reaction:

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

$C_2H_2(g) + 2\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$
$\Delta H = -1300$ kJ mol^{-1}

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

$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -1560$ kJ mol^{-1}

10 Use the data here to calculate the enthalpy change for the following reaction:

$2C_6H_{14}(g) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$

$C_6H_{14}(l) \rightarrow C_6H_{14}(g)$ $\Delta H = 32$ kJ mol^{-1}

$C_6H_{14}(l) + 9.5O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$
$\Delta H = -4163$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = 44$ kJ mol^{-1}

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13.3 Standard enthalpy change of combustion data

Standard enthalpy change of combustion ($\Delta H_c^\ominus$) is the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

The **standard enthalpy change of combustion** is always negative, as combustion is always an exothermic process. For example:

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

$\Delta H_c^\ominus = -891 \text{ kJ mol}^{-1}$

Link

When organic compounds containing C, H and/or O undergo complete combustion, the products of the reaction are carbon dioxide and water. See Chapter 16, section 16.1 for how to balance equations.

When we have been given enthalpy change of combustion data, we can work out the enthalpy change for a reaction using the equation:

$\Delta H^\ominus = \Sigma \Delta H_c^\ominus \text{(reactants)} - \Sigma \Delta H_c^\ominus \text{ (products)}$

where Σ means 'sum of'.

WORKED EXAMPLE 13.6

Given the enthalpy change of combustion data in the table, calculate the enthalpy change for the reaction: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
$C_2H_4(g)$	−1411
$H_2(g)$	−286
$C_2H_6(g)$	−1561

Answer

$\Delta H^\ominus = \Sigma \Delta H_c^\ominus \text{ (reactants)} - \Sigma \Delta H_c^\ominus \text{ (products)}$

So:

$\Delta H^\ominus = [-1411 + (-286)] - [-1561] = -1697 + 1561$

$\Delta H^\ominus = -136 \text{ kJ mol}^{-1}$

WORKED EXAMPLE 13.7

Given the enthalpy changes of combustion in the table, work out the enthalpy change for the reaction:

$7C(s) + 3H_2(g) + O_2(g) \rightarrow C_6H_5COOH(s)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
C(s)	−394
$H_2(g)$	−286
$C_6H_5COOH(s)$	−3228

Answer

Again, we will use the equation:

$\Delta H^\ominus = \Sigma \Delta H_c^\ominus \text{ (reactants)} - \Sigma \Delta H_c^\ominus \text{ (products)}$

This is essentially the same as the previous worked example except here we have to remember to multiply the $\Delta H_c^\ominus$ values by the coefficient in the equation.

The enthalpy change of combustion of oxygen gas is zero – oxygen cannot burn in oxygen.

So:

$\Delta H^\ominus = [(7 \times -394) + (3 \times -286)] - [-3228]$
$= -3616 + 3228$

$\Delta H^\ominus = -388 \text{ kJ mol}^{-1}$

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TEST YOUR UNDERSTANDING

11 Write equations for the complete combustion of

a $C_3H_8(g)$ **b** $C_2H_5OH(l)$.

12 Calculate the enthalpy change for the following reaction, given the data in the table:

$C_4H_8(g) + H_2(g) \rightarrow C_4H_{10}(g)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
$C_4H_8(g)$	–2717
$C_4H_{10}(g)$	–2877
$H_2(g)$	–286

13 Given the data in the table, calculate the enthalpy change for the reaction:

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
$C_2H_6(g)$	–1561
$C_2H_2(g)$	–1301
$H_2(g)$	–286

14 Given the data in the table, calculate the enthalpy change for the reaction:

$3C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
$CH_3COCH_3(l)$	–1817
C(s)	–394
$H_2(g)$	–286

15 Given the data in the table, calculate the enthalpy change for the reaction:

$6C(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$

	$\Delta H_c^\ominus$ / kJ mol^{-1}
$C_6H_{12}O_6(s)$	–2803
C(s)	–394
$H_2(g)$	–286

13.4 Standard enthalpy change of formation

KEY POINT

Standard enthalpy change of formation ($\Delta H_f^\ominus$) is the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.

The equation representing the **standard enthalpy change of formation** of methane is

$C(s) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta H_f^\ominus = -74.6 \text{ kJ mol}^{-1}$

The carbon here is graphite, which is the most stable form of carbon.

The equation for the standard enthalpy change of formation of propanone is

$3C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$
$\Delta H_f^\ominus = -248.4 \text{ kJ mol}^{-1}$

KEY POINT

Standard state refers to the pure substance at 100 kPa and a specified temperature (assume 298.15 K unless another temperature is specified).

For an element, the **standard state** is the pure element in its normal physical state at 100 kPa (and 298.15 K), so, for nitrogen it is $N_2(g)$ and for iodine it is $I_2(s)$

KEY POINT

The standard enthalpy change of formation of any element in its standard state is zero.

This can be seen from the definition: no heat energy is taken in or given out when one mole of an element in its

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standard state is formed from one mole of the element in its standard state:

$Br_2(l) \rightarrow Br_2(l) \quad \Delta H_f^\ominus = 0$

KEY POINT

State symbols must always be included in equations for enthalpy changes.

This is because the enthalpy change will be different depending on the state of a substance. For example, the standard enthalpy change of formation of $Br_2(g)$ is not zero.

$Br_2(l) \rightarrow Br_2(g) \quad \Delta H_f^\ominus = +31 \text{ kJ mol}^{-1}$

KEY POINT

The definition of standard enthalpy change of formation refers to the formation of one mole of the substance *formed*.

For ammonia, the enthalpy change of formation is for the reaction:

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$

which shows the formation of *one mole* of ammonia

For H_2O the equation is:

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

KEY POINT

A standard enthalpy change of formation may be exothermic or endothermic.

This depends on the substance. For example, the standard enthalpy change of formation of $CH_4(g)$ is $-74.6 \text{ kJ mol}^{-1}$, but that of $C_2H_4(g)$ is $+52.4 \text{ kJ mol}^{-1}$.

Using standard enthalpy changes of formation

When we have been given enthalpy change of formation data, we can calculate the enthalpy change for a reaction using the equation:

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

WORKED EXAMPLE 13.7

Given these standard enthalpy change of formation values:

$\Delta H_f^\ominus [NH_3(g)] = -46 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus [NO(g)] = 90 \text{ kJ mol}^{-1}$

$\Delta H_f^\ominus [H_2O(g)] = -242 \text{ kJ mol}^{-1}$

calculate the enthalpy change for the reaction:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Answer

We have not been given the value for $\Delta H_f^\ominus$ for $O_2(g)$, but we know it is zero because it is an element in its standard state.

Using $\Delta H^\ominus = \Sigma \Delta H_f^\ominus \text{ (products)} - \Sigma \Delta H_f^\ominus \text{ (reactants)}$

$\Sigma \Delta H_f^\ominus \text{ (products)} = (4 \times 90) + (6 \times -242)$
$= -1092 \text{ kJ mol}^{-1}$

$\Sigma \Delta H_f^\ominus \text{ (reactants)} = 4 \times -46 + 5 \times 0 = -184 \text{ kJ mol}^{-1}$

$\Delta H^\ominus = -1092 - (-184) = -908 \text{ kJ mol}^{-1}$

So the enthalpy change for this reaction is -908 kJ mol^{-1}.

Determining an enthalpy change of formation from an enthalpy change of reaction

You may be given an enthalpy change of reaction and some enthalpy changes of formation and asked to work out a missing enthalpy change of formation.

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WORKED EXAMPLE 13.8

Given that the standard enthalpy change of formation of ethane [$C_2H_6(g)$] is –85 kJ mol^{-1} and this equation:

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g) \quad \Delta H^\ominus = -311$ kJ mol^{-1}

calculate the enthalpy change of formation of ethyne, $C_2H_2(g)$.

Answer

We have not been given the value for $\Delta H_f^\ominus$ for $H_2(g)$, but we know it is zero because it is an element in its standard state.

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

$-311 = -85 - (\Delta H_f^\ominus[C_2H_2(g)] + [2 \times 0])$

Rearranging the equation gives

$\Delta H_f^\ominus[C_2H_2(g)] = -85 + 311 = +226$ kJ mol^{-1}

KEY POINT

The method you use to solve enthalpy problems depends on the data you are given and not on what you have to find.

WORKED EXAMPLE 13.9

Given the following enthalpy change of combustion values, work out the enthalpy change of formation of ethanol, $C_2H_5OH(l)$:

	$\Delta H_c^\ominus$ / kJ mol^{-1}
C(s)	–394
$H_2(g)$	–286
$C_2H_5OH(l)$	–1367

Answer

The equation for the enthalpy of formation of ethanol is $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

We have looked above at examples involving both enthalpy change of combustion and enthalpy change of formation. This question mentions both, so which method do we use? The key thing is to look at the data you have been *given*, and base your method on that. Here, we have been given enthalpy of combustion data, and so, we will use the equation which contains this:

$\Delta H^\ominus = \Sigma\Delta H_c^\ominus(\text{reactants}) - \Sigma\Delta H_c^\ominus(\text{products})$

So: $\Delta H_f^\ominus = [(2 \times -394) + (3 \times -286)] - [-1367]$
$= -279$ kJ mol^{-1}

Remember: O_2 does not have an enthalpy change of combustion – you cannot burn oxygen in oxygen.

TEST YOUR UNDERSTANDING

16 Write equations for the enthalpy change of formation of the following:

a HF(g) **b** $CH_3Cl(g)$

c $H_2O(l)$ **d** $C_5H_{11}OH(l)$.

17 Calculate the enthalpy change for the following reaction, given the standard enthalpy changes of formation in the table:

$S_2Cl_2(l) + Cl_2(g) \rightarrow 2SCl_2(g)$

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$S_2Cl_2(l)$	–59.4
$SCl_2(g)$	–19.7

18 Calculate the enthalpy change for the following reaction, given the enthalpy changes of formation in the table:

$4BCl_3(l) + 3SF_4(g) \rightarrow 4BF_3(g) + 3SCl_2(g) + 3Cl_2(g)$

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$BCl_3(l)$	–427
$SCl_2(g)$	–19.7
$SF_4(g)$	–775
$BF_3(g)$	–1137

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CONTINUED

19 Use data in the table to answer the following questions:

	$\Delta H_f^\ominus$ / kJ mol^{-1}		$\Delta H_f^\ominus$ / kJ mol^{-1}
$SO_2(g)$	–297	$POCl_3(l)$	–597
$PCl_5(s)$	–444	$NH_3(g)$	–46
$SOCl_2(l)$	–246	$NH_4Cl(s)$	–314
$Cl_2O(g)$	80	$H_2O(g)$	–242

a Calculate the standard enthalpy change for

$SO_2(g) + PCl_5(s) \rightarrow SOCl_2(l) + POCl_3(l)$

b Calculate the standard enthalpy change for

$3Cl_2O(g) + 10NH_3(g) \rightarrow 2N_2(g) + 6NH_4Cl(s) + 3H_2O(g)$

c $PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$ $\Delta H = -124$ kJ mol^{-1}

Calculate the standard enthalpy change of formation of $PCl_3(l)$.

20 Calculate the enthalpy change of formation of $NO_2(g)$ from the following data:

$2Pb(NO_3)_2(s) \rightarrow 4NO_2(g) + 2PbO(s) + O_2(g)$
$\Delta H^\ominus = +602$ kJ mol^{-1}

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$Pb(NO_3)_2(s)$	–452
$PbO(s)$	–217

21 Calculate the standard enthalpy change of combustion of methanol using the standard enthalpies of formation, $\Delta H_f^\ominus$, in the table.

Compound	$CH_3OH(l)$	$CO_2(g)$	$H_2O(l)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	–239	–394	–286

22 Calculate the standard enthalpy change of formation of pentane using the standard enthalpies of combustion, $\Delta H_c^\ominus$, in the table.

Compound	$C_5H_{12}(l)$	$C(s)$	$H_2(g)$
$\Delta H_c^\ominus$ / kJ mol^{-1}	–3509	–394	–286

23 Calculate the standard enthalpy change for the process $H_2O(l) \rightarrow H_2O(g)$, given the following standard enthalpy changes:

$H_2O(g)$: $\Delta H_f^\ominus = -242$ kJ mol^{-1}

$H_2(g)$: $\Delta H_c^\ominus = -286$ kJ mol^{-1}

13.5 Energy cycles for ionic compounds

So far, the energy cycles we have drawn have been for covalent substances. In this section, we will consider an enthalpy level diagram for ionic substances. Before we look at this, we must consider some definitions.

KEY POINT

Standard enthalpy change of atomisation ($\Delta H_{at}^\ominus$) is the enthalpy change when one mole of gaseous atoms is formed from an element in its standard state under standard conditions.

$\Delta H_{at}^\ominus$ is always endothermic, for example:

$\frac{1}{2}H_2(g) \rightarrow H(g)$ $\Delta H_{at}^\ominus = +218$ kJ mol^{-1}

$Na(s) \rightarrow Na(g)$ $\Delta H_{at}^\ominus = +109$ kJ mol^{-1}

KEY POINT

The enthalpy of atomisation for $X_2(g)$ is half the bond enthalpy.

The values for the enthalpy changes of atomisation of hydrogen and chlorine are half the bond enthalpy values given in Table 13.1 in Section 13.1. The *bond* enthalpy for Cl_2 refers to breaking one mole of covalent bonds, which produces two moles of gaseous atoms whereas the enthalpy change of *atomi*sation for Cl_2 refers to breaking half a mole of covalent bonds to produce *one mole* of gaseous *atoms*.

$Cl_2(g) \rightarrow 2Cl(g)$ bond enthalpy = 242 kJ mol^{-1}

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\Delta H_{at}^\ominus = +121$ kJ mol^{-1}

The bond enthalpy for Cl_2 refers to breaking one mole of covalent bonds, which produces two moles of gaseous atoms whereas the enthalpy change of atomisation for

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Cl_2 refers to breaking half a mole of covalent bonds to produce. It is important to remember this, as there is a good chance that you will not be given a value for the enthalpy change of atomisation of, e.g., chlorine or oxygen in the exam, and you will be expected to use bond enthalpy values to deduce it.

KEY POINT

The first ionisation energy is the enthalpy change when one electron is removed from each atom in one mole of gaseous atoms under standard conditions:

$M(g) \rightarrow M^+(g) + e^-$

All ionisation energies are endothermic.

The second ionisation energy is the enthalpy change for the process: $M^+(g) \rightarrow M^{2+}(g) + e^-$

KEY POINT

The first electron affinity is the enthalpy change when one electron is added to each atom in one mole of gaseous atoms under standard conditions:

$X(g) + e^- \rightarrow X^-(g)$

The first electron affinity is exothermic for virtually all elements; it is a favourable process to bring an electron from infinity to where it feels the attractive force of the nucleus in an atom.

The second electron affinity is the enthalpy change for the process:

$X^-(g) + e^- \rightarrow X^{2-}(g)$

The second electron affinity is always endothermic. It is an unfavourable process to add an electron to an ion that is already negatively charged, due to repulsion between the negative charges.

KEY POINT

Standard lattice enthalpy ($\Delta H^{\ominus}_{latt}$) (usually just called *lattice enthalpy*) is the enthalpy change when one mole of an ionic compound is broken apart into its constituent gaseous ions under standard conditions.

For example, for NaCl:

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H^{\ominus}_{latt} = +771 \text{ kJ mol}^{-1}$

It is important to remember that the lattice enthalpy refers to the substance being broken apart into its constituent ions, not into the simplest possible ions, so ammonium nitrate would be broken apart into ammonium and nitrate ions:

$NH_4NO_3(s) \rightarrow NH_4^+(g) + NO_3^-(g)$

Look carefully to determine whether lattice enthalpy is exothermic or endothermic, as it can be defined in either direction, i.e., as the making or breaking of the lattice. Here, it is defined as the breaking of the lattice and is an endothermic process because energy must be supplied to separate the ions against the attractive forces holding them in the lattice.

EXAM TIP

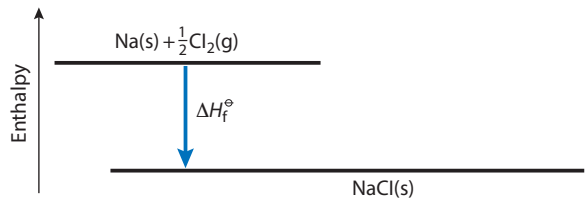
State symbols are essential in all these equations defining the various enthalpy terms.

Born–Haber cycles

A **Born–Haber cycle** is an enthalpy level diagram breaking down the formation of an ionic compound into a series of simpler steps. For example, for sodium chloride, let's look at the stages in the construction of the cycle. The first step we put in is the equation for the enthalpy change of formation:

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

The enthalpy change of formation for NaCl(s) is exothermic and the (blue) arrow, representing this process is shown in the downward, negative, direction.



The aim now is to construct a cycle that gives us an alternative route between the elements, $Na(s) + \frac{1}{2}Cl_2(g)$, and the ionic compound NaCl(s).

NaCl(s) can be broken apart into its constituent gaseous ions, this is the lattice enthalpy: $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

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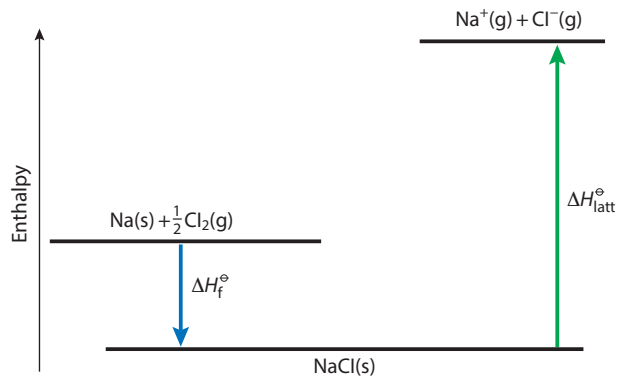
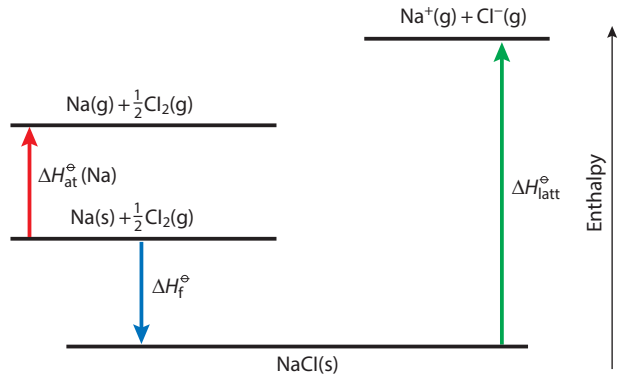
We put this in the cycle using an upwards arrow, indicating that $\Delta H^{\ominus}_{latt}$ is an endothermic process:



Now that the lattice enthalpy is in the cycle, we can see more clearly what we are aiming for. So, to complete the cycle, Na(s) and $\frac{1}{2}Cl_2(g)$ must be converted into gaseous ions.

Let's start with sodium: $Na(s) \rightarrow Na(g)$

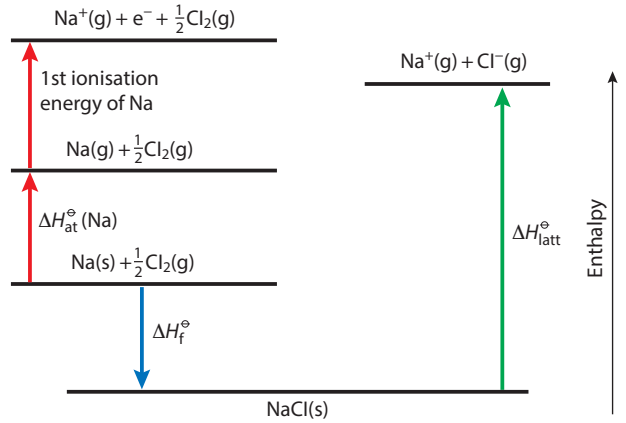
This is the enthalpy change of atomisation for sodium. The process is endothermic, and so, the red arrow goes upwards on the cycle:



The next step involves the first ionisation energy of sodium:

$Na(g) \rightarrow Na^+(g) + e^-$

This process is also endothermic:



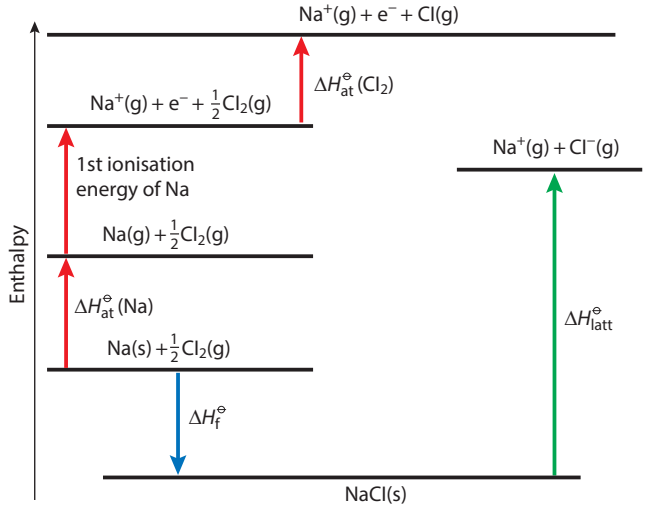
Sodium must be converted into gaseous atoms before it can be ionised because the definition of ionisation energy involves removal of an electron from a *gaseous* atom.

Sodium has been converted into the required species, $Na^+(g)$, and now we must do the same with the chlorine.

The next step is the atomisation of chlorine:

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

This is another endothermic process:



There is no scientific reason why we converted sodium into its gaseous ion before atomising chlorine, but it is probably easier to deal with all the steps with one of the elements first and then with other one.

The cycle is then completed by adding the electron removed from the sodium atom to the chlorine atom:

$Cl(g) + e^- \rightarrow Cl^-(g)$

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This process is the first electron affinity of chlorine and is exothermic, so the arrow goes downwards:

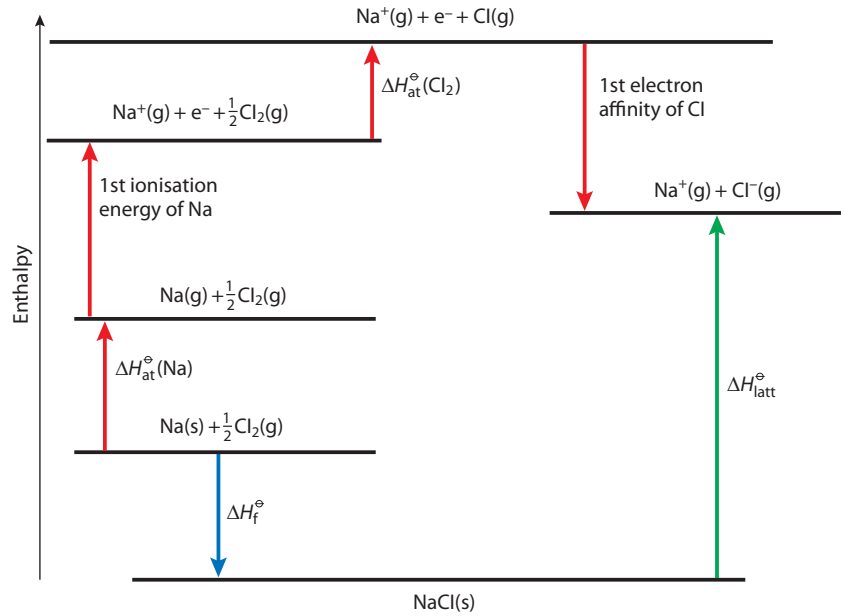

Figure 13.7:

This is now the complete Born–Haber cycle for the formation of NaCl(s).

Working out values from a Born–Haber cycle

If all the quantities in the cycle except one are known, then application of Hess's law allows the missing quantity to be worked out. For example, let us calculate the lattice enthalpy of sodium chloride using data in Table 13.4.

$\Delta H^{\ominus}_{at}$ [Na(s)]	109 kJ mol^{-1}
Cl—Cl bond enthalpy	242 kJ mol^{-1}
first ionisation energy (Na)	494 kJ mol^{-1}
first electron affinity (Cl)	–364 kJ mol^{-1}
$\Delta H^{\ominus}_{f}$[NaCl(s)]	–411 kJ mol^{-1}

Table 13.4: Data for the calculation of the lattice enthalpy of sodium chloride.

We must, first of all, realise that we have been given the Cl—Cl bond enthalpy, but we require the enthalpy change of atomisation of chlorine. This is calculated by halving the bond enthalpy, so $\Delta H^{\ominus}_{at}[Cl_2(g)] = 121$ kJ mol^{-1}.

The values can be put into the Born–Haber cycle (Figure 13.8) and Hess's law used to calculate the missing lattice energy.

The enthalpy change that we are trying to find is that for the lattice enthalpy, so we have two arrows, the direct and the indirect route, between the level of NaCl(s) and that of $Na^+(g) + Cl^-(g)$. The enthalpy change for the direct route is the same as that for the indirect route. The arrow for the indirect route goes in the same direction as all the red arrows, but in the opposite direction to the blue arrow, so the sign of the enthalpy change on the blue arrow must be changed:

$\Delta H^{\ominus}_{latt} = 411 + 109 + 494 + 121 - 364$

$\Delta H^{\ominus}_{latt} = 771$ kJ mol^{-1}

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A Born–Haber cycle for magnesium oxide is shown in Figure 13.9. We will use this cycle and the values in Table 13.5 to work out the second electron affinity of oxygen.

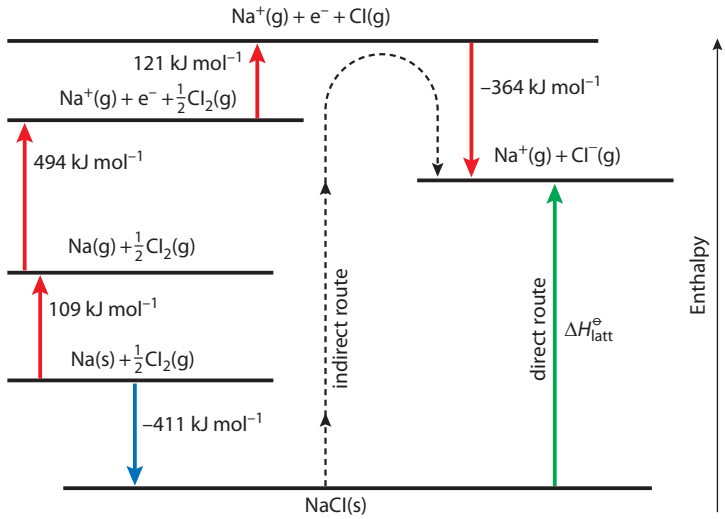

Figure 13.8: Working out the lattice energy for sodium chloride.

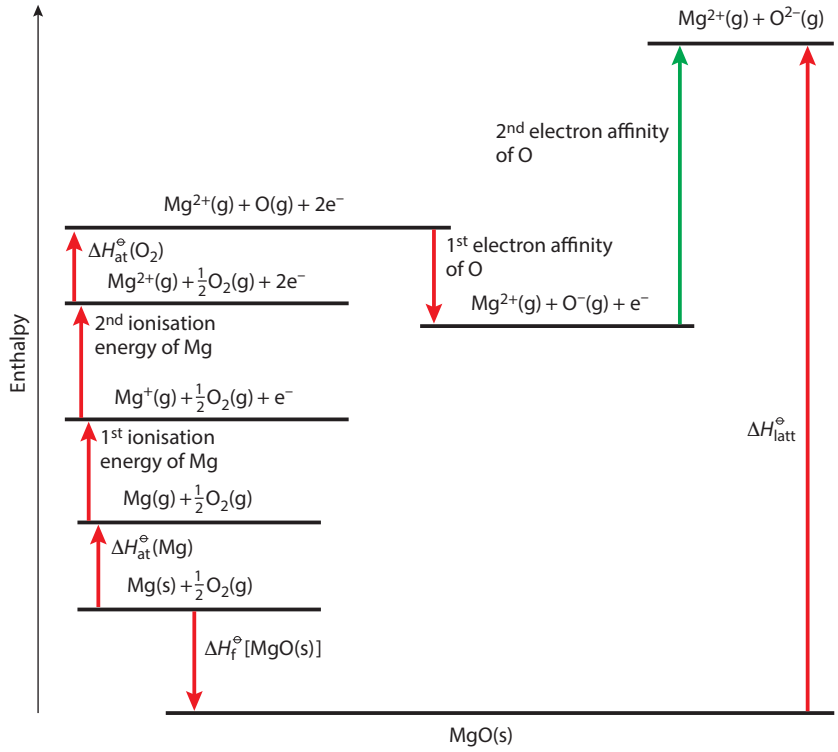

Figure 13.9: Born–Haber cycle for magnesium oxide.

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Enthalpy term	Enthalpy change / kJ mol^{-1}
$\Delta H^{\ominus}_{at}$ [Mg(s)]	150
O=O bond enthalpy	498
first ionisation energy (Mg)	736
second ionisation energy (Mg)	1450
first electron affinity (O)	–142
$\Delta H^{\ominus}_{f}$ [MgO(s)]	–602
$\Delta H^{\ominus}_{latt}$ (MgO)	3889

Table 13.5

This Born–Haber cycle looks a little different to the one for sodium chloride because magnesium and oxygen form 2+ and 2– ions, respectively. We have thus had to include the second ionisation of magnesium and the second electron affinity of oxygen, that is, the enthalpy changes for the processes:

$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$

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

Both of these processes are endothermic, and so, represented by upwards arrows on the diagram.

The principle for constructing the cycle is, however, the same as we looked at for sodium chloride, and the steps are followed through in the same order.

Again, we have to work out the enthalpy of atomisation for $O_2(g)$ by dividing the bond enthalpy by 2 to get a value of 249 kJ mol^{-1}.

The second electron affinity of O, the quantity we have to find, is shown by the green arrow on the cycle. It can be worked out most easily by applying Hess's law and looking at the enthalpy change for the direct route and the indirect route (Figure 13.10).

The start and the end of the indirect route are marked. The signs of the enthalpy changes highlighted in blue in Figure 13.10 are reversed, as the direction of the indirect route is in the opposite direction to the arrows on the diagram.

The enthalpy change for the direct route is the same as that for the indirect route:

$\Delta H^{\ominus} = 142 - 249 - 1450 - 736 - 150 - 602 + 3889$
$= 844$ kJ mol^{-1}

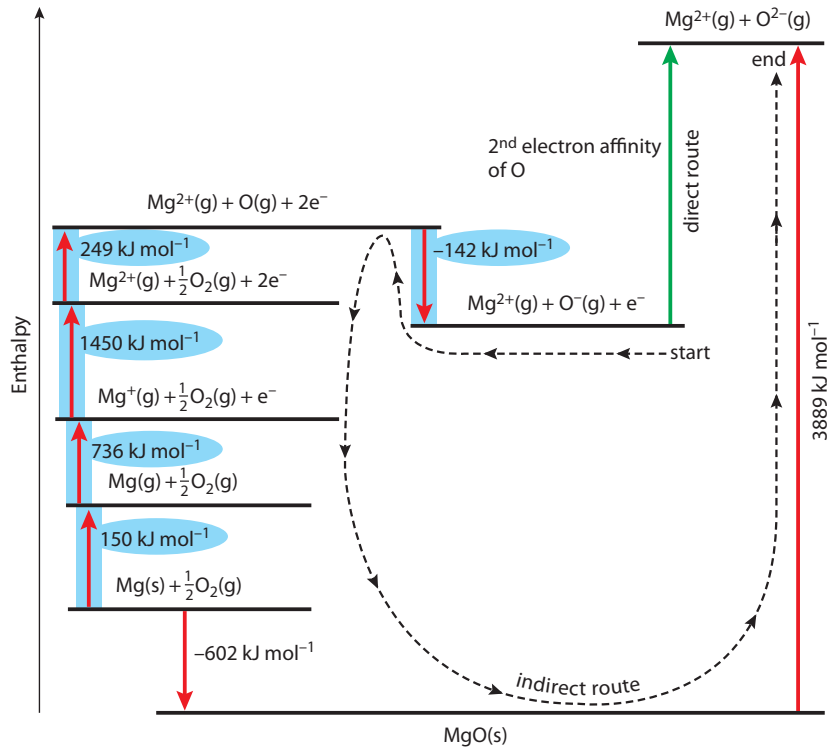

Figure 13.10: Working out the second electron affinity for gaseous oxygen atoms using a Born–Haber cycle.

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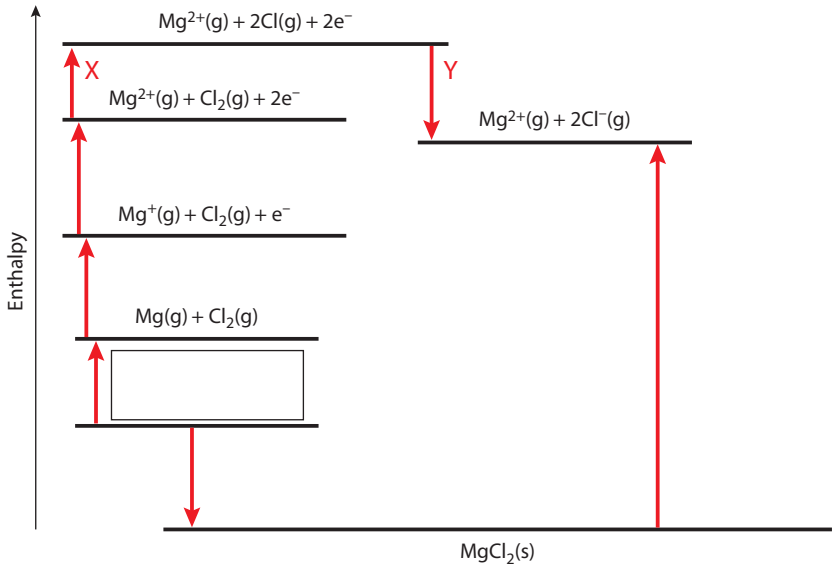
WORKED EXAMPLE 13.10

Part of a Born–Haber cycle for the formation of magnesium chloride is shown below.



a Fill in the missing species in the cycle.

b Use the table of data to deduce values for the enthalpy changes marked X and Y and, hence, determine the lattice enthalpy of magnesium chloride:

Enthalpy term	Enthalpy change / kJ mol^{-1}
$\Delta H^{\ominus}_{at}$[Mg(s)]	150
Cl—Cl bond enthalpy	242
first ionisation energy (Mg)	736
second ionisation energy (Mg)	1450
first electron affinity (Cl)	–364
$\Delta H^{\ominus}_{f}$[$MgCl_2$(s)]	–641

Answer

a The species missing are Mg(s) and Cl_2(g). Both of the previous examples involved $\frac{1}{2}X_2$(g), so it is important to realise that we require Cl_2 here and not $\frac{1}{2}Cl_2$ because the formula of magnesium chloride is $MgCl_2$.

b X represents the process: $Cl_2(g) \rightarrow 2Cl(g)$

This shows the breaking of one mole of covalent bonds and is, therefore, equal to the Cl—Cl bond enthalpy.

[It is also equivalent to $2 \times \Delta H^{\ominus}_{at}$ for Cl_2 since 2 mol gaseous atoms are formed.]

The value for this enthalpy change, from the table, is +242 kJ mol^{-1}.

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CONTINUED

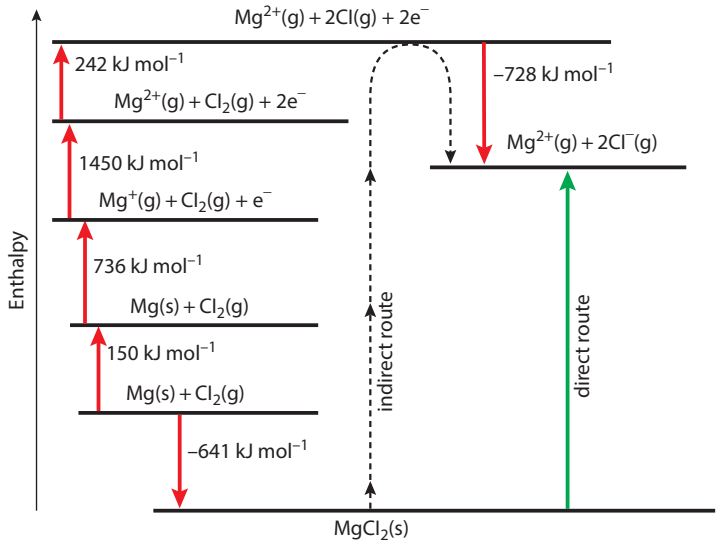
Y represents the process: $2Cl(g) + 2e^- \rightarrow 2Cl^-(g)$

The equation for the first electron affinity of Cl is $Cl(g) + e^- \rightarrow Cl^-(g)$

So, Y represents twice the first electron affinity and the value of the enthalpy change is:

$2 \times -364 = -728$ kJ mol^{-1}

The lattice enthalpy is shown by the green arrow, and this can be calculated from the enthalpy changes on the indirect route:



$\Delta H^{\ominus}_{latt} = -(-641) + 150 + 736 + 1450 + 242 - 728 = 2491$ kJ mol^{-1}

Link

We met lattice enthalpies in Chapter 6. Why is the lattice enthalpy of magnesium chloride higher than than of sodium chloride, but lower than that of magnesium oxide?

INTERNATIONAL MINDEDNESS

The Born–Haber cycle was developed by two Nobel Prize winning German scientists: Fritz Haber (1868–1934) and Max Born (1882–1970). Max Born won the Nobel Prize for Physics in 1954, but in his lifetime he would not have achieved the same level of fame that his granddaughter did; she was Olivia Newton-John, star of the 1978 film 'Grease'.
How many famous scientists working now can you name, any? What about Nobel-Prize-winning scientists of the last 50 years? Why do Nobel-Prize-winning scientists not become as well known as footballers and popstars?

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TEST YOUR UNDERSTANDING

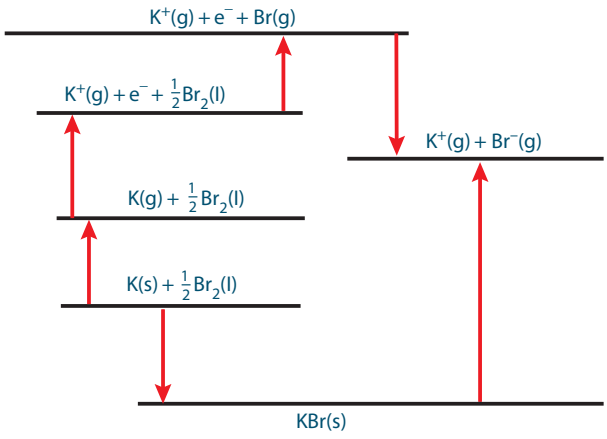
24 Write equations for the following:

- **a** the first ionisation energy of calcium
- **b** the lattice enthalpy of magnesium oxide (MgO)
- **c** the second electron affinity of nitrogen atoms
- **d** the bond enthalpy of bromine
- **e** the enthalpy of atomisation of iodine (I_2(s))
- **f** the second ionisation energy of aluminium.

25 State whether the following enthalpy changes are *always exothermic*, *always endothermic* or *sometimes exothermic and sometimes endothermic*:

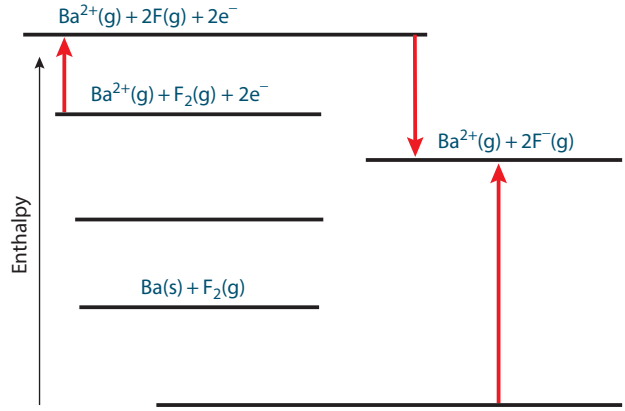
- **a** first ionisation energy
- **b** second ionisation energy
- **c** enthalpy change of atomisation
- **d** enthalpy change of formation
- **e** first electron affinity
- **f** second electron affinity.

26 Use the Born–Haber cycle and data in the table to calculate the first electron affinity of Br.



	/ kJ mol^{-1}
$\Delta H^{\ominus}_{at}$ [K(s)]	90
$\Delta H^{\ominus}_{at}$ [Br_2(l)]	112
first ionisation energy (K)	418
$\Delta H^{\ominus}_{latt}$ (KBr)	670
$\Delta H^{\ominus}_{f}$[KBr(s)]	–394

27 Complete the Born–Haber cycle and use the data in the table to calculate the lattice enthalpy of BaF_2.



	/ kJ mol^{-1}
$\Delta H^{\ominus}_{at}$ [Ba(s)]	178
F—F bond enthalpy	159
first ionisation energy (Ba)	503
second ionisation energy (Ba)	965
first electron affinity (F)	–328
$\Delta H^{\ominus}_{f}$[BaF_2(s)]	–1207

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the term average bond enthalpy	13.1			
calculate enthalpy changes using bond enthalpies	13.1			
use Hess's law to calculate enthalpy changes	13.2			
calculate enthalpy changes using standard enthalpy changes of combustion	13.3			
explain the term standard enthalpy change of formation	13.4			
calculate enthalpy changes using standard enthalpy changes of formation	13.4			
use a Born–Haber cycle to calculate enthalpy changes for ionic compounds.	13.5			

REFLECTION

- What were the most difficult parts of this topic?
- How confident do you feel with the calculations, would more practice help?
- Has this topic identified any other parts of the course that you need to look at again? Try to explain to another student how to use Hess's law to work out enthalpy changes.

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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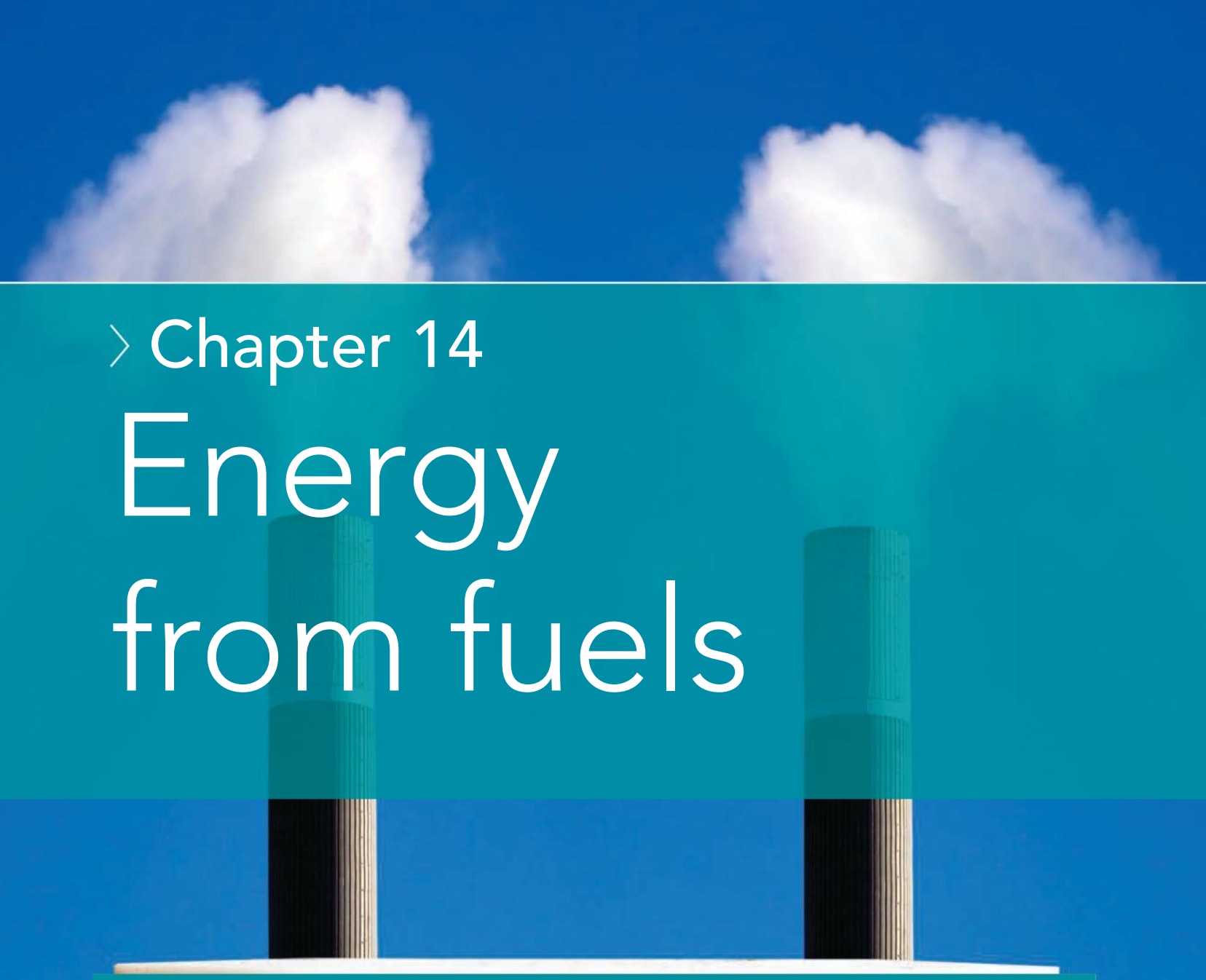

Chapter 14

Energy from fuels

LEARNING OBJECTIVES

In this chapter you will:

- understand that reactive metals, non-metals and organic compounds undergo combustion reactions
- deduce equations for incomplete combustion of organic compounds
- discuss the advantages and disadvantages of fossil fuels
- calculate how much carbon dioxide is formed when fossil fuels burn
- understand what biofuels are
- explain the difference between renewable and non-renewable energy sources
- explain how fuel cells work
- deduce half-equations for the reactions occurring in fuel cells.

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GUIDING QUESTIONS

- What are combustion reactions?
- What are the advantages and disadvantages of different fuels?
- What are fuel cells?

Introduction

Mowgli thrust his dead branch into the fire till the twigs lit and crackled, and whirled it above his head among the cowering wolves.

"Thou art the master," said Bagheera in an undertone'

In Rudyard Kipling's 'The Jungle Book', fire was the thing that was perceived as setting humans apart from the animals – their mastery of a chemical reaction! Fire is a theme, or appears in the titles, of countless books, films, songs and poems; it was one of the four ancient elements – fire, earth, air, water and was often something that was associated with gods – there are fire gods in most ancient mythologies and also many stories about how humans came to acquire fire, as a gift, or, very often, stolen, from the gods.

14.1 Combustion reactions

Combustion is another word for burning. A combustion reaction is an exothermic reaction that occurs when a substance reacts with oxygen. The substances usually have to be heated, or a spark, or other source of ignition, is required, but there are some substances, e.g., phosphorus, that burst into flames when simply exposed to oxygen.

KEY POINT

Reactive metals, non-metals, organic and inorganic compounds can all undergo combustion reactions.

Examples of combustion reactions are

magnesium: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

phosphorus: $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

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

hydrazine: $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$

Not all reactions with oxygen are combustion reactions, and we usually reserve the term for reactions that produce a flame/carry on spontaneously when the source of ignition/heat is removed. So, for instance, copper will react when heated strongly with oxygen to form copper(I) oxide and copper(II) oxide. The equation for the formation of copper(II) oxide is

$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

This reaction would not, however, usually be regarded as a combustion reaction because there is no flame and the reaction will stop when the source of heat is removed.

Not all substances react directly with oxygen – elements that do not react directly with oxygen include extremely unreactive metals, such as platinum and gold, and the noble gases, such as helium, neon and argon. There are also some normally very reactive substances that do not react *directly* with oxygen, for example, chlorine. Many inorganic compounds also do not react with oxygen, e.g., sodium chloride.

Link

It is an interesting question as to whether nitrogen undergoes combustion. Nitrogen does combine with oxygen at very high temperatures:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$

This reaction can occur at the very high temperatures produced when other substances burn in air, for example, in an internal combustion engine, but due to the very high N≡N bond enthalpy, this is an endothermic reaction. This reaction is very important because NO contributes to the destruction of stratospheric ozone (the ozone layer) and is oxidised in the atmosphere to NO_2 and HNO_3, which cause acid rain.

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KEY POINTS

Combustion reactions are redox reactions.

A redox reaction is one that involves both oxidation and reduction.

Oxidation and reduction may be defined in many ways (Table 14.1):

Oxidation	Reduction
gain of oxygen (O)	loss of oxygen (O)
loss of hydrogen (H)	gain of hydrogen (H)
increase in oxidation state	decrease in oxidation state
loss of electrons	gain of electrons

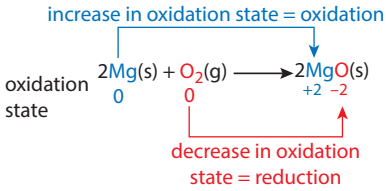
Table 14.1

If we look at the combustion reactions on the previous page in terms of the loss/gain of oxygen, we can see that, in the first three reactions, the substance undergoing combustion is being oxidised, because, in each case, it gains oxygen, e.g., Mg forms MgO and P_4 forms P_4O_{10}. In the third equation, both C and H from CH_4 gain oxygen, so, again, we can say that the methane is oxidised.

The fourth equation is a little different – H from N_2H_4 (hydrazine) gains oxygen, but N does not, it just forms N_2. However, we can also see that N_2H_4 loses hydrogen to form N_2 and loss of hydrogen is oxidation. So, again, we can say that hydrazine is oxidised in this reaction.

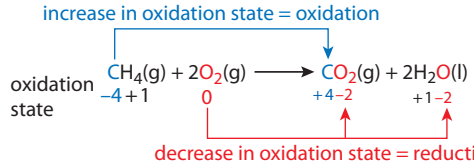
The reactions discussed here are all redox reactions and should, therefore, involve reduction as well as oxidation; however, just by looking at the loss/gain of oxygen/hydrogen, it is not immediately obvious what has been reduced in these equations. This becomes clearer if we look at the reactions in terms of oxidation states.

Oxidation states were discussed in Chapter 10. If we work out the oxidation states in the first equation on the previous page, we get:



So, Mg is oxidised (oxidation state increases from 0 to +2) and O_2 is reduced (oxidation state decreases from 0 to –2).

If we look at the third equation,



it can be seen that only the carbon in CH_4 has a change in oxidation state, but we would still say that CH_4 is oxidised, rather than saying that carbon in CH_4 is oxidised. Again, O_2 is reduced. We can classify the fourth equation in the same way – N_2H_4 is oxidised (the oxidation state of N increases from –2 to 0) and O_2 is reduced.

We can, therefore, say, in general:

KEY POINT

The substance that reacts with oxygen in a combustion reaction gets oxidised and oxygen in a combustion reaction gets reduced.

Oxidising and reducing agents

KEY POINTS

Oxidising agents (oxidants) oxidise other species and, in the process, are themselves reduced.

Reducing agents (reductants) reduce other species and, in the process, are themselves oxidised.

In each of the reactions above, oxygen gets reduced as it oxidises the substance undergoing combustion.

KEY POINT

Oxygen is the oxidising agent in combustion reactions.

The substance undergoing combustion gets oxidised; therefore, it must be the reducing agent – it reduces the oxygen. This is the case in all combustion reactions.

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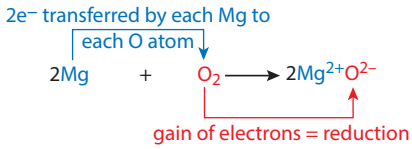
Redox reactions involve transfer of electrons

The most fundamental definitions of oxidation and reduction are as follows:

- oxidation is loss of electrons
- reduction is gain of electrons.

How the distribution of electrons changes in redox reactions can be most easily understood by looking again at the combustion of magnesium.

Magnesium oxide is an ionic compound consisting of Mg^{2+} and O^{2-} ions. We can, therefore, re-write the equation as:



Each O atom takes two electrons away from a Mg atom. Loss of electrons is oxidation, and so, oxygen is oxidising Mg by taking electrons away from it, making oxygen the oxidising agent. In the process, the oxygen has gained electrons, so it has been reduced.

We can also look at this from the point of view of the Mg atoms. Each Mg atom donates two electrons to an O atom. Gain of electrons is reduction, so Mg is reducing oxygen by donating electrons to it, and Mg is, therefore, the reducing agent. Because Mg has lost electrons (by donating them to oxygen), it has been oxidised. We will return to this idea in Chapter 20.

Combustion of organic compounds

Complete combustion

This occurs when there is a plentiful supply of oxygen. The products of the reaction are carbon dioxide and water.

Examples of equations for complete combustion are

ethane: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

ethene: $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Complete combustion produces a cleaner (blue) flame and releases more energy per mole of substance than incomplete combustion.

Balancing equations

All chemical equations must be balanced – there must be the same number of atoms of each type on both sides. The easiest way to balance the combustion reactions of hydrocarbons is as follows:

1. balance the carbons – look at the number of C atoms in your organic compound and put this number in front of CO_2 on the right-hand side
2. balance the hydrogens – look at the number of H atoms in your organic compound, divide the number by two and put this number in front of H_2O on the right-hand side
3. balance the oxygens – add up the total number of oxygen atoms on the right-hand side of the equation, divide the total by two and put this number in front of O_2 on the left-hand side
4. get rid of any halves – if the number in front of O_2 involves a half, then multiply all the coefficients in the equation by two.

TEST YOUR UNDERSTANDING

1 Which substance gets oxidised in each of these reactions?

   a $S(s) + O_2(g) \rightarrow SO_2(g)$

   b $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

   c $2(CH_3)_2CO(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

2 In the following equations, identify the substance that gets oxidised, the substance that gets reduced, the oxidising agent and the reducing agent:

   a $C(s) + O_2(g) \rightarrow CO_2(g)$

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

   c $2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g)$

   d $2Mg(s) + 2NO(g) \rightarrow 2MgO(s) + N_2(g)$

   e $Ca(s) + H_2O(l) \rightarrow CaO(s) + H_2(g)$.

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EXAM TIP

Although it is generally best practice to balance equations using only integers, step 4 is not strictly necessary and equations involving non-integral numbers would generally be accepted.

WORKED EXAMPLE 14.1

Write an equation for the complete combustion of hexane, $C_6H_{14}(l)$.

Answer

Since this is complete combustion, the reaction with oxygen will produce carbon dioxide and water:

$C_6H_{14}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$

There are 6 C atoms in hexane, and so, we write 6 in front of CO_2:

$C_6H_{14}(l) + O_2(g) \rightarrow 6CO_2(g) + H_2O(l)$

There are 14 H atoms in hexane, we divide this by 2 to get 7 – this is the coefficient of H_2O:

$C_6H_{14}(l) + O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$

The total number of O atoms on the right-hand side is $6 \times 2 + 7 \times 1 = 19$

$19 \div 2 = 9\frac{1}{2}$, so the coefficient of O_2 is $9\frac{1}{2}$:

$C_6H_{14}(l) + 9\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$

Everything is now multiplied by 2 to get rid of the half:

$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(l)$

As a final check, you can make sure that there is the same number of each type of atom on each side – in this case, we have the following:

Left-hand side	Right-hand side
$2 \times 6 = 12$ C	$12 \times 1 = 12$ C
$2 \times 14 = 28$ H	$14 \times 2 = 28$ H
$19 \times 2 = 38$ O	$12 \times 2 + 14 \times 1 = 38$ O

When balancing equations for combustion of alcohols, the procedure must be modified slightly because there is also O in the alcohol – you need to subtract the number of oxygens in the alcohol from your total for O atoms on the right-hand side before dividing it by two. See Chapter 16 for further guidance on balancing equations.

Incomplete combustion

Incomplete combustion occurs when there is a limited supply of oxygen. The products of incomplete combustion are water, carbon monoxide (CO) and soot (C). If we compare the equations for complete and incomplete combustion of ethane, we can see the effect of limiting the oxygen supply.

complete combustion:
$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

incomplete combustion producing CO:
$2C_2H_6(g) + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(l)$

incomplete combustion producing C:
$2C_2H_6(g) + 3O_2(g) \rightarrow 4C(s) + 6H_2O(l)$

In reality, all of these processes occur at the same time in a flame, but we write separate equations for each. The presence of soot in the flame due to incomplete combustion makes the flame yellow/orange. Soot will also be seen as a black deposit if an object is placed above a flame where incomplete combustion is occurring. Incomplete combustion releases less energy per mole of fuel than complete combustion.

Equations for complete and incomplete combustion of ethanol are shown below.

complete combustion:
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

incomplete combustion producing CO:
$C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(l)$

incomplete combustion producing C:
$C_2H_5OH(l) + O_2(g) \rightarrow 2C(s) + 3H_2O(l)$

Ethanol normally burns with a clear blue flame, and so, complete combustion is the dominant process.

TEST YOUR UNDERSTANDING

3 Write equations, including state symbols, for the complete combustion of the following:

a $C_2H_4(g)$ **b** $C_5H_{12}(l)$

c $C_8H_{18}(l)$ **d** $CH_3OH(l)$

e $CH_3CH_2CH_2CH_2OH(l)$.

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CONTINUED

4 Write equations, including state symbols, for the following reactions:

a incomplete combustion of ethene [$C_2H_4(g)$] producing carbon monoxide

b incomplete combustion of ethyne [$C_2H_2(g)$] producing carbon

c incomplete combustion of hexane [$C_6H_{14}(l)$] producing carbon monoxide

d incomplete combustion of propanol [$C_3H_7OH(l)$] producing carbon monoxide

e incomplete combustion of pentanol [$C_5H_{11}OH(l)$] producing carbon.

14.2 Fuels

EXAM TIP

A fuel is something that is burnt to produce energy.

Examples of **fuels** include coal, wood, ethanol.

The word fuel is, however, often used a bit more generally than defined here, for example, uranium is usually referred to as a *nuclear fuel* – no combustion is, however, involved in a nuclear reactor – the energy is released when uranium nuclei break apart (fission) to produce smaller nuclei. Food is also talked about as a fuel and, although it is oxidised to release energy in the body, you would have noticed if the reaction involved burning!

Fossil fuels

The three main **fossil fuels** are coal, oil and natural gas. They are called fossil fuels because they were formed from things that were once alive and have been buried underground for millions of years.

Coal is formed from the remains of plants and trees that fell into swamps millions of years ago. Coal is mostly carbon. Crude oil (petroleum) was formed from marine organisms (plankton) that died and sank to the bottom of the sea. Crude oil is a complex mixture of hydrocarbons. Crude oil must be separated into fractions (narrower mixtures) before it can be used. This process is called refining.

Natural gas is formed in basically the same way as crude oil and is often found with it. Natural gas consists mostly of methane. Other light hydrocarbons may also be present.

All fossil fuels have the following positive characteristics:

- they are concentrated forms of energy (compared to **renewable energy sources**), and so, release a lot of energy when they are burnt
- they are reasonably cheap to extract/produce.

All fossil fuels have the following negative characteristics:

- they produce greenhouse gases when burnt, which contribute to climate change
- they are **non-renewable sources** – they will run out in the near future and cannot be replaced.

Advantages and disadvantages of different fossil fuels

Table 14.2 gives details of some advantages and disadvantages of the three main fossil fuels.

INTERNATIONAL MINDEDNESS

Coal can be converted into liquid and gaseous fuels. The processes to do this require energy and money, so why would countries do this? South Africa and Germany have both converted coal to liquid fuels in the last hundred years – to what extent do political factors affect the use of chemical technology?

NATURE OF SCIENCE

The problem of dwindling fossil fuel resources is one that transcends any particular science – scientists and technologists from many different disciplines will have to work together to try to solve some of the problems that we will be facing very soon. The problems are, however, not just scientific, and scientists will also have to collaborate with politicians, economists, environmental agencies, etc. to plan for a world without fossil fuels.

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Fuel	Advantages	Disadvantages
coal	supplies should last hundreds of years; supplies distributed throughout the world; can be converted into synthetic gaseous and liquid fuels	not as easily transported as oil or gas; mining is a dirty (slag heaps) and dangerous process; dirty fuel – lots of incomplete combustion; pollutants include particulates (soot) and sulfur dioxide (acid rain)
oil	easily transported in pipelines or by tankers; convenient fuel for transport – can be easily stored and used in vehicles; source of variety of chemicals for the petrochemical industry	very limited lifespan – supplies could run out in decades; can produce sulfur dioxide (acid rain) when burned; environmental problems associated with extraction and transportation in tankers; only a few countries have reserves
natural gas	a clean fuel – undergoes more complete combustion; produces very few particulates/soot (C) or gases that contribute to acid rain when it burns; easily transported in pipelines and tankers; can be transported easily into homes, through pipelines, for heating and cooking; releases a higher quantity of energy per kg than coal or oil; produces less CO_2 per kJ of energy released than coal or oil	limited lifespan – may be less than 100 years; only certain countries have reserves; methane is a powerful greenhouse gas and leaks during production and transportation of natural gas contribute to climate change; these leaks could offset any advantages due to it producing less CO_2 per kJ or kg; risk of explosions due to leaks; more difficult to store than coal and oil because it is a gas – must be stored under pressure or cooled to liquefy it;

Table 14.2: Advantages and disadvantages of fossil fuels. It is very difficult to estimate reserves of coal, oil and gas and how long they will last. Factors such as undiscovered reserves, how usage will change and new technologies all have to be considered.

Link

A desirable characteristic of a fuel is that it should release energy at a reasonable rate (not too fast or too slow). If a fuel reacts too quickly (explodes), it can be difficult to harness the energy. The rate of a chemical reaction depends, amongst other things, on the activation energy (see Chapter 17), and, if the activation energy for a combustion reaction is very low, the fuel could react upon exposure to air at room temperature (without the requirement for ignition from an external source) and be very difficult to handle.

Incomplete combustion and clean burning fuels

Soot (carbon) is produced when fuels undergo incomplete combustion. Soot belongs to a wider class of pollutants known as particulates (or particulate matter, Figure 14.1); these can be harmful to health (aggravating heart and lung conditions) and the environment (e.g. global warming).

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Figure 14.1: Diesel vehicles can produce large amounts of particulate matter.

KEY POINT

Incomplete combustion releases less energy than complete combustion as well as producing carbon monoxide, which is toxic, and particulates.

Of the fuels here, natural gas is the cleanest burning fuel – when used to generate electricity, it undergoes the least incomplete combustion and, therefore, produces the least (very little) particulate matter. Coal is the dirtiest fuel – it undergoes the most incomplete combustion and it produces the largest amounts of particulates when it is burnt.

Combustion is a complex process, and how much incomplete combustion occurs will be influenced by many factors, which include the following:

- availability of oxygen (less oxygen means more incomplete combustion)
- physical state of the fuel (gaseous fuels mix more easily with oxygen)
- how easy it is to vaporise the fuel (fuels containing shorter-chain molecules will vaporise more easily and mix better with available oxygen)
- chemical make-up of the fuel [aromatic (based on benzene) hydrocarbons with a higher C : H ratio will undergo more incomplete combustion].

Link

What is the effect of carbon chain length on incomplete combustion?

Let's compare two fuels,

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

hexane: $C_6H_{14}(l) + 9.5O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$.

Two moles of oxygen gas, which, at around room temperature and pressure, occupies about 50 dm^3, is required to burn one mole of methane. The air contains about 20% oxygen, and so, the volume of air required to burn 1 mol methane is about 250 dm^3. The corresponding volume of air for hexane will be about 1200 dm^3. So, it could be argued that hexane is more likely to undergo incomplete combustion because much more air is required to completely burn one mole, and this volume of air is less likely to be available. However, if we work out, using the approximate values, the volume of air required per gram of each fuel, we find that methane requires about 16 dm^3 of air to burn 1 g completely, but hexane only requires about 14 dm^3. Of course, how much incomplete combustion we get will depend on the conditions under which each fuel is burnt, and it will make a big difference that hexane is a liquid at room temperature, but methane is a gas.

Comparing fuels

Energy released per gram

When fuels are burned, energy is released in the form of heat (chemical energy is converted into thermal energy). Different fuels may be compared by looking at the energy released per gram of fuel burnt. We sometimes use the term **specific energy** for the energy released per gram of fuel burnt.

KEY POINT

Energy released per gram (specific energy)

$$= \frac{\text{energy released from fuel}}{\text{mass of fuel consumed}}$$

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We can calculate the energy released per gram of fuel burnt from its enthalpy change of combustion. The enthalpy change of combustion is the enthalpy change when one mole of substance undergoes complete combustion.

WORKED EXAMPLE 14.2

The enthalpy change of combustion of methane is –891 kJ mol^{-1}. Calculate the energy released per gram of fuel when methane is burned.

Answer

One mole of methane (CH_4) has a mass of 16.05 g, so burning 16.05 g of methane produces 891 kJ of energy.

$$\text{energy released per gram} = \frac{\text{energy released}}{\text{mass of fuel consumed}} = \frac{891}{16.05} = 55.5 \text{ kJ g}^{-1}$$

SCIENCE IN CONTEXT

Carbon monoxide

Carbon monoxide is formed when fuels such as natural gas undergo incomplete combustion. It is toxic, and it is estimated that around 1 million people each year suffer the effects of accidental carbon monoxide poisoning, with about 30 000 dying. Famous people who have died from accidental carbon monoxide poisoning include Émile Zola (author), Vitas Gerulaitis (tennis grand slam winner), with several more, including Sylvia Plath (poet), using it as a method of killing themselves. Carbon monoxide can build up around the home if, for instance, a heating system or a gas cooker has not been properly maintained or if ventilation is blocked (Figure 14.2). There are also several reported cases of carbon monoxide poisoning arising from smoking hookah (shisha) outdoors as well as indoors – this comes mainly from burning charcoal!

Carbon monoxide is sometimes known as the silent killer because you do not realise it is there – it is a colourless, odourless and tasteless gas. The symptoms of mild carbon monoxide poisoning include a headache, dizziness and nausea, and it can appear similar to influenza (but without the high temperature), so many people just ignore it until it is too late. Carbon monoxide acts as a poison because it binds to the iron in haemoglobin more strongly than oxygen does, to form carboxyhaemoglobin, and so, reduces the capacity of the blood to transport oxygen. An increasing number of people have carbon monoxide alarms installed around their homes to detect the presence of CO. Many of these work on the principle of a **fuel cell**, in which an electric current is generated as carbon monoxide is oxidised to carbon dioxide.

Figure 14.2: A boiler being serviced.

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Another way of expressing the equation for the energy released per gram when a fuel is burned is

$$\text{energy released per gram} = \frac{-(\text{enthalpy change of combustion})}{\text{molar mass of fuel}}$$

The negative sign is required, because we are considering the energy *released*, which is a positive value.

We can compare the value obtained for the energy released per gram for methane in Worked Example 14.2 with values for other fuels.

To do the calculation for coal, we will assume that coal is pure carbon. The enthalpy change of combustion of carbon is –394 kJ mol^{-1} and the molar mass of carbon is 12.01 g mol^{-1}.

$$\text{energy released per gram} = \frac{-(\text{enthalpy change of combustion})}{\text{molar mass of fuel}}$$

$$= \frac{394}{12.01} = 32.8 \text{ kJ g}^{-1}$$

Therefore, considerably less energy is released when 1 g of coal is burned compared to 1 g of methane (natural gas).

We cannot do the calculation for crude oil because it contains a complicated mixture of different substances, but we can do the calculation for octane (molecular formula: C_8H_{18}), which is a representative component of gasoline (petrol) used as fuel for cars. This has a molar mass of 114.26 g mol^{-1} and an enthalpy change of combustion of –5470 kJ mol^{-1}.

$$\text{energy released per gram} = \frac{-(\text{enthalpy change of combustion})}{\text{molar mass of fuel}}$$

$$= \frac{5470}{114.26} = 47.9 \text{ kJ g}^{-1}$$

We can see from the data that natural gas releases the most energy per gram and coal the least.

Carbon dioxide and climate change

When all these fossil fuels burn, carbon dioxide is produced. Each year, over 30 billion tonnes of carbon dioxide is added to the atmosphere from human activities – the vast majority of this comes from burning fossil fuels for heat, electricity, transport, etc. Carbon dioxide is a greenhouse gas and increased levels in the atmosphere are contributing to climate change.

In the 10 000-year period up to 1750, the CO_2 concentration in the atmosphere remained fairly constant at around 280 ppm – this level has now risen to around 420 ppm. In the past 40 years, global temperatures have increased by about 0.2 °C per decade, and the vast majority of scientists believe there is a strong correlation between these two facts – increasing levels of CO_2 in the atmosphere are causing the Earth to get hotter (enhanced greenhouse effect), resulting in climate change. It is difficult to predict the exact nature and extent of the consequences of climate change due to increased levels of greenhouse gases in the atmosphere, but things that we are already seeing include the following:

- Rise in sea levels – sea levels are rising by about 3.6 mm per year. Sea levels are predicted to be up to 0.8 m higher in 2100 than in 2005.
- Melting of polar ice caps and glaciers. Arctic sea ice is currently decreasing at over 10% per decade.
- Increased frequency and severity of extreme weather events, such as heatwaves, droughts and floods. It is difficult to attribute extreme weather events that have occurred over the last few years unequivocally to climate change, but there is reasonable confidence amongst scientists that they are related.

TEST YOUR UNDERSTANDING

5 Calculate the energy released per gram when each of the following fuels is burned:

	Fuel	Formula	Enthalpy change of combustion / kJ mol^{-1}
a	methanol	CH_3OH	–726
b	hexane	C_6H_{14}	–4163
c	ethanol	CH_3CH_2OH	–1367
d	propane	C_3H_8	–2219

6 Calculate the energy released in kJ g^{-1} when each of the following fuels is burned:

a hydrazine (N_2H_4) if burning 2.62 g releases 50.8 kJ

b decane ($C_{10}H_{22}$) if burning 0.180 g releases 8570 J

c ethyne (C_2H_2) if burning 0.0560 g releases 2800 J.

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INTERNATIONAL MINDEDNESS

Climate change

Climate change could be regarded as the biggest challenge facing humans in the foreseeable future. International agreements are essential to minimise the effect of this. One such treaty was the Paris Agreement, which came into force in 2016. The key tenet of the Paris agreement is that the countries of the world should come together to try to keep the increase in global temperatures at well below 2 °C and, if possible, the temperature increase should be less than 1.5 °C above pre-industrial levels. For this to be achieved, it was further set out that every effort should be made to achieve the peak in greenhouse gas emissions as soon as possible. The agreement recognises the needs of developing countries, and there is a commitment to support these countries in implementing the articles of the agreement and to fostering sustainable development with the minimum emissions of greenhouse gases. As of 2020, the agreement had been ratified by 189 countries.

Carbon dioxide production from burning fossil fuels

The mass of CO_2 produced per gram of fuel burned

All fossil fuels contain carbon and when they are burned the carbon is converted into carbon dioxide (and carbon monoxide and soot).

As before, we will use a simplified model to make the calculations easier. We will assume that coal is made entirely of carbon, that natural gas is pure methane and that petrol/gasoline is pure octane.

The equations for the complete combustion of each of these fuels are:

- $C(s) + O_2(g) \rightarrow CO_2(g)$
- $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
- $C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$

From these equations, we can deduce the number of moles of carbon dioxide produced when one mole of each fuel undergoes complete combustion:

- 1 mol carbon produces 1 mol CO_2
- 1 mol methane produces 1 mol CO_2
- 1 mol octane produces 8 mol CO_2.

The mass of 1 mol CO_2 is 44.01 g; therefore, we can calculate the mass of CO_2 produced when 1 mol of each fuel is burned:

- 1 mol carbon produces $1 \times 44.01 = 44.01$ g CO_2
- 1 mol methane produces $1 \times 44.01 = 44.01$ g CO_2
- 1 mol octane produces $8 \times 44.01 = 352.08$ g CO_2.

If we divide each value by the molar mass of the fuel burned, we get the mass of CO_2 produced per gram of fuel burned:

- carbon: $44.01 \div 12.01 = 3.66$ g per gram of fuel burned
- methane: $44.01 \div 16.05 = 2.74$ g per gram of fuel burned
- octane: $352.08 \div 114.26 = 3.08$ g per gram of fuel burned.

Therefore, using our simplified model, we can predict that coal will produce the most CO_2 per gram of fuel undergoing complete combustion and natural gas will produce the least.

The mass of CO_2 produced per kJ of energy released

When we are considering energy production, perhaps a more useful comparison is the mass of CO_2 produced per kJ of energy released. This value can be obtained by dividing the mass of CO_2 produced per mole by the enthalpy change of combustion. Enthalpy change of combustion values are given in Table 14.3.

Substance	Enthalpy change of combustion / kJ mol^{-1}
coal, C(s)	–394
natural gas, $CH_4(g)$	–891
petrol, $C_8H_{18}(l)$	–5470

Table 14.3: The enthalpy change of combustion of fossil fuels.

- carbon: $44.01 \div 394 = 0.112$ g of CO_2 per kJ of energy released
- methane: $44.01 \div 891 = 0.0494$ g of CO_2 per kJ of energy released
- octane: $352.08 \div 5470 = 0.0644$ g of CO_2 per kJ of energy released

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So, in this calculation as well, methane (natural gas) comes out best and carbon (coal) comes out worst – natural gas releases the lowest mass of CO_2 for each gram burnt or kJ of heat energy produced. We also saw above that natural gas produces the greatest amount of energy per gram burnt. Added to this, natural gas is the cleanest burning of the fuels and undergoes less incomplete combustion, producing fewer harmful particulates. It would, therefore, seem to be the ideal fuel for, e.g., power generation and significantly better than coal. However, methane is a more powerful greenhouse gas than carbon dioxide and, for the same mass, has a global warming potential of about 20–30 times that of carbon dioxide over a period 100 years. Methane is present in the atmosphere at much lower concentrations than carbon dioxide, but scientists are becoming increasingly worried about increases in methane concentrations due to leakages in natural gas production and transportation.

NATURE OF SCIENCE

All science must be funded–by governments, international organisations or companies. Science should, however, not be biased or be influenced by the vested interests of large international corporations, such as oil companies. An internet search for 'ExxonMobil climate change' will throw up some interesting stories. Nowadays, most reputable scientific journals require contributing scientists to declare the source of their funding and vested interests. Scientists can sometimes be put in difficult positions when their findings do not fit with the interests of the people funding their research.

THEORY OF KNOWLEDGE

The evidence for climate change being caused by human activity seems clear, so why do some people not 'believe in' climate change? Is climate change something we can believe in or not believe in, like fairies or dragons? How do the words we use affect how something is perceived? Why do some people think that we should be talking about 'climate crisis' rather than 'climate change'?

SCIENCE IN CONTEXT

Carbon footprint

A **carbon footprint** is a measure of the quantity of greenhouse gases (primarily carbon dioxide and methane) emitted as a result of human activities. It is usually expressed as equivalent tonnes of carbon dioxide (e.g. 10 tonne CO_2e or CO_2–eq). Carbon footprints can be worked out at many different levels, for example, by country, region, organisation, household or individual. Your carbon footprint is influenced by many things – major contributions come from transport and electricity usage, but what food you eat, whether you buy a newspaper, etc. all make a difference. Contributions to an individual's carbon footprint can be divided into two broad categories – direct production and indirect production. Direct production of carbon dioxide from, say, a car journey is reasonably straightforward to calculate, but indirect production from something like eating a frozen pizza bought from a supermarket is much more difficult to quantify. Think about your favourite frozen pizza and try to work out all the processes that produce CO_2/CH_4. You will have to consider all the ingredients (you must also think about the workers on farms, etc.), transportation and processing of the ingredients, making the pizza and packaging, transportation of the pizza, keeping it frozen, etc. Do not forget that growing some of the ingredients could also result in a net decrease in the amount of CO_2 in the atmosphere. You will probably realise that the calculation is incredibly difficult!

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TEST YOUR UNDERSTANDING

7 Calculate the mass of CO_2 produced per gram of fuel burned and per kJ of energy released when each of the following fuels is burned:

	Fuel	Formula	Enthalpy change of combustion / kJ mol^{-1}
a	methanol	CH_3OH	−726
b	hexane	C_6H_{14}	−4163
c	ethanol	CH_3CH_2OH	−1367
d	ethane	C_2H_6	−1561
e	ethene	C_2H_4	−1411
f	ethyne	C_2H_2	−1300
g	benzene	C_6H_6	−3268

8 Use your answers from the previous question to compare the environmental impact of using ethanol, ethane, ethene and ethyne as fuels, with respect to:

a mass of CO_2 produced per gram of fuel burned

b mass of CO_2 produced per kJ of energy released.

14.3 Renewable and non-renewable energy sources

KEY POINTS

Renewable energy sources are naturally replenished – they will not run out.

Non-renewable energy sources are finite – they will eventually run out.

Renewable energy sources include solar energy, wind energy and **biofuels**. Solar energy and wind energy will never run out (at least not for a few billion years), and biofuels can be easily replenished (see next). Non-renewable energy sources include fossil fuels – once these run out it, that is it, there is no more – it would take millions of years to create them again!

Biofuels

KEY POINT

Biomass is material of plant or animal origin that is used for fuel.

The **biomass** can be burned directly (e.g. wood) or converted into biofuels such as ethanol (from the fermentation of sugar cane/corn starch), biogas (from decaying matter) and biodiesel (from vegetable oils).

KEY POINT

Biofuel: a fuel produced from organic matter obtained from plants or from waste material of plant/animal origin.

The chemical energy in plants comes from photosynthesis. Photosynthesis involves the conversion of light energy from the sun to chemical energy in plants. In photosynthesis, light energy drives the conversion of carbon dioxide (from the air) and water (from the air and ground) into glucose, which can then be converted into more complex carbohydrates, such as cellulose and starch, the material of plants. This process can be described as the *biological fixation of carbon* – the conversion of carbon dioxide to organic molecules.

The exact nature of the reactions that occur in photosynthesis is complex, but the basic equation is

KEY POINT

$$6CO_2 + 6H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2$$

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INTERNATIONAL MINDEDNESS

Biofuels

Ethanol is an important biofuel that is produced by fermentation of sugar cane or corn starch. The main producers of ethanol as a fuel are Brazil (from sugar cane) and the US (from corn starch). Ethanol can be mixed with gasoline for use as a fuel in cars (Figure 14.3). Various blends of ethanol with gasoline are available and, especially in Brazil and the US, flexible-fuel vehicles are available that have been designed to work with all possible mixtures of ethanol and gasoline.

Figure 14.3: E85 is a fuel that is 85% ethanol and 15% gasoline, whereas E20 is 20% ethanol and 80% gasoline.

Advantages and disadvantages of biofuels

Advantages

- Biofuels are renewable – one of the main advantages of using biofuels over fuels derived from petroleum is that biofuels are renewable, whereas fuels from petroleum are non-renewable. More sugar cane/corn can be grown to make more ethanol, etc.
- Biofuels can be produced locally and reduce reliance on expensive oil imports from other countries. Also, only some countries have reserves of crude oil, but biofuel crops can be grown much more widely.
- Biofuels can be produced from waste materials, e.g., biogas from manure or landfill sites, or biodiesel from waste plant oils.
- Biofuels are biodegradable, and so, the potential environmental impact of spillages of biofuels is considerably lower than that of a spillage of crude oil.

Biofuels are often regarded as **carbon neutral**. The carbon atoms in the biofuel originally came from carbon dioxide in the atmosphere and, when the fuel is burned, these are returned to the atmosphere as carbon dioxide. Therefore, growing and burning biofuels should result in no net change in the number of carbon dioxide molecules in the atmosphere. However, the situation is more complicated than this and, how environmentally friendly a biofuel such as ethanol is, depends on how it is produced. Factors that must be considered include the following:

- the production of fertilisers for use on farms
- the transportation of corn/sugar cane
- the processing of corn starch to produce simple sugars
- distillation and so on.

All these processes require energy and, assuming that most of this comes originally from burning fossil fuels, which produces carbon dioxide (although in Brazil they burn the waste material from the sugar cane to reduce the impact here), it can be seen that ethanol is far from carbon neutral. The debate is ongoing as to whether some biofuels actually have a larger carbon footprint (the amount of greenhouse gases produced in a process) than fuels derived from petroleum. There is also some debate in the US as to whether more energy must be put in to make ethanol from corn than is obtained from it.

Disadvantages

- Growing biofuel crops requires large areas of land.
  - This land could be used for growing crops for food – in a world with a rapidly increasing population, and where there are severe problems with famine, there are ethical implications in using vast areas of land to grow a crop to be converted into a fuel for vehicles.
  - Deforestation to produce land for growing biofuels, could decrease the amount of carbon dioxide being taken from the atmosphere and destroy habitats.

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- Biofuels produce carbon dioxide when they are burnt.
- Burning biomass directly, e.g., wood-burning stoves, produces particulates and other toxic substances [e.g. dioxins and polycyclic aromatic hydrocarbons (PAHs)].

14.4 Fuel cells

A fuel cell is essentially a type of battery but needs a continuous supply of fuel from an external source, whereas the batteries you are more familiar with are self-contained (all the fuel is contained within them) or only need to be re-charged periodically. Hydrogen fuel cells are finding increasing use in vehicles (Figure 14.4) and were used in the space shuttle.

Figure 14.4: A bus powered by hydrogen fuel cells.

KEY POINT

A fuel cell is a device that can be used to convert chemical energy from a fuel directly into electrical energy.

How a fuel cell works

All fuel cells work in basically the same way: the fuel (e.g. hydrogen or methanol) is fed into the anode compartment, where it is oxidised (electrons are lost). The electrons produced flow through the external circuit – this is the flow of current that can be used to power devices – to the cathode compartment where they reduce (electrons are gained) the oxidant (oxygen). The anode and cathode compartments are separated by a membrane/electrolyte through which ions (but not electrons) can flow to complete the circuit. The overall reaction that goes on in a fuel cell is equivalent to a combustion reaction, except the separation of the oxidation and reduction reactions allows the energy to be obtained as electrical energy rather than heat.

Link

See Chapter 20 for further discussion on how redox reactions can be used to generate electricity.

The hydrogen–oxygen fuel cell

An alkaline fuel cell

Figure 14.5 shows an alkaline hydrogen–oxygen fuel cell with a potassium hydroxide electrolyte. Electrodes are typically made of carbon and incorporate a metal catalyst such as nickel or platinum.

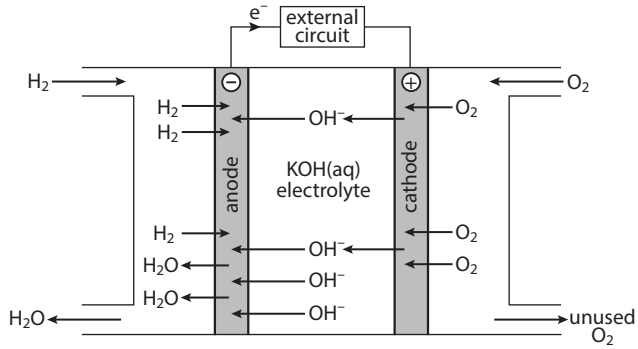

Figure 14.5: An alkaline hydrogen–oxygen fuel cell with a potassium hydroxide electrolyte.

The two electrodes are separated by a porous matrix saturated with an electrolyte, which may be either an alkaline or an acidic solution. In the case of an alkaline electrolyte, typically a solution of potassium hydroxide (KOH) is used.

At the anode, hydrogen undergoes oxidation when it reacts with hydroxide ions (OH^-) to form water:

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

This is called a half-equation: it just shows one of the processes (either oxidation or reduction) in a redox reaction.

Electrons are released in this oxidation process at the anode and flow around the external circuit to the cathode. At the cathode, oxygen undergoes reduction when it reacts with water and gains electrons coming from the external circuit:

$$\tfrac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$$

If these reactions are added together and common terms cancelled, we get:

$$H_2(g) + \cancel{2OH^-(aq)} \rightarrow \cancel{2}H_2O(l) + \cancel{2e^-} \quad \text{oxidation}$$
$$\tfrac{1}{2}O_2(g) + \cancel{H_2O(l)} + \cancel{2e^-} \rightarrow \cancel{2OH^-(aq)} \quad \text{reduction}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \text{overall redox reaction}$$

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The overall reaction is equivalent to the combustion of hydrogen, but the energy has been released as electrical energy rather than heat energy. The separation of the oxidation and reduction reactions permits the flow of electrons and the generation of an electric current.

Link

More details on how to derive these equations are given in Chapter 20.

EXAM TIP

The half-equations here are given in the table of standard reduction potentials in the IB data booklet. All the equations in the data booklet are, however, written as reduction reactions (see Chapter 20), and so must be reversed to produce oxidation half-equations.

An acidic fuel cell

In an acidic fuel cell, the alkaline electrolyte is replaced by an acidic solution, commonly phosphoric acid, or a membrane (proton exchange membrane), through which protons (H^+ ions) can flow from the anode to the cathode (Figure 14.6).

Hydrogen passes through a porous carbon anode that contains a platinum catalyst and is oxidised to form hydrogen ions (protons) and electrons (which travel through the external circuit). The hydrogen ions travel through the electrolyte/proton exchange membrane to the cathode (containing a platinum catalyst) where they combine with oxygen molecules and electrons to form water.

The reactions occurring at the anode and cathode in an acidic fuel cell are different from those in an alkaline fuel cell, but the overall reaction is the same:

$$H_2(g) \rightarrow \cancel{2H^+(aq)} + \cancel{2e^-} \quad \text{anode – oxidation}$$

$$\cancel{2H^+(aq)} + \tfrac{1}{2}O_2(g) + \cancel{2e^-} \rightarrow H_2O(l) \quad \text{cathode – reduction}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \text{overall redox reaction}$$

Methanol fuel cells

One disadvantage of using hydrogen fuels cells is the difficulty of storing hydrogen fuel (a gas), so one solution to the problem is to use a liquid fuel, such as methanol. A direct methanol fuel cell works in a similar way to the acidic hydrogen–oxygen fuel cell described previously. The anode and cathode both contain a platinum catalyst, and there is a membrane between the electrodes that allows protons, but not electrons., to flow from the anode to the cathode. Methanol solution is oxidised in the anode compartment to produce electrons that flow around the external circuit and protons that flow through the membrane to the cathode. In the cathode compartment, oxygen is reduced, as it combines with electrons from the external circuit and protons from the membrane. The equations for the reactions are

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

cathode: $\tfrac{3}{2}O_2(g) + 6H^+(aq) + 6e^- \rightarrow 3H_2O(l)$

overall: $CH_3OH(aq) + \tfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Again, the overall reaction is equivalent to a combustion reaction.

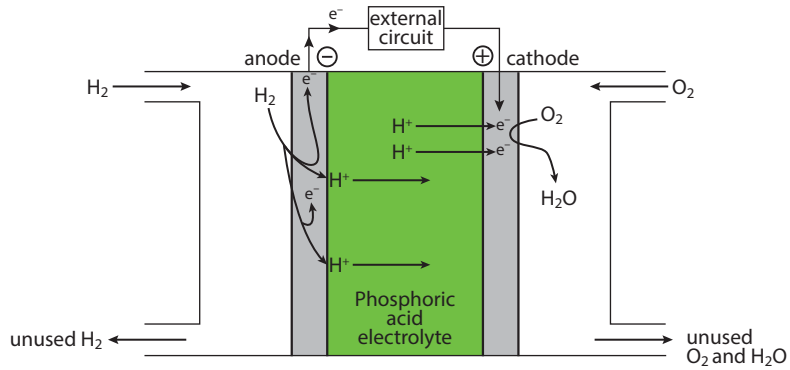

Figure 14.6: An acidic hydrogen–oxygen fuel cell.

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SCIENCE IN CONTEXT

Hydrogen as a fuel

With ambitious worldwide targets to reduce the emission of carbon dioxide, the use of hydrogen fuel cells is likely to increase in the near future. These can be used to power vehicles, and one large advantage over powering a vehicle using gasoline/diesel is that a hydrogen fuel cell vehicle does not produce carbon dioxide in operation. However, hydrogen cannot simply be extracted from the ground or the air and must be made. One of the most important processes for producing hydrogen is called steam reforming (steam methane reforming), where natural gas is reacted with steam at high temperature in the presence of a catalyst:

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

The carbon monoxide is then converted into carbon dioxide and more hydrogen in the water–gas shift reaction:

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

These processes require large amounts of energy, which is likely to come from burning fossil fuels, which produces carbon dioxide. Most other methods of making hydrogen, such as electrolysis of water, also require large amounts of energy; therefore, how environmentally friendly hydrogen is as fuel will depend on how the electricity is produced – from renewable sources or fossil fuels.

An advantage of using hydrogen as a fuel is that it can be produced from water, therefore potential supplies of hydrogen are essentially limitless.

Other problems associated with the use of hydrogen include the fact that it is an explosive gas; therefore, if it is used in vehicles, it must be stored under pressure in very strong tanks.

Direct methanol fuel cells are being developed for use in laptop computers and mobile phones. The fuel cell is built into the device, and a methanol cartridge is plugged in to provide the fuel. When the fuel has been used up, the cartridge is disposed of and replaced with a new one. The use of this sort of technology allows laptops and phones to be used well away from the electricity grid and has many potential military and civilian applications. One disadvantage of direct methanol fuel cells is that they produce carbon dioxide, which is a greenhouse gas.

Reformed methanol fuel cells

In this type of fuel cell, methanol is first reformed to hydrogen and carbon dioxide:

$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

Hydrogen is then used as the fuel for the fuel cell. The reactions that occur are the same as in the acidic fuel cell:

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$	anode – oxidation
$2H^+(aq) + \frac{1}{2}O_2(g) + 2e^- \rightarrow H_2O(l)$	cathode – reduction
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	overall redox reaction

TEST YOUR UNDERSTANDING

9 Write ionic half-equations for each of the following:

- **a** the reaction that occurs at the anode in an alkaline hydrogen-oxygen fuel cell
- **b** the reaction that occurs at the cathode in an acidic hydrogen-oxygen fuel cell
- **c** the reaction that occurs at the anode in a direct methanol fuel cell.

10 Classify each of the reactions in question 9 as oxidation or reduction.

11 Write an equation for

- **a** the overall reaction in a hydrogen-oxygen fuel cell
- **b** the overall reaction in a direct methanol fuel cell.

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
write equations for combustion reactions	14.1			
deduce equations for incomplete combustion of organic compounds	14.1			
discuss the advantages and disadvantages of fossil fuels	14.2			
calculate how much carbon dioxide is formed when fossil fuels burn	14.2			
explain what biofuels are	14.3			
explain the difference between renewable and non-renewable energy sources	14.3			
explain how fuel cells work	14.4			
deduce half-equations for the reactions occurring in fuel cells.	14.4			

REFLECTION

- How confident do you feel comparing different fuels?
- To what extent do you feel that your understanding would be enhanced by reading around the material covered in this chapter?
- What is the most difficult part of this chapter? How could you improve your understanding of that topic?
- Try explaining how a fuel cell works to another student. Does this highlight any gaps in your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 15

Entropy and spontaneity

LEARNING OBJECTIVES

In this chapter you will:

- understand the term entropy
- predict whether a chemical/physical reaction involves an increase or decrease in entropy
- calculate standard entropy changes
- understand the term 'change in Gibbs energy'
- calculate the change in Gibbs energy
- relate the change in Gibbs energy to the spontaneity of a reaction
- explain the changes in Gibbs energy as a system reaches equilibrium
- calculate Gibbs energy changes for systems approaching equilibrium and at equilibrium.

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GUIDING QUESTIONS

- What is entropy?
- How can endothermic reactions occur spontaneously?
- What factors govern whether a reaction occurs spontaneously?

Introduction

In this chapter, we will investigate the fundamental idea of why some chemical reactions occur spontaneously, and others do not. We have met a lot of chemical reactions so far in the book, but why do they occur in one direction rather than in the reverse direction? In the last chapter, we met hydrogen as a fuel – this will spontaneously react with oxygen to form water, but water does not spontaneously break apart into hydrogen and oxygen – if you leave a glass of water on your bedside table, it might evaporate a little overnight, but it will definitely not split apart into hydrogen and oxygen – that process needs a continuous supply of energy in electrolysis.

15.1 Entropy

What is a spontaneous reaction?

KEY POINT

Spontaneous reaction a reaction that occurs without any outside influence.

A **spontaneous reaction** is one that occurs without us having to do anything – it will happen by itself – we do not have to supply energy. A spontaneous reaction does not have to occur quickly – some are very fast, others immeasurably slow.

Do endothermic reactions occur spontaneously?

The dissolving of sodium chloride (common salt) in water is an example of an endothermic process that occurs spontaneously at room temperature. You might say that it is because heat energy flows from the surroundings to cause it to occur – but why should that happen? The idea of an endothermic reaction occurring spontaneously goes against our experience from everyday life that things do not seem to move by themselves from a lower to a higher energy state – a book does not absorb energy from the surroundings to jump from a lower shelf (lower potential energy) to a higher one (higher potential energy). Endothermic processes such as the melting of ice at room temperature and water evaporating are relatively common, which suggests that it is not just a consideration of the energy changes involved that must be used to predict whether a reaction occurs spontaneously.

The examples of endothermic processes mentioned here all have one thing in common: they all involve an increase in disorder. In a sodium chloride solution, the Na^+ and Cl^- ions are dispersed throughout the solution and are moving around, which is a much more disordered, or random, arrangement than a separate crystal of sodium chloride and a beaker of pure water. Similarly, liquid water is much more disordered (dispersed) than a solid lump of ice, as in the liquid form all the molecules are moving around each other randomly. To understand why these processes occur, we need to introduce a new term called **entropy**.

What is entropy?

KEY POINT

Entropy is a measure of the disorder of a system (how the matter is dispersed/distributed) or how the available energy is distributed among the particles.

These two ways of thinking about entropy are equivalent to each other – if a system becomes more disordered, the energy in it can be distributed in more ways among the available particles and the *entropy* of the system is higher. Imagine 100 people sitting on chairs in a hall – there is only a limited number of ways in which they can move but still remain seated. This is a relatively ordered system, and the number of ways of distributing the energy that they have is limited. However, if you have the same 100 people running around in the hall (a much more disordered system), there is an absolutely enormous number of different ways in which they can move (the energy can be distributed).

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Entropy is given the symbol S. The units of entropy are J K^{-1} mol^{-1}, and it is important to notice that joules and not kilojoules are used.

$S^{\ominus}$ is called the standard entropy. It is possible to work out values for standard entropies for substances – for example, the standard entropy of $H_2(g)$ is 131 J K^{-1} mol^{-1}, and the standard entropy of NaCl(s) is 72.4 J K^{-1} mol^{-1}.

Link

Actual values of entropy can be calculated from experimental data – as opposed to enthalpy, for which only enthalpy *changes* can be measured. For us to be able to work out absolute entropies, there must a zero of entropy – this is a perfect crystal at 0 K. A perfect crystal is a perfectly ordered system, and if it is at absolute zero, everything is in the lowest possible energy state, meaning that there is only one way of distributing the energy.

KEY POINT

Gases have higher entropy than liquids, which have higher entropy than solids.

Measured under the same conditions, gases tend to have higher entropy than liquids, which have higher entropy than solids (Figure 15.1).

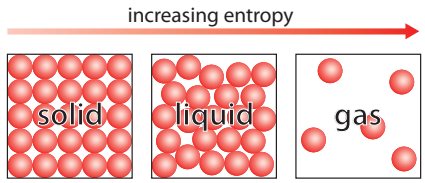

Figure 15.1: In a solid, the particles vibrate about mean positions; in a liquid, the particles move around each other; in a gas, the particles move at high speeds in all directions.

In a gas, all the particles are moving at different speeds in different directions and rotating and vibrating. This is a very disordered state, and there is a huge number of ways in which the energy could be distributed among all the different particles. In a solid, the particles are more constrained (it is less disordered), and there are fewer ways in which the energy could be distributed among the particles (lower entropy).

Table 15.1 shows the values of standard entropies for elements across Period 2 in the periodic table. Lithium to carbon are all solid elements and have low entropy values at 298.15 K, but nitrogen to neon are all gases and have much higher entropy values.

Remembering that gases have higher entropy than liquids, which have higher entropy than solids, is useful when considering the same substance in different states or similar substances. When considering very different substances, it must be used with caution. For instance, $S^{\ominus}$ for $(NH_4)_2SO_4(s)$ is 220 J K^{-1} mol^{-1}, whereas that for $CCl_4(l)$ is 214 J K^{-1} mol^{-1} and that for HCl(g) is 187 J K^{-1} mol^{-1}.

Entropy changes

An entropy change is represented by the symbol ΔS, or $\Delta S^{\ominus}$ for a standard entropy change (measured under standard conditions).

A positive value for ΔS indicates an increase in entropy – increase in disorder (greater dispersal of matter) – the energy can be distributed in more ways.

For example, $\Delta S^{\ominus}$ for the process $H_2O(l) \rightarrow H_2O(g)$ is +119 J K^{-1} mol^{-1}; the positive value indicates that the disorder of the system has increased. The particles in a gas have complete freedom of movement in three dimensions and, therefore, the energy can be distributed in more ways. The movement of the particles in a liquid is more constrained, and so, there are not as many ways to distribute the energy.

A negative value for ΔS indicates a decrease in entropy – a decrease in disorder (less dispersal of matter) – a decrease in the number of ways the available energy can be distributed among the particles.

For example, $\Delta S^{\ominus}$ for the process $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ is –285 J K^{-1} mol^{-1}. Two moles of gas being converted into a solid results in a decrease in disorder.

Element	Li	Be	B	C	N_2	O_2	F_2	Ne
State	solid	solid	solid	solid	gas	gas	gas	gas
$S^{\ominus}$ / J K^{-1} mol^{-1}	29	10	6	6	192	205	203	146

Table 15.1: Standard entropies for elements across Period 2.

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The particles in a solid have less freedom of movement, and so, there are fewer ways of distributing the energy and, therefore, the solid has lower entropy than the gas.

Predicting the sign of entropy changes

To predict the sign of the entropy change in a reaction, the easiest way to think about it is in terms of disorder. If there is an increase in disorder (dispersal of matter), the entropy also increases. Because gases have significantly higher entropy than solids and liquids, the most important factor in determining whether a chemical reaction involves an increase or decrease in entropy is whether there is an increase or decrease in the number of moles of gas.

- An increase in number of moles of gas: ΔS is +ve (entropy increases).
- A decrease in number of moles of gas: ΔS is –ve (entropy decreases).

This can be seen in the reactions in Table 15.2.

If the number of moles of gas is the same on both sides of an equation, for example:

$F_2(g) + Cl_2(g) \rightarrow 2ClF(g)$

the prediction can be made that the entropy change would be approximately zero.

The entropy of a system is also changed by other factors as follows:

- entropy increases as the temperature increases
- entropy increases as the pressure decreases
- the entropy of a mixture is higher than the entropy of pure substances.

INTERNATIONAL MINDEDNESS

Statistical approach to entropy

The Austrian physicist Ludwig Boltzmann (1844–1906) developed a statistical approach to entropy. His famous equation, $S = k \log W$, is inscribed on his gravestone. W represents the possible energy states over which the energy can be distributed, and k is the Boltzmann constant. Other scientists with equations on their graves include Max Born, Erwin Schrödinger and Stephen Hawking. Scientists may not always become as famous as footballers or popstars, but their achievements have been celebrated and they have been featured on bank notes around the world, for example, Erwin Schrödinger was on the 1000 Schilling bank note used in Austria, Niels Bohr was on the Danish 500 Kroner note and Marie Curie has appeared on bank notes in both France and Poland.

Calculating an entropy change for a reaction

Values of $\Delta S^{\ominus}$ can be worked out from standard entropies, $S^{\ominus}$.

KEY POINT

entropy change = total entropy of products – total entropy of reactants

$\Delta S^{\ominus} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$

Reaction	Entropy	ΔS	Explanation
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	decrease	–	four moles of gas on the left-hand side are converted into two moles of gas on the right-hand side; a decrease in the number of moles of gas is a decrease in disorder; therefore, the energy can be distributed in fewer ways in the products
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	increase	+	one mole of solid becomes one mole of solid and one mole of gas; increase in the number of moles of gas means an increase in disorder
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	decrease	–	three moles of gas are converted into one mole of gas; decrease in the number of moles of gas means a decrease in disorder

Table 15.2: Entropy changes for some reactions.

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WORKED EXAMPLE 15.1

Use data in the table to calculate the standard entropy change for the following reaction:

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

	$S^\ominus$ / J K^{-1} mol^{-1}
$N_2(g)$	192
$H_2(g)$	131
$NH_3(g)$	193

Answer

$\Delta S^\ominus = \Sigma S^\ominus_{products} - \Sigma S^\ominus_{reactants}$

The standard entropy values are multiplied by the appropriate coefficients in the equation:

$\Delta S^\ominus = (2 \times 193) - [192 + (3 \times 131)]$

$\Delta S^\ominus = -199$ J K^{-1} mol^{-1}

The decrease in entropy corresponds to the prediction made above based on the number of moles of gas (four moles of gas converted to two moles of gas).

TEST YOUR UNDERSTANDING

1 Deduce whether each of the following processes involves an increase or a decrease in entropy:

a $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

b $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

c $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

d $2C(s) + O_2(g) \rightarrow 2CO(g)$

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

2 Use the entropy values in the table to calculate the standard entropy change in each of the following reactions:

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

b $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$

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

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

e $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

f $4BCl_3(l) + 3SF_4(g) \rightarrow 4BF_3(g) + 3SCl_2(g) + 3Cl_2(g)$.

Substance	$S^\ominus$ / J K^{-1} mol^{-1}
$H_2(g)$	131
$H_2O(l)$	70
$H_2O(g)$	189
$O_2(g)$	205
$CH_4(g)$	186
$CO_2(g)$	214
$C_4H_9OH(l)$	226
$Cu(NO_3)_2(s)$	193
$CuO(s)$	43
$NO_2(g)$	240
$BCl_3(l)$	206
$SF_4(g)$	292
$BF_3(g)$	254
$SCl_2(g)$	282
$Cl_2(g)$	223

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15.2 Spontaneous reactions

KEY POINT

A reaction will occur spontaneously if the entropy of the universe increases.

Remember, a spontaneous reaction is one that occurs without any outside influence. If sodium and oxygen are put together in an isolated container at 25 °C, they will react spontaneously to produce sodium oxide:

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

This reaction will occur by itself – nothing has to be done to make the reaction occur.

A spontaneous reaction does not have to happen quickly. If methane and oxygen are put into an isolated container at 25 °C, they will react together spontaneously to form carbon dioxide and water. This reaction, although it is spontaneous, is not a very fast reaction at room temperature (unless a spark is supplied) and would have to be left for a very long time before a significant amount of carbon dioxide and water could be detected.

Whether a reaction will be spontaneous or not under a certain set of conditions can be deduced by looking at how the entropy of the universe changes as the reaction occurs. The second law of thermodynamics states that, for a process to occur spontaneously, it must result in an increase in the entropy of the universe. (The first law of thermodynamics is basically a statement of the principle of conservation of energy: the energy of the universe remains constant.)

The universe may be regarded as being composed of the system (the chemical reaction) and the surroundings. The entropy change of the universe is given by

$$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$$

If, during a reaction, the value of $\Delta S_{universe}$ is positive, the entropy of the universe increases, and the reaction occurs spontaneously. It is not, however, very useful to us to be trying to work out what is going on in the universe, so this equation would be far better if we could relate it just to a chemical reaction – the system.

When heat is given out in a chemical reaction, the surroundings get hotter and the particles move around more, therefore, the entropy of the surroundings increases. So, the entropy change of the surroundings can be related to the enthalpy change (ΔH) of the system (chemical reaction).

If a certain amount of heat is transferred to the surroundings at a low temperature, it has a much bigger effect on the entropy of the surroundings than if the same amount of heat is transferred at a higher temperature. The entropy change of the surroundings, therefore, depends on the temperature and is given by

$$\Delta S_{surroundings} = -\Delta H_{system} / T$$

$-\Delta H_{system}$ because, if the enthalpy of the system decreases, heat is transferred to the surroundings, so the entropy of the surroundings increases.

Therefore we can write:

$$\Delta S_{universe} = (-\Delta H_{system} / T) + \Delta S_{system}$$

Rearranging this we get: $-T\Delta S_{universe} = \Delta H_{system} - T\Delta S_{system}$

$-T\Delta S_{universe}$ is given the symbol ΔG and so we can write:

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

The subscripts are now omitted, because both ΔH and ΔS refer to the system, i.e., the chemical reaction. ΔG is called the **Gibbs energy change** (sometimes called the free energy change). If $\Delta S_{universe}$ is positive, ΔG will be negative and the reaction will be spontaneous.

Under standard conditions (pressure = 100 kPa), we have $\Delta G^{\ominus}$, which is the standard Gibbs energy change.

KEY POINT

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

The sign of ΔG and spontaneity

KEY POINT

For a reaction to be spontaneous, ΔG for the reaction must be negative.

This refers to reactions occurring at constant pressure, that is, the reactions that we would normally be carrying out in chemical laboratory, which are open to the atmosphere.

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Calculating $\Delta G^{\ominus}$

The standard Gibbs energy change for a reaction can be calculated using the equation: $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Two important points to remember when using this equation are:

- $\Delta H^{\ominus}$ values are usually given in kJ mol^{-1}, but the units for $\Delta S^{\ominus}$ are J K^{-1} mol^{-1}. We cannot subtract a quantity in J from one in kJ without converting the units. The units we usually use for $\Delta G^{\ominus}$ are kJ mol^{-1}, so we normally divide the $\Delta S^{\ominus}$ value by 1000 to convert it to kJ.
- The temperature must be in K.

EXAM TIP

You must remember to divide the entropy value by 1000 – this is a very common mistake.

WORKED EXAMPLE 15.2

$\Delta S^{\ominus} = -233$ J K^{-1} mol^{-1} for the following reaction:

$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g) \quad \Delta H^{\ominus} = -313$ kJ mol^{-1}

Calculate $\Delta G^{\ominus}$ for this reaction and predict whether it will be spontaneous at 25.00 °C.

Answer

$\Delta H^{\ominus}$ is in kJ but $\Delta S^{\ominus}$ is in J, so, to combine them, $\Delta S^{\ominus}$ will be converted into kJ. Therefore:

$\Delta S^{\ominus} = -233 \div 1000 = -0.233$ kJ K^{-1} mol^{-1}

Before substituting the values into the equation for $\Delta G^{\ominus}$, we must remember that temperature must be in kelvin. To convert a temperature in °C to one in kelvin, we add 273.15:

$T = 25.00 + 273.15 = 298.15$ K

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \qquad \Delta G^{\ominus} = -313 - 298.15 \times (-0.233) = -244$ kJ mol^{-1}

Because the value of $\Delta G^{\ominus}$ is negative, the reaction is spontaneous.

TEST YOUR UNDERSTANDING

3 For each of the reactions below, calculate $\Delta G^{\ominus}$ at 298.15 K and predict whether the reaction will be spontaneous:

a $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$\Delta H^{\ominus} = -891$ kJ mol^{-1}
$\Delta S^{\ominus} = -243$ J K^{-1} mol^{-1}

b $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
$\Delta H^{\ominus} = +572$ kJ mol^{-1}
$\Delta S^{\ominus} = 327$ J K^{-1} mol^{-1}

c $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
$\Delta H^{\ominus} = -137$ kJ mol^{-1}
$\Delta S^{\ominus} = -55$ J $K^{-1}mol^{-1}$

d $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
$\Delta H^{\ominus} = -2219$ kJ mol^{-1}
$\Delta S^{\ominus} = -373$ J K^{-1} mol^{-1}

4 For each of the following reactions, determine $\Delta G^{\ominus}$ and predict whether the reaction will be spontaneous at the specified temperature:

a $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$ at 37.00 °C
$\Delta H^{\ominus} = -1170$ kJ mol^{-1}
$\Delta S^{\ominus} = -534$ J K^{-1} mol^{-1}

b $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ at 100.00 °C
$\Delta H^{\ominus} = +178$ kJ mol^{-1}
$\Delta S^{\ominus} = +161$ J K^{-1} mol^{-1}

c $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$ at 500.00 °C
$\Delta H^{\ominus} = -25$ kJ mol^{-1}
$\Delta S^{\ominus} = +16$ J K^{-1} mol^{-1}

d $Zn(s) + MgO(s) \rightarrow ZnO(s) + Mg(s)$ at 1000.00 °C
$\Delta H^{\ominus} = +251$ kJ mol^{-1}
$\Delta S^{\ominus} = 7.8$ J K^{-1} mol^{-1}

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CONTINUED

5 **a** $4KClO_3(s) \rightarrow 3KClO_4(s) + KCl(s)$
$\Delta H^{\ominus} = -144$ kJ mol^{-1}
$\Delta G^{\ominus} = -133$kJ mol^{-1}

Calculate the value of $\Delta S^{\ominus}$ (in J K^{-1} mol^{-1}) at 25.00 °C.

b $Mg(s) + O_2(g) \rightarrow 2MgO(s)$
$\Delta G^{\ominus} = -1139$ kJ mol^{-1}
$\Delta S^{\ominus} = -184$ J K^{-1} mol^{-1}

Calculate the value of $\Delta H^{\ominus}$ at 25.00 °C.

Spontaneity depends on temperature

Let's consider the melting of ice: $H_2O(s) \rightarrow H_2O(l)$

$\Delta H^{\ominus}$ for this reaction is 6.01 kJ mol^{-1} and $\Delta S^{\ominus} = 22.0$ J mol^{-1} K^{-1}

The values used here were measured at a pressure of 100 kPa, so they are standard values, but the temperature was 0 °C.

If we work out $\Delta G^{\ominus}$ for this process at 5 °C (278.15 K) (assuming that we can ignore any variation of the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ with temperature), we get:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus} = 6.01 - 278.15 \times (22.0 \div 1000)$

$= -0.109$ kJ mol^{-1}

The value is negative, so we can conclude that this process is spontaneous at 5 °C; in other words, ice melts at 5 °C.

If we do the same calculation at −5 °C (268.15 K), we get:

$\Delta G^{\ominus} = 6.01 - 268.15 \times (22.0 \div 1000) = +0.111$ kJ mol^{-1}

The value is positive here, so this process is not spontaneous – ice does not melt at −5 °C. The reverse reaction, the freezing of water, will have $\Delta G^{\ominus} = -0.111$ kJ mol^{-1}, so that will be spontaneous at −5 °C – water freezes at −5 °C.

If we imagine heating up some ice from −5 °C, the value of $\Delta G^{\ominus}$ for the process $H_2O(s) \rightarrow H_2O(l)$ will become less and less positive because $\Delta S^{\ominus}$ is positive, and when we multiply it by a higher temperature (remember that T must be in K), $-T\Delta S^{\ominus}$ becomes more negative. The variation of $\Delta G^{\ominus}$ with temperature is plotted in Figure 15.2.

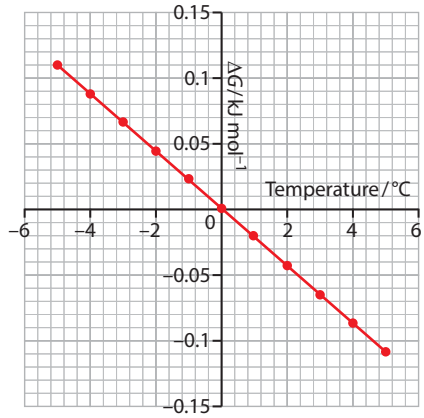

Figure 15.2: The melting of ice becomes spontaneous as the temperature is raised above 0 °C.

It can be seen that $\Delta G^{\ominus}$ for the melting of ice is positive, and therefore not spontaneous, below 0 °C, but negative, and therefore spontaneous, above 0 °C. The temperature at which $\Delta G^{\ominus} = 0$ represents the boundary between the process being spontaneous and non-spontaneous. When $\Delta G^{\ominus} = 0$, the reaction has no tendency to go in either direction – it is in a state of equilibrium. Here, this represents the melting point of ice: at 0 °C ice and water are in equilibrium.

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WORKED EXAMPLE 15.3

Consider the decomposition of magnesium nitrate:

$2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

	$Mg(NO_3)_2(s)$	$MgO(s)$	$NO_2(g)$	$O_2(g)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	–790	–602	34	0
$S^\ominus$/J K^{-1} mol^{-1}	164	27	240	205

a Use the data in the table to work out $\Delta G^\ominus$ and, hence, whether or not the reaction will be spontaneous at 25.00 °C.

b As the temperature is increased from absolute zero, work out the temperature (in °C) at which the reaction first becomes spontaneous.

Answer

a To calculate the enthalpy change, we have been given $\Delta H_f^\ominus$. In Chapter 13, we saw the equation

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

$\Delta H^\ominus = [(2 \times -602) + (4 \times 34) + 0] - [(2 \times -790)]$

$= 512 \text{ kJ mol}^{-1}$

To calculate the entropy change, we use

$\Delta S^\ominus = \Sigma S^\ominus_{\text{products}} - \Sigma S^\ominus_{\text{reactants}}$

$\Delta S^\ominus = [(2 \times 27) + (4 \times 240) + 205] - [(2 \times 164)]$

$= 891 \text{ J K}^{-1} \text{ mol}^{-1}$

To work out $\Delta G^\ominus$, we use the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

The temperature must, however, be in K and, therefore, we have

$T = 25.00 + 273.15 = 298.15 \text{ K}$

$\Delta G^\ominus = 512 - 298.15 \times (891 \div 1000) = 246 \text{ kJ mol}^{-1}$

Remember: $\Delta S^\ominus$ is divided by 1000 to convert it into kJ.

At 298.15 K, the reaction is *not* spontaneous because $\Delta G^\ominus$ is positive.

b Because $\Delta S^\ominus$ is positive, as the temperature is increased, $T\Delta S^\ominus$ will become larger until it is eventually bigger than $\Delta H^\ominus$, and the reaction will become spontaneous.

We can estimate the temperature at which this reaction is going to become spontaneous. As the temperature is increased, $\Delta G^\ominus$ will become less and less positive, until it becomes zero, and then it will be negative. So, if we work out the temperature at which $\Delta G^\ominus$ becomes zero, the reaction will be spontaneous at any temperature above that.

Using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$0 = 512 - T \times (891 \div 1000)$

Rearranging the equation gives $T = 575 \text{ K}$

This means that this reaction is likely to become spontaneous above 575 K, that is, 302 °C.

This calculation is only approximate because the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ change with temperature, and we have used the values for 298.15 K.

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EXAM TIP

The temperature (in K) at which a reaction first becomes spontaneous can be calculated using the following equation:

$T = \Delta H^{\ominus}/\Delta S^{\ominus}$

but you must remember to convert $\Delta H^{\ominus}$ to J or $\Delta S^{\ominus}$ to kJ.

The effect of changing temperature on the spontaneity of a reaction

We will use the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ to explain the effect of temperature on the value of $\Delta G^{\ominus}$ and, hence, on the spontaneity of a reaction. We will consider some different combinations.

$\Delta H^{\ominus}$ is positive and $\Delta S^{\ominus}$ is positive

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

If $T\Delta S^{\ominus}$ is smaller than $\Delta H^{\ominus}$, $\Delta G^{\ominus}$ will be positive and the reaction will not be spontaneous. So, a reaction like this is non-spontaneous at low temperatures. As the temperature is raised, $T\Delta S^{\ominus}$ becomes larger and, because this is being subtracted from $\Delta H^{\ominus}$, $\Delta G^{\ominus}$ becomes less positive/more negative – the reaction becomes more spontaneous. Eventually, when $T\Delta S^{\ominus}$ becomes greater than $\Delta H^{\ominus}$, $\Delta G^{\ominus}$ will be negative and the reaction will be spontaneous.

$\Delta H^{\ominus}$ is positive and $\Delta S^{\ominus}$ is negative

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Because $\Delta S^{\ominus}$ is negative, $-T\Delta S^{\ominus}$ in the equation is positive. $\Delta H^{\ominus}$ is also positive, so overall $\Delta G^{\ominus}$ is positive, and the reaction is not spontaneous. Because both $\Delta H^{\ominus}$ and $-T\Delta S^{\ominus}$ are positive, this reaction is non-spontaneous at all temperatures; $\Delta G^{\ominus}$ can never be negative.

Both reactions considered so far have been endothermic.

KEY POINT

An endothermic reaction can only occur spontaneously if it involves an increase in entropy (and the temperature is sufficiently high).

An exothermic reaction ($\Delta H^{\ominus}$ negative) will always be spontaneous at some temperature.

$\Delta H^{\ominus}$ is negative and $\Delta S^{\ominus}$ is positive

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

The reaction involves an increase in entropy ($\Delta S^{\ominus}$ positive) so $-T\Delta S^{\ominus}$ will be negative. Because $\Delta H^{\ominus}$ is also negative, $\Delta G^{\ominus}$ will always be negative, and the reaction will be spontaneous at all temperatures.

$\Delta H^{\ominus}$ is negative and $\Delta S^{\ominus}$ is negative

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

The reaction involves a decrease in entropy ($\Delta S^{\ominus}$ negative), and so, will be spontaneous at low temperatures, when the absolute value of $\Delta H^{\ominus}$ (negative) is greater than that of $-T\Delta S^{\ominus}$ (positive). It will, however, become less spontaneous as the temperature increases (because $-T\Delta S^{\ominus}$ is positive and becomes more positive as the temperature increases). At higher temperatures, the absolute value of $-T\Delta S^{\ominus}$ (positive) will be greater than that of $\Delta H^{\ominus}$ (negative) and, therefore, $\Delta G^{\ominus}$ will be positive, and the reaction will be non-spontaneous.

Table 15.3 gives an overview of this discussion.

KEY POINT

Reactions in which $\Delta S^{\ominus}$ is positive become more spontaneous as temperature increases, but reactions in which $\Delta S^{\ominus}$ is negative become less spontaneous as temperature increases.

$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$-T\Delta S^{\ominus}$	$\Delta G^{\ominus}$	Spontaneous?
negative	positive	negative	negative	at all temperatures
positive	positive	negative	becomes more negative as temperature increases	becomes more spontaneous as temperature increases
negative	negative	positive	becomes less negative as temperature increases	becomes less spontaneous as temperature increases
positive	negative	positive	positive	never

Table 15.3: Determining whether a reaction will be spontaneous.

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Non-spontaneous reactions

If a reaction is non-spontaneous, it does not mean that it can never happen – it just means that it will not happen without external influence. For instance, in the previous examples, we can change the temperature to make the reaction spontaneous.

Let us go back to the reaction discussed right at the beginning of the chapter:

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta G^\ominus = +474 \text{ kJ mol}^{-1}$

This reaction is not spontaneous at 25 °C, but it can be made to happen at this temperature by the continuous passage of an electric current (electrolysis).

TEST YOUR UNDERSTANDING

6 Consider the decomposition of calcium carbonate:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$\Delta H^\ominus = +179 \text{ kJ mol}^{-1}$

$\Delta S^\ominus = +160 \text{ J K}^{-1} \text{ mol}^{-1}$

Assuming that ΔH and ΔS do not change with temperature, calculate the temperature, in K, above which this reaction will become spontaneous.

7 Consider the reaction:

$2CoO(s) + C(s) \rightarrow 2Co(s) + CO_2(g)$

$\Delta H^\ominus = +82 \text{ kJ mol}^{-1}$

$\Delta S^\ominus = +108 \text{ J K}^{-1} \text{ mol}^{-1}$

Assuming that ΔH and ΔS do not change with temperature, calculate the temperature, in K, above which this reaction will become spontaneous.

8 Consider the decomposition of potassium nitrate(V):

$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

$\Delta H^\ominus = +250 \text{ kJ mol}^{-1}$

$\Delta S^\ominus = +243 \text{ J K}^{-1} \text{ mol}^{-1}$

Assuming that ΔH and ΔS do not change with temperature, calculate the temperature, in K, above which this reaction will become spontaneous.

9 Consider the decomposition of lead(II) nitrate:

$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$

$\Delta H^\ominus = +598 \text{ kJ mol}^{-1}$

$\Delta G^\ominus = +333 \text{ kJ mol}^{-1}$

a Work out the value for ΔS at 298.15 K.

b Assuming that ΔH and ΔS do not change with temperature, calculate the temperature, in °C, above which this reaction will become spontaneous.

10 Consider the process:

$Br_2(l) \rightarrow Br_2(g)$

$\Delta H^\ominus = +30.9 \text{ kJ mol}^{-1}$

$\Delta S^\ominus = +93.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Assuming that ΔH and ΔS do not change with temperature, determine the boiling point of bromine in °C.

11 For each of the following reactions, predict whether it becomes more or less spontaneous as temperature increases:

a $N_2O_4(g) \rightarrow 2NO_2(g)$

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

c $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

d $2AgNO_3(s) \rightarrow 2Ag(s) + 2NO_2(s) + O_2(g)$.

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SCIENCE IN CONTEXT

A diamond is not forever

The advertising slogan 'a diamond is forever' was first used by The De Beers group in the late 1940s and had a huge influence on social behaviour, virtually creating the idea of a diamond engagement ring being an essential part of the marriage ritual. This is probably one of the most famous advertising slogans of all time, but unfortunately it is not true – diamonds are not forever (Figure 15.3).

Figure 15.3: A diamond is not forever.

Diamond and graphite are both allotropes of carbon. Consider the following process:

$C_{diamond} \rightarrow C_{graphite}$

$\Delta H^{\ominus} = -1.9$ kJ mol^{-1}

$\Delta S^{\ominus} = +3.3$ J K^{-1} mol^{-1}

We can calculate then that $\Delta G^{\ominus} = -2.9$ kJ mol^{-1}; therefore, this process is spontaneous at around room temperature, so that diamonds will spontaneously become graphite. Also, because $\Delta H^{\ominus}$ is negative and $\Delta S^{\ominus}$ is positive, it is spontaneous at all temperatures.

Similarly, if we look at the following process:

$C_{diamond} + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^{\ominus} = -397$ kJ mol^{-1}

Once again, it is looking bad for diamonds – they will spontaneously react with the oxygen in the air to form carbon dioxide.

However, if you are lucky enough to possess any diamonds, you have probably not noticed any change in them over the last week, month, year… and the reason for this is that these reactions are extremely slow at room temperature (the activation energy is very high) – we say that diamond is thermodynamically unstable but kinetically stable with regard to graphite and carbon dioxide at room temperature. However, if you heat diamond, the reaction becomes much more rapid and at a temperature of above about 2000 °C, in the absence of air, you would probably notice your diamond becoming graphite fairly rapidly.

It is not all bad news, and graphite can be made to turn into diamond if we increase the pressure (diamond is more dense than graphite); however, this is not going to be achieved by just standing on a pencil; the pressures required are many thousands of times atmospheric pressure. The first synthetic diamonds were made in the 1950s by subjecting graphite to very high pressure and temperatures and, although these were not gem-quality diamonds, they could be used in cutting tools. Since then, other methods of making diamonds have also been developed, and the first gem-quality synthetic diamonds were made in the 1970s.

15.3 Gibbs energy and equilibrium

The process for the production of ammonia involves a reversible reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta G^{\ominus} = -33$ kJ mol^{-1}

According to the previous discussion, at 298.15 K, this reaction will proceed from left to right – nitrogen and hydrogen will spontaneously become ammonia – but the reverse reaction ($\Delta G^{\ominus} = +33$ kJ mol^{-1}) will not occur spontaneously. If we start with nitrogen and hydrogen in a closed container, they will react together spontaneously to form an equilibrium mixture in which nitrogen, hydrogen and ammonia are present. However, what we also find is that, if we start with just ammonia

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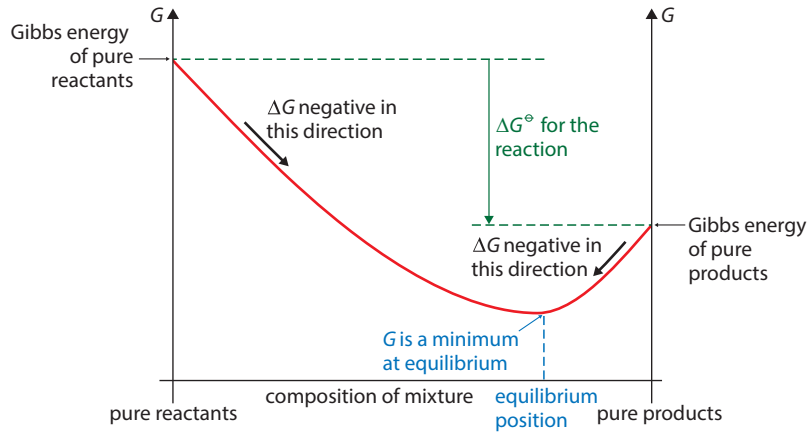

Figure 15.4: Variation in the Gibbs energy for a reaction for which $\Delta G^{\ominus}$ is negative overall.

in a sealed container, some will also spontaneously react to form nitrogen and hydrogen and, again, all three will be present in the equilibrium mixture.

This does not, however, violate the second law of thermodynamics because the value of $\Delta G^{\ominus}$ that was given is for complete conversion of one mole of nitrogen and three moles of hydrogen to two moles of ammonia. The equilibrium mixture, however, always has a lower Gibbs energy than either the pure reactants or the pure products; therefore, the conversion of either reactants or products into the equilibrium mixture results in a process in which ΔG is negative and a spontaneous process (Figure 15.4).

The overall Gibbs energy of a system [note that we are looking at the Gibbs energy (G) here and not the change in Gibbs energy (ΔG)] depends on how much of each substance is present – the equilibrium mixture represents the composition that gives the minimum value of the Gibbs energy.

The equation that relates the Gibbs energy change to the composition of the reaction mixture is

$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

When using this equation, it is important to remember that ΔG and $\Delta G^{\ominus}$ must be in J mol^{-1} (because R is in J K^{-1} mol^{-1}) and T must be in K.

Q is called the **reaction quotient**, and more details about what it means and calculations involving it will be explained in Chapter 18.

Consider a simple system, where we convert imaginary substance A into imaginary substance B (not boron!):

$$A \rightleftharpoons B \qquad \Delta G^{\ominus} = -5 \text{ kJ mol}^{-1}$$

$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

$\Delta G^{\ominus}$ represents the difference in Gibbs energy between molar quantities as in the chemical equation – in this case, the difference in Gibbs energy between 1 mol A and 1 mol B.

ΔG represents the difference in Gibbs energy between however much A is present in the reaction mixture at any time and however much B is present, that is, $\Delta G = G_B - G_A$, where G_B is the Gibbs energy of the amount of B present.

Let us imagine that we have a sealed reaction vessel of volume 1 dm^3 that contains 1 mol A and 1 mol B at 298.15 K. This means that the concentration of A is 1 mol dm^{-3} and that of B is 1 mol dm^{-3} (concentration = amount in mol ÷ volume).

The expression for Q for this reaction is given by $Q = \dfrac{[B]}{[A]}$

$$Q = \frac{[B]}{[A]} = \frac{1}{1} = 1$$

$$\ln Q = \ln 1 = 0$$

$$\Delta G = \Delta G^{\ominus} + RT\ln Q = -5000 + 8.31 \times 298.15 \times 0$$
$$= -5000 \text{ J mol}^{-1}$$

Remember, $\Delta G^{\ominus}$ must be in J mol^{-1}.

So, when the concentrations of A and B are both 1 mol dm^{-3}, $\Delta G = -5000$ J mol^{-1}, and the negative sign indicates that the reaction will proceed spontaneously in the direction as shown, that is, from A to B. So, if the reaction proceeds in that direction and 0.2 mol A is converted into B, we have 0.8 mol A and 1.2 mol B.

This means that the concentration of A is 0.8 mol dm^{-3} and that of B is 1.2 mol dm^{-3}.

$$Q = \frac{[B]}{[A]} = \frac{1.2}{0.8} = 1.5$$

$$\ln Q = \ln 1.5 = 0.405$$

$$\Delta G = \Delta G^{\ominus} + RT\ln Q = -5000 + 8.31 \times 298.15 \times 0.405$$
$$= -4000 \text{ J mol}^{-1}$$

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The difference in Gibbs energy between 0.8 mol A and 1.2 mol B is, thus, smaller than that between 1 mol A and 1 mol B; however, the sign of ΔG is still negative, so the reaction still spontaneously proceeds from A to B. If we do the same calculation when [A] = 0.6 mol dm^{-3} and [B] = 1.4 mol dm^{-3}, we get $\Delta G = -2900$ J mol^{-1}, so the value is continuing to get numerically smaller but is still negative, so the spontaneous reaction is still from A to B. Because the difference between the Gibbs energy of the amount of A present and the amount of B present is getting numerically smaller, if A keeps spontaneously being converted into B, there is going to come a point when $\Delta G = 0$. We can work out that, for this reaction, this will come when there are 0.23 mol A and 1.77 mol B present. The Gibbs energy of this amount of A and this amount of B are the same, and so, $\Delta G = 0$. This means that there is no tendency for the reaction to proceed to the left or the right – the system has reached a state of equilibrium, where the concentrations stay constant.

KEY POINT

As a system moves towards equilibrium, ΔG becomes less and less negative, until, at equilibrium, it is equal to zero.

If we imagine going past the equilibrium point, say to [A] = 0.2 mol dm^{-3} and [B] = 1.8 mol dm^{-3}, ΔG comes out as +441 J mol^{-1}. The positive value means that the reverse reaction, from B to A, is spontaneous, so the reaction would proceed spontaneously in that direction until the point at which $\Delta G = 0$ (equilibrium).

KEY POINT

When the system is at equilibrium, the Gibbs energy of the amount of reactants present is the same as that of the amount of products present, and so, ΔG is zero, and there is no tendency to spontaneously move in either direction away from equilibrium. Any shift away from the equilibrium position results in an increase in G and, therefore, a process for which ΔG is positive, i.e., non-spontaneous.

Since $\Delta G = 0$ at equilibrium, we get a new equation at that point:

$$\Delta G^{\ominus} = -RT \ln K$$

where K is the equilibrium constant. The expression for the equilibrium constant is the same as that of Q, except all the concentrations are equilibrium concentrations. The equilibrium constant and calculations involving this equation will be discussed in Chapter 18.

Link

The connection between the sign of $\Delta G^{\ominus}$ and the position of equilibrium

The value and sign of $\Delta G^{\ominus}$ give us information about the position of equilibrium (the relative amounts of reactants and products present at equilibrium). If $\Delta G^{\ominus}$ is negative, this indicates that pure products have a lower Gibbs energy than pure reactants, and then the position of equilibrium will lie closer to the products than the reactants (Figure 15.5**a**).

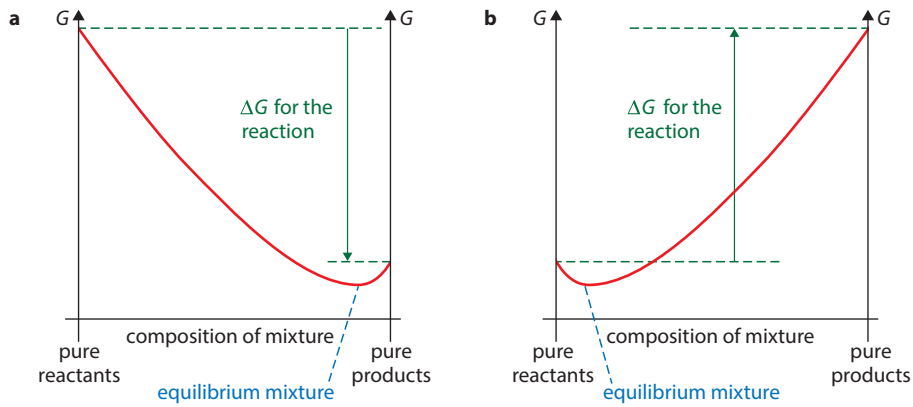

Figure 15.5: a $\Delta G^{\ominus}$ is negative and the position of equilibrium lies closer to the products; **b** $\Delta G^{\ominus}$ is positive and the position of equilibrium lies closer to the reactants.

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The more negative the value of $\Delta G^{\ominus}$, the closer the position of equilibrium lies towards the products. If $\Delta G^{\ominus}$ is numerically very large and negative, then the position of equilibrium lies very close to pure products. If $\Delta G^{\ominus}$ is positive, then the position of equilibrium lies more towards the reactants (Figure 15.5**b**) – the more positive the value, the closer the position of equilibrium lies towards pure reactants.

A value of $\Delta G^{\ominus}$ of -30 kJ mol^{-1} (or more negative) indicates that a reaction essentially goes to completion at around room temperature; one of $+30$ kJ mol^{-1} (or more positive) indicates a reaction that does not really proceed towards products at all. The relationship between equilibrium constants and Gibbs energy is discussed again in Chapter 18.

TEST YOUR UNDERSTANDING

In each of the questions, we will be looking at a reaction of the form: X $\rightleftharpoons$ Z for which the expression for Q is $Q = \frac{[Z]}{[X]}$

12 a Consider the reaction: X $\rightleftharpoons$ Z
$\Delta G^{\ominus} = -3.0$ kJ mol^{-1}

i Calculate ΔG when [X] = 2.0 mol dm^{-3} and [Z] = 1.0 mol dm^{-3} and the temperature is 298.15 K.

ii Calculate ΔG when [X] = 1.0 mol dm^{-3} and [Z] = 2.0 mol dm^{-3} and the temperature is 298.15 K.

In each case, indicate the direction in which the system will move towards equilibrium.

c Consider the reaction: C $\rightleftharpoons$ D
$\Delta G^{\ominus} = -5.0$ kJ mol^{-1}

i Calculate ΔG when [C] = 0.020 mol dm^{-3} and [D] = 4.0×10^{-4} mol dm^{-3} and the temperature is 298.15 K.

ii Calculate ΔG when [C] = 0.050 mol dm^{-3} and [D] = 0.10 mol dm^{-3} and the temperature is 298.15 K.

In each case, indicate the direction in which the system will move towards equilibrium.

b Consider the reaction: A $\rightleftharpoons$ B
$\Delta G^{\ominus} = +2.0$ kJ mol^{-1}

i Calculate ΔG when [A] = 0.50 mol dm^{-3} and [B] = 10.0 mol dm^{-3} and the temperature is 27.00 °C.

ii Calculate ΔG when [A] = 0.10 mol dm^{-3} and [B] = 0.010 mol dm^{-3} and the temperature is 50.00 °C.

In each case, indicate the direction in which the system will move towards equilibrium.

d Consider the reaction: E $\rightleftharpoons$ F
$\Delta G^{\ominus} = +20.0$ kJ mol^{-1}

i Calculate ΔG when [E] = 5.0×10^{-3} mol dm^{-3} and [F] = 0.80 mol dm^{-3} and the temperature is 20.00 °C.

ii Calculate ΔG when [E] = 0.10 mol dm^{-3} and [F] = 5.0×10^{-4} mol dm^{-3} and the temperature is 23.00 °C.

In each case, indicate the direction in which the system will move towards equilibrium.

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the term entropy	15.1			
predict whether a chemical/physical process involves an increase or decrease in entropy	15.1			
calculate standard entropy changes	15.1			
explain the term *change in Gibbs energy*	15.2			
calculate the change in Gibbs energy	15.2			
relate the change in Gibbs energy to the spontaneity of a reaction	15.2			
explain the changes in Gibbs energy as a system reaches equilibrium	15.3			
calculate Gibbs energy changes for systems approaching equilibrium and at equilibrium.	15.3			

REFLECTION

Try to assess your understanding of this chapter. Which statement best describes your level?

- I understand everything and am able to do all the calculations.
- I am not sure that I understand everything, but I can do the calculations.
- I do not really understand the material and find the questions very difficult.

What can you do to bring your understanding to the next level?

Try explaining entropy changes to another student. Does this highlight gaps in your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Unit 5

How much, how fast, how far?

INTRODUCTION

The title of this unit is 'How much, how fast, how far?' All these are questions that a chemist working in industry, for example, as a chemical engineer, would ask about a particular process. The chemical industry is vast, contributes trillions of dollars to the global economy and employs millions of people. It is not, however, a simple task to define what is meant by the chemical industry; it is usually taken to mean industry producing basic chemicals such as sulfuric acid, ammonia and sodium hydroxide, manufacturing agrochemicals such as fertilisers and pesticides, manufacture of plastics and artificial fibres, manufacture of soaps, detergents, dyes, explosives… the list goes on.

The pharmaceutical industry, producing medicines and drugs, is not usually classified as part of the chemical industry, but this also contributes over a trillion US dollars to the global economy. Other major industries having chemical reactions at their heart, but not usually classified as chemical industries, include the production of iron and steel or cement/concrete. Overall, putting everything together, industries using chemical reactions to manufacture substances contribute well over 10% of the global gross domestic product. An understanding of the extent (how much product is produced) and speed of chemical reactions is essential in all these industries and, although 'how much' is not meant in this context in this unit, it is critical to how much money is made.

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Chapter 16

How much? The amount of chemical change

LEARNING OBJECTIVES

In this chapter you will:

- understand how to write chemical equations
- learn how to use the mole ratio from a chemical equation in calculations
- understand how to work out which are the limiting reactants
- understand how to calculate theoretical and percentage yield
- understand the term atom economy.

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GUIDING QUESTIONS

- What does a chemical equation mean?
- How can chemical equations be used to work out reacting quantities?
- How can chemical equations be used to work out how much is produced in a reaction?

Introduction

Chemistry is often likened to cookery; in both, we make things by combining ingredients and in both we follow a recipe. You would not make a cake by adding random amounts of sugar, butter, eggs and flour into a bowl and hoping it turns out alright, and it is the same in chemistry: we usually use carefully measured out amounts of reactants. We do not, however, necessarily need a written list of masses/volumes of chemicals; the recipe is summarised in a chemical equation.

16.1 The meaning of chemical equations

Chemical equations show the ratio in which chemical species (atoms, molecules, compounds, ions…) combine with each other and the relationship to the amounts of products formed.

Consider the equation: $2C + O_2 \rightarrow 2CO$

We could show this equation diagrammatically, as in Figure 16.1 and, if we were to describe the reaction in words, we would say 'two carbon atoms combine with one oxygen molecule to form two molecules of carbon monoxide'.

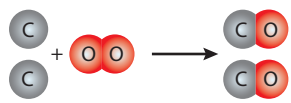

Figure 16.1: Two carbon atoms react with one oxygen molecule to form two molecules of carbon monoxide.

The equation tells us the *ratio* in which carbon and oxygen combine and the ratio to the number of molecules of carbon monoxide formed. This ratio is fixed (for this reaction) – the number of molecules of oxygen is always half the number of carbon atoms, and the number of carbon monoxide molecules produced is the same as the number of carbon atoms. So, if we started with four carbon atoms, they would react with two oxygen molecules to form four molecules of carbon monoxide (Figure 16.2) and, if we started with eight carbon atoms, we would produce eight molecules of carbon monoxide (Figure 16.3).

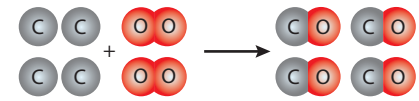

Figure 16.2: Four carbon atoms react with two oxygen molecules to form four molecules of carbon monoxide.

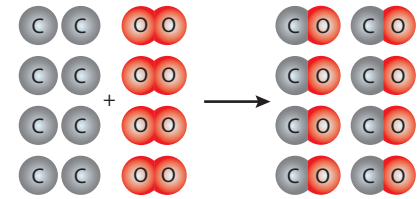

Figure 16.3: Eight carbon atoms react with four oxygen molecules to form eight molecules of carbon monoxide.

If we imagine a very large number of C atoms, e.g., 1.204×10^{24} atoms, these would combine with 6.02×10^{23} O_2 molecules (half as many oxygen molecules) to form 1.204×10^{24} CO molecules. But 1.204×10^{24} is the number of particles in 2 mol and, therefore, we can say: 2 mol C reacts with 1 mol O_2 to form 2 mol CO. A chemical equation is usually interpreted as involving molar quantities, and the term *mole ratio* is used to describe the relationship between the numbers of moles of the various substances in a reaction. This is given by the coefficients (large numbers) in the equation, so carbon and oxygen combine in a mole ratio of 2:1 (see the section on 'Chemical equations and mole ratios').

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KEY POINT

Mass is conserved in all chemical reactions.

If a reaction involves 5.00 g of one substance reacting with 10.00 g of another substance in a closed container (nothing can be added or can escape), then, at the end of the reaction, there will still be exactly 15.00 g of matter present. This 15.00 g may be made up of just products or products and some reactants that have not fully reacted, but the key point is that there will no more and no less than 15.00 g present.

Balancing equations

A chemical reaction involves atoms joining together in different ways and electrons redistributing themselves between the atoms, but no atoms or electrons are created or destroyed in the reaction and no atoms change into an atom of a different element. This means that there must be the same number of atoms of each type at the end of a reaction as at the beginning.

When a chemical reaction is represented by a chemical equation, there must be the same number and type of atoms on either side of the equation, representing the same number of atoms before and after the reaction has taken place. For example:

$C_3H_8 + 5O_2$ reactants	→	$3CO_2 + 4H_2O$ products
C 3	atoms	C 3
H 8		H 8
O 10		O 10

So, this equation is balanced – before the reaction occurred (the left-hand side) there were 3 C atoms, 8 H atoms and 10 O atoms present; once the reaction had occurred (the right-hand side), there are still exactly the same number of atoms; they are just joined together differently.

It is important to realise that only coefficients (large numbers in front of the substances) may be added to balance a chemical equation. The chemical formula for water is H_2O, and this cannot be changed in any way when balancing an equation. If, for instance, the formula is changed to H_2O_2, then it represents a completely different chemical substance, hydrogen peroxide.

WORKED EXAMPLE 16.1

Balance the following equation:

$\ldots N_2(g) + \ldots H_2(g) \rightarrow \ldots NH_3(g)$

and work out the sum of the coefficients in the equation.

Answer

In the equation, there are two N atoms and two H atoms on the left-hand side of the equation, but one N atom and three H atoms on the right-hand side. It is not possible for two N atoms to react with two H atoms to produce one N atom and three H atoms; therefore, this equation is not balanced.

It can be balanced as:

$$\ldots N_2 + 3H_2 \rightarrow 2NH_3$$

atoms: 2 N 6 H 2N 6 H

This equation is now balanced because there is the same number of each type of atom on both sides of the equation.

The sum of the coefficients in this equation is $1 + 3 + 2 = 6$. The coefficient of N_2 is 1, although we do not usually write this in an equation.

EXAM TIP

You may be asked about the *sum of the coefficients* in a multiple-choice question. It is important not to forget that, if there is no number in front of a substance, the coefficient is one.

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WORKED EXAMPLE 16.2

Balance the following equation:

… $C_4H_{10}(g)$ + … $O_2(g)$ → … $CO_2(g)$ + … $H_2O(l)$

Answer

We looked at equations similar to this in Chapter 14.

Compounds are balanced first, then elements:

… $C_4H_{10}(g)$ + … $O_2(g)$ → $4CO_2(g)$ + $5H_2O(l)$

There are 2 oxygen atoms on the left-hand side of the equation, and O_2 needs to be multiplied by 6.5 to give 13 oxygen atoms, which is the number of oxygen atoms on the other side [(4 × 2) + (5 × 1)]:

… $C_4H_{10}(g)$ + $6.5O_2(g)$ → $4CO_2(g)$ + $5H_2O(l)$

The equation is balanced as shown, but it looks much neater when balanced with whole numbers. To achieve this, all the coefficients are multiplied by two:

$2C_4H_{10}(g)$ + $13O_2(g)$ → $8CO_2(g)$ + $10H_2O(l)$

TEST YOUR UNDERSTANDING

1 Balance the following equations:

a $NO + O_2 \rightarrow NO_2$

b $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$

c $CaCO_3 + HCl \rightarrow CaCl_2 + CO_2 + H_2O$

d $C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$

e $WO_3 + H_2 \rightarrow W + H_2O$

f $H_2O_2 \rightarrow O_2 + H_2O$

g $CrO_3 \rightarrow Cr_2O_3 + O_2$

h $Al_4C_3 + H_2O \rightarrow CH_4 + Al_2O_3$

i $HI + H_2SO_4 \rightarrow H_2S + H_2O + I_2$

j $PH_3 + O_2 \rightarrow P_4O_{10} + H_2O$

Ionic equations

Consider the reaction between a chlorine solution and a solution of potassium bromide, that we met in Chapter 10:

$2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$

In a solution of an ionic salt, the ions are separate from each other, so KBr(aq) contains separate $K^+(aq)$ and $Br^-(aq)$ ions, and we could re-write the above equation as:

$2K^+(aq) + 2Br^-(aq) + Cl_2(aq) \rightarrow 2K^+(aq) + 2Cl^-(aq) + Br_2(aq)$

We can see that there are two $K^+(aq)$ ions on the left and the same number on the right; these have not changed at all during the reaction and are sometimes called *spectator ions*. We often want to just concentrate on the species that actually react and can show this in an ionic equation that leaves out the spectator ions:

$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

It is important to remember, when balancing ionic equations, that the atoms *and the charges* must be the same on both sides. For, example, consider the following equation:

$MnO_4^-(aq) + 8H^+(aq) + Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O(l) + Fe^{3+}$

Although there is the same number of each atom on both sides, the equation is not balanced because the total charge on the left-hand side is 9+ but 5+ on the right-hand side. This would indicate that four electrons just appeared out of nowhere when the reactants were converted into the products, which cannot be the case.

The balanced equation is:

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}$

The total charge is now 17+ on each side.

Link

We will consider how to balance redox equations such as this in Chapter 20.

Half equations are used to show the individual processes of oxidation and reduction in a redox reaction. Half-equations differ from other equations in that they contain electrons. The half equations for the reaction shown above would be:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

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

Half-equations also balance in terms of the atoms present and the total charge on each side.

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KEY POINT

Chemical equations tell us the mole ratios in which the reactants combine and the relationship to the number of moles of products formed.

Chemical equations and mole ratios

Although it is easier to talk about atoms, molecules and ions when balancing equations, when interpreting equations, we should refer to molar amounts.

Consider the equation:

$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$

In this reaction, 2 mol iron atoms reacts with 3 mol chlorine molecules to form 2 mol iron(III) chloride units (not molecules because it is not covalent). The ratio between the number of moles of iron atoms and chlorine molecules that react is fixed as 2:3, that is, the number of moles of chlorine molecules is always 1.5 times the number of moles of iron atoms, and the number of moles of iron(III) chloride formed is always the same as the number of moles of iron that reacted. So, if we started with 0.100 mol Fe, it would react with 0.150 mol chlorine and 0.100 mol $FeCl_3$ would be formed. If we started with 0.300 mol of chlorine, it would react exactly with 0.200 mol Fe and 0.200 mol $FeCl_3$ would be produced.

Moles

We learnt how to work out the amount of substance (in mol) in Chapters 4 and 5. This is summarised in the triangles in Figure 16.4.

Before working through the rest of the chapter, it would be good to check that you are confident with converting between masses, volumes, concentrations and amount (in mol) by attempting the Test Your Understanding questions on the next page.

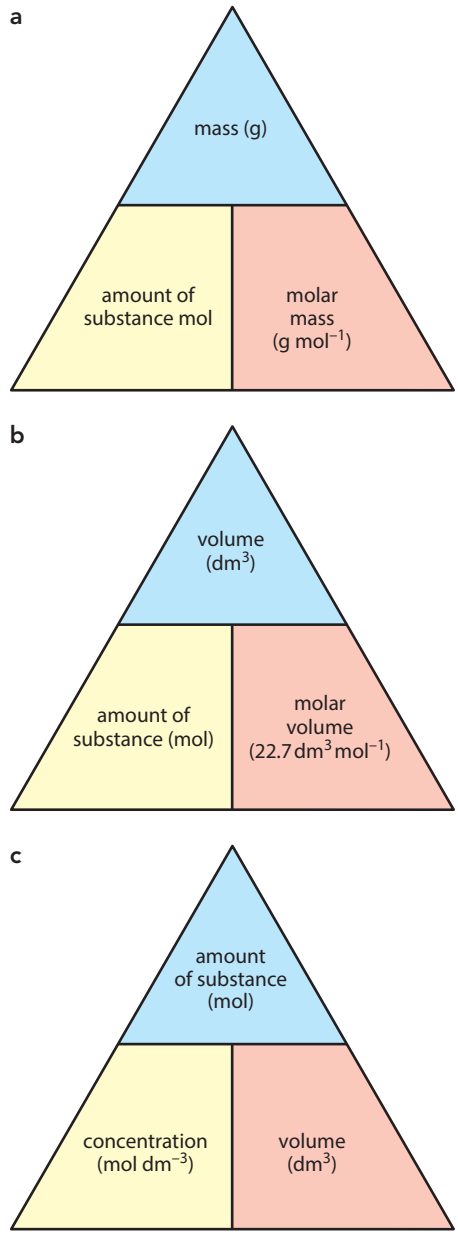

Figure 16.4: a The relationship between the mass of a substance, the amount (in mol) and molar mass. **b** The relationship between the amount of a gas and its volume at STP. **c** The relationship between concentration, amount and volume of solution.

Solving problems involving mole ratios

There are three main steps in moles calculations.

1 Work out the amount (in mol) of anything you can.

2 Use the mole ratio from the balanced chemical (stoichiometric) equation to work out the amount (in mol) of the quantity you require.

3 Convert the amount (in mol) into the required quantity – volume, mass, etc.

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TEST YOUR UNDERSTANDING

2 For each of the following, calculate the amount in mol. Assume that all gases behave as ideal gases and that all volumes are measured at STP.

a 2.00 g Fe
b 0.400 g NaOH
c 1.20 kg CO_2
d 5.00 g $CuSO_4 \cdot 5H_2O$
e 10.0 dm^3 $H_2(g)$
f 500 cm^3 O_2
g 30.0 cm^3 CO_2.

3 Calculate the amount in mol of solute present in

a 25.0 cm^3 of 0.200 mol dm^{-3} HCl(aq)
b 28.2 cm^3 of 0.100 mol dm^{-3} NaOH(aq)
c 32.0 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$(aq)
d 500 cm^3 of 1.00 mol dm^{-3} H_2SO_4(aq).

4 Convert the following amounts to masses in g:

a 0.600 mol CH_4
b 2.30 mol H_2O
c 0.165 mol Na_2SO_4
d 0.830 mol $Na_2S_2O_3 \cdot 5H_2O$.

5 Convert the following amounts in mol to volumes in cm^3 at STP:

a 0.100 mol C_2H_4(g)
b 2.40×10^{-3} mol CO_2(g)
c 0.0750 mol H_2(g)
d 0.820 mol O_2(g).

6 Work out the concentrations of the following solutions in mol dm^{-3}:

a 4.00 g of NaOH was used to make 250 cm^3 of solution
b 10.0 g of $MgCl_2$ was used to make 500 cm^3 of solution
c 0.800 g of $KMnO_4$ was used to make 100.0 cm^3 of solution
d 0.250 g of $CuSO_4 \cdot 5H_2O$ was used to make 10.0 cm^3 of solution.

WORKED EXAMPLE 16.3

Consider the reaction of sodium with oxygen:

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

a What mass of sodium reacts exactly with 3.20 g of oxygen?

b What mass of Na_2O is produced?

Answer

a

Step 1: the mass of oxygen is given, so the amount in mol of oxygen can be worked out:

$$\text{amount in mol of oxygen} = \frac{3.20}{32.00} = 0.100 \text{ mol}$$

Note: the mass of oxygen was given to three significant figures, so all subsequent answers are also given to three significant figures.

Step 2: the coefficients in the chemical (stoichiometric) equation tell us that 1 mol O_2 reacts with 4 mol sodium. Therefore, 0.100 mol O_2 reacts with 4×0.100 mol sodium, i.e., 0.400 mol sodium.

Step 3: convert the amount in mol to the required quantity, mass in this case:

mass of sodium $= 0.400 \times 22.99 = 9.20$ g

Note: the mass of sodium is worked out by multiplying the mass of one mole by the amount in mol – the amount in mol is not multiplied by the mass of 4Na – the four was already taken into account when 0.100 mol was multiplied by four to give the amount in mol of sodium.

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b From the coefficients in the equation, we know that 1 mol O_2 reacts with 4 mol sodium to produce 2 mol Na_2O. Therefore, 0.100 mol O_2 reacts with 0.400 mol sodium to give 2×0.100 mol Na_2O, i.e., 0.200 mol Na_2O.

molar mass of $Na_2O = 61.98$ g mol^{-1}

So, mass of $Na_2O = 0.200 \times 61.98 = 12.4$ g

We could also use the idea of conservation of mass to work out the mass of sodium oxide produced. The key point in the question is that this is an *exact* reaction, so that all the sodium and oxygen will be used up, therefore:

mass of Na_2O = mass of O_2 + mass of sodium

KEY POINT

Excess of a reagent means that there is more than enough to react, so you can ignore this when calculating the amount of product formed.

WORKED EXAMPLE 16.4

Consider the equation:

$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3H_2O(l) + 3Cu(s)$

If 186 cm^3 (measured at STP) of ammonia (NH_3) is reacted with excess CuO, calculate the mass of copper produced.

Answer

CuO is in excess – this means that there is more than enough to react with all the NH_3, so we do not need to worry about the amount of CuO.

Step 1: the amount in mol of NH_3 can be calculated using the molar volume of a gas at STP.
The molar volume is 22.7 dm^3 mol^{-1}, so the volume of ammonia must be converted into dm^3 by dividing by 1000.

$$\text{volume of ammonia in dm}^3 = \frac{186}{1000} = 0.186 \text{ dm}^3$$

$$\text{amount in mol of ammonia} = \frac{\text{volume}}{22.7} = \frac{0.186}{22.7} = 8.19 \times 10^{-3} \text{ mol}$$

Step 2: 2 mol NH_3 produce 3 mol of Cu, so 8.19×10^{-3} mol NH_3 produces $8.19 \times 10^{-3} \times \frac{3}{2}$ mol Cu, i.e. 1.23×10^{-2} mol copper.

Step 3: the molar mass of Cu = 63.55 g mol^{-1}, so the mass of copper produced $= 1.23 \times 10^{-2} \times 63.55 = 0.781$ g

WORKED EXAMPLE 16.5

Consider the reaction:

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

Excess calcium carbonate is added to 50.0 cm^3 of 0.400 mol dm^{-3} hydrochloric acid. Determine the volume of carbon dioxide (measured at STP) produced.

Answer

Excess calcium carbonate is added, so we can ignore this and just consider hydrochloric acid.

Step 1: we have the volume and concentration of hydrochloric acid, and so, we can calculate the amount in mol.

$$\text{amount of hydrochloric acid} = \frac{50.0}{1000} \times 0.400 = 0.0200 \text{ mol}$$

NOTE: 50.0 and 0.400 are both 3 significant figures, so the amount has been given as 3 significant figures.

Step 2: from the equation, 2 mol HCl produce 1 mol CO_2; therefore, 0.0200 mol HCl will produce $\frac{0.0200}{2}$ mol CO_2, i.e., 0.0100 mol CO_2.

Step 3: we have worked out the amount in mol of carbon dioxide, but the volume at STP is required, so we need to multiply the amount by the molar volume at STP (22.7 dm^3 mol^{-1}).

volume of $CO_2 = 0.0100 \times 22.7 = 0.227$ dm^3

The molar volume was in dm^3, and so, the volume of CO_2 also comes out in dm^3. No units were specified in the question, so we can leave the answer in dm^3. If the answer had been required in cm^3, then we would multiply by 1000 to get 227 cm^3.

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Link

If you try doing this experiment with these amounts in the laboratory to collect the carbon dioxide, it is extremely likely that the volume will be different to this. First of all, the gas will not be collected at STP but, more significantly, some gas is likely to escape before the apparatus is sealed. The loss of gas before the apparatus is sealed will mean that the volume collected will be less than 227 cm^3 – this is a systematic error.

We are not always given information about the reactants, sometimes we are told about the products of a reaction. This, however, makes no difference to how we approach the question.

WORKED EXAMPLE 16.6

Potassium chlorate(V) decomposes when heated:

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

What mass of potassium chlorate(V) decomposes to produce 100.0 cm^3 of oxygen gas measured at STP?

Answer

Step 1: work out the amount in mol of O_2:

The volume of O_2 must first be converted into dm^3:

$$\text{volume of O in dm}^3 = \left(\frac{100.0}{1000}\right) = 0.1000 \text{ dm}^3$$

$$\text{amount of } O_2 = \left(\frac{0.1000}{22.7}\right) = 4.41 \times 10^{-3} \text{ mol}$$

22.7 is 3 significant figures, so the answer has been given to 3 significant figures [your answer should have the same number of significant figures as the least precise (fewest significant figures) piece of data].

Step 2: the chemical equation shows that 3 mol O_2 are produced from 2 mol $KClO_3$. Therefore, the amount in mol of $KClO_3$ is two-thirds the amount in mol of O_2:

$$\frac{2}{3} \times 4.41 \times 10^{-3} = 2.94 \times 10^{-3} \text{ mol}$$

Step 3: convert the amount of $KClO_3$ to mass:

molar mass of $KClO_3 = 122.55 \text{ g mol}^{-1}$

mass of $KClO_3 = 122.55 \times 2.94 \times 10^{-3} = 0.360$ g

The mass of $KClO_3$ required is 0.360 g.

EXAM TIP

If you had carried all the figures in this calculation through on the calculator, you would have got the answer 0.3599118943 g, which is the same as the answer given here to 3 significant figures. If in doubt in the exam, it is generally better to quote more, rather than fewer significant figures.

Masses may also be given in kilograms or tonnes

1 kg = 1000 g 1 tonne (1 t) = 1×10^6 g

Before working out the amount in mol, you must convert the mass into grams.

To convert kilograms to grams, multiply by 1000; to convert tonnes to grams, multiply the mass by 1×10^6.

WORKED EXAMPLE 16.7

Tin can be extracted from its ore by heating the ore, cassiterite (mostly tin(IV) oxide), with carbon. The reaction that occurs is:

$SnO_2(s) + 2C(s) \rightarrow Sn(l) + 2CO(g)$

Calculate the mass of tin(IV) oxide (in tonnes) that must be heated with excess carbon to produce 2.00 t tin.

Answer

Step 1: the only substance for which we can work out the amount in mol is tin.

The mass of tin must be converted into g by multiplying by 10^6:

mass of tin in g is 2.00×10^6 g

$$\text{amount of tin} = \frac{2.00 \times 10^6}{118.71} = 1.68 \times 10^4 \text{ mol}$$

Step 2: from the chemical equation, 1 mol Sn is produced from 1 mol SnO_2; therefore, 1.68×10^4 mol of SnO_2 is required to produce 1.68×10^4 mol Sn.

Step 3: the mass of SnO_2 is required. This is obtained by multiplying the amount in mol by the molar mass:

mass of $SnO_2 = 1.68 \times 10^4 \times 150.71 = 2.54 \times 10^6$ g

This can be converted into tonnes by dividing by 10^6.

Therefore, the mass of tin is 2.54 t.

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There are various other ways of doing this question. The quickest of which is to just use the ratio of the molar masses of Sn and SnO_2:

$$\text{mass of } SnO_2 = \frac{150.71}{118.71} \times 2.00 = 2.54 \text{ t}$$

Link

The mass of tin was written in standard form in this question, and it is clear that there are 3 significant figures; if it had been written as 2 000 000 g, then it is not at all clear how many significant figures are present – it could be any number from 1 to 7.

EXAM TIP

You should carry through all figures on the calculator to calculate the final answer.

You may have realised that you would have obtained the same answer if you did not convert into g and worked out the amount in mol as if the mass had been in g. Most mark schemes give full marks for just the correct final answers, and so, if you did it like that and wrote down the answer 2.54 t at the end, you would get full marks. However, if you did this and made a mistake at the last stage, in that you, say, calculated the molar mass of SnO instead of SnO_2, giving the answer 2.27 t, you could receive zero marks because none of the intermediate answers were correct.

TEST YOUR UNDERSTANDING

Assume that all gases behave as ideal gases and that the molar volume of an ideal gas at STP is 22.7 $dm^3\ mol^{-1}$.

7 **a** Calculate the amount in mol of hydrogen gas produced when 0.4 mol sodium reacts with excess water.

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

b Calculate the amount in mol of O_2 that reacts with 0.01 mol C_3H_8.

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

c Calculate the amount in mol of H_2S formed when 0.02 mol HCl reacts with excess Sb_2S_3.

$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$

d Calculate the amount in mol of oxygen formed when 0.6 mol $KClO_3$ decomposes.

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

e Calculate the amount in mol of iron formed when 0.9 mol CO reacts with excess iron(III) oxide.

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

f Calculate the amount in mol of hydrogen required to make 2.4×10^{-3} mol NH_3.

$N_2 + 3H_2 \rightarrow 2NH_3$

8 **a** Calculate the mass of arsenic(III) chloride produced when 0.150 g of arsenic reacts with excess chlorine according to the equation:

$2As + 3Cl_2 \rightarrow 2AsCl_3$

b What mass of sulfur is produced when 5.78 g of iron(III) sulfide is reacted with excess oxygen?

$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$

c Calculate the mass of iodine that must be reacted with excess phosphorus to produce 5.00 g of phosphorus(III) iodide according to the equation:

$2P + 3I_2 \rightarrow 2PI_3$

d Consider the reaction:

$3SCl_2 + 4NaF \rightarrow S_2Cl_2 + SF_4 + 4NaCl$

What mass of SCl_2 must be reacted with excess NaF to produce 2.25 g of NaCl?

9 Sodium nitrate(V) decomposes according to the equation:

$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$

Calculate the volume (in cm^3) of oxygen produced (measured at STP) when 0.850 g of sodium nitrate(V) decomposes.

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CONTINUED

10 Tin reacts with nitric acid according to the equation:

$Sn(s) + 4HNO_3(aq) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$

If 2.50 g of tin is reacted with excess nitric acid, what volume of nitrogen dioxide (in cm^3) is produced at STP?

11 Calculate the mass of sodium carbonate that must be reacted with excess hydrochloric acid to produce 100.0 cm^3 of carbon dioxide at STP.

$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

12 Calcium carbonate is reacted with 50.0 cm^3 of 0.500 mol dm^{-3} hydrochloric acid.

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

a What mass of calcium carbonate is required for an exact reaction?

b What volume of carbon dioxide, measured at STP, will be produced?

13 If 25.00 cm^3 of 0.200 mol dm^{-3} hydrochloric acid is reacted with excess magnesium, calculate the volume of hydrogen gas produced at STP.

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

14 What volume (in cm^3) of 0.0100 mol dm^{-3} barium chloride must be reacted with excess sodium sulfate to produce 0.100 g of barium sulfate?

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

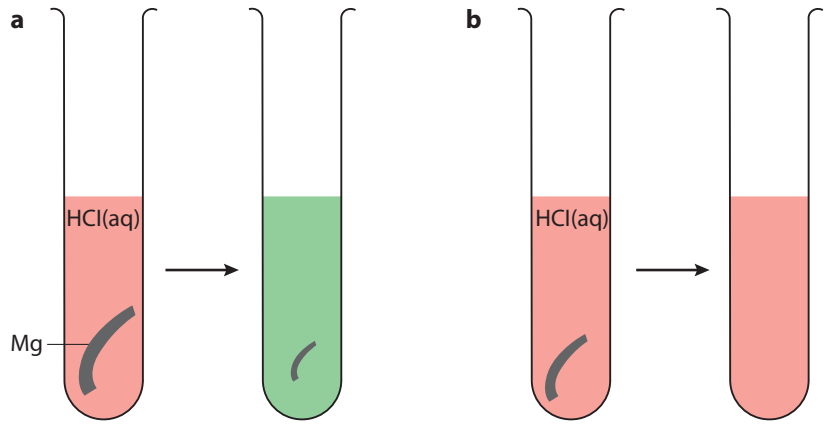

Figure 16.5: The reaction between magnesium and hydrochloric acid. **a** In this test tube, magnesium is in excess. **b** In this test tube, hydrochloric acid is in excess.

Limiting reactant

Very often we do not use exact quantities in a chemical reaction, but rather we use an excess of one or more reactants. One reactant is, therefore, used up before the others and is called the **limiting reactant**. When the limiting reactant is completely used up, the reaction stops.

Figure 16.5 illustrates the idea of a limiting reactant.

The equation for the reaction is:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

A small amount of universal indicator has been added to each test tube.

In Figure 16.5**a**, magnesium is in excess, and hydrochloric acid is the limiting reactant. The reaction finishes when the hydrochloric acid runs out. Because magnesium is in excess, there will still be some left in the test tube – there is not enough hydrochloric acid to react with all the magnesium. The resulting solution will be neutral (universal indicator is green) because all the hydrochloric acid has reacted.

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In Figure 16.5**b**, hydrochloric acid is in excess, and magnesium is the limiting reactant. The reaction stops when the magnesium has been used up. There is excess hydrochloric acid, and so, there will still be some left at the end once all the magnesium has reacted, and therefore, the solution is still acidic at the end (universal indicator is red).

WORKED EXAMPLE 16.8

Consider the reaction between magnesium and nitrogen: $3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

10.00 g of magnesium is reacted with 5.00 g of nitrogen. Which is the limiting reactant?

Answer

$$\text{amount in mol of magnesium} = \frac{10.00}{24.31} = 0.4114 \text{ mol}$$

$$\text{amount in mol of } N_2 = \frac{5.00}{28.02} = 0.178 \text{ mol}$$

From the equation, 3 mol magnesium reacts with 1 mol N_2.

So, 0.4114 mol magnesium reacts with $\frac{0.4114}{3 \text{ mol}}$ N_2, i.e., 0.1371 mol N_2.

Therefore, for an exact reaction, 0.1371 mol N_2 is required to react with 0.4114 mol magnesium. However, 0.178 mol N_2 is present, which is more than the 0.1371 mol required for exact reaction; therefore, there is more than enough nitrogen to react with all the magnesium. This means that N_2 is in excess, and magnesium is, therefore, the limiting reactant.

This can also be seen from working with the amount of N_2. 0.178 mol N_2 was used in this reaction, and this amount of N_2 would require 3×0.178 mol magnesium for an exact reaction, i.e., 0.534 mol magnesium. However, only 0.4114 mol magnesium is present; there is not enough magnesium to react with all the nitrogen and, therefore, magnesium will run out before all the N_2 has reacted.

The limiting reactant can be found quickly by dividing the amount in mol of each reactant by its coefficient in the chemical (stoichiometric) equation; the smallest number indicates the limiting reactant.

WORKED EXAMPLE 16.9

Consider the reaction between sulfur and fluorine: $S(s) + 3F_2(g) \rightarrow SF_6(g)$

10.00 g of sulfur reacts with 10.00 g of fluorine. Which is the limiting reactant?

Answer

$$\text{amount in mol of sulfur} = \frac{10.00}{32.07} = 0.3118 \text{ mol}$$

$$\text{amount in mol of } F_2 = \frac{10.00}{38.00} = 0.2632 \text{ mol}$$

The coefficient of sulfur in the chemical equation is 1 and that of F_2 is 3.

S: $\frac{0.3118}{1} = 0.3118$ and F_2: $\frac{0.2632}{3} = 0.08773$;

therefore, F_2 is the limiting reactant (smaller number) and sulfur is in excess.

Alternatively, we can reason from the chemical equation that 0.2632 mol F_2 should react with 0.08773 mol sulfur (0.2632 mol divided by 3). There is more than 0.08773 mol sulfur present, so sulfur is present in excess, and F_2 is the limiting reactant.

KEY POINT

To find the amount of product, you must always work with the limiting reactant.

All of the limiting reactant will react in a reaction, but only some of the substance in excess will react. Therefore, when working out how much product is formed, we must work with the number of moles of the limiting reactant, as we know that all of this reacts.

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WORKED EXAMPLE 16.10

0.200 g of magnesium was added to 25.0 cm^3 of 0.500 mol dm^{-3} hydrochloric acid.
The equation for the reaction is:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

Calculate the volume of hydrogen gas (measured at STP) produced.

Answer

To answer a moles question, you only need to be given enough information to work out the amount in mol of just one of the reactants. If you are given enough information to work out the amount in mol of more than one reactant, you must consider that one of these reactants will be the limiting reactant and use this one for all calculations.

Here, we have enough information to work out the amount in mol of magnesium and of hydrochloric acid, so we need to find out if one of these is a limiting reactant.

$$\text{amount in mol of Mg} = \frac{0.200}{24.31} = 8.23 \times 10^{-3} \text{ mol}$$

$$\text{amount in mol of HCl} = \frac{25.0}{1000} \times 0.500 = 0.0125 \text{ mol}$$

Although we have more moles of HCl, we cannot assume that this is in excess without looking at the chemical equation.

From the equation, we need $2 \times 8.23 \times 10^{-3}$ mol HCl to react with 8.23×10^{-3} mol Mg, that is, 0.0165 mol. However, only 0.0125 mol HCl is present, which is not enough to react with all the Mg and, therefore, HCl is the limiting reactant, and Mg is in excess.

All of the HCl will react, but only some of the Mg will react; therefore, to work out the number of moles of H_2 produced, we must use the amount in mol of HCl, the limiting reactant.

From the chemical equation, 2 mol HCl reacts to form 1 mol H_2; therefore, 0.0125 mol HCl will form $\frac{0.0125}{2} = 6.25 \times 10^{-3}$ mol H_2

The volume of 6.25×10^{-3} mol H_2 at STP is given by:

volume of $H_2 = 6.25 \times 10^{-3} \times 22.7 = 0.142$ dm^3 or 142 cm^3

WORKED EXAMPLE 16.11

For the following reaction:

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

there is 100.0 g of each reactant available. Which is the limiting reactant?

Answer

This question could be done by working out the amount in mol of each reactant and then comparing them, but there is a shortcut – work out the masses of each substance if molar quantities reacted, that is, if 4 mol $FeCr_2O_4$ reacted with 8 mol Na_2CO_3 and 7 mol O_2:

	$4FeCr_2O_4$	+	$8Na_2CO_3$	+	$7O_2$	→	$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
mass in g	$4 \times 223.85 = 895.40$		$8 \times 105.99 = 847.92$		$7 \times 32.00 = 224.00$		

These are the masses that are required for the exact reaction. Because the highest mass required is that of $FeCr_2O_4$, if the same mass of each substance is taken, $FeCr_2O_4$ will run out first and must be the limiting reactant.

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TEST YOUR UNDERSTANDING

15 What is the limiting reactant in each of the following reactions?

a 0.1 mol Sb_4O_6 reacts with 0.5 mol H_2SO_4

$Sb_4O_6 + 6H_2SO_4 \rightarrow 2Sb_2(SO_4)_3 + 6H_2O$

b 0.20 mol $AsCl_3$ reacts with 0.25 mol H_2O

$4AsCl_3 + 6H_2O \rightarrow As_4O_6 + 12HCl$

c 0.25 mol copper reacts with 0.50 mol dilute HNO_3

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

d 0.10 mol NaCl reacts with 0.15 mol MnO_2 and 0.20 mol H_2SO_4

$2NaCl + MnO_2 + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

16 Identify the limiting reactant in each case.

a 1.00 g of $CaCO_3$ reacts with 25.0 cm^3 of 0.200 mol dm^{-3} hydrochloric acid:

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

b 2.00 g of sulfur reacts with 2.00 dm^3 of oxygen (measured at STP):

$S(s) + O_2(g) \rightarrow SO_2(g)$

c 1.00 kg iron(III) oxide reacts with 500 dm^3 (measured at STP) of carbon monoxide:

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

d 25.0 cm^3 of 0.0500 mol dm^{-3} silver nitrate solution reacts with 30.0 cm^3 of 0.0400 mol dm^{-3} sodium chloride solution:

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

e 2.00 dm^3 propane reacts with 4.00 dm^3 oxygen gas:

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

Assume both gas volumes were measured at STP.

17 Boron can be prepared by reacting B_2O_3 with magnesium at high temperatures:

$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$

What mass of boron is obtained if 0.75 g B_2O_3 is reacted with 0.50 g magnesium?

18 Iron(III) oxide reacts with carbon to produce iron:

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

What mass of iron is obtained if 10.0 t of Fe_2O_3 is reacted with 1.00 t of carbon?

19 Lead (II) nitrate solution reacts with sodium iodide solution to form a precipitate of lead(II) iodide:

$Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$

Calculate the mass of lead(II) iodide formed when 20.0 cm^3 of 0.100 mol dm^{-3} lead(II) nitrate solution is reacted with 10.0 cm^3 of 0.150 mol dm^{-3} sodium iodide solution.

20 Copper(II) sulfate reacts with potassium iodide to form a precipitate of copper(I) iodide:

$2CuSO_4(aq) + 4KI(aq) \rightarrow 2CuI(s) + I_2(aq)$

Calculate the mass of copper(I) iodide produced when 25.00 cm^3 of 0.100 mol dm^{-3} $CuSO_4$ reacts with 30.00 cm^3 of 0.120 mol dm^{-3} KI.

21 Zinc metal reacts with dilute hydrochloric acid according to the equation:

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Calculate the volume (in cm^3) of hydrogen produced (measured at STP) if 5.00 g of zinc is added to 30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

Link

Look back at Avogadro's law in Chapter 4.

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16.2 Yield and atom economy of chemical reactions

Calculating the yield of a chemical reaction

KEY POINT

The yield of a chemical reaction is the amount/mass of the desired product obtained.

In any commercial process, it is very important to know the **yield** of a chemical reaction.

The yield of a chemical reaction is usually quoted as a percentage.

KEY POINT

$$\% \text{ yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

The **percentage yield** gives more information than just quoting the yield of the product as a mass. For example, if a scientist stated that they started with 1 g of A, reacted it with B and produced 1.2 g of C, this could sound quite good, until someone works out that this is only a 40% yield!

The **theoretical yield** is the maximum possible amount/mass/volume that can be obtained – this is determined by doing a moles calculation. In all the calculations previously, we have calculated the theoretical yield of the product. The **experimental (or actual) yield** is the amount/mass/volume actually obtained when you do the experiment. You have to be told what the experimental yield is in a question. The experimental yield should always be less than the theoretical yield.

Example

Consider the preparation of 1,2-dibromoethane ($C_2H_4Br_2$):

$C_2H_4(g) + Br_2(l) \rightarrow C_2H_4Br_2(l)$

10.00 g of ethene (C_2H_4) will react *exactly* with 56.95 g of bromine, therefore the theoretical yield for this reaction is 10.00 + 56.95 = 66.95 g – this is the maximum possible mass that can be obtained.

If the experimental yield of $C_2H_4Br_2$ is 50.00 g, we get

$$\% \text{ yield} = \frac{50.00}{66.95} \times 100 = 74.68\%$$

WORKED EXAMPLE 16.12

$$\underset{\text{ethanol}}{C_2H_5OH(l)} + \underset{\text{ethanoic acid}}{CH_3COOH(l)} \rightleftharpoons \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5(l)} + \underset{\text{water}}{H_2O(l)}$$

If the yield of ethyl ethanoate obtained when 20.00 g of ethanol is reacted with excess ethanoic acid is 30.27 g, calculate the percentage yield.

Answer

The first step is to calculate the maximum possible yield, i.e., the theoretical yield:

molar mass of $C_2H_5OH = 46.08$ g mol^{-1}

amount in mol of $C_2H_5OH = \frac{20.00}{46.08} = 0.4340$ mol

CH_3COOH is in excess, i.e., more than enough is present to react with all the C_2H_5OH. This means that we do not need to worry about the amount in mol of CH_3COOH.

From the chemical equation, 1 mol C_2H_5OH produces 1 mol $CH_3COOC_2H_5$.
Therefore, 0.4340 mol C_2H_5OH produces 0.4340 mol $CH_3COOC_2H_5$.

molar mass of $CH_3COOC_2H_5 = 88.12$ g mol^{-1}

The mass of ethyl ethanoate, $CH_3COOC_2H_5$, produced is $0.4340 \times 88.12 = 38.24$ g.

So, the theoretical yield is 38.24 g.

The experimental yield is 30.27 g (given in the question).

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CONTINUED

$$\% \text{ yield} = \frac{30.27}{38.24} \times 100 = 79.15\%$$

The percentage yield of $CH_3COOC_2H_5$ is 79.15%.

Here, reasons that the yield is less than 100% include the fact that the reaction is reversible, and so will reach a state of equilibrium.

Why is the experimental yield usually lower than the theoretical yield?

There are many reasons why the experimental yield is less than the theoretical yield. These include the following:

- losses when substances are transferred between vessels (not including spilling the material) and in physical processes, such as filtration, crystallisation and solvent extraction
- side reactions producing other products
- the product of a reaction reacting further to produce a different product, or products decomposing
- incomplete reactions, for instance, if the reaction is not left long enough to go to completion or if the reaction is reversible
- reactants not being pure.

Consider a very simple reaction, such as the reaction between calcium carbonate powder and hydrochloric acid:

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

If we reacted together exact amounts of the two reactants required (i.e. neither was in excess), then reasons that the volume of carbon dioxide collected is less than that predicted include the following:

- not all the calcium carbonate was transferred to the reaction vessel
- some gas escaped before the apparatus was sealed
- some gas dissolved in the water
- the calcium carbonate was impure
- the hydrochloric acid was not the stated concentration.

TEST YOUR UNDERSTANDING

22 Calculate the percentage yield in each of the following reactions:

a When 10.0 g of arsenic is heated in excess oxygen, 12.5 g of As_4O_6 is produced.

$4As + 3O_2 \rightarrow As_4O_6$

b When 1.20 g of C_2H_4 reacts with excess bromine, 5.23 g of CH_2BrCH_2Br is produced.

$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$

c When 2.0 g of S is heated with excess oxygen, 1.00 dm^3 of SO_2 (measured at STP) is obtained.

$S(s) + O_2(g) \rightarrow SO_2(g)$

d 0.362 g of barium sulfate is obtained when excess barium chloride solution is added to 20.0 cm^3 of 0.100 mol dm^{-3} sodium sulfate solution.

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(aq) + 2NaCl(aq)$

e 3.21 g of copper(II) sulfate crystals are formed when excess copper(II) oxide is reacted with 30.0 cm^3 of 0.600 mol dm^{-3} sulfuric acid.

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

$CuSO_4(aq) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$

f 124 cm^3 of ammonia is obtained when 250 cm^3 of nitrogen gas is reacted with excess hydrogen. All gas volumes are measured at STP.

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

g Aspirin, $C_9H_8O_4$, can be prepared by reacting 2-hydroxybenzoic acid, $C_7H_6O_3$, with ethanoic anhydride, $C_4H_6O_3$.

$2C_7H_6O_3 + C_4H_6O_3 \rightarrow 2C_9H_8O_4 + H_2O$

When 13.81 g of 2-hydroxybenzoic acid was reacted with excess ethanoic anhydride, 9.01 g of aspirin was obtained.

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The main reason that an experimental yield could be *greater* than the theoretical yield is residual solvent in a sample of a solid product.

Atom economy

The idea of **atom economy** can be used as a measure of how efficient a particular reaction is in converting as much of the starting materials as possible into useful products. This is often used a guide as to how 'green' a particular synthetic pathway is.

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{total molar mass of all reactants}} \times 100\%$$

The higher the atom economy, the greener the process, because more of the starting materials end up in the desired product.

We will use the preparation of Cl_2O to illustrate how atom economy is worked out:

$$2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow 2NaHCO_3 + 2NaCl + Cl_2O$$

The total molar mass of all reactants is calculated by working out the molar mass of each reactant, multiplying by the coefficients in the chemical equation and then adding them all up:

$(2 \times 70.90) + (2 \times 105.99) + 18.02 = 371.80 \text{ g mol}^{-1}$

The desired product is Cl_2O, which has a molar mass of 86.90 g mol^{-1}.

So, atom economy $= \left(\frac{86.90}{371.80}\right) \times 100 = 23.37\%$

This is quite a low value because Cl_2O is only one of several products in this reaction – there is a lot of waste.

KEY POINT

There is an inverse relationship between the atom economy and the amount of waste – the lower the atom economy, the more waste there will be.

Quite apart from the environmental issues, the aim of any industrial process would be to reduce waste to a minimum because waste costs money – this can be achieved by redesigning the process so that a different reaction is used, which has a higher atom economy (assuming that this does not make the whole process more wasteful/expensive in other ways), or finding a use/market for the 'waste' products. If the above reaction were an industrial process, it would be greener if the other products (NaCl and $NaHCO_3$) were also used in some way and not simply wasted. For instance, if the NaCl and $NaHCO_3$ produced in this reaction were both ultrapure and easily separated (which will not be the case!), they could be sold for food use ($NaHCO_3$ is commonly known as sodium bicarbonate or bicarbonate of soda and is used in baking), which would increase the atom economy of this process to 100%.

Atom economy is one of the principles of *green chemistry* (or sustainable chemistry), which is an approach to chemical research and chemical industrial processes that seeks to minimise the environmental impact of these processes. Other factors that are looked at when trying to make a process as green as possible include:

- using readily available and safe materials that are renewable
- using as little solvent as possible
- using as little energy as possible.

WORKED EXAMPLE 16.13

Consider two different ways of making 1-phenylethanone from 1-phenylethanol:

Method 1: $3C_6H_5CH(OH)CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3C_6H_5COCH_3 + Cr_2(SO_4)_3 + 6H_2O$

Method 2: $C_6H_5CH(OH)CH_3 + \frac{1}{2}O_2 \rightarrow C_6H_5COCH_3 + H_2O$

Work out the atom economy for each process and suggest which is more efficient.

Answer

Method 1

total molar mass of all reactants $= (3 \times 122.18) + (2 \times 100.00) + (3 \times 98.09) = 860.81 \text{ g mol}^{-1}$

molar mass of desired product $= 3 \times 120.16 = 360.48 \text{ g mol}^{-1}$

atom economy $= \left(\frac{360.48}{860.81}\right) \times 100 = 41.88\%$

Method 2

total molar mass of all reactants $= 122.18 + (0.5 \times 32.00) = 138.18 \text{ g mol}^{-1}$

molar mass of desired product $= 120.16 \text{ g mol}^{-1}$

atom economy $= \left(\frac{120.16}{138.18}\right) \times 100 = 86.96\%$

Method 2 has a much higher atom economy and is, therefore, much more efficient – more atoms of the reactants have ended up in the desired product.

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Atom economy and yield

It is important to realise that atom economy is not the same as the yield of a reaction. Atom economy is a theoretical quantity based on a balanced equation and allows evaluation of how much of the starting materials are incorporated into the desired product and, therefore, how much waste material will be produced. The yield of a reaction is an experimental quantity worked out from how much of the desired product is actually made in a chemical reaction. In the calculation of atom economy, it has been assumed that all reactions have 100% yield, which, in practice, will not be the case.

For example, if we look at the reaction for the industrial preparation of ammonia:

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

we can see that this has an atom economy of 100% because all of the reactants are incorporated into the desired product. However, this is a reversible reaction and the yield of ammonia under the conditions used in the industrial process is typically only around 15%.

When evaluating how green or environmentally friendly a particular process is, both atom economy and yield must be considered, as well as several other factors, such as how much energy must be supplied (usually as heat), the amounts of solvents required, the nature of the solvents and disposal of solvents.

TEST YOUR UNDERSTANDING

23 Calculate the atom economy for each of the following reactions:

a $CaC_2 + H_2O \rightarrow C_2H_2 + CaO$, where the desired product is ethyne

b $C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl$, where the desired product is ethanal

c $4HgS + 4CaO \rightarrow 4Hg + 3CaS + CaSO_4$, where the desired product is mercury

d $C_2H_4 + H_2O \rightarrow C_2H_5OH$

e $2C_7H_6O_3 + C_4H_6O_3 \rightarrow 2C_9H_8O_4 + H_2O$, where the desired product is aspirin, $C_9H_8O_4$.

16.3 Titrations

Titration is a technique for finding the volumes of solutions that react exactly with each other.
The following procedure should be followed for carrying out an acid–base titration:

- measure out a known volume of a standard solution using a pipette (this could be the acid or the alkali) and transfer this to a conical (Erlenmeyer) flask
- add a few drops of an acid–base indicator
- fill the burette with the other solution (either the alkali or the acid)
- record the initial reading on the burette (to two decimal places)
- add the solution from the burette to the solution in the conical flask until the indicator changes colour (Figure 16.6)
- record the final reading on the burette
- subtract the initial reading from the final reading to work out the *titre*.

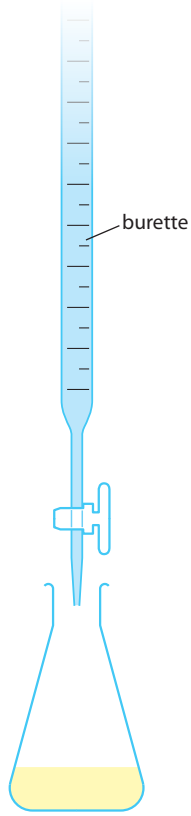

Figure 16.6: Titration set-up.

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For the technique to be used to determine the concentration of a solution, the concentration of the solution it reacts with must be known accurately – this is a standard solution. Standard solutions are discussed in Chapter 4, Section 4.5.

WORKED EXAMPLE 16.14

Sulfuric acid (H_2SO_4) is titrated against 25.00 cm^3 of 0.2000 mol dm^{-3} sodium hydroxide solution (NaOH). It is found that 23.20 cm^3 of sulfuric acid is required for neutralisation. Calculate the concentration of the sulfuric acid.

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

Answer

Step 1: work out the amount in mol of NaOH:

amount in mol = concentration × volume in dm^3

$$\text{amount in mol} = 0.2000 \times \left(\frac{25.00}{1000}\right)$$

$$= 5.000 \times 10^{-3} \text{ mol}$$

Step 2: from the balanced equation, 2 mol NaOH reacts with 1 mol H_2SO_4. Therefore, 5.000×10^{-3} mol NaOH reacts with $5.000 \times \frac{10^{-3}}{2}$, i.e. 2.500×10^{-3} mol H_2SO_4.

This is the amount of H_2SO_4 in 23.20 cm^3 of H_2SO_4(aq)

Step 3: convert amount in mol to concentration:
concentration = amount / volume in dm^3

23.20 cm^3 is $\frac{23.20}{1000} = 0.02320$ dm^3

$$[H_2SO_4] = 2.500 \times \frac{10^{-3}}{0.02320} = 0.1078 \text{ mol dm}^{-3}$$

The concentration of the H_2SO_4 is 0.1078 mol dm^{-3}.

Equation for solving moles questions involving solutions

The following equation can be useful for solving titration problems:

$$\frac{C_1V_1}{n_1} = \frac{C_2V_2}{n_2}$$

where:

C_1 = concentration of first substance

V_1 = volume of first substance

N_1 = coefficient of first substance in the balanced equation

C_2 = concentration of second substance

V_2 = volume of second substance

N_2 = coefficient of second substance in the balanced equation

WORKED EXAMPLE 16.15

Neutralisation of 25.00 cm^3 of sulfuric acid (H_2SO_4) requires 28.70 cm^3 of sodium hydroxide (NaOH) of concentration 0.1500 mol dm^{-3}. What is the concentration of the sulfuric acid?

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

Answer

Let H_2SO_4 be substance 1 and NaOH be substance 2.

$C_1 = ?$ $\quad C_2 = 0.1500$ mol dm^{-3}

$V_1 = 25.00$ cm^3 $\quad V_2 = 28.70$ cm^3

$N_1 = 1$ $\quad N_2 = 2$

$$\frac{C_1V_1}{n_1} = \frac{C_2V_2}{n_2}$$

There is no need to convert the volume to dm^3 when this equation is used, so we can use the volume in cm^3 directly.

$$\frac{(C_1 \times 25.00)}{1} = \frac{(0.1500 \times 28.70)}{2}$$

Rearranging the equation:

$$C_1 = \frac{(0.1500 \times 28.70)}{(2 \times 25.00)} = 0.08610 \text{ mol dm}^{-3}$$

The concentration of H_2SO_4 is 0.08610 mol dm^{-3}.

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Back titration

This is a technique by which a known excess of a reagent, A, is added to another substance, X, so that they react. Then the excess A is titrated against another reagent, B, to work out how much A had reacted with X, and therefore how many moles of X were present. This is useful when X is a solid – titration involving a solid does not work well, as it would react too slowly.

TEST YOUR UNDERSTANDING

24 If 22.30 cm^3 of hydrochloric acid of concentration 0.1000 mol dm^{-3} is required for neutralisation of 25.00 cm^3 of sodium hydroxide solution, calculate the concentration of the sodium hydroxide solution.

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

25 If 29.70 cm^3 of sulfuric acid of concentration 0.2000 mol dm^{-3} is required for neutralisation of 25.00 cm^3 of potassium hydroxide solution, calculate the concentration of the potassium hydroxide solution.

$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

26 28.20 cm^3 of barium hydroxide solution was required for the neutralisation of 25.00 cm^3 of 0.1200 mol dm^{-3} hydrochloric acid. Calculate the concentration of the barium hydroxide solution.

$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

27 5.30 g of anhydrous sodium carbonate is added to water and the solution made up to a total volume of 250.0 cm^3. If 25.00 cm^3 of this solution required 26.30 cm^3 of HCl for neutralisation, calculate the concentration of the hydrochloric acid.

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

28 0.20 g of lithium metal was put into 100.0 cm^3 of water. The solution was then made up to a total volume of 250.0 cm^3 in a volumetric flask. 25.00 cm^3 of this solution was titrated against 0.100 mol dm^{-3} hydrochloric acid. 28.85 cm^3 of hydrochloric acid was required for neutralisation. Calculate the molar mass of lithium.

$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$

$LiOH(aq) + HCl(aq) \rightarrow LiCl(aq) + H_2O(l)$

WORKED EXAMPLE 16.16

The following procedure was followed to determine the percentage calcium carbonate in an eggshell:

- An egg was cracked, the membrane removed and the eggshell was washed with distilled water then dried.
- The eggshell was ground to a powder using a mortar and pestle.
- 1.20 g of powdered eggshell was put into a beaker.
- 20.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (HCl) was added to the eggshell.
- The mixture was left to react.
- The mixture was titrated against 1.00 mol dm^{-3} sodium hydroxide (NaOH).
- 17.20 cm^3 of sodium hydroxide was required for neutralisation.

Determine the percentage calcium carbonate in the eggshell (assume that none of the impurities react with hydrochloric acid).

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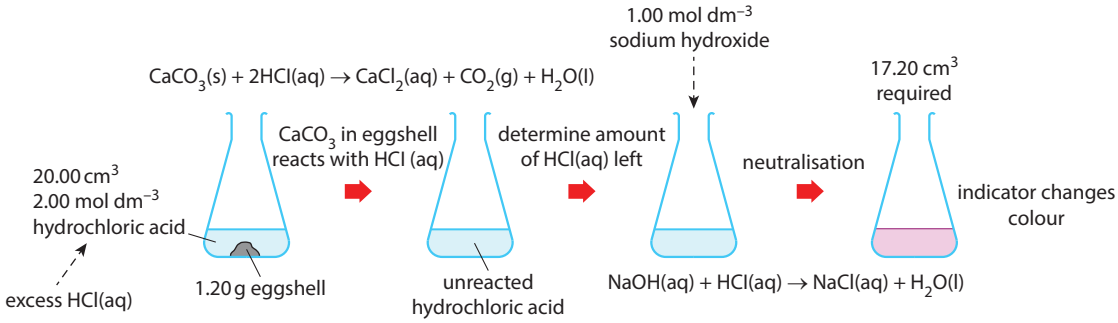
Answer

Sometimes it is good to draw a quick sketch to summarise what is happening in a procedure:



Let us consider the first piece of quantitative information: 1.20 g of eggshell is put into a beaker and 20.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid added. The reaction that occurs is as follows:

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

The eggshell is impure, so we cannot work out the amount in mol of $CaCO_3$ present, but we do have enough information to work out the amount in mol of HCl added:

$$\text{amount in mol of HCl} = \text{concentration} \times \text{volume in dm}^3 = 2.00 \times \frac{20.00}{1000} = 0.0400 \text{ mol}$$

Three significant figures because the concentration of HCl was given to three significant figures.

If the eggshell were pure $CaCO_3$, the amount in mol present in 1.20 g would be 0.0120 mol, which would react with 0.0240 mol HCl. So, excess HCl has been added and, after the eggshell has reacted with it, there will be some HCl left over. We can determine how much HCl is left over by reacting it with sodium hydroxide solution.

The hydrochloric acid required 17.20 cm^3 of 1.00 mol dm^{-3} sodium hydroxide for neutralisation.

$$\text{amount in mol of NaOH} = \text{concentration} \times \text{volume in dm}^3 = 1.00 \times \left(\frac{17.20}{1000}\right) = 0.0172 \text{ mol}$$

This reacts with HCl according to the equation:

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

Therefore, 0.0172 mol NaOH reacted with 0.0172 mol HCl. This is the amount of HCl left over after it has reacted with $CaCO_3$ in the eggshell.

Because 0.04000 mol HCl was originally added to the eggshell and 0.0172 mol was left after the reaction with calcium carbonate, the amount that reacted with $CaCO_3$ was 0.0400 − 0.0172, i.e., 0.0228 mol.

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

0.0228 mol HCl reacts with $\frac{0.0228}{2}$, i.e., 0.0114, mol $CaCO_3$

molar mass of $CaCO_3$ = 100.09 g mol^{-1}

mass of $CaCO_3$ = amount in mol × molar mass = 100.09 × 0.0114 = 1.14 g

$$\%\ CaCO_3 \text{ in the eggshell} = \left(\frac{1.141}{1.20}\right) \times 100 = 95.1\%$$

All figures were carried through on the calculator to get this answer.

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SCIENCE IN CONTEXT

DDT (dichlorodiphenyltrichloroethane – there are more systematic names!) is probably the most famous pesticide ever, and one of the most controversial chemicals in use today (Figure 16.7).

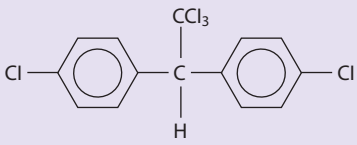

Figure 16.7: DDT

DDT became famous in the 1940s when it was used extensively by the allied forces for killing insects associated with diseases such as malaria and typhus. After World War II, widespread spraying of DDT to control these diseases continued, and it also became widely used by farmers to control insects that could damage crops. Swiss chemist Paul Muller was awarded the Nobel Prize for Medicine or Physiology in 1948 for discovering the effect that DDT had on insects that carry disease, and there are claims that the use of DDT has saved hundreds of millions of lives since the 1940s.

However, there is another side to DDT, and there had been concerns about the use of DDT for many years before the publication of the book 'Silent Spring' by Rachel Carson in 1962. This book raised public awareness of the environmental problems associated with DDT and other pesticides and is regarded by many as the start of the environmental movement. One of the problems with DDT is that, when areas of land were sprayed, some of the DDT found its way into rivers and lakes. It was taken up by microscopic plants, which were eaten by microscopic animals, which were eaten by fish, which were eaten by larger fish, which were eaten by birds. At each level, the concentration of DDT in the organism increased. The effect of DDT on birds is a thinning and, thus, weakening of the shells of eggs so that they are unable to support the weight of the mother (studies have shown that the calcium carbonate percentage is not affected!). This led to a decline in the populations of several species of birds. There are also concerns about DDT in breast milk and its effect on human health, and the US and several other countries banned DDT for agricultural use in the 1970s.

Many people believe that there should be an outright ban on the use of DDT. However, the use of DDT for indoor residual spraying (spraying on inside walls and ceilings of dwellings) is recommended by the World Health Organisation. Each year, according to World Health Organisation statistics, about 400 000 people die from malaria, with about two-thirds of them being children under five, and DDT is one of the most important weapons against this disease.

The use of DDT worldwide is controlled by the Stockholm Convention.

The debate still goes on about DDT – is it one of the chemicals that has had the greatest benefit to mankind or an environmental disaster?

Linked reactions

Sometimes the product of one reaction becomes the reactant in a second reaction. A common example of this is the determination of the concentration of copper ions in solution using sodium thiosulfate. This is an example of a redox titration and redox reactions will be considered again in Chapter 20.

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WORKED EXAMPLE 16.17

10.0 cm^3 of 1 mol dm^{-3} potassium iodide is added to 25.0 cm^3 of copper(II) nitrate solution. The iodine produced is titrated against 0.0200 mol dm^{-3} sodium thiosulfate solution using starch indicator near the end point. 22.50 cm^3 of the sodium thiosulfate solution was required for the titration. Calculate the concentration of the copper(II) nitrate solution.

Answer

The initial reaction of copper(II) ions with iodide ions is:

reaction 1: $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

A large excess of iodide ions is added to make sure that all the copper(II) ions react. Iodine is produced in the reaction and, if we can determine the amount of iodine produced, we can also find the amount of copper(II) ions that reacted.

The amount of iodine is determined by titration with sodium thiosulfate solution:

reaction 2: $\underset{\text{thiosulfate ion}}{2S_2O_3^{2-}(aq)} + I_2(aq) \rightarrow 2I^-(aq) + \underset{\text{tetrathionate ion}}{S_4O_6^{2-}(aq)}$

We know the volume and concentration of the thiosulfate solution, and so, we can work out the amount in mol of this.

The amount in mol of thiosulfate in 22.50 cm^3 of 0.0200 mol dm^{-3} solution is:

$$\text{amount in mol} = \text{volume in dm}^3 \times \text{concentration} = \left(\frac{22.50}{1000}\right) \times 0.0200 = 4.50 \times 10^{-4} \text{ mol } S_2O_3^{2-}$$

From **reaction 2**, we can see that 2 mol $S_2O_3^{2-}$ reacts with 1 mol I_2. Therefore, 4.50×10^{-4} mol $S_2O_3^{2-}$ reacts with $4.50 \times \frac{10^{-4}}{2 \text{ mol}}$ I_2, i.e., 2.25×10^{-4} mol I_2.

This iodine was produced in **reaction 1**. Since we now know the amount of iodine produced in **reaction 1**, we can work out the amount of Cu^{2+} ions that reacted in **reaction 1**.

From **reaction 1**, 2 mol Cu^{2+} produces 1 mol I_2, so the amount of Cu^{2+} is twice the amount of I_2.

Therefore, the amount of Cu^{2+} is $2 \times 2.25 \times 10^{-4}$, i.e., 4.50×10^{-4} mol.

The volume of the solution containing Cu^{2+} ions was 25.0 cm^3, and this allows us to work out the concentration:

$$\text{concentration} = \frac{\text{amount in mol}}{\text{volume in dm}^3} = \frac{4.50 \times 10^{-4}}{0.0250} = 0.0180 \text{ mol dm}^{-3}$$

Therefore, the concentration of the copper(II) nitrate solution was 0.0180 mol dm^{-3}.

The relationship between the amount in mol of thiosulfate and the amount in mol of Cu^{2+} could also be worked out by looking at the two equations together:

reaction 1: $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

reaction 2: $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

From **reaction 1**, 2 mol Cu^{2+} react to form 1 mol I_2. All of this I_2 from **reaction 1** reacts with the $S_2O_3^{2-}$ in **reaction 2**. In **reaction 2**, 1 mol I_2 reacts with 2 mol $S_2O_3^{2-}$. Therefore, overall, the number of moles of Cu^{2+} is equivalent to the number of moles of $S_2O_3^{2-}$.

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More examples of question types

Some questions can look very difficult at first sight, but a good place to start is to work out the amount in mol of whatever you can and see where you can go from there.

WORKED EXAMPLE 16.18

A 3.92 g sample of hydrated sodium carbonate ($Na_2CO_3 \cdot xH_2O$) was dissolved in water and made up to a total volume of 250.0 cm^3. Of this solution, 25.00 cm^3 was titrated against 0.100 mol dm^{-3} hydrochloric acid, and 27.40 cm^3 of the acid was required for neutralisation. Calculate the value of x in $Na_2CO_3 \cdot xH_2O$.

Answer

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

Step 1: work out the amount in mol of HCl:

amount in mol = concentration × volume in dm^3

$$\text{amount in mol} = 0.100 \times \frac{27.40}{1000} = 2.74 \times 10^{-3} \text{ mol}$$

Step 2: from the balanced equation, 2 mol HCl reacts with 1 mol Na_2CO_3. Therefore, 2.74×10^{-3} mol HCl reacts with $2.74 \times \frac{10^{-3}}{2} = 1.37 \times 10^{-3}$ mol Na_2CO_3. This is the number of moles of Na_2CO_3 in 25.00 cm^3.

The original mass of $Na_2CO_3 \cdot xH_2O$ was dissolved in a total volume of 250.0 cm^3. Therefore, the number of moles of Na_2CO_3 in 250.0 cm^3 of solution is $1.37 \times 10^{-3} \times 10$, i.e., 1.37×10^{-2} mol.

Step 3: convert amount in mol to mass:

molar mass of $Na_2CO_3 = 105.99$ g mol^{-1}

mass of 1.37×10^{-2} mol Na_2CO_3 = amount in mol × molar mass of $Na_2CO_3 = 1.37 \times 10^{-2} \times 105.99 = 1.45$ g

This is the mass of Na_2CO_3 that was in the 3.92 g of $Na_2CO_3 \cdot xH_2O$ that we started with. The rest of the mass was the water of crystallisation.

mass due to the water of crystallisation = 3.92 − 1.45 = 2.47 g

$$\text{amount of water of crystallisation} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.74}{18.02} = 0.137 \text{ mol}$$

The ratio between the amount of water of crystallisation and the amount of sodium carbonate can be worked out by dividing the amount of water by the amount of sodium carbonate:

$$\text{ratio} = \frac{0.137}{(1.37 \times 10^{-2})} = 10$$

The value of x is 10, and the formula for the hydrated sodium carbonate is $Na_2CO_3 \cdot 10H_2O$.

WORKED EXAMPLE 16.19

A solution of a chloride of formula MCl_x (concentration 0.0170 mol dm^{-3}) reacts with silver nitrate ($AgNO_3$) solution to precipitate silver chloride (AgCl). It is found that 25.0 cm^3 of 0.0110 mol dm^{-3} silver nitrate solution reacts with 5.40 cm^3 of the chloride solution.

a Calculate the amount in mol of silver nitrate.

b Calculate the amount in mol of the chloride (MCl_x).

c Calculate the formula of the chloride (MCl_x).

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CONTINUED

Answer

a amount in mol = concentration × volume in dm^3

amount of $AgNO_3 = \left(\frac{25.0}{1000}\right) \times 0.0110 = 2.75 \times 10^{-4}$ mol

b amount in mol of $MCl_x = \left(\frac{5.40}{1000}\right) \times 0.0170 = 9.18 \times 10^{-5}$ mol

c The reaction that occurs here is the silver ions from the silver nitrate and the chloride ions from the MCl_x solution coming together to form a precipitate of silver chloride. This can be shown by the ionic equation:

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

If $x = 1$, then 1 MCl unit produces 1 Cl^- ion in solution and 1 mol MCl would produce 1 mol Cl^- ions in solution.

$MCl(aq) \rightarrow M^+(aq) + Cl^-(aq)$

1 mol MCl would react with 1 mol $AgNO_3$, since this is the amount required to produce 1 mol Ag^+ ions in solution:

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

If $x = 2$, then each MCl_2 unit produces 2 Cl^- ions in solution and 1 mol MCl_2 would produce 2 mol Cl^- ions in solution.

$MCl_2(aq) \rightarrow M^{2+}(aq) + 2Cl^-(aq)$

1 mol MCl_2 would, therefore, react with 2 mol $AgNO_3$. Here, we need 2 mol $AgNO_3$ to produce 2 mol Ag^+ in solution:

$2Ag^+(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s)$

We can, therefore, write a general equation for the reaction:

$MCl_x(aq) + xAgNO_3(aq) \rightarrow xAgCl(s) + M(NO_3)_x(aq)$

The ratio of the amount in mol of $AgNO_3$ to the amount in mol of MCl_x will give us the value of x.

$$\frac{\text{amount in mol of } AgNO_3}{\text{amount in mol of } MCl_x} = \frac{2.75 \times 10^{-4}}{9.18 \times 10^{-5}} = 3$$

Therefore, the value of x is 3, and the formula of the chloride is MCl_3.

WORKED EXAMPLE 16.20

One of the stages in the extraction of arsenic, antimony and bismuth from their ores involves the roasting of the sulfide in oxygen:

$2M_2S_3 + 9O_2 \rightarrow 2M_2O_3 + 6SO_2$

A certain mass of the sulfide reacted with 180.0 cm^3 of oxygen gas, measured at 14.85 °C and 101 kPa pressure to produce 0.335 g of M_2O_3. Determine the identity of the element M.

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CONTINUED

Answer

We have enough information to determine the amount in mol of oxygen. The volume of gas is not, however, measured at STP; therefore, we cannot use the molar volume of 22.7 $dm^3\ mol^{-1}$ and have to use $PV = nRT$ to work out the amount in mol of oxygen. Look back at Chapter 5 if you cannot remember how to use this equation.

We must use a consistent set of units, so pressure must be converted to Pa, volume to m^3 and temperature to K. Therefore, we have:

$P = 101\ 000$ Pa

$V = 1.800 \times 10^{-4}\ m^3$

$n = ?$

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

$T = 288.00$ K

$$n = \frac{101\,000 \times 1.800 \times 10^{-4}}{8.31 \times 288.00} = 7.60 \times 10^{-3}\ \text{mol}$$

We can now use the balanced chemical equation to work out the amount in mol of M_2O_3.

From the chemical equation, 9 mol O_2 react to form 2 mol M_2O_3. Therefore, the amount in mol of M_2O_3 is two-ninths of the amount in mol of O_2:

$$\text{amount of } M_2O_3 = \frac{2}{9} \times 7.60 \times 10^{-3} = 1.69 \times 10^{-3}\ \text{mol}$$

Now that we have the amount in mol and the mass of M_2O_3, we can work out the molar mass:

$$\text{molar mass} = \frac{\text{mass}}{\text{amount in mol}} = \frac{0.335}{1.69 \times 10^{-3}} = 198\ \text{g mol}^{-1}$$

The formula of the compound is M_2O_3, and its molar mass is 198 $g\ mol^{-1}$. The relative atomic mass of M can be worked out by taking away three times the relative atomic mass of O and then dividing the answer by 2:

$$\text{mass of } M_2 = 198 - (3 \times 16.00) = 150$$

$$\text{relative atomic mass of M} = \frac{150}{2} = 75$$

This value is closest to the relative atomic mass of arsenic (74.92); therefore, the element M is arsenic.

TEST YOUR UNDERSTANDING

The gas constant may be required in some questions: $R = 8.31\ J\ K^{-1}\ mol^{-1}$

29 Iron can be extracted from its ore by heating with carbon monoxide:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

When 10.00 kg of iron ore, containing mostly Fe_2O_3, was heated with excess carbon monoxide, 6.72 kg of iron was obtained. Determine the percentage Fe_2O_3 in the iron ore. *(Assume that no other compounds in the iron ore react with carbon monoxide.)*

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CONTINUED

30 Hydrogen peroxide decomposes rapidly in the presence of a catalyst, such as MnO_2.

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Determine the concentration of the hydrogen peroxide solution (in mol dm^{-3}) if 50.0 cm^3 of the solution decomposed to form 1.00 dm^3 of oxygen, measured at 19.85 °C and 100 kPa.

31 Zinc metal reacts with dilute hydrochloric acid according to the equation:

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Calculate the volume (in cm^3) of hydrogen produced, measured at 21.85 °C and 9.88×10^4 Pa, if 5.00 g of zinc is reacted with 30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

32 4.09 g of hydrated iron(II) sulfate ($FeSO_4 \cdot xH_2O$) is dissolved in water and made up to a total volume of 100.0 cm^3. 20.0 cm^3 of this solution is acidified and then reacted with 0.0200 mol dm^{-3} potassium manganate(VII) solution [$KMnO_4(aq)$]. 29.40 cm^3 of $KMnO_4(aq)$ is required for exact reaction. Calculate the value of x in $FeSO_4 \cdot xH_2O$.

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

33 Pure chromium can be extracted from chromite ($FeCr_2O_4$) in the following series of reactions:

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + 2C \rightarrow Cr_2O_3 + Na_2CO_3 + CO$

$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

If 2.000 kg of pure chromium is obtained, how much chromite was used?

34 1.12 g of hydrated copper(II) nitrate [$Cu(NO_3)_2 \cdot xH_2O$] is dissolved in water and the solution made up to a total volume of 250.0 cm^3. 25.00 cm^3 of this solution is taken and excess potassium iodide solution added. The iodine liberated completely reacted with 23.20 cm^3 of 0.0200 mol dm^{-3} sodium thiosulfate solution. Calculate the value of x in $Cu(NO_3)_2 \cdot xH_2O$. The ionic equations for the reactions involved are:

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$

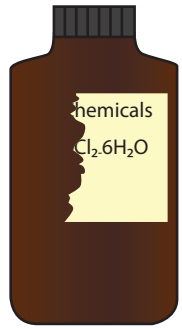
$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

35 1.020 g of magnesium was placed in a beaker and 50.00 cm^3 of 2.000 mol dm^{-3} hydrochloric acid added. The resulting solution was transferred to a volumetric flask and made up to a total volume of 100.0 cm^3 with water. 25.00 cm^3 of this solution was titrated against 0.1120 mol dm^{-3} sodium hydroxide solution and 34.30 cm^3 of the sodium hydroxide was required for neutralisation.
Use this information to work out the relative atomic mass of magnesium to two decimal places.
The relevant equations are as follows:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

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

36 A bottle of a white crystalline salt was found in a cupboard. All that was left of the label is shown in the diagram. 5.000 g of the substance was dissolved in water and made up to a total volume of 50.00 cm^3.



10.00 cm^3 of this solution was reacted with 25 cm^3 of 2.0 mol dm^{-3} silver nitrate solution (this was an excess). The precipitate was filtered off, washed, dried and weighed. The total mass of precipitate formed was 1.410 g. Work out the element missing from the formula of the substance.

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

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
write chemical equations	16.1			
use the mole ratio from a chemical equation in calculations	16.1			
work out which is the limiting reactant	16.1			
calculate theoretical and percentage yield	16.2			
calculate the atom economy.	16.2			
solve calculations involving titrations.	16.3			
solve more complex moles questions	16.4			

REFLECTION

Try to assess the level of your understanding of this topic. Which of the following best applies to you?

- I understand everything and am very confident with the calculations.
- I understand the concepts and am confident on most questions but find the multistage problems challenging.
- I need to go back through the concepts and work through the worked examples again

Do you think that you need to go through Chapters 4 and 5 again to help with your understanding?

Would further practice on the Test Yourself questions help?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 17

How fast? The rate of chemical change

LEARNING OBJECTIVES

In this chapter you will:

- understand what is meant by the rate of a reaction
- understand how to calculate rates of reaction
- explain collision theory
- explain the factors that affect the rate of a reaction
- explain the effect of temperature on the rate of reaction
- explain the effect of a catalyst on the rate of reaction

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CONTINUED

- deduce rate equations for reactions and calculate rate constants
- sketch concentration–time and rate–concentration graphs
- understand the connection between the rate equation and the reaction mechanism and evaluate reaction mechanisms
- draw energy profiles for reactions
- understand the effect of temperature on the rate constant
- calculate the activation energy and Arrhenius *A* factor (pre-exponential factor).

GUIDING QUESTIONS

- What factors affect the rate of reaction?
- In what ways does concentration affect the rate of reaction?
- How does temperature affect the rate of reaction?
- How can we work out the mechanism of a reaction?

Introduction

There are two fundamental factors that govern whether a chemical reaction will happen – is it spontaneous (what is the value of $\Delta G^{\ominus}$)? and how fast does it go? There are many reactions that are spontaneous but are extremely slow. Sometimes this is a good thing, as in the conversion of diamond to graphite, but, at other times, this makes things extremely difficult, and many industrial processes need extreme conditions to make a process happen at a reasonable rate.

17.1 What is 'rate' of reaction?

When we consider the rate of a chemical reaction, what we are looking at is how fast or slow the reaction is. This can be thought of in terms of the speed at which the reactants are used up or the products are formed.

Consider the reaction: A → B

If we start with 1.0 g of A and 10 s later there is only 0.9 g A left, then during the first 10 s we can say that the average rate at which A is being used up is $\frac{0.1}{10} = 0.01$ g s^{-1}. 0.1 g of B would also be produced during that time, so we could also say that the average rate at which B is being produced is 0.01 g s^{-1}.

A formal definition of rate of reaction is in terms of concentrations, and this will be considered in more detail later in this chapter, but, when measuring rates of reaction experimentally, we often monitor other quantities, such as changes in mass and volume, so a good working definition of **rate of reaction** is

$$\text{rate of reaction} = \frac{\text{change in concentration/mass/volume, etc.}}{\text{time}}$$

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17.2 Experiments to measure the rate of reaction

Consider the reaction between calcium carbonate and hydrochloric acid:

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

The rate of this reaction can be measured in various ways, two of which will be considered here:

- measurement of the rate at which the gas is produced
- measurement of the rate at which the mass decreases.

Measurement of the rate at which the gas is produced

The apparatus is set up as shown in Figure 17.1 without calcium carbonate.

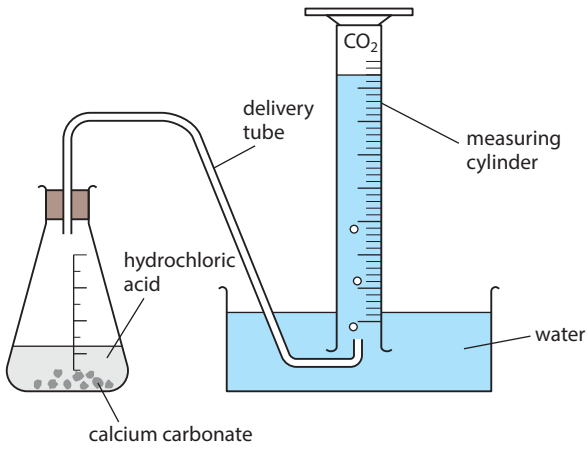

Figure 17.1: An experiment to measure rate of gas production. Instead of a measuring cylinder, a gas burette or a gas syringe could be used.

The bung in the conical flask (Erlenmeyer flask) is removed, calcium carbonate added, the bung quickly replaced and the timer started. This experiment can be used to generate a graph of volume of carbon dioxide produced against time by recording the volume on the measuring cylinder every 10 s and then plotting the data. Sample data for this experiment are shown in Table 17.1.

Time / s	Volume of CO_2 / cm^3
0	0.0
10	19.0
20	33.0
30	44.0
40	50.0
50	54.0
60	56.5
70	58.5
80	59.5
90	60.0
100	60.0
110	60.0

Table 17.1: Sample data for the experiment shown in Figure 17.1.

These data are plotted in Figure 17.2.

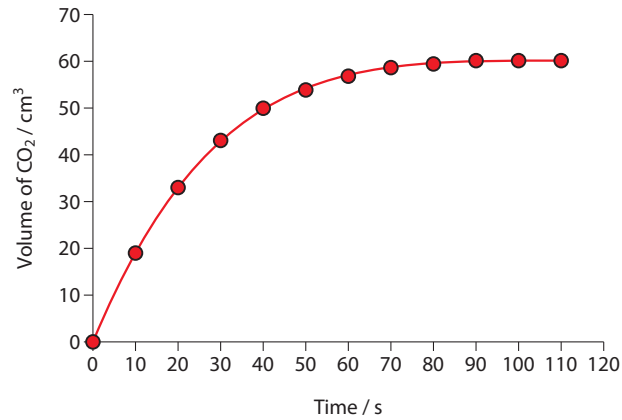

Figure 17.2: Change in volume with time.

The volume increases at first – carbon dioxide is being produced. The graph levels off at 90 s, showing that the reaction has finished – no more gas is produced after that. The *average* rate of reaction during the first 90 s can be worked out as follows:

$$\text{average rate} = \frac{\text{change in volume}}{\text{time}} = \frac{60.0}{90} = 0.67 \text{ cm}^3 \text{ s}^{-1}$$

If we look at the first 10 s, however, the rate is significantly higher than this:

$$\text{average rate} = \frac{\text{change in volume}}{\text{time}} = \frac{19.0}{10} = 1.9 \text{ cm}^3 \text{ s}^{-1}$$

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If you look at each 10 s section of the graph, you can see that the average rate for each of these sections decreases over the course of the experiment.

The rate at any time is given by the gradient (slope) of the graph at that time. From Figure 17.2, we can see that the graph is steepest (largest gradient) at the beginning, indicating that more gas is being produced per second, and the rate of reaction is highest, but decreases to eventually become zero when the graph is horizontal.

KEY POINT

The rate at a particular time can be determined from the gradient of a tangent to the curve at that point.

The rate of reaction at any point can be worked out by drawing a tangent to the curve at that point (Figure 17.3).

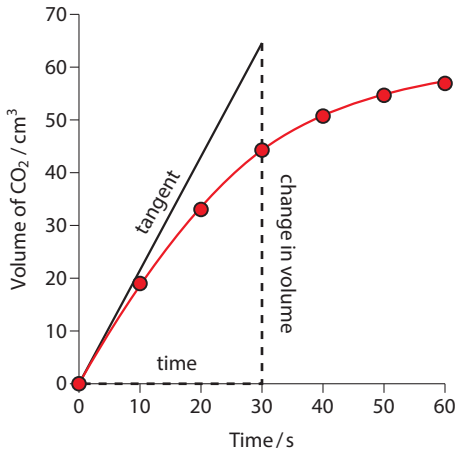

Figure 17.3: The tangent is drawn at the initial point to determine the initial rate.

The rate that we are finding in Figure 17.3 is the *initial* rate of reaction, which is the rate at the beginning of the experiment, when time = 0.

The gradient of the tangent is given by:

$$\text{gradient} = \frac{\text{change in volume}}{\text{time}} = \frac{64}{30} = 2.1 \text{ cm}^3 \text{ s}^{-1}$$

Therefore, the initial rate of reaction is 2.1 cm^3 s^{-1}, which means that, right at the start of the experiment, the gas is being produced at a rate of 2.1 cm^3 per second.

This is higher than the average rate in the first 10 s and significantly higher than the average rate over the course of the experiment.

Link

Possible problems with experiments like this include the fact that some gas is likely to escape before the bung is put on the flask (resulting in all values for the volume of carbon dioxide being lower than expected) and variations in the sizes of the calcium carbonate pieces.

The same experimental set-up can be used for investigating the rate of reaction between magnesium and hydrochloric acid. That reaction is highly exothermic and the reaction mixture becomes hotter during the experiment; this will cause the rate to be higher than 'expected'.

Measurement of the rate at which the mass decreases

The rate of this reaction can also be determined by measuring the speed at which the mass decreases. The experimental set-up for this is shown in Figure 17.4.

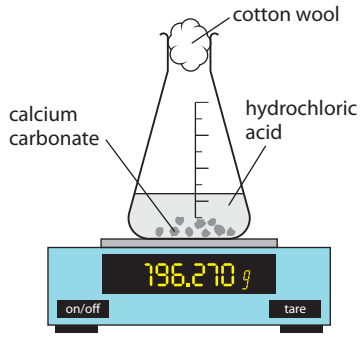

Figure 17.4: The cotton wool allows the gas to escape but stops mass being lost as a result of splashes due to fizzing – next time you drink a glass of fizzy water, watch out for all the tiny droplets escaping from the glass!

The mass decreases as carbon dioxide is given off. The results from this experiment are plotted in the graph in Figure 17.5.

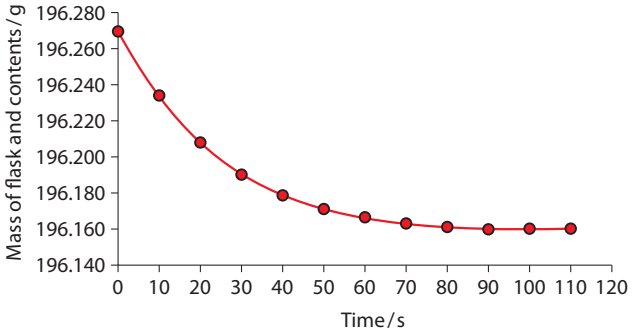

Figure 17.5: Change in mass with time.

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Alternatively, the mass of carbon dioxide lost can be worked out as follows:

mass of CO_2 lost = initial mass – mass at any time

These results are plotted in Figure 17.6.

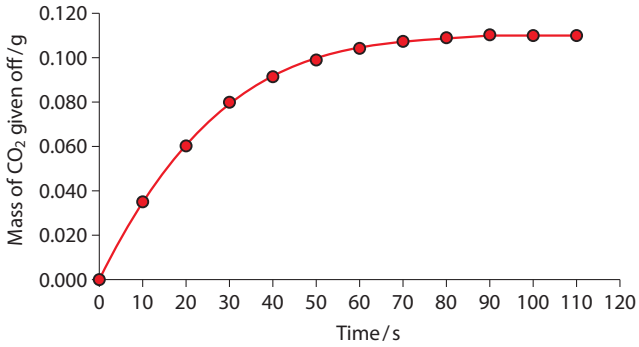

Figure 17.6: Mass of CO_2 produced with time.

The average rate of reaction and initial rate of reaction can be worked out from either graph, using the same techniques as before. In this case, we get

$$\text{average rate} = \frac{\text{change in mass}}{\text{time}} = \frac{0.110}{90} = 1.2 \times 10^{-3} \text{ g s}^{-1}$$

The initial rate is found by drawing a tangent at $t = 0$ and, in this case, the initial rate is 4.0×10^{-3} g s^{-1}. If you try doing this yourself, then you may get a slightly different value – the idea is to match the gradient of the tangent to the gradient of the graph at the initial point, but there is always an element of personal judgement in drawing a tangent. This introduces an uncertainty (random error) into your value and you must think about how many significant figures you can quote.

Following the rate of a chemical reaction using changes in colour

Some reactions involve a change in colour, and this can be used to determine the rate of reaction. Situations you may encounter are when a coloured substance is used up (the colour fades) or a coloured substance is produced. Common coloured substances that you may come across in rate experiments are solutions of bromine (orange/yellow), iodine (brown) and potassium manganate(VII) (purple). The colour changes can either be followed by eye, or by using a colorimeter. The principles of a colorimeter have already been discussed in Chapter 4 (Section 4.5).

The iodination of propanone [$(CH_3)_2CO(aq)$] in the presence of an acid **catalyst** is a commonly encountered reaction involving a colour change:

$$(CH_3)_2CO(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$$

Iodine is brown and all the other species are colourless. The reaction mixture fades from brown through yellow to colourless as iodine is used up in the reaction, and we can either time how long it takes for the reaction mixture to go colourless, which will give us the average rate of reaction, or use a colorimeter to follow how the absorbance changes over the course of the experiment (Figure 17.7), from which the initial rate of reaction can be determined.

If a colorimeter is used, a calibration curve (see Chapter 4) can be generated to convert absorbance values to concentrations, and so, work out the rate of reaction as change in concentration per unit time.

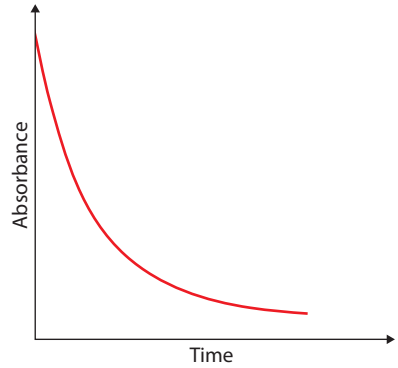

Figure 17.7: The absorbance falls with time as iodine is used up.

Rate of reaction defined

Although we can also determine rates of reaction based on changes in volume, mass, etc., rate of reaction is defined in terms of concentrations.

KEY POINT

Rate of reaction is the change in concentration of a particular reactant or product per unit time:

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

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Units for time could be s, min etc., so the units for rate of reaction are, mol dm^{-3} s^{-1}, mol dm^{-3} min^{-1}, etc.

Consider the reaction A + B → C with the following initial concentrations:

[A] = 0.100 mol dm^{-3}

[B] = 0.200 mol dm^{-3}

[C] = 0

If the initial concentration of A was 0.100 mol dm^{-3} and we measure the concentration of A after 30 s as 0.040 mol dm^{-3}, we can work out the rate of reaction for A as follows:

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}} = \frac{0.100 - 0.040}{30}$$
$$= 2.0 \times 10^{-3} \text{ mol dm}^{-3}\text{s}^{-1}$$

From the chemical equation, we can see that 1 mol A reacts with 1 mol B, so the change in concentration of B will be the same as that of A, and the rate at which B is used up will also be 2.0×10^{-3} mol dm^{-3} s^{-1}. Each time 1 mol A reacts with 1 mol B, 1 mol C is produced, so the rate at which C is produced is also 2.0×10^{-3} mol dm^{-3} s^{-1}.

Consider the reaction A → 2D

The rate at which D is produced will be twice the rate at which A is used up, because one mole of A will produce two moles of D. Therefore, if, at a particular time, the rate at which A is being used up is 0.16 mol dm^{-3} s^{-1}, the rate at which D is being produced will be 0.32 mol dm^{-3} s^{-1}.

The rate of reaction at any time can be found from a graph of concentration against time by drawing a tangent at the particular time and finding the gradient (slope) of the tangent, in a similar way to that shown for a volume against time graph in Figure 17.3. Figure 17.8a shows the how the concentration of A varies in the reaction A → 2D. The initial rate of reaction ($t = 0$) can be determined from the gradient of the tangent shown $\left(\frac{2.00}{24} = 0.083 \text{ mol dm}^{-3} \text{ s}^{-1}\right)$. The gradient of the tangent would actually be a negative value (A is being used up), but, at this level, we write all rates of reactions as positive values.

The graph in Figure 17.8b shows how the concentration of the product, D, changes in the same reaction. The rate at 40 s can be determined from the graph using the tangent shown: $\frac{2.00}{76} = 0.026$ mol dm^{-3} s^{-1}.

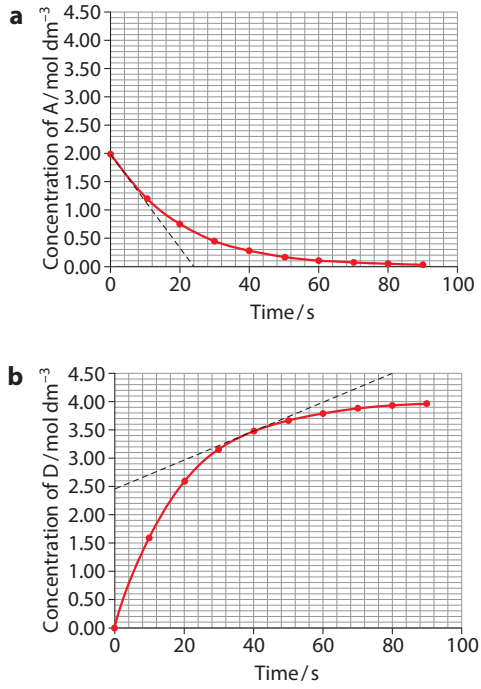

Figure 17.8: Graphs showing how the concentrations of **a** the reactant and **b** the product vary for the reaction A → 2D.

17.3 Collision theory

Reaction rates are generally discussed in terms of **collision theory**. For a reaction to occur particles must collide; however, not every collision results in a reaction, sometimes the particles just bounce off each other. A collision that results in a reaction is called a *successful* or effective collision.

KEY POINT

For a collision to result in a reaction:

- the collision must involve more than a certain minimum amount of energy, the **activation energy**, E_a: $E \geq E_a$
- molecules must collide with the correct orientations.

Activation Energy

Particles must collide with sufficient energy to react.

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If two particles with less than the activation energy collide, they will just bounce off each other and no reaction will result; however, if the particles have energy greater than or equal to the activation energy then, assuming the orientation of the collision is also correct, the particles will react.

KEY POINT

Activation energy (E_a) is the minimum amount of energy that colliding particles must possess for a collision to result in a reaction.

The activation energy is the energy needed to overcome repulsions, to start breaking bonds, to deform molecules and to allow rearrangement of atoms, electrons, etc.

The activation energy for an exothermic reaction is shown on an energy profile in Figure 17.9.

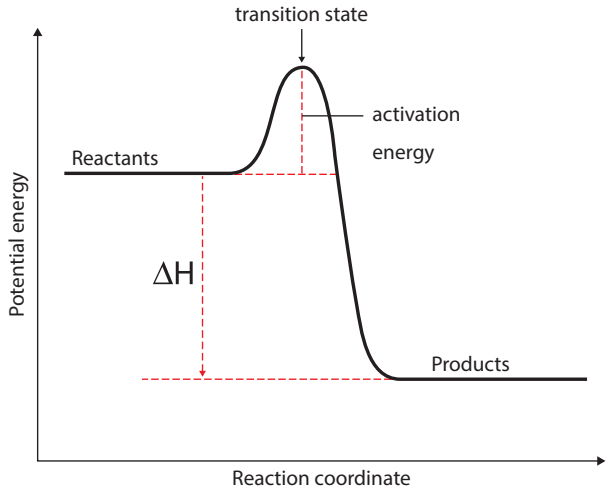

Figure 17.9: An energy profile, showing the activation energy for an exothermic reaction.

Imagine the reaction between two particles, A and B—C:

$A + B—C \rightarrow A—B + C$

As the two particles approach, repulsion between the atoms (internuclear and between electrons) causes an increase in the potential energy (this is a bit like compressing a spring or forcing together the like poles of two magnets – the potential energy increases). The B—C bond begins to break and the A—B bond begins to form. The highest point along the curve is called the **transition state (activated complex)** and all three atoms are joined together by partial bonds (A···B···C). As the A—B bond continues to form, the potential energy decreases.

Collision geometry

Not every collision with energy greater than or equal to the activation energy results in a reaction. If molecules do not collide with the correct orientation, they will not react (Figure 17.10).

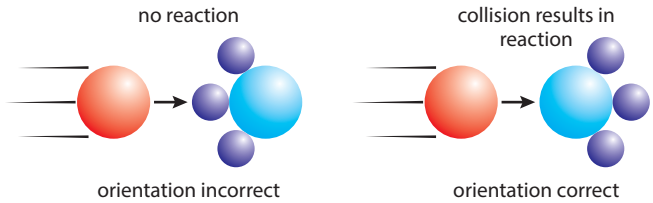

Figure 17.10: Orientation is important.

The larger and more complex the molecules, the less likely it is that they will collide in the correct orientation to react.

17.4 Factors affecting reaction rate

The main factors that affect the rate of a chemical reaction are:

- concentration of reactants
- pressure (for reactions involving gases)
- surface area of solid reactants
- temperature
- catalysis.

These factors will be considered in turn.

The effect of concentration on the reaction rate

With more particles in a certain volume, the particles collide more often (the collision frequency is higher) and, therefore, more successful collisions (i.e. ones that results in a reaction) occur in a certain time (Figure 17.11).

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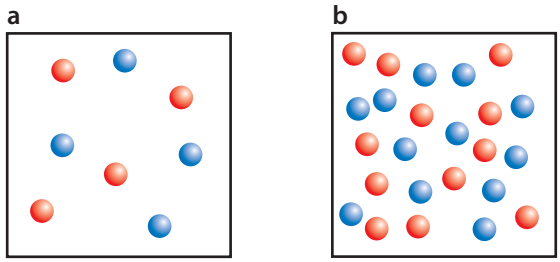

Figure 17.11: a Lower concentration – the particles are further apart and collide less frequently; **b** higher concentration – the particles are closer together and collide more frequently.

EXAM TIP

We are dealing here with how *quickly* a reaction occurs, and you must, therefore, have the idea of *time* in your explanation – it is not correct here to say that 'the particles collide more', you must write something like 'the particles collide more often/more frequently' or 'there are more collisions in a certain time'.

If you look again at Figure 17.2 and all the other graphs that show how the mass/concentration changes with time, you can see the reaction rate (gradient) is always highest at the beginning and decreases as the reaction proceeds. At the beginning, the concentrations of the reactants are highest, so the particles collide more frequently and there are more successful collisions per second, but, as the reaction proceeds, the concentration of the reactants decreases, as they get used up, so the particles collide less frequently and the reaction rate decreases.

The effect of pressure on the reaction rate

Only reactions involving gases are significantly affected by changing the pressure. The effect of increasing the pressure is essentially the same as that of increasing the concentration of gaseous reactants – there are more particles in a certain volume and the collision frequency increases (Figure 17.12).

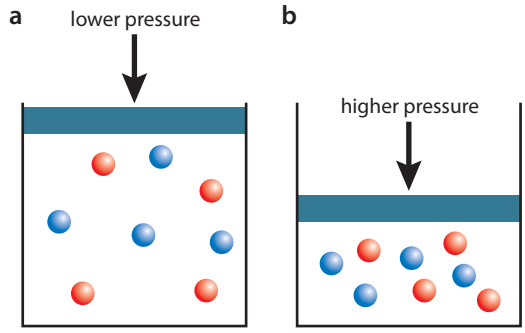

Figure 17.12: a Lower pressure – the particles are further apart and collide less frequently; **b** higher pressure – the particles are closer together and collide more frequently.

The effect of surface area of solid reactants

Reactions generally only occur at the surface of a solid. Making a solid more finely divided increases the surface area and, therefore, the number of particles exposed at the surface. The effective concentration of the particles of the solid has, thus, been increased, and there will be more frequent collisions between a particle of the other reactant and a particle on the surface of the solid (Figure 17.13).

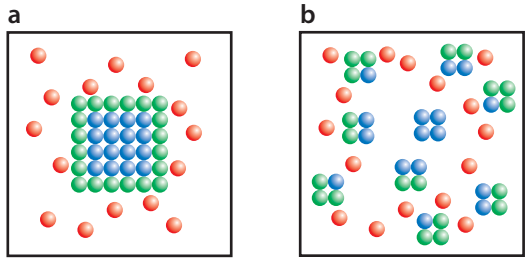

Figure 17.13: a Low surface area – only the particles coloured green are exposed on the surface and able to collide with the red particles; **b** high surface area – particles coloured both green and blue are exposed and are able to collide with the red particles.

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The effect of temperature on rate of reaction

The relationship between temperature and the energy of particles in a gas

Before we can understand the effect of temperature on the rate of a chemical reaction, we must look at how changing the temperature affects how the particles in a gas move.

KEY POINT

For an ideal gas, the average kinetic energy of the particles in a gas is proportional to its temperature in kelvin.

Therefore, if a sample of oxygen is heated from 300 to 600 K, the average kinetic energy of the particles is doubled.

We can get an idea of how increasing the temperature affects the speed of the particles in the gas by doing a quick calculation. Imagine heating a sample of gas from 300 to 310 K.

kinetic energy $(K_E) = \frac{1}{2}mv^2$

So, if we take v_T as the average speed of the gas particles at temperature T, we get

average K_E at 300 K $= \frac{1}{2}mv_{300}^2$

average K_E at 310 K $= \frac{1}{2}mv_{310}^2$

Note: v here is actually the root mean square speed.

Average K_E is proportional to temperature, so the ratio of the average K_E at 310 K to that at 300 K is $\left(\frac{310}{300}\right) = 1.033$.

So, $\frac{\frac{1}{2}mv_{310}^2}{\frac{1}{2}mv_{300}^2} = 1.033$

The $\frac{1}{2}$ and m cancel, and so, we have $\frac{v_{310}^2}{v_{300}^2} = 1.033$

and $v_{310} = \sqrt{1.033}\, v_{300} = 1.02 v_{300}$

This means that at 310 K the particles are only moving about 2% faster than at 300 K.

How much does temperature affect rate?

Increasing the temperature has a large effect on the rate of the reaction. As the temperature increases, the rate of reaction increases exponentially (Figure 17.14).

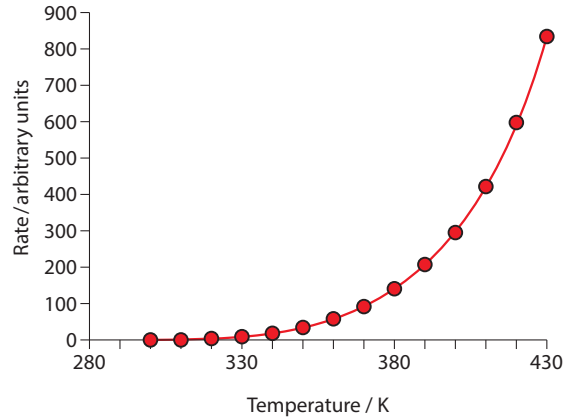

Figure 17.14: The rate of a reaction increases exponentially as the temperature rises.

It is often said that, as a rough rule of thumb, a rise in temperature of 10 K causes the reaction rate to approximately double. This applies reasonably well to many of the reactions we encounter in a school laboratory over the temperature range we usually look at, but it is only a guide and not generally applicable.

KEY POINT

Collision frequency increases as temperature increases.

As the temperature increases, the molecules have more kinetic energy and, therefore, move faster. This means that the collision frequency increases, i.e., the particles collide more often. However, we saw that increasing the temperature by 10 K only caused the speed of the particles to increase by about 2%, so such a large increase in reaction rate as the temperature is increased by 10 K cannot be explained solely by an increase in collision frequency.

The major cause of the increase in rate as the temperature increases is that the particles collide harder, that is, with more energy, so that there is greater chance that a collision will result in reaction. This is usually explained further using the Maxwell-Boltzmann distribution.

The Maxwell–Boltzmann energy distribution

Let us consider a sample of gas – the molecules are constantly colliding with each other and, therefore, do not all have the same speed and, hence, kinetic energy. This is shown in Figure 17.15, which represents the

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Maxwell–Boltzmann distribution of molecular kinetic energies at a particular temperature.

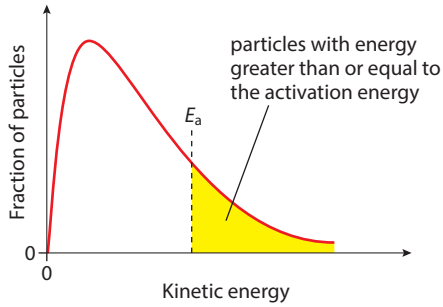

Figure 17.15: The Maxwell–Boltzmann distribution of the energy of the particles in a sample of gas.

Features to note in Figure 17.15:

- it is *not* symmetrical
- no molecules have zero kinetic energy
- at higher energy, the line does not reach the kinetic energy axis.

The shaded region in Figure 17.15 shows the proportion of particles that have suffcient energy to react when they collide, that is, those particles with energy greater than or equal to the activation energy.

The graph in Figure 17.15 is actually a histogram, where each bar in the histogram represents the fraction of molecules in a certain narrow range of kinetic energies.

EXAM TIP

The vertical axis of the Maxwell–Boltzmann distribution can be labelled in various ways:

- fraction/proportion of particles/molecules
- fraction/proportion of particles/molecules with a certain amount of energy
- probability density
- probability of particles/molecules
- number of particles/molecules
- number of particles/molecules with a certain amount of energy.

Of these labels, the one that is probably used most frequently in exams is fraction/proportion of particles/molecules, but questions have been set where it has been required, for instance, to know that probability density is also a possible label.

KEY POINT

The main reason that the rate of reaction increases with temperature is an increase in the proportion of particles with energy greater than or equal to the activation energy.

Why does temperature have such a large effect on rate of reaction?

As the temperature is increased, the distribution of energies in a sample of gas changes (Figure 17.16).

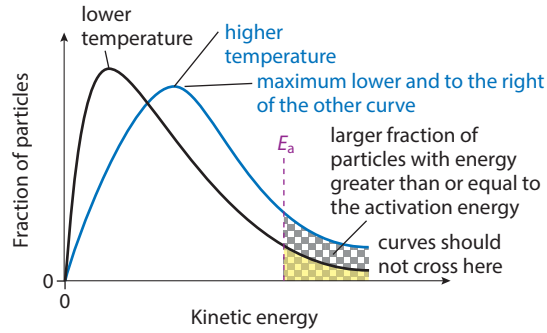

Figure 17.16: The Maxwell-Boltzmann distribution changes as temperature changes.

At higher temperatures, the average kinetic energy of the particles is higher – there are fewer particles with lower energy and more particles with higher energy. This is shown in the Maxwell–Boltzmann distribution by the curve being flatter and the maximum having moved to the right. The areas underneath the curves are the same because we are looking at fractions of particles, and the total when we add up the fractions of something is one (the whole thing).

The yellow-shaded area in Figure 17.16 represents the fraction of particles with energy greater than or equal to the activation energy at the lower temperature. The checked area represents the fraction of particles with energy greater than or equal to the activation energy (E_a) at the higher temperature. At a higher temperature, a greater proportion of particles have energy greater than or equal to the activation energy (E_a), therefore a greater proportion of collisions will be successful. This means that there will be more successful collisions per second and the rate of reaction will increase.

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Catalysis

KEY POINT

A catalyst is a substance that increases the rate of a chemical reaction but is chemically unchanged at the end (it is not used up).

An example of a catalyst is manganese(IV) oxide in the decomposition of hydrogen peroxide solution:

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

Note that the catalyst is often written above the reaction arrow – it does not appear in the chemical equation because it is not used up in the reaction.

Without the catalyst, the reaction occurs very slowly, but it is very rapid once the catalyst has been added. This reaction can also be catalysed by a biological catalyst called catalase, which is found in liver, potatoes, etc.

KEY POINT

Biological catalysts are called enzymes.

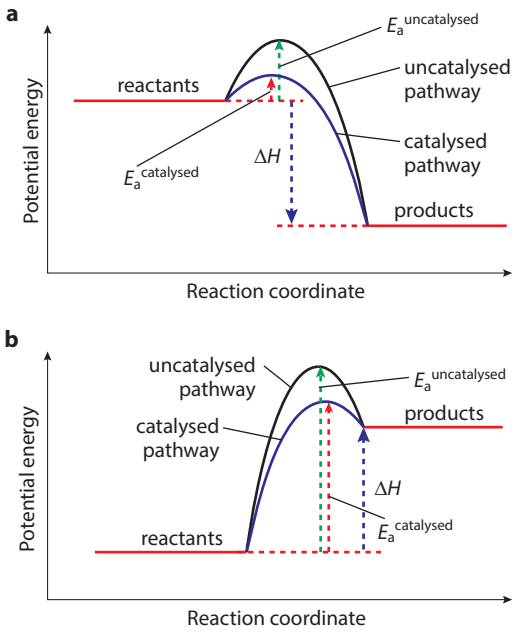

Figure 17.17: Energy profiles showing the effect of a catalyst on the activation energy of **a** an exothermic reaction and **b** an endothermic reaction.

Figure 17.17 shows the energy profiles for exothermic and endothermic reactions with and without a catalyst.

KEY POINT

A catalyst acts by allowing the reaction to proceed by an alternative pathway of lower activation energy.

Link

Higher Level only: the mechanism is different for a catalysed reaction (see Section 17.5).

If we look at the Maxwell–Boltzmann distribution, we can understand why a lower activation energy results in a faster reaction (Figure 17.18).

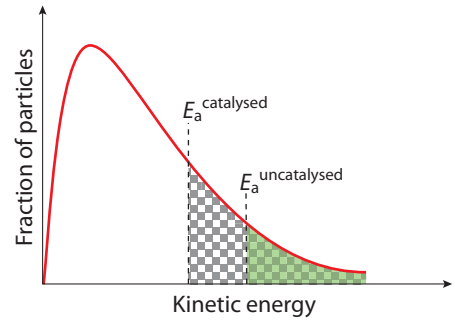

Figure 17.18: The green-shaded area represents the fraction of particles with energy greater than or equal to the activation energy for the uncatalysed reaction. The checked area represents the fraction of particles with energy greater than or equal to the activation energy for the catalysed reaction.

The presence of a catalyst means that a larger fraction of particles have energy greater than or equal to the activation energy; therefore, a greater proportion of collisions results in reaction. There will therefore be more successful collisions per second and the rate of reaction increases.

EXAM TIP

It is important to remember that a catalyst does not 'lower the activation energy' but allows the reaction to occur in a different way, and this alternative pathway has a lower activation energy.

The role of a catalyst is sometimes likened to the idea of there being a mountain between your home and school – a catalyst makes the journey to and from school faster by providing a tunnel through the mountain; it does not lower the mountain.

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SCIENCE IN CONTEXT

Hydrogen peroxide and catalysts

One of the most exciting chemical reactions you might see in a chemical laboratory is the 'elephant's toothpaste' reaction. This involves the decomposition of hydrogen peroxide to oxygen gas using a potassium iodide catalyst to speed up the reaction. The reaction that occurs is

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Washing-up liquid (dishwashing liquid) is added to the reaction mixture to generate a foam as oxygen is produced, and the results can be quite spectacular (try a quick internet search for videos). Potassium iodide is a homogeneous catalyst (in the same phase as the reactants) and allows the reaction to occur by an alternative pathway of lower activation energy by reacting with the hydrogen peroxide. The reaction mechanism is usually described as

$I^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + IO^-(aq)$

$IO^-(aq) + H_2O_2(aq) \rightarrow O_2(g) + H_2O(l) + I^-(aq)$

Things are, however, not quite that simple and, as can be seen from Figure 17.19, some of the iodide is converted to iodine, so other reactions are also occurring.

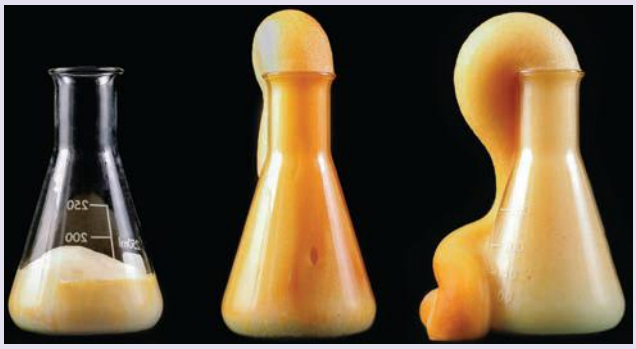

Figure 17.19: The elephant's toothpaste reaction. Try an internet search for 'elephant toothpaste world record' to see how spectacular this reaction can be.

But there is much more to catalysts than just lab demonstrations – other homogeneous catalysts, enzymes, speed up thousands of reactions in your body. These are usually proteins with a specific three-dimensional shape and are involved in all aspects of human biochemistry from breaking down food to DNA replication. There is even an enzyme, catalase, to speed up the decomposition of hydrogen peroxide to oxygen – hydrogen peroxide is involved in cell signalling in the body, but its concentration has to be carefully controlled because it can also severely damage cells – a process called oxidative stress.

Hydrogen peroxide has its entertaining side, and it has a biological role, but it is also an extremely useful industrial chemical and over 4 million tonnes are made each year. Its primary use is for bleaching wood pulp for making paper and de-inking paper in the recycling process; it may have been used in making the paper for this book. It is manufactured from an anthraquinone (Figure 17.20) using a palladium catalyst.

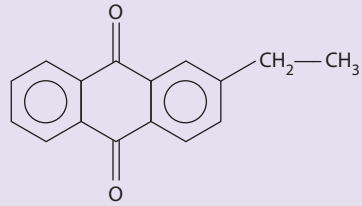

Figure 17.20: An anthraquinone used in the manufacture of hydrogen peroxide.

This time the catalyst, like many others in industrial processes, is a heterogeneous catalyst (catalyst in a different phase to the reactants) and the reaction occurs on the surface. Catalysts are essential in industrial processes because they allow them to operate at lower temperatures and, therefore, reduce the energy requirements of a sector that is already a major contributor to global energy demand.

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THEORY OF KNOWLEDGE

How do we know when we encounter a new reaction that the rate will increase when we increase the temperature? This comes from the idea of inductive reasoning. Inductive reasoning is a fundamental tool of scientists, and, to a certain extent, chemistry would not exist in the form it does without inductive reasoning. Inductive reasoning allows us to generalise from the specific – for instance, if we carry out a series of experiments and each one gives us the result that increasing the temperature increases the rate of reaction, then we postulate a general law – that the rate of reaction increases with temperature.

How is it possible to do this when we have not studied every single chemical reaction? Indeed, a philosopher would say that this is not rational, and there is no logical basis for being able to do this – that is the problem with induction. Common sense, however, would tell us that the rate of reaction for every simple reaction should increase as temperature increases – we rely on the uniformity of nature, and we cannot imagine a situation in which it would not be true. But can we know this or only believe it to be true? Is there a difference between a scientist having faith in induction and religious faith?

TEST YOUR UNDERSTANDING

1 A series of experiments was carried out to measure the volume of gas produced when magnesium reacted with dilute hydrochloric acid. The equation for the reaction is

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

In the first experiment, 0.10 g of Mg ribbon was reacted with 30 cm^3 of 0.50 mol dm^{-3} HCl, which is excess hydrochloric acid. Data for this experiment is recorded in the table. The reaction was carried out at 20 °C.

Time / s	Volume of gas / cm^3
0	0.0
15	18.6
30	32.3
45	44.3
60	54.8
75	62.7
90	68.4
105	72.6
120	74.9
135	75.4
150	75.6
165	75.6
180	75.6

a Draw a graph of the data and state and explain, in terms of collision theory, how the rate of reaction changes with time.

b Use your graph to calculate the initial rate of the reaction with units.

c Calculate the average rate for the first 120 s.

d The experiment was repeated under the same conditions, except that 0.10 g of powdered Mg was used. On the same set of axes you used in part **a**, sketch the graph that would be obtained. Label this graph X. Hint: think about the rate of reaction (initial slope of the graph) and the volume of gas that will be produced.

e The original experiment was repeated, except that 0.05 g of Mg ribbon was used. On the same axes, sketch the graph that would be obtained. Label this graph Y.

f The original experiment was repeated at 10 °C. On the same axes, sketch the graph that would be obtained. Label this graph Z.

g Sketch the Maxwell–Boltzmann distribution for the original experiment and the experiment at 10 °C and use this to explain the effect of a change in temperature on the rate of this reaction.

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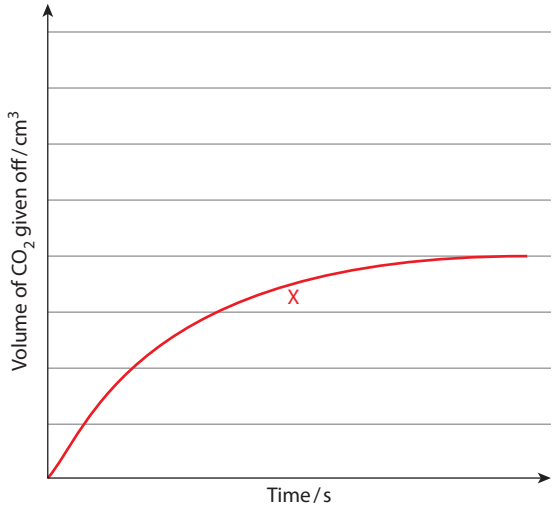
2 The graph shown is for 25.0 cm^3 of 1 mol dm^{-3} HCl reacting with excess calcium carbonate (medium lumps) at 25 °C.



Sketch graphs for the following set of conditions. In each case, consider the initial rate of reaction and the volume of gas produced:

a 25.0 cm^3 of 2 mol dm^{-3} HCl reacting with excess calcium carbonate (medium lumps) at 25 °C

b 50.0 cm^3 of 0.5 mol dm^{-3} HCl reacting with excess calcium carbonate (medium lumps) at 25 °C

c 25.0 cm^3 of 1 mol dm^{-3} HCl reacting with excess calcium carbonate (medium lumps) at 35 °C

d 25.0 cm^3 of 1 mol dm^{-3} HCl reacting with excess calcium carbonate (powder) at 25 °C.

3 State the relationship between the average kinetic energy of particles in a gas and the temperature in K.

4 Explain what a catalyst is.

5 Explain how a catalyst speeds up a chemical reaction.

6 Sketch energy profiles for exo- and endothermic reactions with and without catalysts.

17.5 The rate equation

A rate of reaction is usually affected by a change in concentration of the reactants. Consider the reaction A → B. If a series of experiments are carried out in which the concentration of A is varied and the rate of reaction measured, a graph like the one in Figure 17.21 might be plotted.

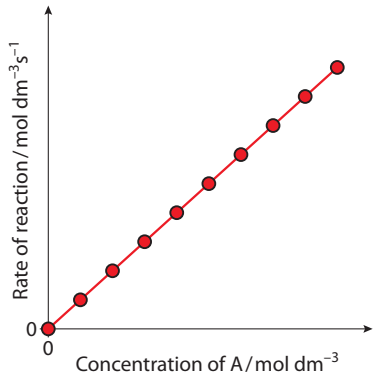


Figure 7.21: Possible rate–concentration graph for the reaction A → B.

This graph shows that the rate of reaction is directly proportional to the concentration of A, and we can write:

$\text{rate} \propto [A]$

where [A] is the concentration of A. By putting in a constant of proportionality, we have

$\text{rate} = k[A]$

This equation is called a **rate equation**, *rate expression* or *rate law* – k is called the **rate constant**.

KEY POINT

The rate equation is an experimentally determined equation that relates rate of reaction to the concentrations of substances in the reaction mixture.

'Substances in the reaction mixture' include the reactants and catalysts. There are also some reactions where the concentrations of the products can affect the rate of a reaction, but these will not be considered here.

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KEY POINT

k, the rate constant, is a constant of proportionality relating the concentrations in the experimentally determined rate equation to the rate of a chemical reaction.

A general rate equation

We can write a rate equation for any reaction.
For example, for the following reaction:

$W + X \rightarrow Y + Z$

we can write rate = $k[W]^m[X]^n$

where, k is the rate constant – note: small k, not capital K

m is the order with respect to W

n is the order with respect to X.

KEY POINTS

The rate constant is only a constant for a particular reaction at a particular temperature.

The order of a reaction with respect to a particular reactant is the power (exponent) of the reactant's concentration in the experimentally determined rate equation.

An **overall order of reaction** is the sum of the powers (exponents) of the concentration terms in the experimentally determined rate equation.

Therefore, in the general rate equation, the overall order is $m + n$.

If we consider our original rate equation, rate = $k[A]$, again: we say that this reaction is *first order with respect to A* because the power of [A] is one. It is also first order overall. If we have the rate expression rate = $k[X][Y]^2$ we say that the reaction is first order with respect to X and second order with respect to Y.
The overall order is $1 + 2 = 3$.

KEY POINT

A rate equation can be determined only from experimental data.

The rate equation cannot be deduced from the chemical (stoichiometric) equation for a reaction, i.e., we cannot simply look at an equation such as $2A + B \rightarrow C + D$ and deduce that the order with respect to A is two and with respect to B is one. The reason for this is that the reaction may not occur in one single step – this will be considered in more detail in section 17.6. To determine the rate equation, we must carry out a series of experiments in which the effect of changing the concentration of the reactants on the rate of reaction is investigated.

Experimental determination of a rate equation

Consider the reaction $A + B \rightarrow C$. The dependence of the reaction rate on the concentrations of A and B can be determined by conducting the following set of experiments.

First, a series of experiments are carried out using a fixed concentration of B and changing the concentration of A each time. Each experiment should yield a graph of concentration of A against time. The initial rates can be worked out from these graphs by drawing tangents at $t = 0$. From these data, the order of the reaction with respect to A can be determined by plotting a graph of initial rate against concentration of A. The initial rate is taken because this is the only point at which we know the concentration of A and concentration of B – none has been used up.

Next, the experiments are repeated using a fixed concentration of A and varying the concentration of B. This allows the **order of reaction** with respect to B to be calculated.

When the orders with respect to A and B are known, the rate equation and, hence, a value for the rate constant can be worked out.

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Determining the order of reaction and the rate equation from experimental data

WORKED EXAMPLE 17.1

Consider the data for the reaction $2A \rightarrow B$ given in the table.

Experiment	[A] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.0	0.60
2	2.0	1.2
3	5.0	3.0

where [A] is the initial concentration of A.

a Deduce the order of reaction with respect to A.

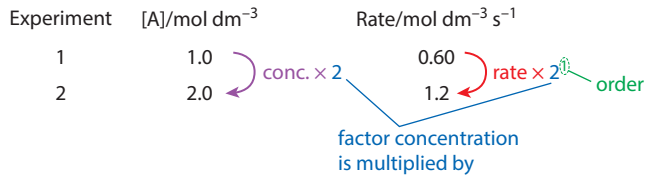
b Deduce the rate equation.

c Calculate the value of the rate constant (with units).

d Calculate the rate of reaction when [A] = 1.3 mol dm^{-3}.

Answer

a If we consider experiments 1 and 2, we can see that, as the concentration of A is doubled from 1.0 to 2.0 mol dm^{-3}, the rate of reaction also doubles from 0.60 to 1.2 mol dm^{-3} s^{-1}. So, concentration is multiplied by a factor of 2 and the rate goes up by a factor of 2^1. This means that the order with respect to A is 1 – in other words, the reaction is first order with respect to A. This can be summarised as



The fact that the order of reaction with respect to A is 1 can be further confirmed by looking at experiments 1 and 3. As the concentration of A is multiplied by a factor of 5, the rate of reaction is multiplied by a factor of 5^1.

b The reaction is first order with respect to A, so the rate equation is: rate = k[A]

If the order with respect to a particular reactant is 1, we do not usually write this explicitly in the rate equation.

c To find the value of k, we substitute the values from any one of the experiments into the rate equation. If this is done using the values from experiment 1, we get:

$0.60 = k \times 1.0$

This can be rearranged to give $k = 0.60$.

k has units, and these can be worked out from the rate equation by substituting units into the rate equation:

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rate = k[A] ⇒ mol dm^{-3} s^{-1} = k × mol dm^{-3}

'mol dm^{-3}' can be cancelled from each side:

~~mol dm^{-3}~~ s^{-1} = k × ~~mol dm^{-3}~~

so, s^{-1} = k

Therefore, the units of k are s^{-1} in this case, and the rate constant is 0.60 s^{-1}.

d The rate of reaction when [A] = 1.3 mol dm^{-3} can be worked out by substituting this value into the rate equation along with the value of k:

rate = k[A]

rate = 0.60 × 1.3

Therefore, the rate of reaction is 0.78 mol dm^{-3} s^{-1}.

This could also have been worked out by realising that the reaction is first order with respect to A and that 1.3 mol dm^{-3} is 1.3 times the concentration of A in experiment 1 and, therefore, the rate of reaction is 1.3 times the rate of reaction in experiment 1.

WORKED EXAMPLE 17.2

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} h^{-1}
1	0.10	0.10	0.50
2	0.30	0.10	4.50
3	0.30	0.20	4.50

Given this data for the reaction 3A + B → C + D determine the following:

a the order with respect to A

b the order with respect to B

c the overall order of the reaction

d the rate equation

e the value of the rate constant (with units)

f the rate of reaction when [A] = 1.60 mol dm^{-3} and [B] = 0.30 mol dm^{-3}.

Answer

a To find the order with respect to A, we must consider experiments 1 and 2, because the only thing that changes in these two experiments is the concentration of A (the concentration of B remains constant). From experiment 1 to experiment 2, the concentration of A is multiplied by a factor of 3 and the rate goes up by a factor of 9, which is 3^2. This means that the order with respect to A is 2 – the reaction is second order with respect to A.

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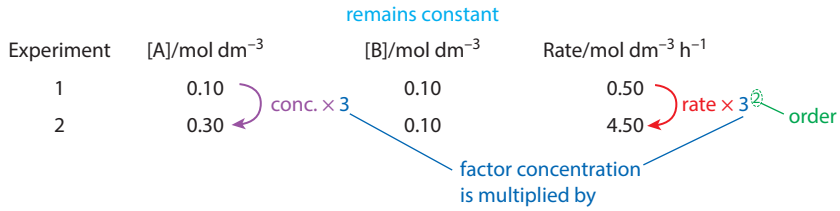
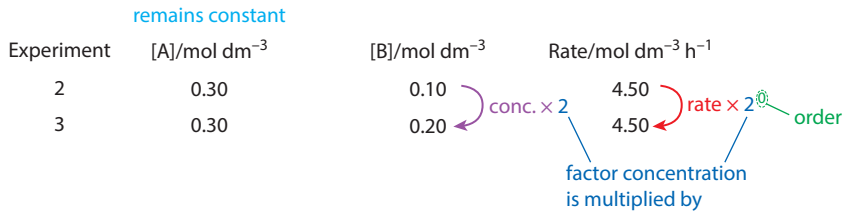


b To find the order with respect to B, we must consider experiments 2 and 3, because the only thing that changes in these two experiments is the concentration of B (the concentration of A remains constant). From experiment 2 to experiment 3, the concentration of B is multiplied by a factor of 2 and the rate does not change, i.e., it is multiplied by a factor of 2^0. This means that the order with respect to B is 0 – the reaction is zero order with respect to B.



Remember: any number to the power zero is 1.

c The overall order of reaction is the sum of the orders with respect to A and B – in this case 2 + 0. Therefore, the overall order is 2.

d The rate equation is: rate = $k[A]^2[B]^0$, which is usually just written as: rate = $k[A]^2$.

e The value of the rate constant can be calculated by substituting values from any experiment into the rate equation. It does not matter which experiment is taken, but values must not be taken from different experiments. If we use data from experiment 2:

$\text{rate} = k[A]^2$

$4.50 = k \times 0.30^2$

$k = 50$

To work out the units for k, the units of concentration and rate are substituted into the rate equation:

$\text{mol dm}^{-3}\ \text{h}^{-1} = k(\text{mol dm}^{-3})^2$

mol dm^{-3} can be cancelled from each side:

$\cancel{\text{mol dm}^{-3}}\ \text{h}^{-1} = k(\text{mol dm}^{-3})^{\cancel{2}}$

$\text{h}^{-1} = k\ \text{mol dm}^{-3}$

This can be rearranged to give:

$$\frac{h^{-1}}{\text{mol dm}^{-3}} = k$$

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i.e. $k = \text{mol}^{-1}\ \text{dm}^3\ \text{h}^{-1}$

Remember: to bring a quantity from the bottom to the top of an expression, the sign of the power is changed, i.e., $\frac{1}{x^2}$ is equivalent to x^{-2}.

Therefore, the value of the rate constant, k, is 50 $\text{mol}^{-1}\ \text{dm}^3\ \text{h}^{-1}$.

It is good practice to write any positive powers in units first, so this is better written as 50 $\text{dm}^3\ \text{mol}^{-1}\ \text{h}^{-1}$.

f The rate of reaction when [A] = 1.60 mol dm^{-3} and [B] = 0.30 mol dm^{-3} can be worked out by substituting these values, together with the value of k, into the rate equation:

rate = $k[\text{A}]^2 = 50 \times 1.60^2 = 128$ mol $\text{dm}^{-3}\ \text{h}^{-1}$

WORKED EXAMPLE 17.3

The table shows experimental data for the reaction $2\text{P} + \text{Q} \rightarrow \text{R} + \text{S}$

Experiment	[P] / mol dm^{-3}	[Q] / mol dm^{-3}	Rate / mol $\text{dm}^{-3}\ \text{s}^{-1}$
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
3	6.00	8.00	0.100

Determine the following:

a the order with respect to P

b the order with respect to Q

c the overall order of the reaction

d the rate equation

e the value of the rate constant (with units).

Answer

a To find the order with respect to P, we must consider experiments 1 and 2, because the only thing that changes in these two experiments is the concentration of P (the concentration of Q remains constant). From experiment 1 to experiment 2, the concentration of P is multiplied by a factor of 2 and the rate goes up by a factor of 2, i.e., 2^1. This means that the order with respect to P is 1 – the reaction is first order with respect to P.

b It is a more difficult problem to find the order with respect to Q because there are no two experiments in which the concentration of P remains constant, and so, we cannot easily see how just changing [Q] affects the rate. One way of getting around this is to add another row to the table:

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Experiment	[P] / mol dm^{-3}	[Q] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	1.20	2.00	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
2A			
3	6.00	8.00	0.100

The concentration of P is chosen to be the same as that in experiment 3 to produce two experiments where the concentration of P remains constant and the concentration of Q must be the same as in experiment 1 (or 2) so that the only thing that changes between experiment 1 and experiment 3 is the concentration of P.

Experiment	[P] / mol dm^{-3}	[Q] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	1.20	*2.00*	5.00×10^{-3}
2	2.40	2.00	1.00×10^{-2}
2A	*6.00*	*2.00*	$\mathbf{2.50 \times 10^{-2}}$
3	*6.00*	8.00	0.100

We can deduce the rate of experiment 2A because we have already worked out that the order with respect to P is 1. The concentration of P in experiment 2A is 5 times that in experiment 1, and because [Q] is the same in both experiments, the rate in experiment 2A will be $5^1 \times 5.00 \times 10^{-3}$, i.e., 2.50×10^{-2} mol dm^{-3} s^{-1}.

We can now consider experiments 2A and 3 and see the effect of just changing the concentration of Q on the rate of reaction. From experiment 2A to experiment 3, the concentration of Q is multiplied by a factor of 4 and the rate changes by a factor of 4^1. This means that the order with respect to Q is 1.

Another way to approach this, without adding another row to the table, is to just consider experiments 1 and 3. We know that going from experiment 1 to experiment 3 the concentration of P has increased by a factor of 5. Because the reaction is first order with respect to P, the result of this will be to multiply the rate of reaction by a factor of 5^1. If this were done without any change in the concentration of Q, the rate of reaction would be $5 \times 5.00 \times 10^{-3}$, i.e., 2.50×10^{-2} mol dm^{-3} s^{-1}. However, the rate of reaction in experiment 3 is 0.100, which is 4 times 2.50×10^{-2}. Thus, the effect of multiplying the concentration of Q by 4 is that the rate of reaction is multiplied by 4^1; therefore, the order with respect to Q is 1. This approach is, of course, equivalent to adding an extra row to the table.

c The order with respect to P is 1 and the order with respect to Q is 1, so the overall order is 1 + 1, i.e., 2.

d The rate equation is: rate = k[P]^1[Q]^1, which is usually just written as: rate = k[P][Q].

e The value of the rate constant can be calculated by substituting values from any one experiment into the rate equation. If we use data from experiment 3:

$0.100 = k \times 6.00 \times 8.00$

$k = 2.08 \times 10^{-3}$

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To work out the units for k, the units of concentration and rate must be substituted into the rate equation:

$\text{mol dm}^{-3}\ \text{s}^{-1} = k \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}$

mol dm^{-3} can be cancelled from each side:

$\cancel{\text{mol dm}^{-3}}\ \text{s}^{-1} = k \times \cancel{\text{mol dm}^{-3}} \times \text{mol dm}^{-3}$

So, $\text{s}^{-1} = k \times \text{mol dm}^{-3}$

This can be rearranged to give $\dfrac{\text{s}^{-1}}{\text{mol dm}^{-3}} = k$

Thus, $k = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$

Therefore, the rate constant, k, is $2.08 \times 10^{-3}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$.

Reaction orders

Zero-order reactions

Consider a zero-order reaction – the decomposition of ammonia on a tungsten surface:

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

The concentration of ammonia decreases at a constant rate in this reaction. The constant rate is indicated by the graph of concentration against time being a straight line (Figure 17.22). A straight line has a constant gradient (slope) and indicates that the rate does not change as the concentration of NH_3 changes (the NH_3 is being used up).

The concentration of nitrogen also increases at a constant rate, as indicated by the straight dashed line in Figure 17.22.

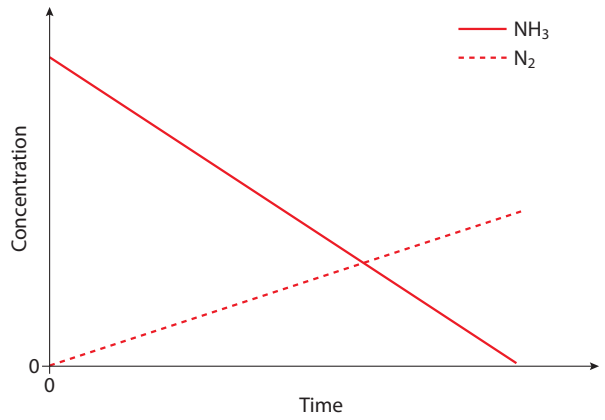

Figure 17.22: Concentration of reactant and product against time for a zero-order reaction.

The two graphs of concentration against time are drawn to the same scale, so the magnitude of the gradient of the line for N_2 is half that for NH_3. This is because in the chemical equation for this reaction the coefficient of NH_3 is 2 but that of N_2 is 1 – so, for every 2 mol of NH_3 used up, only 1 mol of N_2 is produced – N_2 is produced at half the rate at which NH_3 is used up.

Changing the concentration of ammonia has no effect on the rate of the reaction (Figure 17.23). The graph of rate against concentration is a horizontal straight line.

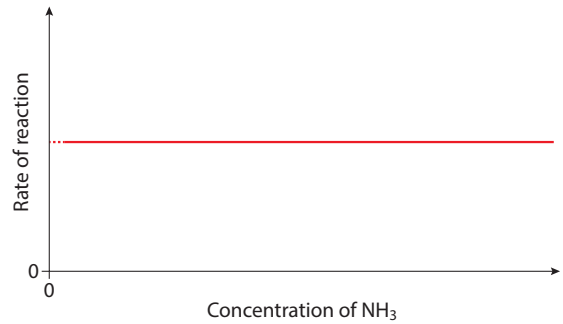

Figure 17.23: Rate against concentration for a zero-order reaction.

KEY POINT

For a zero-order reaction:

- the rate is independent of concentration
- the rate equation is: rate = k
- the units of k are concentration × time^{-1} (i.e. units could be mol dm^{-3} s^{-1}, mol dm^{-3} h^{-1}, etc.)

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First-order reactions

A first-order reaction is the decomposition of hydrogen iodide on a platinum surface:

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

The rate of this reaction is directly proportional to the concentration of HI, as shown by the straight line through the origin in Figure 17.24 and the rate equation is rate = k[HI].

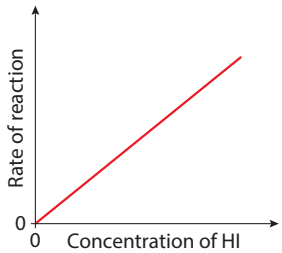

Figure 17.24: Rate against concentration for a first-order reaction.

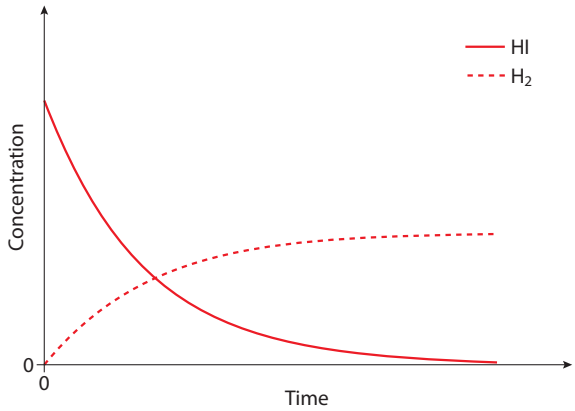

Figure 17.25: Concentration of reactant and product against time for a first-order reaction.

The graph in Figure 17.25 shows how the concentration of HI decreases with time. This shows an exponential decay and a constant *half-life*. The time for the concentration to drop by half does not depend on concentration in a first-order reaction, for example, the time taken for the concentration to fall from 0.1 to 0.05 mol dm^{-3} is the same as the time taken for the concentration to fall from 0.08 to 0.04 mol dm^{-3}.

The dashed line in Figure 17.25 shows the increase in concentration of one of the products (H_2) with time. The rate of production of H_2 is half the rate at which HI is used up, which can be seen from the coefficients in the chemical equation:

$2HI \rightarrow H_2 + I_2$

KEY POINT

For a first-order reaction:

- the rate is directly proportional to the concentration
- the rate equation is: rate = k[A]
- the units of k are time^{-1} (i.e. units could be s^{-1}, h^{-1}, etc.)

Second-order reactions

Consider a second-order reaction – the decomposition of hydrogen iodide without a catalyst:

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

Figure 17.26 shows how the rate of the reaction varies with the concentration of hydrogen iodide.

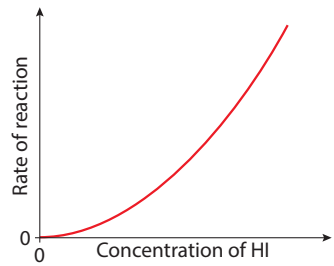

Figure 17.26: Rate against concentration for a second-order reaction.

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The rate equation is: rate = $k[HI]^2$

It can be proved that a reaction is second order (rather than third order, etc.) by plotting a graph of rate against concentration of HI squared (Figure 17.27). As the rate is proportional to $[HI]^2$, this graph is a straight line through the origin.

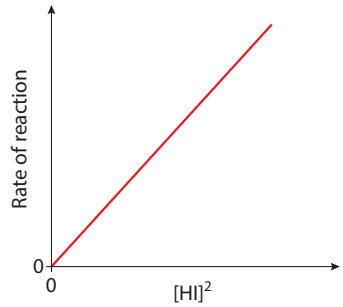

Figure 17.27: Rate against concentration squared for a second-order reaction.

Figure 17.28 shows how the concentration of HI changes with time. This is not an exponential relationship and does not have a constant half-life.

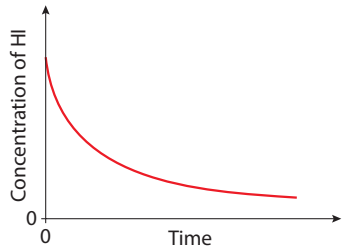

Figure 17.28: Concentration of reactant against time for a second-order reaction.

KEY POINT

For a second-order reaction:

- the rate of reaction is proportional to concentration squared
- the rate equation is: rate = $k[A]^2$

The units of the rate constant are concentration^{-1} time^{-1} (i.e. units could be mol^{-1} dm^3 s^{-1}).

The units of the rate constant

It can be seen from this treatment that the units of the rate constant are related to the overall order of the reaction. This is summarised in Table 17.3.

Overall order	Units of k	Example of units
0	concentration time^{-1}	mol dm^{-3} s^{-1}
1	time^{-1}	s^{-1}
2	concentration^{-1} time^{-1}	mol^{-1} dm^3 s^{-1}
3	concentration^{-2} time^{-1}	mol^{-2} dm^6 s^{-1}

Table 17.3: The relationship between overall order of the reaction and the units of the rate constant.

For a zero-order reaction, the units of k are the same as that of the rate.

Each time the overall order increases by one, the units of k are divided by concentration.

KEY POINT

Generally, the units of k are: concentration$^{(1-\text{overall order})}$ time^{-1}.

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TEST YOUR UNDERSTANDING

7 Consider the following data for the reaction

$A + 2B \rightarrow C + D$

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.0200
2	0.400	0.100	0.0400
3	0.400	0.200	0.160

a Deduce the order of reaction with respect to A and with respect to B.

b What is the overall order of reaction?

c Work out a value for the rate constant of this reaction with units.

d What will be the rate of reaction when the concentration of A is 0.100 mol dm^{-3} and that of B is 0.0500 mol dm^{-3}?

8 Consider the following data for the reaction

$2X + 4Y \rightarrow Q + 2R$

Experiment	[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	1.50×10^{-2}	3.00×10^{-2}	1.78×10^{-3}
2	4.50×10^{-2}	3.00×10^{-2}	5.34×10^{-3}
3	4.50×10^{-2}	1.20×10^{-1}	2.14×10^{-2}

a Write the rate equation for this reaction.

b Calculate a value for the rate constant from these data.

c What are the units of the rate constant?

9 Write the rate equation and calculate the rate constant (including units) for the following reaction: $A + B \rightarrow P + Q$

[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1.0	1.0	2.0×10^{-3}
2.0	1.0	4.0×10^{-3}
2.0	3.0	36×10^{-3}

10 Write the rate equation and calculate the rate constant (including units) for the following reaction:

$2Z + 3Y \rightarrow W + X$

Expt.	[Z] / mol dm^{-3}	[Y] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	2.0×10^{-3}	2.0×10^{-3}	0.050
2	8.0×10^{-3}	2.0×10^{-3}	0.800
3	1.0×10^{-2}	6.0×10^{-3}	3.750

11 **a** A reaction is zero order with respect to P and second order with respect to Q. What would be the effect of doubling the concentration of P and the concentration of Q on the overall rate of reaction?

b A reaction has rate equation: rate = k[A][B]^2. What would be the effect on the rate of doubling the concentration of A and halving the concentration of B?

c A reaction has rate equation: rate = k[Q]^2[X]. What would be the effect on the rate of halving the concentrations of Q and X?

12 Consider the following data for the reaction

$2D + 3E \rightarrow 2C + B$

Experiment	[D] / mol dm^{-3}	[E] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	2.50×10^{-3}	5.00×10^{-3}	4.28×10^{-4}
2	1.00×10^{-2}	5.00×10^{-3}	1.71×10^{-3}
3	4.00×10^{-2}	2.00×10^{-2}	6.84×10^{-3}

a Work out the order of reaction with respect to D.

b Work out the order of reaction with respect to E.

c What is the rate equation for the reaction?

d Work out a value, with units, for k, the rate constant, for this reaction.

e What is the rate of reaction when the concentration of D is 0.0600 mol dm^{-3} and that of E is 0.0300 mol dm^{-3}?

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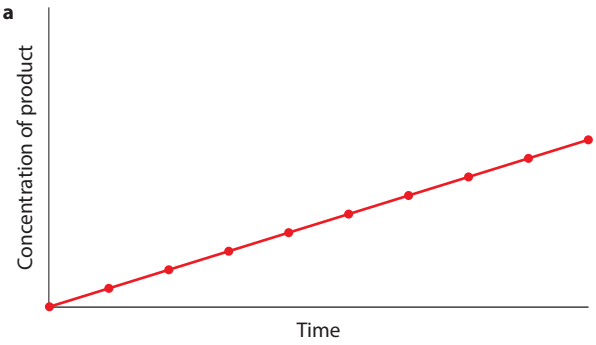
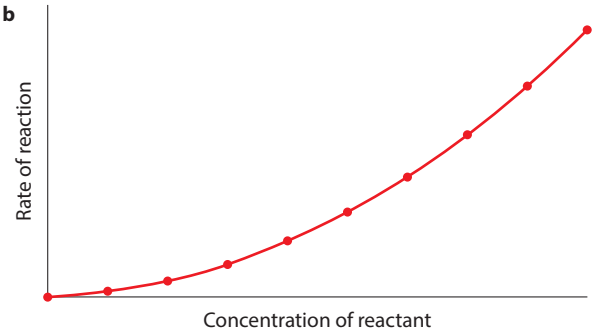
CONTINUED

13 Deduce whether the graphs represent zero-, first- or second-order reactions.

a



b



17.6 Mechanisms of reactions

In this section, we consider why a rate equation cannot be derived directly from the chemical equation for a reaction. Consider the reaction:

$A + B + C \rightarrow T + X$

If this reaction were to occur in one single step, all three molecules must collide together at exactly the same time, and we would expect that doubling the concentration of any one of the three reactant molecules would double the chance of a collision and, therefore, the rate of the reaction. The rate of reaction in this case would, therefore, depend on [A], [B] and [C], and the rate equation would be:

rate = k[A][B][C]

The actual rate equation obtained from experiments is, however rate = k[A][B].

How is it possible that the rate of reaction does not depend on the concentration of C?

The fact that the experimental rate equation is not the same as our hypothesis suggests that the reaction does not occur in just one step in which all three molecules collide to form one activated complex, which then breaks apart to form the products. This was always going to be unlikely because the chance of three gas molecules all colliding at *exactly* the same time is extremely small. What if the reaction occurs as a series of simpler steps?

KEY POINT

A reaction mechanism consists of a series of elementary steps that make up a more complex reaction. Each elementary step involves a maximum of two molecules colliding.

A mechanism that has been proposed for this reaction is:

step 1: $A + B \rightarrow Y$

step 2: $Y + C \rightarrow T + X$

Y, produced in the first step, is called an *intermediate* – intermediates are produced in the reaction, exist in the reaction mixture for a very short amount of time, and are then used up again. Intermediates do not occur in the overall equation for the reaction because they are produced and then used up again.

KEY POINT

The mechanism must be consistent with the overall chemical (stoichiometric) equation.

We can check that the mechanism agrees with the overall chemical equation. In order to do this, species that are the same on both sides of the equations are cancelled and then the two equations are added together:

step 1: $A + B \rightarrow \cancel{Y}$

step 2: $\cancel{Y} + C \rightarrow T + X$

overall: $A + B + C \rightarrow T + X$

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Intermediates will always cancel out so they do not appear in the overall equation.

KEY POINT

The mechanism must be consistent with the rate equation.

The overall reaction has now been divided into two elementary steps in which two species collide. Doubling the concentration of the reactants in each of these steps will cause the reaction rate to double because the particles will collide twice as frequently and, therefore, we can derive the rate equation for each step:

step 1: rate = k_1[A][B]

step 2: rate = k_2[Y][C]

where k_1 is the rate constant for step 1.

This time, we can go directly from the chemical equation to the rate equation because each step is an elementary step in which we know what species are colliding.

It can be seen that the rate equation for step 1 is the same as the experimental rate equation, so when we put in values for concentration the rate of reaction for step 1 is the same as the overall rate of reaction. So how is it possible that only this step is important in determining the overall rate and we can ignore the second step? One way of thinking about it is like queuing at an amusement park for a ride – if you had to queue for 2 hours for a ride that took 30 s, the overall time that you were at the ride is essentially 2 hours – the 30 s is negligible compared to the 2 hours. What if they doubled the speed of the ride, so it took 15 s, overall you still spent 2 hours at the ride – the length of the ride makes virtually no difference to the overall time.

Imagine that we had the following conditions:

- we started with a million molecules of each of A, B and C
- there are 1 million collisions between A and B molecules every second.
- 1 in 10 million collisions between A and B result in a successful reaction (the activation energy is high).

This means that we will, on average, produce 1 molecule of Y every 10s.

Y and C collide 500 000 times per second, but this step has a very low activation energy and now 1 in 500 collisions results in a reaction, so it takes, overage a further $\frac{1}{1000}$s to produce the products X and T. This means that 1 molecule of X and 1 molecule of T are produced, on average, every 10.001 s. The overall rate of the reaction is therefore essentially the same as the rate of step 1.

Step 1 the governs the overall rate of reaction and the second step has no noticeable effect on the rate - if we doubled the concentration of C, there would be 1 million collisions between Y and C every second and X and T would be produced in 10.0005 s, which is still essentially 10 s – changing the concentration of C has essentially not affected the rate of the reaction. However, if we double the concentration of A there will be 2 million collisions between A and B molecules every second, so a molecule of Y will be produced, on average every 5 s and, as this goes on to react further almost instantaneously, the rate of reaction doubles.

Step 1 is called the **rate-determining step (RDS)** of the mechanism and occurs significantly more slowly than step 2.

KEY POINT

The rate-determining step is the slowest step in a reaction mechanism.

We can now show the mecahnism as:

$A + B \xrightarrow{\text{slow}} Y$ step 1 rate-determining

$Y + C \xrightarrow{\text{fast}} T + X$ step 2

KEY POINT

The rate-determining step (RDS) is the step in a reaction mechanism with the highest activation energy.

The energy profile for this reaction is shown in Figure 17.29, and it can be seen that the rate-determining step (step 1) has a much higher activation energy than the other step.

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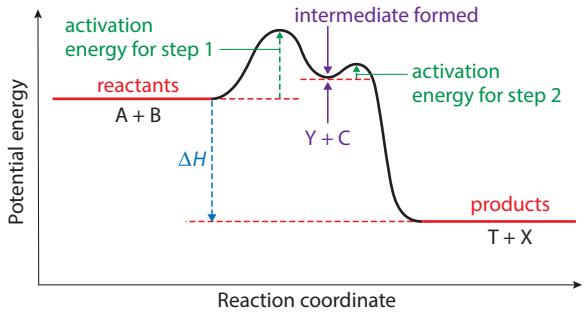

Figure 17.29: Energy profile for a two-step reaction. The formation of an intermediate Y is shown by the potential energy well in the profile.

Another mechanism

Let us consider another mechanism, this time for the reaction $A + 2B \rightarrow C$:

step 1: $B + B \rightarrow Q$ rate-determining step

step 2: $Q + A \rightarrow C$ fast

Let us first check that the mechanism agrees with the chemical equation:

$B + B \rightarrow \cancel{Q}$ step 1

$\cancel{Q} + A \rightarrow C$ step 2

$2B + A \rightarrow C$ overall equation

Q is an intermediate – it is produced in the first step and used up in the second step – it does not appear in the overall equation.

Step 1 is the rate-determining step, so the concentrations of the reactants involved in this step affect the rate of the overall reaction and occur in the rate equation. Step 2 is a fast step that occurs after the rate-determining step and, therefore, the species involved in this step do not affect the rate of reaction or occur in the rate equation.

Since there are two molecules of B in the rate-determining step, doubling the concentration of B will cause the rate of reaction to go up by a factor of 2^2
(you can think of this from the point of view of each of the two B molecules in this step separately – each one will have twice as many other B molecules to collide with).
The rate equation consistent with this mechanism is:

$\text{rate} = k[B]^2$

The concentration of A does not appear in this rate equation because it is only involved in a fast step after the rate-determining step. Q is highly reactive and, once it is formed, it will collide almost immediately and react with an A molecule. Because collisions occur so rapidly and virtually every collision results in a reaction, changing the concentration of A will have essentially no effect on the overall rate.

The rate-determining step is not necessarily the first step

In both examples we have considered so far, the rate-determining step is the first step. Now consider a mechanism in which the rate-determining step is the second step.

Let us look at the reaction, $A + B + C \rightarrow D$, with the following mechanism:

step 1: $A + B \rightleftharpoons Z$ fast

step 2: $Z + C \rightarrow D$ rate-determining step

A and B react together to form the intermediate, Z, and, if we double the concentration of A or B, Z will be produced twice as quickly, so the amount of Z present at any time that is available to react with C will be twice as much, which will double the rate of the second step. The second step is the rate-determining step, and, the rate of this step is essentially the overall rate of the reaction. The rate equation for this second step is:

$\text{rate} = k[Z][C]$

But the concentration of Z at any time depends on the concentration of A and B from the first step (if we double [A] or [B] we double [Z]), so we can write

$\text{rate} = k[A][B][C]$

This contains all the reactants involved in the mechanism up to and including the rate-determining step.

If we assume that this reaction is an exothermic reaction overall, the energy profile for the reaction would be as shown in Figure 17.30.

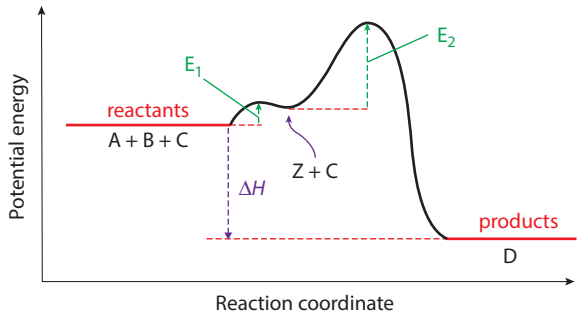

Figure 17.30: The energy profile for an exothermic reaction in which the second step is the rate-determining step. E_1 is the activation energy for the first step and E_2 is the activation energy for the second step.

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KEY POINTS

The rate equation contains concentrations of reactants involved up to and including the rate-determining step.

The order of a particular reactant indicates how many times it is involved in the mechanism up to and including the rate-determining step.

Let us consider another possible mechanism for the reaction $A + 2B \rightarrow C$:

step 1: $A + B \rightleftharpoons S$ fast

step 2: $S + B \rightarrow C$ rate-determining step

The reactants involved up to and including the rate-determining step are A once and B twice, so the order with respect to A is 1 and the order with respect to B is 2 and the rate equation is:

rate = $k[B]^2[A]$

Reactions involving a catalyst

Consider the iodination of propanone:

$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This reaction is acid (H^+) catalysed.

The experimental rate equation is:

rate = $k[CH_3COCH_3][H^+]$

The rate equation does not include I_2, so this must be involved only after the rate-determining step (RDS).

At a simple level, the mechanism could be proposed as:

$CH_3COCH_3 + H^+ \rightarrow X$ rate-determining step

$X + I_2 \rightarrow CH_3COCH_2I + HI + H^+$ fast

In this reaction, X is an intermediate and H^+ is the catalyst. The catalyst is involved in the rate-determining step but is regenerated in the second step and, therefore, does not appear in the overall chemical equation. You should recognise the difference between a catalyst and an intermediate.

KEY POINTS

A catalyst is used up in one step and then produced again in a later step.

An intermediate is produced in one step and then used up again in a later step.

Catalysts change a reaction mechanism, allowing the reaction to occur via an alternative pathway that has a lower activation energy. A homogeneous catalyst (in the same phase as the reactants) usually works by forming an intermediate with one or other of the reactant molecules – this step has a lower activation energy than the original reaction. Once the intermediate has been formed, this is more reactive than the original reactant, and reacts quickly in a further, lower activation, energy step.

Consider the reaction $A \rightarrow X + Y$, which occurs in a single step, with activation energy E_1. If a catalyst (C) is introduced, the reaction will happen by a different mechanism involving two steps:

$A + C \rightarrow A—C$ RDS (activation energy E_2)

$A—C \rightarrow X + Y + C$ fast (activation energy E_3)

The rate equation for the original reaction would be rate = $k[A]$ (it occurs in a single step) and that for the catalysed reaction would be rate = $k[A][C]$; the catalyst appears in the rate equation. The energy profile for this reaction is shown in Figure 17.31.

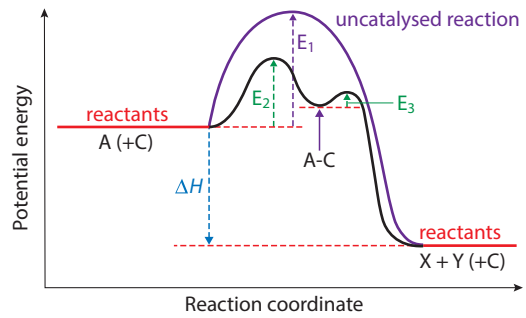

Figure 17.31: The effect of a catalyst on activation energy. E_1 is the activation energy for the uncatalysed reaction, E_2 is the activation energy for the first step of the catalysed reaction (the rate-determining step) and E_3 is the activation energy for the second step (fast) of the catalysed reaction.

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Summary of guidance for writing mechanisms

1 The mechanism must agree with the overall chemical (stoichiometric) equation.

2 A maximum of two particles can react in any one step.

3 The power of a particular reactant's concentration (the order with respect to that reactant) in the rate equation indicates the number of times it appears in the mechanism up to and including the rate-determining step.

4 If a reaction is zero order with respect to a particular reactant, it can only occur in the mechanism in a fast step after the rate-determining step. This has essentially been covered in 3, above, but is worth stating as a separate point.

WORKED EXAMPLE 17.4

Nitrogen(I) oxide and hydrogen react according to the equation:

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

The rate equation for this reaction is rate = $k[NO]^2[H_2]$

Four possible mechanisms for this reaction are:

Mechanism 1

step 1: $2NO(g) + H_2(g) \rightarrow H_2O(g) + N_2O(g)$ slow – rate-determining step

step 2: $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ fast

Mechanism 2

step 1: $2NO(g) \rightleftharpoons N_2O_2(g)$ fast

step 2: $N_2O_2(g) + H_2(g) \rightarrow H_2O(g) + N_2O(g)$ slow – rate-determining step

step 3: $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ fast

Mechanism 3

step 1: $H_2 + NO(g) \rightleftharpoons H_2NO(g)$ fast

step 2: $H_2NO(g) + H_2(g) \rightarrow H_2O(g) + H_2N(g)$ slow – rate-determining step

step 3: $NO(g) + H_2N(g) \rightarrow N_2(g) + H_2O(g)$ fast

Mechanism 4

step 1: $H_2 + NO(g) \rightleftharpoons H_2NO(g)$ fast

step 2: $NO(g) + 2H_2(g) \rightarrow H_2O(g) + H_2N(g)$ slow – rate-determining step

step 3: $H_2N(g) + NO(g) \rightarrow H_2O(g) + N_2(g)$ fast

Evaluate these reaction mechanisms.

Answer

Let's work through each mechanism in turn, considering each one in terms of the guidance steps above.

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Mechanism 1

If we can cancel out any intermediates, we can see that it agrees with the stoichiometric equation:

$2NO(g) + H_2(g) \rightarrow H_2O(g) + \cancel{N_2O(g)}$ step 1 slow – rate-determining step

$\cancel{N_2O(g)} + H_2(g) \rightarrow N_2(g) + H_2O(g)$ step 2 fast

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

The rate equation contains $[NO]^2$ and $[H_2]$, which indicates that NO will appear twice and H_2 once in steps up to and including the rate-determining step. We can, therefore, see that this mechanism agrees with the rate equation, as there are two NO and one H_2 in step 1, which is the rate-determining step.

If, however, we look at step 1 in more detail, we can see that this mechanism would require three molecules to collide at exactly the same time, which is highly unlikely, so we can discount this mechanism on this basis.

Mechanism 2

This also agrees with the stoichiometric equation:

$2NO(g) \rightleftharpoons \cancel{N_2O_2(g)}$ step 1 fast

$\cancel{N_2O_2(g)} + H_2(g) \rightarrow H_2O(g) + \cancel{N_2O(g)}$ step 2 slow – rate-determining step

$\cancel{N_2O(g)} + H_2(g) \rightarrow N_2(g) + H_2O(g)$ step 3 fast

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

There are two NO and one H_2 involved up to and including the rate-determining step; therefore, this mechanism is also consistent with the rate equation. The second H_2 does not appear in the mechanism until a fast step after the rate-determining step, and so, does not feature in the rate equation. All the steps involve a maximum of two species colliding, and so, overall, this mechanism is consistent with experimental data, and we can accept it as a *possible* mechanism. This does not, however, mean that it is necessarily *the* mechanism for the reaction because there could be other mechanisms that are also consistent with these data.

Mechanism 3

$H_2 + NO(g) \rightleftharpoons \cancel{H_2NO(g)}$ step 1 fast

$\cancel{H_2NO(g)} + H_2(g) \rightarrow H_2O(g) + \cancel{H_2N(g)}$ step 2 slow – rate-determining step

$NO(g) + \cancel{H_2N(g)} \rightarrow N_2(g) + H_2O(g)$ step 3 fast

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

Mechanism 3 is also consistent with the stoichiometric equation and there is a maximum of two species reacting in any one step. However, the reactants involved up to and including the rate-determining step are two H_2 and one NO, so this would give the following rate equation:

$\text{rate} = k[H_2]^2[NO]$

so we can dismiss this mechanism on the grounds that it is not consistent with the experimental rate equation.

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Mechanism 4

Mechanism 4 is not consistent with the stoichiometric equation; therefore, it can be dismissed immediately:

$H_2 + NO(g) \rightleftharpoons H_2NO(g)$ step 1 fast

$NO(g) + 2H_2(g) \rightarrow H_2O(g) + \cancel{H_2N(g)}$ step 2 slow – rate-determining step

$\cancel{H_2N(g)} + NO(g) \rightarrow H_2O(g) + N_2(g)$ step 3 fast

$3NO(g) + 3H_2(g) \rightarrow H_2NO(g) + N_2(g) + 2H_2O(g)$

It is also not consistent with the experimental rate equation as it would produce the following rate equation:

rate = $k[H_2]^3[NO]^2$

NATURE OF SCIENCE

A mechanism being consistent with the experimental rate equation does not mean that the mechanism is correct. It can never be proved that a mechanism is correct, only that it is incorrect. A mechanism is accepted as long as it agrees with experimental data, but if new experimental data are produced that are not consistent with the mechanism, the mechanism is disproved, and a new mechanism must be developed that agrees with these and other experimental data.

If we look at Mechanism 2 in the worked example, we could try to gather more evidence for this being the actual mechanism by designing methods to detect the presence of N_2O_2 and N_2O in the reaction mixture. If we detected these species in the reaction mixture, this would provide further weight for this being the *actual* mechanism, although it would still not *prove* it *is* the actual mechanism. Failure to detect these species would not necessarily disprove the mechanism, as this could be due to a weakness in our experimental procedure, and further research may be necessary to design better methods for the detection of these species. If a different species, e.g., H_2NO, were detected, it would make our mechanism inconsistent with the experimental data, and we would have to revise our hypothesis – perhaps H_2 and NO reacting in the first step is more likely?

TEST YOUR UNDERSTANDING

14 Consider the following reaction:

$2A + 3B \rightarrow 4C + D$

The rate equation is: rate = $k[B]^2$.

A proposed mechanism for this reaction is:

step 1: $A + B \rightarrow 2C + D$ slow – RDS

step 2: $A + 2B \rightarrow C + D$ fast

Suggest *three* reasons why this is not a suitable mechanism for this reaction.

15 Consider the reaction: $P + 2Q \rightarrow R + S$

A student has suggested some possible two-step mechanisms for this reaction:

Mechanism 1

$Q + Q \rightarrow X$ slow – RDS

$P + X \rightarrow R + S$ fast

Mechanism 2

$Q + P \rightleftharpoons Z + R$ fast

$Q + Z \rightarrow S$ slow – RDS

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CONTINUED

Mechanism 3

$Q + P \rightarrow Y + S$ slow – RDS

$Q + Y \rightarrow R$ fast

Mechanism 4

$Q + P \rightarrow Y + S$ slow – RDS

$Q + Z \rightarrow R$ fast

a Write the rate equation that would be consistent with Mechanism 1.

b Explain why Mechanism 4 cannot be the mechanism for this reaction.

c The experimentally determined rate equation for this reaction is: rate = $k[P][Q]$.

Which mechanism is consistent with the experimental data?

16 Consider the following reaction:

$2NO + Br_2 \rightarrow 2NOBr$

The rate equation is: rate = $k[NO]^2[Br_2]$.

Suggest two different mechanisms that are consistent with this rate equation.

17 Consider the reaction:

$2X + Y \rightarrow 2Z$

The rate equation for this reaction is: rate = $k[X][Y]$

Suggest a mechanism for this reaction.

18 Explain the difference between a species that acts as a *catalyst* and one that is an *intermediate* in a reaction. Classify X and Y as catalyst or intermediate in the mechanism:

Step 1: $A + X \rightarrow Y$ fast

Step 2: $Y + B \rightarrow C + X$ slow – RDS

Molecularity

KEY POINT

Molecularity is the number of reacting particles that take part in a particular elementary step in a reaction mechanism.

Consider three reactions which are elementary steps in different reaction mechanisms:

- $A \rightarrow B + C$

This reaction has a **molecularity** of 1 and is called *unimolecular* –there is one particle (A) involved in the reaction.

- $X + Y \rightarrow Z$

This reaction has a molecularity of 2 –it is *bimolecular* –there are two reacting particles (X and Y) involved.

- $Q + Q + X \rightarrow D$

This reaction has a molecularity of 3 –it is *termolecular* –there are three reacting particles (2 molecules of Q and 1 molecule of X) involved. Termolecular reactions are extremely rare – there is a very low probability that three particles would collide at exactly the same time.

Molecularity and order are not the same thing. The order is an experimentally determined quantity that relates the concentrations of the reactants to the overall rate of reaction – no knowledge of the reaction mechanism is required to determine the order. Molecularity refers to individual elementary steps in a reaction mechanism and can only be determined from a proposed mechanism.

Molecularity refers to each *elementary step* in a reaction mechanism and not to the overall reaction; however, there are a few cases where an overall reaction mechanism is named according to the molecularity of the rate-determining step – an example is given in the section on S_N1 versus S_N2 mechanisms below.

Energy profiles

An energy profile (potential energy profile) can be used to show how the potential energy changes during a chemical reaction as the reactants are converted into products. The reaction coordinate represents the progress of a reaction from reactants to products. As reactant particles approach each other, repulsion between the particles and the partial breaking of bonds

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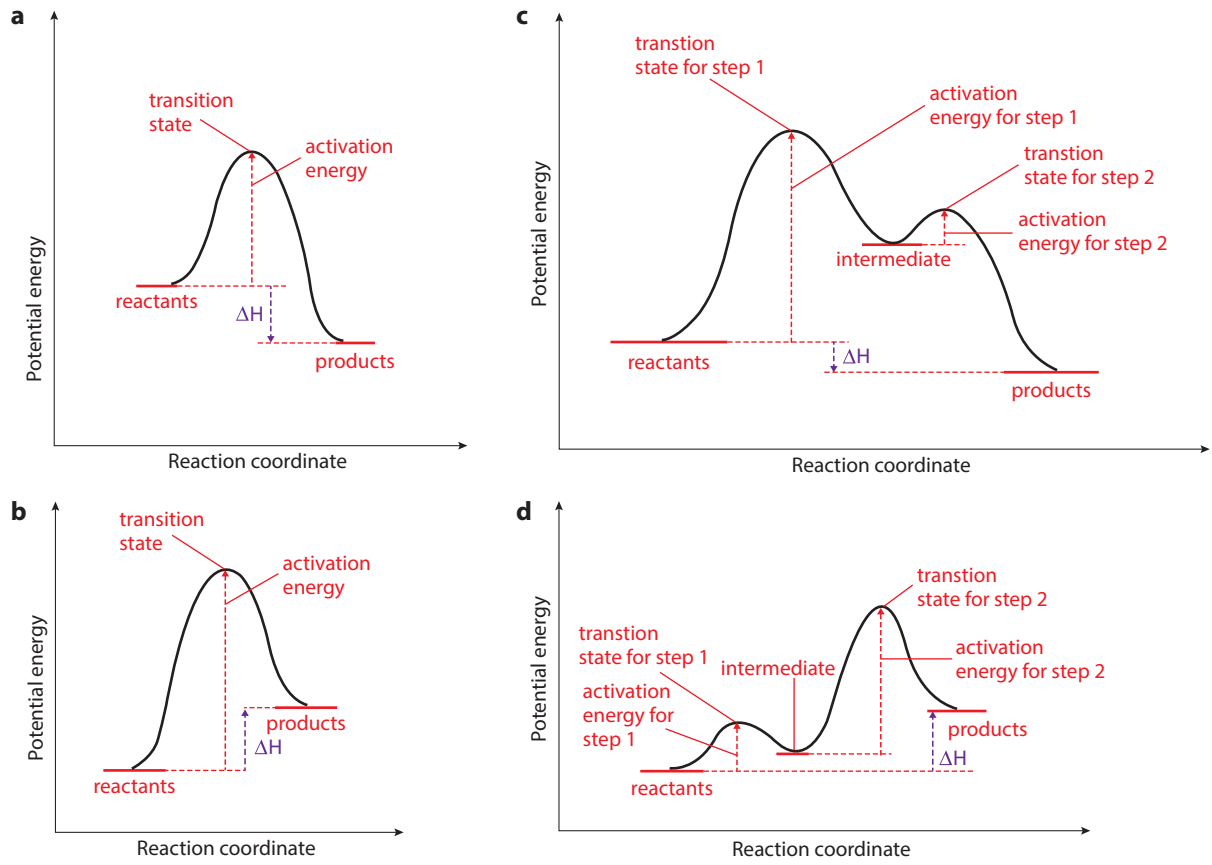

Figure 17.32: Some energy profiles **a** Single-step exothermic reaction; **b** single-step endothermic reaction; **c** two-step exothermic reaction (first step is RDS) **d** two-step endothermic reaction (second step is RDS).

causes the potential energy of the system to increase. The highest point of a particular part of the pathway is the *transition state* and the species present at this point is called the transition state or the activated complex. Reactants, products or intermediates are present at the minima in a potential energy profile. The activation energy is the energy difference between successive minima and maxima in the potential energy profile.

We have already seen several potential energy profiles, and these are collated in Figure 17.32.

The difference between an intermediate and a transition state

Consider the reaction:

$2A + B—C \rightarrow A—B + A—C$

with the proposed mechanism

$A + B—C \rightarrow A—B + C$

$A + C \rightarrow A—C$

In the first step, A will approach the B—C molecule and, as it does, there will be repulsion between the electron clouds of A and B—C, a bond will start forming between A and B and the B—C bond will start breaking – the potential energy of the species will increase until we get to the transition state – the highest point along the potential energy profile for a particular step. The species present at the highest point along the energy profile will have partial bonds (dashed lines) between A and B and between B and C:

$[A\text{---}B\text{---}C]^{‡}$

The species present at the transition state (double dagger symbol) is sometimes called the activated complex and has the maximum potential energy – it does not exist for any measurable amount of time – there is a continuous progression through the transition state. As the reaction proceeds, the A—B bond will continue to form and the

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B—C bond will continue breaking until we get A—B and C. A—B is one of the products and C is an intermediate. C will be a highly reactive species but will exist in the reaction mixture for a finite amount of time. C has only fully formed bonds – there are no partially formed/broken bonds. C will then go on to react with another molecule of A to form the product. The reaction profile for this mechanism is shown in Figure 17.33.

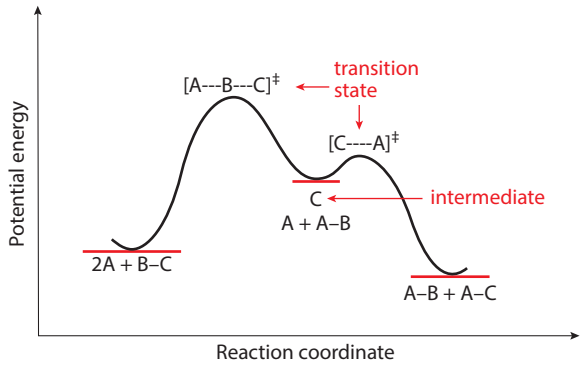


Figure 17.33: The energy profile for 2A + BC → AB + AC, showing the transition states/activated complexes and the intermediate.

If you imagine jumping down a flight of stairs one step at a time, the highest point in each of your jumps is equivalent to a transition state, and you standing on each step is equivalent to an intermediate.

KEY POINT

A transition state is at a maximum in an energy profile. It has partially formed/broken bonds.

An intermediate is at a (local) minimum in an energy profile. There are no partially formed/broken bonds.

Link

S_N1 versus S_N2 mechanisms

In this section, we will investigate the kinetics of the reactions that will be studied further in Chapter 22. Consider the reaction:

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

This is a nucleophilic substitution reaction of 2-bromo-2-methylpropane. The experimentally determined rate equation for this reaction is

rate = $k[(CH_3)_3CBr]$

OH^- does not appear in the rate equation and, therefore, can be involved only in a fast step after the rate-determining step.

The mechanism for this reaction has been suggested as:

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ rate-determining step

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast

The reaction is described as an S_N1 mechanism, where S stands for substitution, N for nucleophilic (the attacking species is a nucleophile in this case) and 1 is the molecularity of the rate-determining step – the molecularity is 1 because one molecule reacts in the rate-determining step. Note that step 2 is a bimolecular step with molecularity two.

$(CH_3)_3C^+$ is an intermediate in this reaction.

$CH_3CH_2CH_2Br$ (1-bromopropane) also undergoes a nucleophilic substitution reaction:

$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$

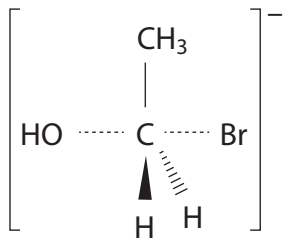
The rate equation is different:

rate = $k[CH_3CH_2CH_2Br][OH^-]$

With both reactants from the original equation appearing once only in the rate equation, this suggests that this reaction occurs in just one step and the mechanism is simply

$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$

There are two reactant species involved in this single step, and it, therefore, has a molecularity of two – it is bimolecular. This reaction mechanism is described as S_N2, where the 2 refers to the molecularity of the single step. There is no intermediate in this reaction because it occurs in a single step, but the transition state/activated complex (with partial bonds between O and C and between Br and C) is sometimes shown when drawing out the reaction mechanism.



trigonal bipyramidal transition state

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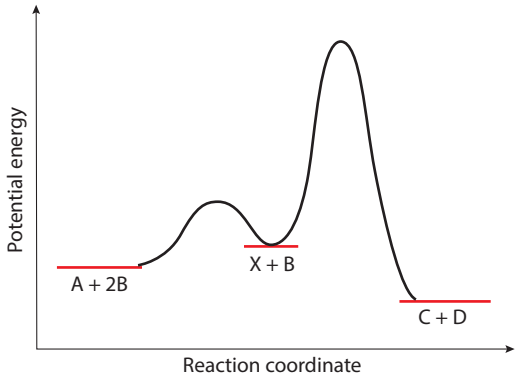
TEST YOUR UNDERSTANDING

19 An energy profile for a reaction is shown.



a Is the reaction exothermic or endothermic?

b What is the overall equation for the reaction?

c Which step is the rate-determining step?

d Write the mechanism for the reaction.

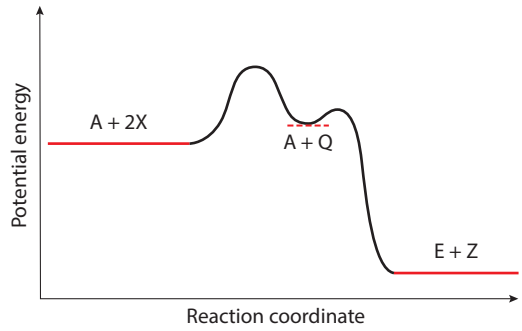
e State the molecularity of each step in the mechanism.

f Deduce the rate equation.

g Mark the transition states on the diagram.

h Identify an intermediate in this reaction.

20 Deduce the mechanism, including which is the rate-determining step, from the energy profile.



17.7 Variation of the rate constant with temperature

Consider a rate equation such as: rate = k[A][B]

If the temperature changes, the value of the rate constant changes.

KEY POINT

As the temperature increases, the rate constant increases exponentially.

The variation of the rate constant with temperature is shown in Figure 17.34.

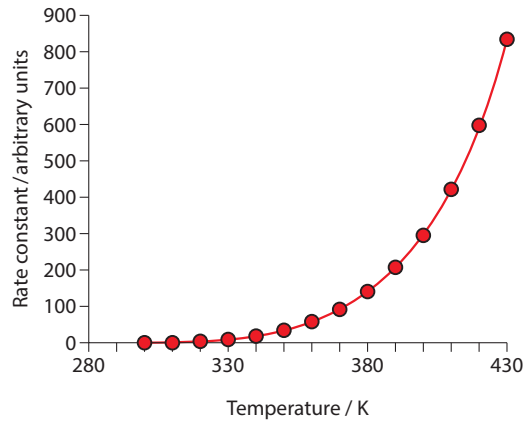


Figure 17.34: The rate constant increases exponentially as the temperature rises.

The Arrhenius equation

The **Arrhenius equation** can be used to model the variation of the rate constant with temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

E_a is the activation energy in J mol^{-1}

R is the gas constant, i.e., 8.31 J K^{-1} mol^{-1}

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T is the temperature in kelvin

$e^{\frac{-E_a}{RT}}$ represents the fraction of collisions that have energy greater than or equal to the activation energy ($E \geq E_a$).

A is called the *pre-exponential factor* or *A-factor* or *Arrhenius A factor* and takes account of the *frequency* of collisions and the *orientation* of the collisions. A can be regarded as the product of two terms – one that is the collision frequency (per unit concentration) and the other takes account of the fact that not all collisions with $E \geq E_a$ result in reaction because the molecules do not always collide with the correct orientation. A can be regarded as a *constant* (theory predicts a very slight variation with temperature, but this is generally not seen experimentally).

KEY POINT

The units of A are the same as the units of the rate constant.

EXAM TIP

The Arrhenius A factor is just called the 'Arrhenius factor' in the IB syllabus.

Calculating the activation energy for a reaction

The Arrhenius equation may also be written in the following form:

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A$$

This is sometimes called the linear form of the Arrhenius equation – we will see why below.

The Arrhenius equation in this form can be used to work out a value for the activation energy for a reaction. To do this, we use the following procedure:

1. Conduct a series of experiments measuring the rate of reaction at a range of temperatures.
2. Calculate a rate constant (k) for each temperature.
3. Plot a graph of $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis), where T is the absolute temperature (in kelvin).
4. The activation energy is equal to $-R$ times the gradient of the straight line obtained.

After we have carried out a series of experiments, measuring the rate at different temperatures, we could have data such as that listed in the first two columns of Table 17.4.

T / K	k / s^{-1}	$\frac{1}{T}$ / K^{-1}	$\ln k$
300	0.000880	0.00333	–7.03
350	0.00370	0.00286	–5.60
400	0.0108	0.00250	–4.53
450	0.0250	0.00222	–3.69
500	0.0487	0.00200	–3.02
550	0.0842	0.00182	–2.47
600	0.133	0.00167	–2.02
650	0.195	0.00154	–1.63
700	0.272	0.00143	–1.30

Table 17.4: Sample experimental data and processed values.

$\frac{1}{T}$ and $\ln k$ are then calculated. A graph of $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis) produces a straight-line graph (Figure 17.35).

We can understand why a straight-line graph is produced by comparing the Arrhenius equation with the equation of a straight line ($y = mx + c$, where m is the gradient and c is the intercept on the y-axis):

$$\underbrace{\ln k}_{y} = \underbrace{\frac{-E_a}{R}}_{m} \times \underbrace{\frac{1}{T}}_{x} + \underbrace{\ln A}_{c}$$

So, the Arrhenius equation is the equation of a straight line, where $\ln k$ is y and $\frac{1}{T}$ is x. From this equation, we can see that the gradient of this straight line is $\frac{-E_a}{R}$.

From the graph in Figure 17.35, we can work out the gradient of the straight line:

$$\text{gradient} = \frac{(-1.3)-(-7.0)}{0.00143-0.00333}$$

i.e., gradient = –3000 K

The gradient of the line is equal to $\frac{-E_a}{R}$, so

$$\frac{-E_a}{R} = -3000$$

$$E_a = 3000 \times R$$

$$E_a = 3000 \times 8.31 = 24\,900 \text{ J mol}^{-1}$$

i.e., the activation energy is 24.9 kJ mol^{-1}.

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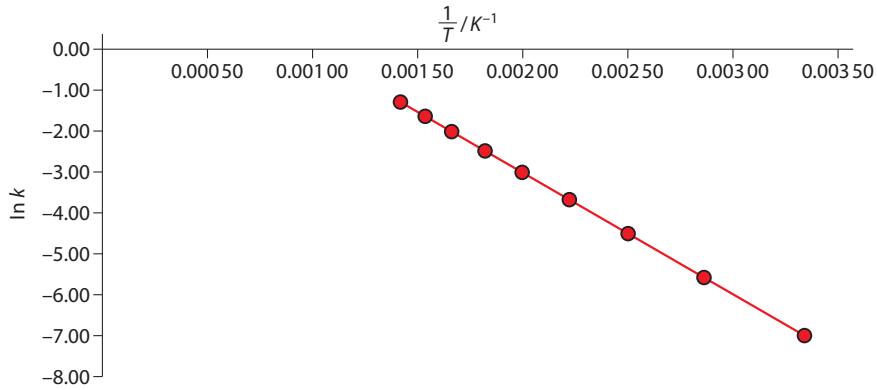

Figure 17.35: A straight line is obtained when ln k (y-axis) is plotted against $\frac{1}{T}$ (x-axis).

Note on units:

The units of the gradient are obtained by dividing the units of ln k (no units) by the units of $\frac{1}{T}$ (K^{-1}). Therefore, the units of the gradient are K.

The units of E_a are obtained as follows:

$E_a = 3000 \times R$

Substituting units into this equation:

$E_a = \text{K} \times \text{J K}^{-1}\text{ mol}^{-1}$

K cancels with K^{-1}, so the units of E_a are J mol^{-1}.

EXAM TIP

Look carefully at the scale on any graph given in the examination. The scale on the x-axis in the graph here could have been written as $\frac{\left(\frac{1}{T}\right)}{10^{-3}}$ K^{-1}, and the values on the axis changed appropriately (0.500...1.00...1.50 etc.). In this case, you must remember to multiply the values by 10^{-3} when working out the gradient.

Using an equation to work out the activation energy

The value of E_a can also be worked out using an equation derived from the Arrhenius equation, if the values of the rate constant are known at two different temperatures:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

It is important to remember that E_a is in units of J mol^{-1} and T must be in K.

WORKED EXAMPLE 17.5

Calculate a value for the activation energy, with units, for a reaction given the values of the rate constant at two different temperatures:

$T = 25.00$ °C; $\quad k = 1.20 \times 10^{-4}$ s^{-1}

$T = 270.00$ °C; $\quad k = 5.63 \times 10^{-2}$ s

Answer

It does not matter which way round we label k_1 and k_2 – if k_1 is the rate constant at the lower temperature, then both numbers in brackets will come out as negative, but, if k_1 is the rate constant at the higher temperature, both values will come out as positive. Here, we will just use them in the order we have been given them:

$T_1 = 25.00$ °C $\quad k_1 = 1.20 \times 10^{-4}$ s^{-1}

$T_2 = 270.00$ °C $\quad k_2 = 5.63 \times 10^{-2}$ s^{-1}

Before we can substitute into the equation, we must convert the temperatures to kelvin:

$T_1 = 25.00 + 273.15 = 298.15$ K

$T_2 = 270.00 + 273.15 = 543.15$ K

Substituting into the equation,

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{1.20\times10^{-4}}{5.63\times10^{-2}}\right) = \frac{E_a}{8.31}\left(\frac{1}{543.15} - \frac{1}{298.15}\right)$$

Carrying all the figures through on a calculator and rearranging this gives $E_a = 33786$

The units of E_a are J mol^{-1} and because the data is to 3 significant figures, we should quote the answer as 33 800 J mol^{-1} or 33.8 kJ mol^{-1}.

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EXAM TIP

It is important to remember that

$$\ln\left(\frac{k_1}{k_2}\right) \neq \ln\frac{k_1}{\ln k_2}$$

Calculating the Arrhenius *A* factor

Comparing again the Arrhenius equation to the equation for a straight line, we can see that ln A will be the intercept on the y-axis (ln k axis).

$$\underset{y}{\ln k} = \underset{m}{\frac{-E_a}{R}} \times \underset{x}{\frac{1}{T}} + \underset{c}{\ln A}$$

Therefore, if we use again the data from Table 17.4 and extend (extrapolate) the graph in Figure 17.35, we get the graph shown in Figure 17.36.

From Figure 17.36, it can be seen that the 'y-intercept' occurs at 3.00 and, therefore, ln A = 3.00.

The value of A can be obtained by raising each side as a power of e (e^x is the inverse function of ln x).

Therefore, $A = e^{3.00}$ i.e., $A = 20.1\ s^{-1}$.

The units of A are s^{-1} here because the reaction is first order overall, and the units of k are s^{-1}. In general, the units of A will be the same as the unit of k, so, for example, if the reaction studied is first order overall, the units of A will be time^{-1} (e.g. s^{-1}) and, if it is second order overall, the units will be concentration^{-1} time^{-1} (e.g. $mol^{-1}\ dm^3\ s^{-1}$).

Alternatively, the value of A can be calculated from the Arrhenius equation once the activation energy is known by putting the values into the Arrhenius equation.

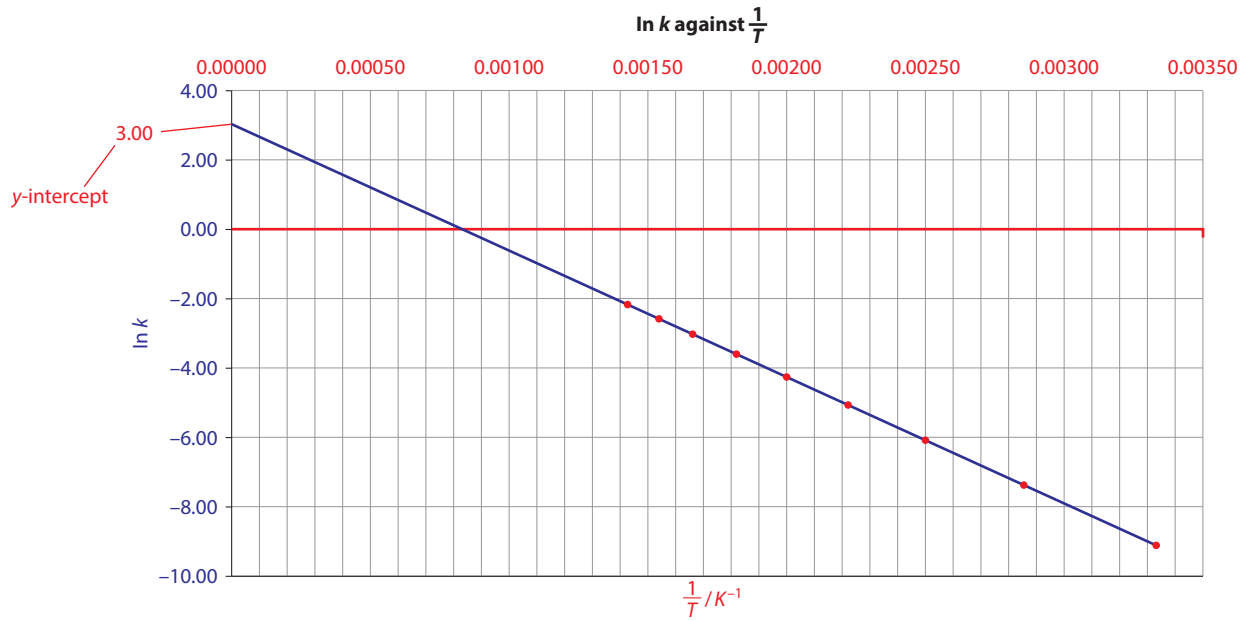

Figure 17.36: Extrapolation of the line to the ln k-axis allows us to determine a value for ln A.

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WORKED EXAMPLE 17.6

The rate constant for a reaction at 180.00 °C is 0.0223 mol^{-1} dm^3 s^{-1}. Given that the activation energy for this reaction is 98.2 kJ mol^{-1}, calculate the Arrhenius *A* factor with units.

Answer

This can be done by putting these values into the Arrhenius equation in either of the following forms:

$\ln k = \frac{-E_a}{R} \times \frac{1}{T} + \ln A$ or $k = Ae^{\frac{-E_a}{RT}}$

It is probably slightly easier mathematically, however, to use the first form.

Things to be careful with when using these equations are that the activation energy must be in J mol^{-1} and temperature must be in K.

Converting the activation energy to J mol^{-1}, we get

$E_a = 98.2 \times 1000 = 98\,200$ J mol^{-1}

Converting the temperature to kelvin, we get

$T = 180.00 + 273.15 = 453.15$ K

Substituting these values into the first equation:

$\ln 0.0223 = \left(-98\frac{200}{8.31}\right) \times \left(\frac{1}{453.15}\right) + \ln A$

Rearranging this, we get $\ln A = 22.3$

Therefore $A = e^{22.3}$

i.e., $A = 4.71 \times 10^9$ mol^{-1} dm^3 s^{-1}.

Interpretation of activation energy and Arrhenius A factor values

$k = Ae^{\frac{-E_a}{RT}}$

In general, all other things being equal, if a reaction has a high activation energy, it will be slow.

$e^{\frac{-E_a}{RT}}$ can be rewritten as $\frac{1}{e^{\frac{E_a}{RT}}}$ so if E_a is larger, $e^{\frac{E_a}{RT}}$ will be larger and $\frac{1}{e^{\frac{E_a}{RT}}}$ will be smaller and *k* will be smaller.

Remember that A can be regarded as the product of two terms – one that is the collision frequency and the other takes account of the fact that molecules do not always collide with the correct orientation.

All other things being equal, the value of the Arrhenius *A* factor will be smaller for reactions between more complicated molecules because these can collide in many different ways, and only a small proportion of collisions will be in the correct orientation for reaction. However, if two *atoms* collide, virtually all the collisions will be in the correct orientation and *A*, should be larger.

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TEST YOUR UNDERSTANDING

The value of the gas constant is 8.31 J K^{-1} mol^{-1}.

21 For each of the following, calculate the activation energy and the value of the Arrhenius *A* factor:

a

T / K	300	500
k / s^{-1}	1.20×10^{-4}	1.80×10^{-3}

b

T / K	300	400
k / mol^{-1} dm^3 s^{-1}	5.70×10^{-6}	2.40×10^{-2}

c

T / °C	25.00	80.00
k / min^{-1}	0.220	7.36

d

T / °C	18.00	59.00
k / s^{-1}	1.56×10^{-3}	5.30×10^{-3}

22 Use the following data to calculate values for the activation energy and Arrhenius *A* factor for the second-order reaction P + Q → Z

1 / temperature/K^{-1}	ln (k / mol^{-1} dm^3 s^{-1})
0.00250	2.27
0.00222	4.14
0.00200	5.64
0.00182	6.86
0.00167	7.88
0.00154	8.75
0.00143	9.49
0.00133	10.1
0.00125	10.7

23 Use the following data to calculate values for the activation energy and Arrhenius *A* factor for the reaction: X + B → C

T / K	k / mol^{-1} dm^3 s^{-1}
400	1.74×10^{-2}
450	3.53×10^{-1}
500	3.92
550	28.1
600	145
650	581
700	1.91×10^{3}
750	5.35×10^{3}
800	1.32×10^{4}

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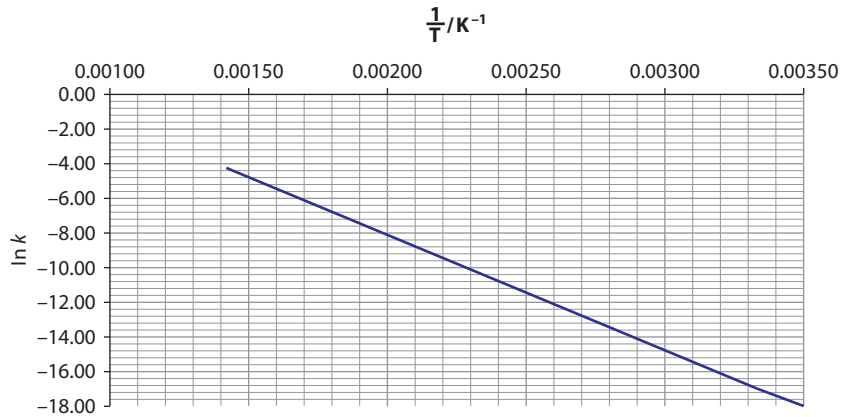
CONTINUED

24 Use the graph to determine

a the activation energy for the reaction.

b the value of the Arrhenius *A* factor and suggest a possible unit for *A* if the reaction is first order.



SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain what is meant by the rate of a reaction	17.1			
describe and evaluate methods of measuring rates of reaction	17.2			
calculate rates of reaction	17.2			
explain collision theory	17.3			
explain the factors that affect the rate of a reaction	17.4			
explain the effect of temperature on the rate of reaction	17.4			
explain the effect of a catalyst on the rate of reaction	17.4			
deduce rate equations for reactions and calculate rate constants	17.5			
sketch concentration–time and rate–concentration graphs	17.5			
explain the connection between the rate equation and the reaction mechanism and evaluate reaction mechanisms	17.6			
draw energy profiles for reactions	17.6			
explain the effect of temperature on the rate constant	17.7			
calculate the activation energy and Arrhenius *A* factor (pre-exponential factor).	17.7			

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REFLECTION

- What is the most difficult part of this chapter?
- What can you do to improve your understanding of the concepts covered here?
- To what extent do you feel that you are able to link the concepts covered here to practical work?
- Do you find it easier to work through the questions by yourself, or is it better with someone else whom you can bounce ideas off?
- Try to explain how to determine activation energy to another student. Does this highlight any gaps in your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 18

How far? The extent of chemical change

LEARNING OBJECTIVES

In this chapter you will:

- understand what is meant by the term dynamic equilibrium
- understand how to write an equilibrium law expression
- understand the connection between the value of the equilibrium constant and the extent of reaction
- understand the connection between the value of the equilibrium constant and how the chemical equation is written
- use Le Chatelier's principle to explain how changes in conditions affect the position of equilibrium

- calculate the value of the reaction quotient
- solve problems involving the equilibrium constant

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CONTINUED

- understand the connection between the change in Gibbs energy, the equilibrium constant and the reaction quotient
- solve problems involving the change in Gibbs energy, the equilibrium constant and the reaction quotient.

GUIDING QUESTIONS

- What is a reversible reaction?
- What factors determine how far a reversible reaction goes in one direction or the other?
- How can we work out how far a reversible reaction goes in one direction or the other?

Introduction

In this chapter, we will look at reversible reactions and how changing conditions can affect them. Reversible processes are remarkably common – any change in state is a reversible physical process – by changing the conditions, water, for example, can be interconverted between liquid and solid (ice) forms. Technically, all chemical reactions are reversible, but many go essentially to completion and are classified as irreversible. The classic example of an irreversible reaction that is often quoted by science teachers is boiling or frying an egg, although, in 2015, scientists reported that they had actually developed a process for unboiling an egg (or at least the egg white)!

18.1 Reversible reactions and equilibrium

Reversible reactions

As the name suggests, **reversible reactions** are reactions that can go either way, so the reactants become the products but the products of the reaction can also react to re-form the reactants.

When calcium carbonate is heated strongly it decomposes to form calcium oxide and carbon dioxide. But calcium oxide also reacts with carbon dioxide to form calcium carbonate:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The double arrow ($\rightleftharpoons$) shows that the reaction is reversible.

Equilibrium

The decomposition of $CaCO_3$ is reversible, but what happens if we put solid calcium carbonate in an open container and keep it at a constant high temperature for an extended period of time (Figure 18.1)?

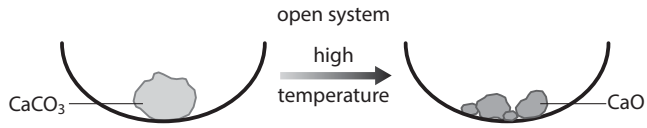

Figure 18.1: In an open container, all the calcium carbonate is completely converted into calcium oxide.

There will be no calcium carbonate left in the container – it is all converted into calcium oxide because carbon dioxide escapes and is not available to react with calcium oxide to re-form calcium carbonate.

If we do the same experiment, at the same temperature, but with calcium carbonate in a sealed container (Figure 18.2), we find that, after the same amount of time, we still have some calcium carbonate present.

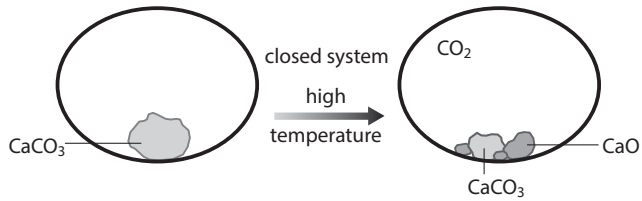

Figure 18.2: In a closed system, a state of equilibrium is attained.

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No matter how long we continue the experiment (keeping it at a constant temperature), the amounts of calcium carbonate, calcium oxide and carbon dioxide stay the same. The reaction appears to have stopped, and we say that the system has reached a state of **equilibrium**.

KEY POINT

A system has reached equilibrium when no further change appears to occur – all concentrations remain constant.

The reaction has not actually stopped but is proceeding in both directions at equal rates. In other words, calcium carbonate is decomposing to give calcium oxide and carbon dioxide at exactly the same rate as calcium oxide and carbon dioxide are recombining to form calcium carbonate.

$$CaCO_3 \xrightarrow{\text{forward}} CaO + CO_2$$
$$CaCO_3 \xleftarrow{\text{reverse}} CaO + CO_2$$
$$Rate_{forward} = Rate_{reverse}$$

This type of equilibrium is called a **dynamic equilibrium**. All equilibria in chemistry are dynamic.

KEY POINT

Dynamic equilibrium: macroscopic properties are constant (concentrations of all reactants and products remains constant) and the rate of the forward reaction is equal to the rate of the reverse reaction.

EXAM TIP

When asked to define dynamic equilibrium, you must address both the 'dynamic' part and the 'equilibrium' part.

Be careful with the words 'constant', 'equal' or 'the same'. The concentrations remain constant (they do not change) – they are not necessarily equal (have the same value). You could also say that they 'stay the same', but, be careful, because they are not 'the same' (equal), so this phrase is best avoided.

Equilibrium and rate of reaction

Consider the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If we start with just hydrogen and iodine vapour in a closed container at a certain temperature and follow how the concentrations of hydrogen and hydrogen iodide change with time, we obtain a graph of the form shown in Figure 18.3.

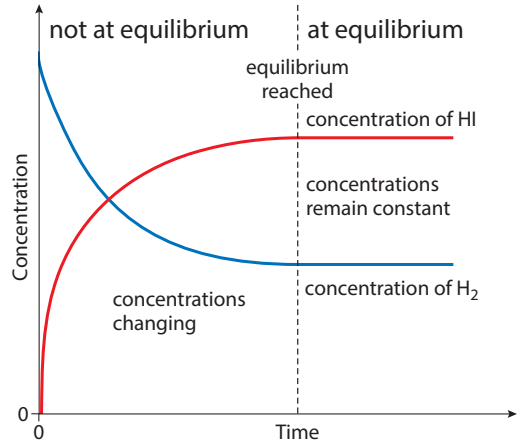

Figure 18.3: Graph showing how the concentrations of hydrogen and hydrogen iodide change with time.

The concentration of H_2 decreases at first, until it levels off (no further change) when equilibrium is reached. The concentration of HI is initially zero, but it increases up to a certain point (the graph flattens off) and then does not change any more after equilibrium has been reached. The concentration of H_2 is not *equal* to the concentration of HI at equilibrium, but the key point is that the *concentrations no longer change* once equilibrium has been established. If we plot a graph of rate against time for the forward and reverse reactions, we get a graph of the form shown in Figure 18.4.

The rate of the forward reaction is initially high because the concentrations of H_2 and I_2 are high. The rate of the forward reaction decreases as H_2 and I_2 are used up, so their concentrations decrease. The rate of the reverse reaction is initially zero because there is no HI present, but this increases as HI is produced by the reaction between H_2 and I_2, so its concentration increases. The rate of the forward reaction keeps decreasing (as the concentration of H_2 and I_2 decrease) and the rate of the reverse reaction keep increasing (as the concentration of HI increases), until the rate of the forward reaction is

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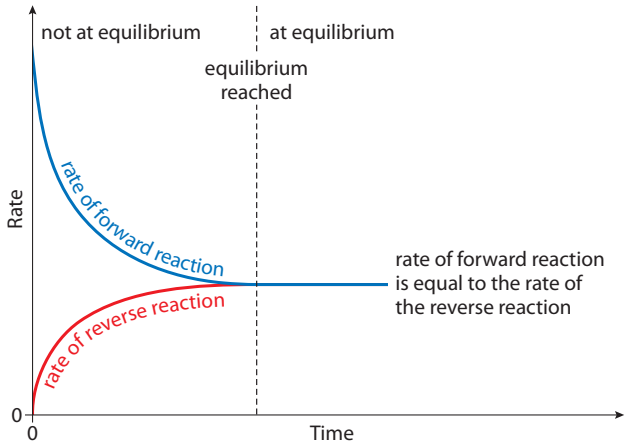

Figure 18.4: Graph showing how the rates of the forward and reverse reactions change as a reversible reaction comes to equilibrium.

equal to the rate of the reverse reaction and equilibrium has been established.

The characteristics of the equilibrium state

Some of these have been discussed previously.

1 Macroscopic properties are constant at equilibrium – at equilibrium, the concentrations of all reactants and products remain constant.

2 At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

3 Equilibrium can be attained only in a **closed system** – a closed system is one in which there is no exchange of matter with the surroundings (nothing can get in or out). As we saw before, if calcium carbonate is heated in an open container, equilibrium is never reached because carbon dioxide escapes and has no opportunity to recombine with calcium oxide. In effect, a reaction in solution, but not involving the production of a gas, represents a closed system.

4 All species in the chemical equation are present in the equilibrium reaction mixture – for example, if nitrogen and hydrogen are allowed to come to equilibrium according to the equation:

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

the reaction mixture at equilibrium contains nitrogen, hydrogen and ammonia.

5 Equilibrium can be attained from either direction – consider the reversible reaction:

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$

ethanoic acid ethanol ethyl ethanoate water

If we mix together ethanoic acid and ethanol in the presence of an acid catalyst and incubate them at 60 °C, they come to equilibrium. If we do the same starting with ethyl ethanoate and water, they also come to equilibrium. A state of equilibrium, in which all four species are present, can be reached by mixing:

- ethanoic acid and ethanol
- ethyl ethanoate and water
- all four substances
- any three of the substances.

In each case, equilibrium is reached, but the actual concentrations present at equilibrium depend on how much of each substance we started with.

Physical equilibria

All the above reactions involved chemical equilibria – equilibria established as a result of chemical reactions. There are also *physical equilibria*, for example equilibria involving a change in state.

Consider a volatile liquid, such as bromine, in a closed container (Figure 18.5).

At the beginning, molecules escape from the liquid (evaporation), but there is no condensation because there are no molecules of vapour above the liquid (Figure 18.5a). As molecules of vapour appear, these strike the surface of the liquid and some re-enter it – condensation. At first, the rate of condensation is low, but, as the number of molecules in the vapour phase increases, the rate of condensation increases (Figure 18.5b). Eventually, the rate of condensation becomes equal to the rate of evaporation (Figure 18.5c) and nothing more appears to change – the colour of the vapour remains constant (it does not get any darker or lighter) – a state of equilibrium has been reached.

Because the rate of evaporation and the rate of condensation are equal, this is a dynamic equilibrium.

This is known as a *phase* equilibrium because it involves a change of phase (state).

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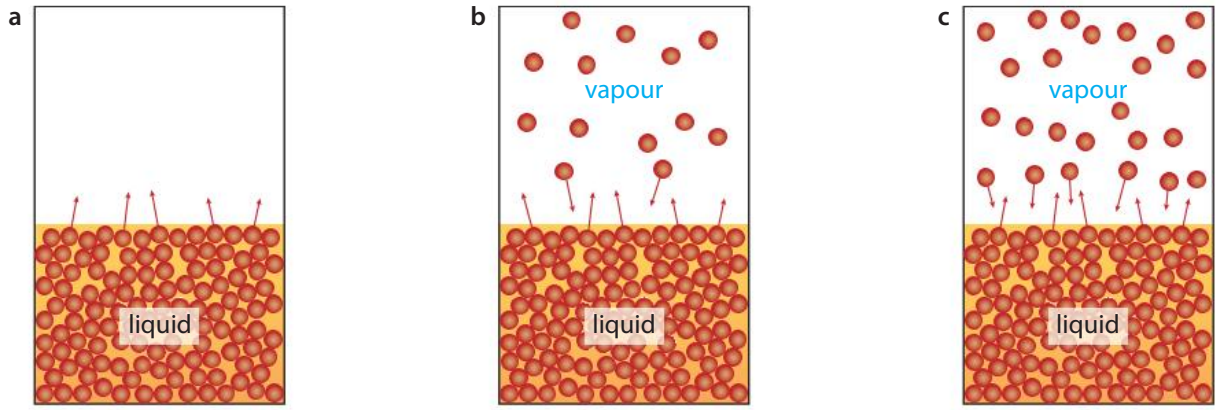

Figure 18.5: Equilibrium is attained when the rate of evaporation is equal to the rate of condensation.

18.2 The position of equilibrium

The **position of equilibrium** refers to the relative amounts of reactants and products present at equilibrium. Some reactions go almost to completion, for example:

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

At 700 K, the position of equilibrium lies a long way to the *right*. There are large amounts of N_2 and O_2 and not very much NO at equilibrium – roughly one and a half million times as many N_2 and O_2 molecules as NO molecules. However, for

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

at 1100 K, the total number of H_2 and CO_2 molecules at equilibrium is roughly equal to the total number of H_2O and CO molecules – the equilibrium is evenly balanced.

Water dissociates according to the equation:

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

At 298.15 K, the number of water molecules present at equilibrium is over 250 million times greater than the total number of H^+ and OH^- ions. The position of this equilibrium lies a long way to the *left* – not many (compared to water molecules) H^+ and OH^- ions are present at equilibrium.

The effect of changing conditions on the position of equilibrium

Le Chatelier's principle

KEY POINT

If a system at equilibrium is subjected to a change, the position of equilibrium will shift to minimise the effect of the change.

This means that, if we take a system at equilibrium under a certain set of conditions and change one of those conditions, such as the temperature or pressure, the system will move to a new position of equilibrium. **Le Chatelier's principle** allows us to predict in which direction the position of equilibrium will shift.

The effect of temperature

Consider the reversible reaction:

$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H^\ominus = +10 \text{ kJ mol}^{-1}$

At room temperature (298.15 K), the number of molecules of HI is roughly 28 times the total number of molecules of H_2 and I_2:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
$$96.6\% \qquad 3.4\%$$

When this system is heated, changes will occur – so the system will no longer be at equilibrium. If the temperature is then held constant at 700 K and time is allowed for equilibrium to be established again, we find

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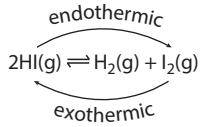
that the number of HI molecules is only approximately 7 times the total number of H_2 and I_2 molecules:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
$$88\% \qquad 12\%$$

This means that there are relatively more H_2 and I_2 molecules present at equilibrium at 700 K than at 298.15 K. In this case, as the temperature increases, *the position of equilibrium shifts to the right* (to the side with H_2 and I_2).

The effect of a temperature change on the position of an equilibrium can be considered in terms of Le Chatelier's principle. The value of $\Delta H^\ominus$ given at the start of this section refers to the forward direction, so, in this case, the forward reaction is endothermic and the reverse reaction is exothermic.



As the temperature is increased, the position of equilibrium shifts in the direction that will minimise the effect of the change. So, to minimise the effect of the increase in temperature in this reaction, the position of equilibrium shifts in the endothermic direction to take in the heat that is added (heat energy is converted into chemical energy). The endothermic direction is to the right and, therefore, as the temperature is increased the position of equilibrium shifts to the right to produce relatively more H_2 and I_2.

Consider another reaction:

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

This time, at 300 K and 10 bar pressure, at equilibrium we have

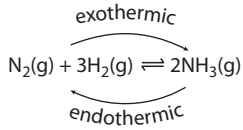
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$85\% \qquad 15\%$$

When equilibrium is established at 700 K and the same pressure, we have:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$99.8\% \qquad 0.2\%$$

In this case, increasing the temperature causes the position of equilibrium to shift to the left, i.e., there is less ammonia present at equilibrium at the higher temperature.

As the temperature is increased, the position of equilibrium shifts in the endothermic direction to take in heat and minimise the effect of the change. This time, the endothermic direction is to the left and, therefore, as the temperature is increased the position of equilibrium shifts to the left.



This is analogous to the idea that, if the heating is turned up, you might take off a jumper – you react to counteract the change in temperature, to minimise the effect of the change on you.

KEY POINTS

Heat a reaction mixture: the position of equilibrium is shifted in the endothermic direction.

Cool a reaction mixture: the position of equilibrium is shifted in the exothermic direction.

EXAM TIP

There is no exothermic or endothermic *side* in a reaction, only an exothermic or endothermic *direction*.

The effect of pressure

Consider again the reaction:

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

If we increase the pressure at constant temperature, the percentage of ammonia (NH_3) present at equilibrium increases – the position of equilibrium shifts to the right.

We know from Avogadro's law (Chapter 4, section 4.6) that the number of moles of gas is proportional to the volume (at constant temperature) and, so, if we imagine the complete conversion of 1 mol $N_2(g)$ and 3 mol $H_2(g)$ to 2 mol $NH_3(g)$, the total number of moles of gas halves (from 4 mol to 2 mol), causing the volume and, therefore, also the pressure, to halve. Converting nitrogen and hydrogen into ammonia reduces the pressure and, therefore, counteracts the effect of increasing the pressure.

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KEY POINTS

Increasing the pressure causes the position of equilibrium to shift towards the side with fewer moles of gas.

Decreasing the pressure causes the position of equilibrium to shift towards the side with more moles of gas.

Consider the reaction:

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

This reaction involves the conversion of two moles of gas (on the left-hand side) to three moles of gas (on the right-hand side). As the pressure is increased, the position of equilibrium shifts to the left, i.e., towards the side with fewer moles of gas, to minimise the effect of the change.

Now consider this reversible reaction:

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

Because there is the same number of moles of *gas* on both sides, changing the pressure has *no effect* on the position of equilibrium.

Liquids and solids are affected very little by changes in pressure, so it is usually the number of moles of *gas* that we need to look at when predicting the effect of a change in pressure on the position of equilibrium.

Consider once again the decomposition of calcium carbonate:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

There is one mole of gas on the right-hand side but none on the left-hand side, therefore, increasing the pressure causes the position of equilibrium to shift to the left.

This reaction is different to the other reactions we have looked at so far – it is a *heterogeneous* equilibrium system as not all substances are in the same physical state.

EXAM TIP

You must remember the word 'gas' in explanations of how changing the pressure affects the position of equilibrium.

The effect of concentration

Consider this system at equilibrium:

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

yellow chromate(VI) ion — acid — orange dichromate(VI) ion

Remember that all species are present at equilibrium. If our solution is yellow this indicates that the position of equilibrium lies much more to to left – there is significantly more of the yellow ion present than the orange ion, and we perceive the colour as yellow.

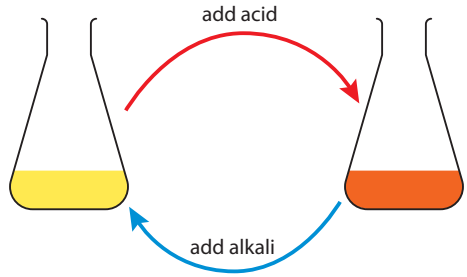

Figure 18.7: The chromate(VI)/dichromate(VI) equilibrium.

When some acid (H^+) is added to the mixture in the flask (Figure 18.7), the colour of the solution changes to orange. There is now much more of the orange dichromate(VI) ion present, which means that the position of equilibrium has shifted to the right. This can be explained in terms of Le Chatelier's principle – as more acid is added, the position of equilibrium shifts to the right to use up (some of) the excess acid, and so, minimise the effect of the change.

If we now add an alkali (OH^-) to the solution, the colour changes back to yellow. The OH^- ions react with the H^+ ions to form water:

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

So, adding alkali reduces the concentration of H^+ ions in the solution, and the position of the chromate(VI)/dichromate(VI) equilibrium must shift to the left to minimise the effect of the change by replacing (some of) the H^+ ions.

KEY POINT

In general, if the concentration of one of the species in an equilibrium mixture is increased, the position of equilibrium shifts towards the opposite side to reduce the concentration of this species.

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TEST YOUR UNDERSTANDING

1 Explain what you understand by the term *dynamic equilibrium*.

2 Predict the effect of increasing pressure on the position of equilibrium in the following systems:

a $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$

b $N_2O_5(g) + NO(g) \rightleftharpoons 3NO_2(g)$

c $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$

d $H_2O(g) \rightleftharpoons H_2O(l)$

3 Predict the effect of decreasing pressure on the position of equilibrium in the following systems:

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

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

c $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

4 Predict the effect of increasing temperature on the position of equilibrium in the following systems:

a $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$
$\Delta H^{\ominus} = -40$ kJ mol^{-1}

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
$\Delta H^{\ominus} = -206$ kJ mol^{-1}

c $C_{graphite}(s) \rightleftharpoons C_{diamond}(s)$ $\Delta H^{\ominus} = +2$ kJ mol^{-1}

d $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
$\Delta H^{\ominus} = +56$ kJ mol^{-1}

5 Predict the effect of decreasing temperature on the position of equilibrium in the following systems:

a $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ $\Delta H^{\ominus} = -88$ kJ mol^{-1}

b $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ $\Delta H^{\ominus} = +73$ kJ mol^{-1}

c $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
$\Delta H^{\ominus} = -90$ kJ mol^{-1}

6 Predict the effect of the following changes on the position of equilibrium:

a Removing the CO_2 from the system:
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

b Adding acid (H^+) to the system:
$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$

c Adding sodium hydroxide to the system:
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

d Adding sodium hydroxide to the system:
$3I_2(aq) + 3H_2O(l) \rightleftharpoons 5HI(aq) + HIO_3(aq)$

Le Chatelier's Principle and heterogeneous equilibria

Ocean acidification was discussed in Chapter 10, and we saw there that an equilibrium is set up between carbon dioxide in the atmosphere and aqueous carbon dioxide in the oceans:

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

Most of the systems we have looked at so far can be described as *homogeneous* equilibria because all species were in the same physical state. The equation here, however, represents a *heterogeneous* equilibrium system – all species are not in the same physical state.

Le Chatelier's principle can, however, be applied in the same way to systems such as this. As the concentration of carbon dioxide in the atmosphere increases, the position of the above equilibrium shifts to the right to use up (some of the) the gaseous carbon dioxide. Therefore, there will be more carbon dioxide dissolved in the oceans.

18.3 Equilibrium constants

A series of experiments are carried out on the reaction:

$$\underset{\text{ethanoic acid}}{CH_3COOH(l)} + \underset{\text{ethanol}}{C_2H_5OH(l)} \rightleftharpoons \underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3(l)} + \underset{\text{water}}{H_2O(l)}$$

Various known amounts of ethanol and ethanoic acid are reacted together and allowed to come to equilibrium at the same temperature. The equilibrium concentrations of each component of the reaction mixture are determined, and it is found that the following ratio:

$$\frac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][C_2H_5OH(l)]}$$

is constant for all the experiments.

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If the same procedure is repeated for the reaction:

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

it is found that the following ratio of equilibrium concentrations is constant at a particular temperature:

$$\frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

This leads us to the general **equilibrium law**.
For the reaction:

$aA + bB \rightleftharpoons cC + dD$

(where all reactants are in the same phase – a *homogeneous equilibrium*), we find that

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

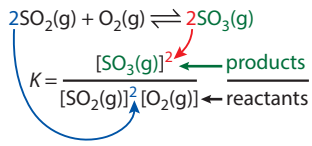
K is the **equilibrium constant** and [A] represents the concentration of A at equilibrium.

KEY POINT

K is constant for a particular reaction at a particular temperature.

How to write the equilibrium constant expression (equilibrium law)

To write an expression for an equilibrium constant, it is important, first of all, to write the chemical equation for the reaction, because these reactions are reversible and can be written either way round. The species on the right-hand side of your equation always go on the top of the expression and the power of each concentration is given by the coefficient in the chemical equation:



This equation is called an equilibrium constant expression or an equilibrium law.

It is important to remember that the expression refers to the system at equilibrium, so these are all concentrations at equilibrium.

The expressions for the equilibrium constant for some other reactions are given:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\qquad K = \dfrac{[NO_2(g)]^2}{[N_2O_4(g)]}$

$N_2O_5(g) + NO(g) \rightleftharpoons 3NO_2(g)$ $\qquad K = \dfrac{[NO_2(g)]^3}{[N_2O_5][NO(g)]}$

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ $\qquad K = \dfrac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3}$

You only need to write equilibrium constants for homogeneous equilibria (all reactants and products in the same physical state). Reactions involving both solids and gases, for example, are more complicated, and the concentrations of pure solids do not appear in the equilibrium constant expression.

EXAM TIP

The equilibrium constant could also be given the symbol Kc in the examination. The 'c' just means that it is written in terms of concentrations.

What use is an equilibrium constant?

Consider the reaction $A \rightleftharpoons B$. The expression for the equilibrium constant for this reaction is $K = \dfrac{[B]}{[A]}$.

From this expression, it can be seen that, if $K > 1$, there will be more B than A present at equilibrium, and, if $K < 1$, there will be more A than B present at equilibrium. If $K = 1$, then the concentrations of A and B at equilibrium will be equal.

KEY POINT

An equilibrium constant provides information about how far a reaction proceeds at a particular temperature (the extent of reaction).

That this is not always so simple can be seen if we look at the following reaction:

$X + Y \rightleftharpoons Z$

for which the expression for K is: $K = \dfrac{[Z]}{[X][Y]}$

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If $[Z] = 0.05$ mol dm^{-3} and $[X] = [Y] = 0.1$ mol dm^{-3}, we can calculate K as $\frac{0.05}{(0.1 \times 0.1)} = 5$, which is greater than 1, but the concentration of the products is lower than that of the reactants.

In general, though:

KEY POINTS

$K >> 1$ – the reaction proceeds almost totally towards the products.

$K << 1$ – the reaction hardly proceeds at all towards the products.

Reaction	K
$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$	10^{95}
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	10^{19}

Table 18.1: Equilibrium constants for reactions at 298.15 K.

The values of the equilibrium constants for a series of reactions at 298.15 K are given in Table 18.1. The expressions for the equilibrium constant for each of these reactions is of the form:

$$K = \frac{[HX]^2}{[H_2][X_2]}$$

Since the value of K is very much greater than one, the concentration of HX at equilibrium is much larger than that of the concentrations of H_2 and X_2. These values are so large that we can assume that these reactions proceed almost totally towards the products, so that there is virtually no hydrogen and halogen in the equilibrium mixture.

However, for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the value of the equilibrium constant is 10^{-31} at 298.15 K. This value is very much less than 1, indicating that the reaction hardly proceeds at all towards the products, that is, the position of equilibrium lies a long way to the left.

The value of the equilibrium constant at a particular temperature depends on how the chemical equation is written

The expression and value for K depend on how the chemical equation is written.

Consider the reaction $A \rightleftharpoons B$. The expression for the equilibrium constant for this reaction is $K = \frac{[B]}{[A]}$.

If we write the reaction the other way round: $B \rightleftharpoons A$

The expression for the equilibrium constant for this reaction is $K' = \frac{[A]}{[B]}$, which is the inverse of the previous expression, so $K' = \frac{1}{K}$

If the value of K at a certain temperature is 10, the value of K' at the same temperature will be $\frac{1}{10} = 0.1$. Both values are 'correct'; it just depends on how the original equation is written.

You would also get a different value for K if you wrote the equation

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ as $\frac{1}{2}H_2(g) + \frac{1}{2}I(g) \rightleftharpoons HI(g)$

The value derived from the second equation would be the square root of the value derived from the first.

It can be seen then that the value of the equilibrium constant depends on how the reaction is written and, therefore, these constants are only useful when quoted in conjunction with a chemical equation for the reaction they represent.

TEST YOUR UNDERSTANDING

7 Write expressions for the equilibrium constants for the following reactions:

a $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$

b $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

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

d $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

8 Write expressions for the equilibrium constants for the following reactions:

a $N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

c $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$

d $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$

e $NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g)$

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CONTINUED

9 Given the following equilibrium constants:

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ $K = 10^{33}$

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $K = 10^{19}$

deduce the values for the equilibrium constants for these reactions:

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

$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

10 a Consider the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $K = 1.03 \times 10^{12}$, at 500 K.

Does the position of equilibrium lie more to the left or to the right at 500 K?

b Consider the equilibrium: $I_2(g) \rightleftharpoons 2I(g)$, $K = 1 \times 10^{-21}$, at 298.15 K

i Does the position of equilibrium lie more to the left or to the right at 298.15 K? What can you deduce about the amount of iodine that exists as separate atoms at 298.15 K?

ii At 1500 K, the value of the equilibrium constant is 2.5. How does the position of equilibrium compare with that in i?

How changing the conditions affects the value of the equilibrium constant

Previously, we used Le Chatelier's principle to predict how changing the conditions affects the position of equilibrium. Here, we will look at the effect of these changes on the value of the equilibrium constant.

KEY POINT

The value of the equilibrium constant for a particular reaction is *only* affected by a change in temperature.

The effect of temperature

Exothermic reactions

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H^\ominus = -90$ kJ mol^{-1}

The equilibrium constant expression for this reaction is:

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2}$$

We can use Le Chatelier's principle to explain the effect of temperature changes on the equilibrium. The reaction is exothermic in the forward direction and so, according to Le Chatelier' s principle, an increase in temperature causes the position of equilibrium to shift in the endothermic direction – the position of equilibrium shifts to the left. The concentration on the top of the expression for K decreases and the concentrations on the bottom increases. Therefore, the overall value of K decreases.

$$\frac{[CH_3OH(g)] \downarrow \text{ concentration decreases}}{[CO(g)]\,[H_2(g)]^2 \uparrow \text{ concentrations increase}}$$

KEY POINT

For an exothermic reaction, the value of the equilibrium constant decreases as the temperature is increased.

Endothermic reactions

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H^\ominus = +181$ kJ mol^{-1}

$$K = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

This is an endothermic reaction in the forward direction. According to Le Chatelier' s principle, as the temperature increases, the position of equilibrium shifts in the endothermic direction. The position of equilibrium is shifted to the right, so that more NO and less N_2 and O_2 are present at equilibrium. This results in the value of the equilibrium constant increasing.

KEY POINT

For an endothermic reaction, the value of the equilibrium constant increases as the temperature is increased.

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The effect of changing pressure or concentration

Changing the pressure and/or concentration can cause the position of equilibrium to shift to the left or the right but does not affect the value of K. We can see how this can be possible by looking at an example.

Consider the reaction: $2A(g) \rightleftharpoons B(g)$

The expression for the equilibrium constant is:

$$K = \frac{[B]}{[A]^2}$$

If we have these gases in a container of volume V, and n_A and n_B are the amounts in mol of A and B at equilibrium, we can work out the concentrations of A and B as follows:

$$[A] = \frac{n_A}{V} \text{ and } [B] = \frac{n_B}{V}$$

The expression for K becomes

$$K = \frac{n_B/V}{(n_A/V)^2}$$

which can be rearranged to $K = \frac{n_B}{(n_A)^2} \times V$

The reaction involves a decrease in the number of moles of gas from left to right, and so, increasing the pressure will cause the position of equilibrium to shift towards the right (the side with fewer moles of gas) so that n_B will increase and n_A will decrease. $\frac{n_B}{(n_A)^2}$ thus increases, which might be expected to increase the value of K, however, the pressure is increased by decreasing the volume of the container, so V goes down. The decrease in V offsets the increase in $\frac{n_B}{(n_A)^2}$ and K stays the same.

Catalysts and equilibrium

Catalysts are substances that increase the rate of a chemical reaction without being permanently changed in the process.

KEY POINT

The presence of a catalyst does not affect the position of equilibrium or the value of the equilibrium constant because it speeds up forward and reverse reactions equally.

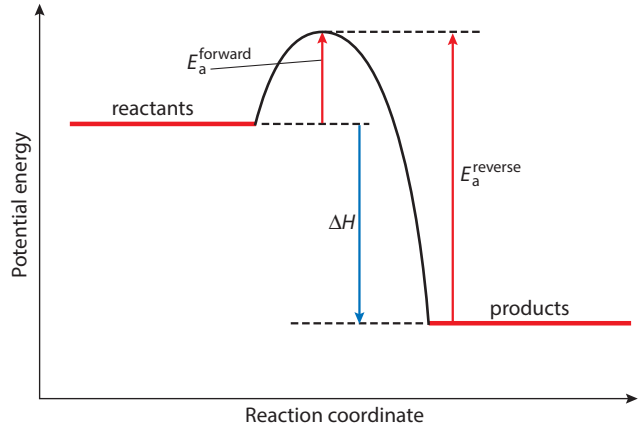

Figure 18.8: An energy profile for a reversible reaction.

An energy profile for a reversible reaction is shown in Figure 18.8.

Catalysts work by providing an alternative pathway of lower activation energy (E_a) for the reaction (Figure 18.9).

In a reversible reaction, a catalyst not only reduces the activation energy for the forward reaction but also that for the reverse reaction. The lowering of the activation energy is the same for both forward and reverse reactions. This means that a catalyst speeds up forward and reverse reactions *equally* and reduces the time taken to reach equilibrium. This is the only change that results from the introduction of a catalyst – a catalyst has no effect on the position of equilibrium or on the value of the equilibrium constant.

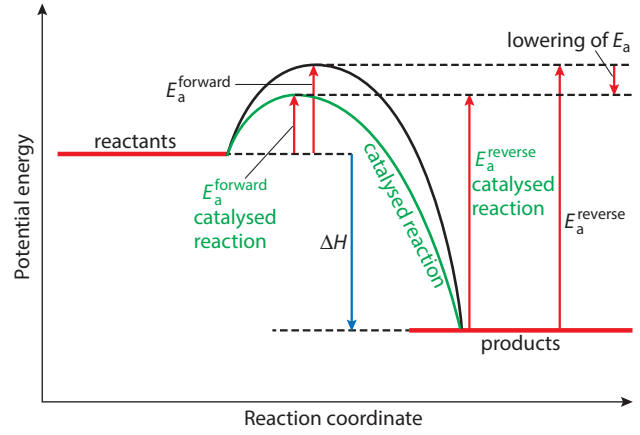

Figure 18.9: A catalyst lowers the activation energy for forward and reverse reactions equally.

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The equilibrium constant and rate

KEY POINT

The equilibrium constant gives us information about how far a reaction goes towards completion (that is, about the extent of the reaction). It gives us absolutely no information about how quickly the reaction occurs. Kinetic data (such as the rate constant) indicate how quickly equilibrium is attained but provide no information whatsoever about the position of equilibrium and how far the reaction proceeds.

So, for example, despite the fact that the equilibrium constant for the following reaction is so large:

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \quad K = 10^{33}$

we cannot make any deductions about what will happen if we put some hydrogen and chlorine into a sealed container and leave them for one week – will there be any significant conversion to hydrogen chloride?

Summary

A summary of the effect of changes in conditions on the position of equilibrium and the value of the equilibrium constant is given in Table 18.2.

Condition	Effect on position of equilibrium	Effect on value of *K*
pressure	if a reaction involves a change in the number of moles of gas, an increase in pressure results in the position of equilibrium shifting in the direction that gives a decrease in the number of moles of gas	no change
concentration	the position of equilibrium will shift to use up any substance that has been added or replace any substance that has been removed from the equilibrium mixture	no change
catalyst	no effect	no change
temperature	if the temperature is increased, the position of equilibrium shifts in the endothermic direction; if the temperature is decreased, the position of equilibrium shifts in the exothermic direction	for an exothermic reaction, *K* decreases as the temperature is increased; for an endothermic reaction, *K* increases as the temperature is increased

Table 18.2: The effect of changes in conditions on the position of equilibrium and the value of the equilibrium constant.

TEST YOUR UNDERSTANDING

11 Explain the effect of the stated changes in conditions on the position of equilibrium and the value of the equilibrium constant. In each case, state whether the value of the equilibrium constant increases, decreases or stays the same.

a Increasing pressure in $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\quad \Delta H^\ominus = +206$ kJ mol^{-1}

b Increasing temperature in $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\quad \Delta H^\ominus = +206$ kJ mol^{-1}

c Decreasing temperature in $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ $\quad \Delta H^\ominus = -40$ kJ mol^{-1}

d Increasing concentration of H_2 in $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H^\ominus = -92$ kJ mol^{-1}

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

f Introducing a catalyst into the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\quad \Delta H^\ominus = -197$ kJ mol^{-1}

g Decreasing the pressure in $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $\quad \Delta H^\ominus = +10$ kJ mol^{-1}

h Increasing concentration of H_2 in $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $\quad \Delta H^\ominus = +10$ kJ mol^{-1}

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SCIENCE IN CONTEXT

With over 170 million tonnes being produced annually, ammonia is one of the most important chemicals in the world today. Most of this ammonia is used to make fertilisers, and some estimates suggest that half the world's population are supported by nitrogen-based fertilisers. However, the process that enables the manufacture of fertilisers on a massive scale has only been around for about 100 years.

Nitrogen is an important element for plant growth, and because most plants are unable to 'fix' nitrogen from the air, they rely on absorbing it in some soluble form from the soil. At the beginning of the 20th century, scientists were struggling to come up with a method for producing ammonia, which could be used to provide this soluble form of nitrogen, and Germany, along with other countries, was reliant on imported guano as a fertiliser. It was Fritz Haber (Figure 18.10) and his co-workers who came up with a solution. Their process was scaled up to industrial level by Carl Bosch of BASF, and the first industrial ammonia production plant opened in Germany in 1913.

The key reaction in the Haber (Haber–Bosch) process is a reversible reaction:

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

Ammonia can be applied directly to soil, but it is also converted into other fertilisers, such as ammonium nitrate. Without artificial fertilisers, it is likely that, in the last hundred years, millions of people around the world would have died of starvation. For his work on this process, which was regarded as benefiting the 'whole of humanity', Haber was awarded the Nobel Prize for Chemistry in 1918 (Carl Bosch had to wait until 1931 for his Nobel Prize!).

There is, however, another side to ammonia. As well as being the basis of artificial fertilisers, ammonia can be used to make explosives Without Haber's process, Germany would have very quickly run out of explosives in World War I; the war would almost certainly have been shorter and millions of lives might have been saved. Haber is also regarded by many as the founder of modern chemical warfare, developing the use of chlorine and other toxic gases as a weapon in World War I; so was the award of the 1918 Nobel Prize for Chemistry one of the most controversial ever?

Just over 100 years later, Haber's process is probably more important than ever – with the world population estimated to grow to about 10 billion by 2050, the production of fertiliser will be essential to feed this population. However, the production of ammonia is very energy intensive and accounts for about 1% of global energy consumption and emissions of greenhouse gases; therefore, the development of greener processes to produce fertilisers will be vital to maintaining a sustainable world.

Figure 18.10: Fritz Haber

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18.4 Calculations involving equilibrium constants

If the concentrations of all reaction components at equilibrium are given, calculating a value for the equilibrium constant simply involves putting these values into the equilibrium constant expression.

WORKED EXAMPLE 18.1

Use the data given to calculate the value of the equilibrium constant at 700 K for the following reaction:

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

Substance	$H_2(g)$	$I_2(g)$	HI(g)
Equilibrium concentration / mol dm^{-3}	0.18	0.39	1.95

Answer

$$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

Substituting in the equilibrium concentrations, we get

$$K = \frac{1.95^2}{0.18 \times 0.39} = 54$$

If we are given a value for the equilibrium constant, we can work out the concentration of any of the species at equilibrium.

WORKED EXAMPLE 18.2

Given that the equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 600 K is 76 and that the concentrations of H_2 and I_2 at equilibrium are 0.25 and 0.50 mol dm^{-3}, respectively, what is the equilibrium concentration of HI?

Answer

$$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

Substituting in equilibrium concentrations, we get

$$76 = \frac{[HI(g)]^2}{0.25 \times 0.50}$$

CONTINUED

Rearranging this expression, we get

$[HI(g)]^2 = 76 \times 0.25 \times 0.50 = 9.5$

Therefore, the equilibrium concentration of hydrogen iodide is 3.1 mol dm^{-3}. A variation on this calculation is given in the next example.

WORKED EXAMPLE 18.3

Equal concentrations of hydrogen and iodine are mixed together in a closed container at 800 K and allowed to come to equilibrium. If the concentration of HI at equilibrium is 0.85 mol dm^{-3}, calculate the equilibrium concentrations of H_2 and I_2. $K = 41$ at this temperature.

Answer

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

$$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

We can substitute the values we know:

$$41 = \frac{0.85^2}{[H_2(g)][I_2(g)]}$$

From the chemical equation, 1 mol H_2 reacts with 1 mol I_2, and since the initial concentrations of these two species are equal, their concentrations must stay equal as they react together. This means that the equilibrium concentration of H_2 is the same as that of I_2 and we can write

$$41 = \frac{0.85^2}{[H_2(g)]^2}$$

Rearranging this expression, we get $[H_2(g)]^2 = \frac{0.85^2}{41}$

$[H_2(g)] = 0.13$ mol dm^{-3}

Therefore, the equilibrium concentrations of H_2 and I_2 are both 0.13 mol dm^{-3}.

Note: if we had the equation $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ and started off with equal concentrations of SO_2 and O_2, the concentrations would not be equal at equilibrium because 2 mol SO_2 react with 1 mol O_2 and, therefore, as the reaction proceeds to equilibrium, the concentration of SO_2 drops by twice as much as the concentration of O_2.

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Next, we will look at questions in which we need to find the value of the equilibrium constant but have not been given all the equilibrium concentrations.

WORKED EXAMPLE 18.4

2.00 mol butane is placed in a closed container of volume 10.0 dm^3 at 25 °C and allowed to come to equilibrium with methyl propane in the presence of a catalyst. The equation for the reaction is:

$CH_3CH_2CH_2CH_3(g) \rightleftharpoons (CH_3)_3CH(g)$

At equilibrium, there was 0.56 mol of butane in the container. Calculate the value of the equilibrium constant at this temperature.

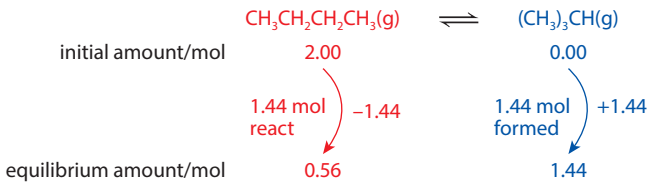
Answer

We can start by setting out the information we have:

	$CH_3CH_2CH_2CH_3(g) \rightleftharpoons (CH_3)_3CH(g)$	
initial amount / mol	2.00	0.00
equilibrium amount / mol	0.56	?

We can see from this that 2.00 – 0.56 = 1.44 mol butane has reacted.

From the chemical equation, we can see that, if 1.44 mol butane reacts, 1.44 mol methylpropane will form. We started with no methylpropane, and so, we can deduce that there must be 1.44 mol methylpropane present at equilibrium. This can be summarised as



The expression for the equilibrium constant is $K = \dfrac{[(CH_3)_3CH]}{[CH_3CH_2CH_2CH_3]}$

We have the equilibrium amount in mol, but we need equilibrium *concentrations* of each species. To work these out, we use the following equation:

$$\text{concentration}(C) = \frac{\text{amount in mol}(n)}{\text{volume}(V)}$$

Because the volume of the reaction vessel is 10.0 dm^3, we must divide each amount by 10.0 and, therefore, the equilibrium concentrations are as follows:

	$CH_3CH_2CH_2CH_3(g) \rightleftharpoons (CH_3)_3CH(g)$	
equilibrium amount / mol	0.56	1.44
equilibrium concentration / mol dm^{-3}	0.056	0.144

We can now put these values into the expression for K: $K = \dfrac{0.144}{0.056} = 2.6$

Because there are equal numbers of moles of gas on both sides, it would not actually have mattered if you had forgotten to divide the number of moles by the volume – the volumes cancel out. This will not, however, always be the case!

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WORKED EXAMPLE 18.5

5.00 mol H_2 and 3.00 mol I_2 are mixed together in a vessel of volume 10.0 dm^3 and allowed to come to equilibrium at 1100 K. At equilibrium, there is 0.44 mol I_2 present in the reaction mixture. Calculate the value of the equilibrium constant.

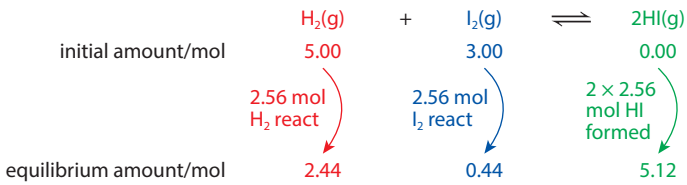
Answer

Here is a summary of the information we have been given:

	$H_2(g)$ +	$I_2(g)$ ⇌	2HI(g)
Initial amount / mol	5.00	3.00	0.00
Equilibrium amount / mol	?	0.44	?

3.00 mol I_2 were originally present, and this became 0.44 mol I_2 at equilibrium. This means that 3.00 – 0.44, i.e., 2.56, mol I_2 reacted.
From the chemical equation, we can see that 1 mol I_2 reacts with 1 mol H_2, so 2.56 mol I_2 reacts with 2.56 mol H_2. If there were 5.00 mol H_2 originally present and 2.56 mol H_2 reacted, this leaves 5.00 – 2.56, i.e., 2.44 mol H_2 present at equilibrium.
From the chemical equation, we can see that, when 1 mol I_2 reacts, 2 mol HI are formed. Therefore, 2.56 mol I_2 will react to form 2 × 2.56, i.e., 5.12 mol HI.

This can be summarised as



Now that we have the equilibrium amounts, we must work out the equilibrium concentrations of each species using $C = \frac{n}{V}$

The volume of the reaction vessel is 10.0 dm^3; therefore, the equilibrium concentrations are

	$H_2(g)$ +	$I_2(g)$ ⇌	2HI(g)
equilibrium amount / mol	2.44	0.44	5.12
equilibrium concentration / mol dm^{-3}	0.244	0.044	0.512

The expression for the equilibrium constant is $K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

The equilibrium concentrations are substituted into this equation:

$$K = \frac{0.512^2}{0.244 \times 0.0444} = 24.4$$

The equilibrium constant for this reaction at 1100 K is, therefore, 24.4.

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EXAM TIP

It is important to remember in all these calculations that the chemical equation shows the ratio is which species *react* and not the ratio in which they are present in the equilibrium mixture.

KEY POINT

The equilibrium constant has no units.

In the calculation we carried out before, we did not have to worry about the units of the equilibrium constant because there were the same number of molecules on each side, but this will not always be the case. However, in general, you can assume that all equilibrium constants do not have units.

Link

All the equilibrium constants here have no units because we are assuming that they are worked out in terms of activities (effective concentrations), which are calculated relative to a standard concentration of 1 mol dm^{-3}. Equilibrium concentrations do have units (mol dm^{-3}), but in expressions for K we use concentration/mol dm^{-3}, which does not have any units and, therefore, overall equilibrium constants have no units. You may come across several different equilibrium constants, K_c, K_p or K, some of which may be defined in a different way, so they do have units.

TEST YOUR UNDERSTANDING

12 Given the equilibrium concentrations, calculate the value of the equilibrium constant for each reaction:

a $2A(g) \rightleftharpoons Z(g)$

equilibrium concentrations are
$[A] = 0.150$ mol dm^{-3} and
$[Z] = 0.500$ mol dm^{-3}

b $2D(g) + 3X(g) \rightleftharpoons 2Z(g) + 4E(g)$

equilibrium concentrations are
$[D] = 1.50 \times 10^{-3}$ mol dm^{-3},
$[X] = 2.75 \times 10^{-3}$ mol dm^{-3},
$[Z] = 7.86 \times 10^{-4}$ mol dm^{-3} and
$[E] = 9.37 \times 10^{-5}$ mol dm^{-3}

13 In each of the following reactions use the data given to calculate the equilibrium amount (in mol) of each substance.

a $2A(g) \rightleftharpoons Z(g)$

	A	Z
Initial amount / mol	0.100	0.500

amount of A at equilibrium = 0.0600 mol

b $2A(g) + X(g) \rightleftharpoons 2Z(g)$

	A	X	Z
Initial amount / mol	1.00	2.00	0.00

amount of Z at equilibrium = 0.400 mol

c $A(g) + 2X(g) \rightleftharpoons R(g) + Z(g)$

	A	X	R	Z
Initial amount / mol	0.200	0.200	0.00	0.00

amount of X at equilibrium = 0.0600 mol

d $A(g) + 2X(g) \rightleftharpoons R(g) + 2Z(g)$

	A	X	R	Z
Initial amount / mol	0.100	0.400	0.100	0.600

amount of Z at equilibrium = 0.580 mol

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CONTINUED

14 Consider the reversible reaction:
$A(g) + X(g) \rightleftharpoons Z(g)$

a Write the expression for K for this reaction.

b In each of the following situations, calculate a value for the equilibrium constant from the data given:

i

	A	X	Z
Initial amount / mol	0.200	0.400	0.000

amount of A at equilibrium = 0.100 mol

volume of container = 1.00 dm^3

temperature = 300 K

ii

	A	X	Z
Initial amount / mol	0.200	0.100	0.100

amount of A at equilibrium = 0.150 mol

volume of container = 10.0 dm^3

temperature = 400 K

c Use the values of K that you have calculated to work out whether the forward reaction is exothermic or endothermic.

15 Consider the reversible reaction:
$2A(g) + X(g) \rightleftharpoons 4R(g) + Z(g)$

a Write the expression for K for this reaction.

b In each of the following situations, calculate a value for the equilibrium constant from the data given:

i

	A	X	R	Z
Initial amount / mol	0.800	0.400	0.000	0.000

amount of Z at equilibrium = 0.100 mol

volume of container = 10.0 dm^3

temperature = 800 K

ii

	A	X	R	Z
Initial amount / mol	0.000	0.000	1.000	2.000

amount of A at equilibrium = 0.200 mol

volume of container = 20.0 dm^3

temperature = 500 K

c Use the values of K that you have calculated to work out whether the forward reaction is exothermic or endothermic.

The reaction quotient

KEY POINT

The reaction quotient, Q, is the ratio of the concentrations of reactants and products (raised to the appropriate powers) at any point in time.

An expression for Q is exactly the same as that for the equilibrium constant, except that the concentrations are not equilibrium concentrations.

So, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$Q = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

When the system is at equilibrium, the concentrations are all equilibrium concentrations, and the value of Q is equal to the value of K at that temperature.

If we mix 2 mol HI, 1 mol H_2 and 1 mol I_2 in a 1 dm^3 vessel at 700 K, then the concentrations of the species present in the reaction mixture are:

$[HI] = 2$ mol dm^{-3}, $[H_2] = 1$ mol dm^{-3} and $[I_2] = 1$ mol dm^{-3}

So, the value of Q is: $Q = \frac{2^2}{1 \times 1} = 4$

The value of K for this reaction is 54 at 700 K.

Because the value of Q is not equal to the value of the equilibrium constant, we can see immediately that the system is not at equilibrium.

We can also see that, because the value of Q is less than that of K, the reaction must proceed to the right (to produce more HI) to reach equilibrium. If the

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reaction proceeds to the right, there will be more HI and less H_2 and I_2 in the reaction mixture, and the value of Q will increase.

If 0.5 mol of the H_2 reacts with 0.5 mol I_2 to produce an extra 1 mol HI, then the new concentrations are as follows:

$[HI] = 3$ mol dm^{-3}, $[H_2] = 0.5$ mol dm^{-3} and $[I_2] = 0.5$ mol dm^{-3}

So, the new value of Q is: $Q = \frac{3^2}{0.5 \times 0.5} = 36$

The system is still not at equilibrium because Q is not equal to K, but it is closer to equilibrium. Because the value of Q is still smaller than K, more H_2 and I_2 must react together to form HI. This happens until $Q = K$ and the system has reached equilibrium.

If we add some HI to this system, so that the concentration of HI is now 6 mol dm^{-3}, we can work out the value of Q again.

$[HI] = 6$ mol dm^{-3}, $[H_2] = 0.5$ mol dm^{-3} and $[I_2] = 0.5$ mol dm^{-3}

So, the new value of Q is: $Q = \frac{6^2}{0.5 \times 0.5} = 144$

In this case, $Q > K$, so the reaction must proceed to the left towards equilibrium. HI will then react to form H_2 and I_2 until the value of $Q = 54$ and the system is at equilibrium.

KEY POINT

In general:

- If $Q \neq K$, the system is not at equilibrium.
- If $Q < K$, then the reaction must proceed towards the products (to the right) to reach equilibrium.
- If $Q > K$, then the reaction must proceed towards the reactants (to the left) to reach equilibrium.

Calculating the equilibrium amounts from the equilibrium constant

WORKED EXAMPLE 18.6

2.00 mol butane and 2.00 mol methylpropane are placed in a closed container of volume 1.00 dm^3 at 800 K and allowed to come to equilibrium in the presence of a catalyst. The value of the equilibrium constant at this temperature is 0.48. The equation for the reaction is:

$CH_3CH_2CH_2CH_3(g) \rightleftharpoons (CH_3)_3CH(g)$

Determine in which direction the system will move to equilibrium and the amounts in mol of butane and methylpropane present at equilibrium at 800 K.

Answer

To work out in which direction this system will move towards equilibrium, we need to work out the value of the reaction quotient, Q, and compare it to the value of K.

$$Q = \frac{[(CH_3)_3CH]}{[CH_3CH_2CH_2CH_3]}$$

The volume of the container is 1.00 dm^3; therefore, the concentrations $\left(n = \frac{C}{V}\right)$ are:

$[CH_3CH_2CH_2CH_3] = [(CH_3)_3CH] = 2.00$ mol dm^{-3}

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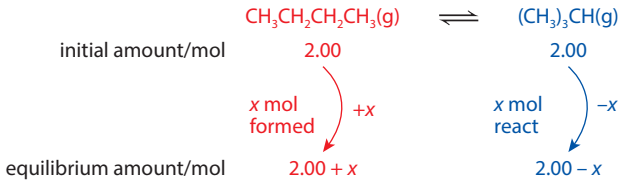
CONTINUED

$$Q = \frac{2.00}{2.00} = 1.00$$

$K = 0.48$; therefore, $Q > K$ and the reaction must proceed to the left towards equilibrium.
In other words, to reach equilibrium, some methylpropane must be converted into butane.

Let the amount of methylpropane that must react to form the equilibrium mixture be x.
From the chemical equation, we can see that x mol of methylpropane would form x mol butane and we have



The concentrations at equilibrium are obtained by dividing the equilibrium amounts by the volume of the container (1.00 dm^3), and so, the equilibrium concentrations are numerically the same as the amounts.

$$K = \frac{[(CH_3)_3CH]}{[CH_3CH_2CH_2CH_3]} = \frac{2.00 - x}{2.00 + x}$$

The value of K is 0.48, so we have

$$0.48 = \frac{2.00 - x}{2.00 + x}$$

Solving this equation we get $x = 0.70$ mol

We can substitute this back into our expressions for the equilibrium amounts of each species:

amount of butane = 2.00 + 0.70 = 2.70 mol

amount of methylpropane = 2.00 – 0.70 = 1.30 mol

WORKED EXAMPLE 18.7

Consider the reaction $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

2.00 mol H_2 and 2.00 mol CO_2 are put into a container of volume 10.0 dm^3 together with 1.00 mol H_2O and 1.00 mol CO. They are allowed to come to equilibrium at 1200 K.
Given that the value of the equilibrium constant at 1200 K is 2.10, work out the composition of the equilibrium mixture in terms of concentrations.

Answer

We could do a quick calculation of Q to work out in which direction the system moves towards equilibrium, but it does not actually make any difference to the calculation – if we get the direction wrong, our value of x will just come out as negative.

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CONTINUED

	$H_2(g)$ + $CO_2(g)$	⇌	$H_2O(g)$ + $CO(g)$
initial amount / mol	2.00 2.00		1.00 1.00
We will assume that x mol H_2 react with x mol CO_2 to form x mol H_2O and x mol CO.			
equilibrium amount / mol	$2.00 - x$ $2.00 - x$		$1.00 + x$ $1.00 + x$
We must divide each of these values by 10.0 to get equilibrium concentrations:			
equilibrium concentration / mol dm^{-3}	$\frac{2.00 - x}{10.0}$ $\frac{2.00 - x}{10.0}$		$\frac{1.00 + x}{10.0}$ $\frac{1.00 + x}{10.0}$

The equilibrium concentrations and the value of K are substituted into the expression for K:

$$K = \frac{[H_2O(g)][CO(g)]}{[H_2(g)][CO_2(g)]}$$

The numbers of species on both sides of the equation are the same, so the volumes cancel.

$$2.10 = \frac{\frac{1.00 + x}{\cancel{10.0}} \times \frac{1.00 + x}{\cancel{10.0}}}{\frac{2.00 - x}{\cancel{10.0}} \times \frac{2.00 - x}{\cancel{10.0}}}$$

$$2.10 = \frac{(1.00 + x)(1.00 + x)}{(2.00 - x)(2.00 - x)} \quad \text{i.e. } 2.10 = \frac{(1.00 + x)^2}{(2.00 - x)^2}$$

The right-hand side is a perfect square, and so the square root of each side can be taken:

$$\sqrt{2.10} = \frac{1.00 + x}{2.00 - x} \quad \text{i.e. } 1.45 = \frac{1.00 + x}{2.00 - x}$$

Solving this, we get $x = 0.776$ mol.

The equilibrium concentrations are worked out from

	$H_2(g)$ + $CO_2(g)$	⇌	$H_2O(g)$ + $CO(g)$
equilibrium concentration / mol dm^{-3}	$\frac{2.00 - x}{10.0}$ $\frac{2.00 - x}{10.0}$		$\frac{1.00 + x}{10.0}$ $\frac{1.00 + x}{10.0}$
Substituting in the value of x we get			
equilibrium concentration / mol dm^{-3}	0.122 0.122		0.178 0.178

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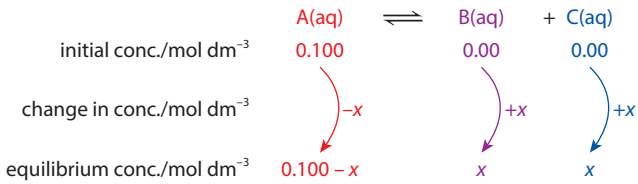
Using an approximation in calculations

Sometimes, when K is very small, we can make an approximation to simplify the calculation. Consider the reaction A(aq) ⇌ B(aq) + C(aq).

If $K = 1.00 \times 10^{-7}$ and the initial concentration of A is 0.100 mol dm^{-3}, we can find the equilibrium concentrations of B and C by assuming that the change in concentration of A, as the system moves to equilibrium, is x mol dm^{-3}:



We have worked here with concentrations rather than amounts (in mol), as before, because that is how we were given the data. Since the total volume of the solution is fixed, the amount is proportional to the concentration. The previous questions could also have been done in terms of concentrations from the beginning (the volume of the container was fixed), but we were given amounts; therefore, it was easier to work with them and then convert to concentrations.

The expression for K is: $K = \dfrac{[B][C]}{[A]}$

and, if we substitute in the known values, we have

$$1.00 \times 10^{-7} = \frac{x^2}{0.100 - x}$$

To solve this for x, we have to solve a quadratic equation, but we can take a shortcut by assuming that, because K is so small, the position of equilibrium lies a long way to the left, and so, the quantity of A that reacts to form B and C is small compared to the initial concentration of A. In other words, we will assume that the equilibrium concentration of A is approximately equal to the initial concentration of A and use this in the calculation. Although we are assuming that $x \approx 0$ when compared to the concentration of A, this does not mean we ignore the concentrations of B and C – the change in concentration for them is significant compared to the initial amounts (0). This is a bit like saying, if person A has $1 000 000 and gives away $10 to person B, who has nothing, it makes very little difference to how much money A has (they still have essentially a million dollars) and their lifestyle is unlikely to change, but it makes a big difference to person B!

Making this approximation means that the previous expression simplifies to

$$1.00 \times 10^{-7} = \frac{x^2}{0.100}$$

This is much easier to solve.

Re-arranging this expression, we get $x = 1.00 \times 10^{-4}$ and the equilibrium concentrations of B and C are, therefore, 1.00×10^{-4} mol dm^{-3}.

If we do the calculation without making the approximation, we get $x = 9.995 \times 10^{-5}$, which, to 3 significant figures, is also 1.00×10^{-4}, so making the approximation makes no difference.

Table 18.3 shows how good the approximation is for various values of K in this calculation.

It can be seen that the approximation results in very good agreement, in this case, when $K < 10^{-5}$. You may be thinking, why bother with the approximation because solving quadratic equations is a lot simpler than some of the other things in chemistry, but we will see how it can make the calculations much faster when we are looking at the dissociation of weak acids in Chapter 19, and, if the original equation had been of the form A ⇌ 2B + C, it does make the maths a lot easier!

K	[B] calculated from the quadratic expression / mol dm^{-3}	[B] using approximation / mol dm^{-3}	Percentage error (%)
0.100	0.0618	0.100	61.8
1.00×10^{-3}	9.51×10^{-3}	1.00×10^{-2}	5.15
1.00×10^{-5}	9.95×10^{-4}	1.00×10^{-3}	0.503
1.00×10^{-7}	1.00×10^{-4}	1.00×10^{-4}	0.00

Table 18.3: A comparison of calculations with and without making the approximation that $[A]_{equilibrium} = [A]_{initial}$. The percentage error was worked out as the difference between the two values, divided by the actual value, × 100.

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TEST YOUR UNDERSTANDING

16 Write expressions for the reaction quotient, Q, for the following reactions:

a $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$

b $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

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

d $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

17 For each of the following systems:

i calculate the value of Q

ii determine whether the system is at equilibrium

iii if the system is not at equilibrium, determine in which direction (to the left or right) it must move towards equilibrium.

a $2A(g) \rightleftharpoons Z(g)$ $K = 50.0$

Concentrations are:

$[A] = 0.100$ mol dm^{-3}

$[Z] = 0.200$ mol dm^{-3}

b $A(g) \rightleftharpoons 2Z(g)$ $K = 0.0200$

Concentrations are:

$[A] = 0.320$ mol dm^{-3}

$[Z] = 0.0800$ mol dm^{-3}

c $R(g) + 2X(g) \rightleftharpoons Z(g) + 2E(g)$ $K = 35.2$

Concentrations are:

$[R] = 1.20 \times 10^{-3}$ mol dm^{-3}

$[X] = 2.50 \times 10^{-3}$ mol dm^{-3}

$[Z] = 7.40 \times 10^{-3}$ mol dm^{-3}

$[E] = 9.30 \times 10^{-3}$ mol dm^{-3}

d $2R(g) + 3X(g) \rightleftharpoons 2Z(g) + E(g)$ $K = 5200$

Concentrations are:

$[R] = 5.70 \times 10^{-2}$ mol dm^{-3}

$[X] = 8.20 \times 10^{-2}$ mol dm^{-3}

$[Z] = 3.65 \times 10^{-1}$ mol dm^{-3}

$[E] = 7.40 \times 10^{-1}$ mol dm^{-3}

e $2R(g) + X(g) \rightleftharpoons 3Z(g) + 2E(g)$ $K = 0.122$

Concentrations are:

$[R] = 1.56 \times 10^{-3}$ mol dm^{-3}

$[X] = 4.78 \times 10^{-2}$ mol dm^{-3}

$[Z] = 9.86 \times 10^{-2}$ mol dm^{-3}

$[E] = 2.47 \times 10^{-3}$ mol dm^{-3}

18 Consider the reversible reaction: $Z(g) \rightleftharpoons X(g)$

a At a certain temperature, the value of the equilibrium constant for this reaction is 20.0. At this temperature, 0.100 mol Z and 0.200 mol X are placed in a container of volume 1.00 dm^3 and allowed to come to equilibrium.

i Determine in which direction the system will move towards equilibrium.

ii Calculate the amount of X present at equilibrium.

b At a different temperature, the value of the equilibrium constant for this reaction is 4.20. At this temperature 1.56×10^{-3} mol Z and 8.24×10^{-3} mol X are placed in a container of volume 5.00 dm^3 and allowed to come to equilibrium.

i Determine in which direction the system will move towards equilibrium.

ii Calculate the amount of Z present at equilibrium.

19 Consider the reversible reaction: $A(g) + Z(g) \rightleftharpoons X(g) + B(g)$

a At a certain temperature, the value of the equilibrium constant for this reaction is 9.00. At this temperature 0.100 mol A and 0.100 mol Z are placed in a container of volume 1.00 dm^3 and allowed to come to equilibrium.

Calculate the amount of X present at equilibrium.

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CONTINUED

b At a different temperature, the value of the equilibrium constant for this reaction is 16.0. At this temperature 0.200 mol A, 0.200 mol Z, 0.200 mol X and 0.200 mol B are placed in a container of volume 2.00 dm^3 and allowed to come to equilibrium.

i Deduce the direction in which the system will move towards equilibrium.

ii Calculate the concentration of A at equilibrium.

20 Consider the system: $A(aq) \rightleftharpoons B(aq) + C(aq)$

$K = 1.58 \times 10^{-9}$ at 300 K

If the initial concentration of A was 0.100 mol dm^{-3}, calculate the concentration of B at equilibrium.

21 Consider the system: $A(aq) \rightleftharpoons B(aq) + C(aq) + D(aq)$

$K = 6.23 \times 10^{-18}$ at 500 K

If the initial concentration of A was 0.0200 mol dm^{-3}, calculate the concentration of C at equilibrium.

18.5 Relationship between equilibrium constants and Gibbs energy

We have already seen in Chapter 15 that the Gibbs energy is a minimum at equilibrium.

KEY POINT

The position of equilibrium corresponds to the mixture of reactants and products that produces the minimum value of the Gibbs energy.

This corresponds to our idea that equilibrium can be reached from either direction, that is, starting from either pure reactants or pure products. Since the equilibrium mixture always has a lower Gibbs energy than either the pure reactants or the pure products, the conversion of either reactants or products into the equilibrium mixture results in a process for which ΔG is negative and, therefore, spontaneous.

It can be seen from Figure 18.11 that the overall Gibbs energy of a system depends on how much of each substance is present. The Gibbs energy change is related to the composition of the reaction mixture.

KEY POINT

$\Delta G = \Delta G^{\ominus} + RT\ln Q$

$\Delta G^{\ominus}$ is the standard change in Gibbs energy for the complete conversion of molar amounts of reactants to products, as in the stoichiometric equation. So, for instance, if the reaction is $X \rightleftharpoons Y$, $\Delta G^{\ominus}$ would be for the complete conversion of 1 mol X into 1 mol Y.

ΔG represents the difference in Gibbs energy between however much of the reactants and however much of the products are present in the reaction mixture at a particular point in time. So, for instance, for the conversion $X \rightleftharpoons Y$, if we started with 1 mol X and 0.2 mol reacts to form 0.2 mol Y, then ΔG is the difference in Gibbs energy between 0.8 mol X and 0.2 mol Y.

Q is the reaction quotient.

R is the gas constant (8.31 $J\ K^{-1}\ mol^{-1}$).

T is the temperature in kelvin.

It is important to remember that ΔG and $\Delta G^{\ominus}$ must be in $J\ mol^{-1}$ because R is in $J\ K^{-1}\ mol^{-1}$.

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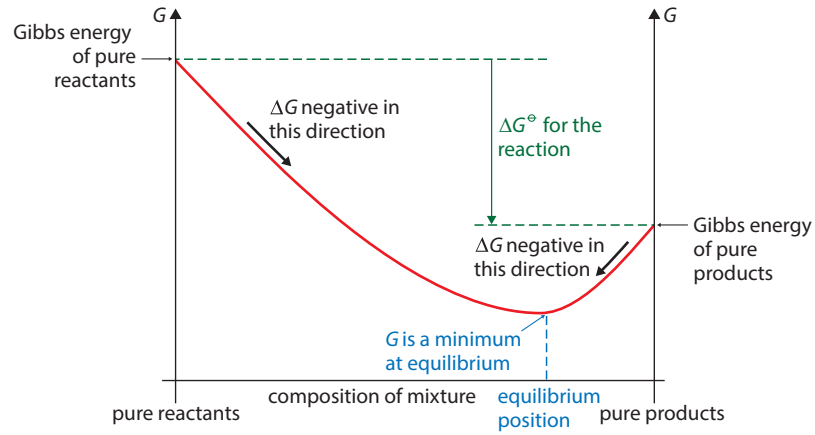

Figure 18.11: Variation in the Gibbs energy for a reaction for which $\Delta G^{\ominus}$ is negative overall.

Using $\Delta G = \Delta G^{\ominus} + RT\ln Q$ in calculations

Let us consider again the conversion of butane into methylpropane:

$CH_3CH_2CH_2CH_3(g) \rightleftharpoons (CH_3)_3CH(g)$
$\Delta G^{\ominus} = -2.32\ \text{kJ mol}^{-1}$

If we mix together 3 mol butane and 2 mol methylpropane in a sealed container with volume 1.00 dm^3, the concentrations of butane and methylpropane are:

$[CH_3CH_2CH_2CH_3] = 3.00\ \text{mol dm}^{-3}$

$[(CH_3)_3CH] = 2.00\ \text{mol dm}^{-3}$

$$Q = \frac{[(CH_3)_3CH]}{[CH_3CH_2CH_2CH_3]} = \frac{2.00}{3.00} = 0.667$$

When substituting values into the equation $\Delta G = \Delta G^{\ominus} + RT\ln Q$ we should remember that $\Delta G^{\ominus}$ must be in J mol^{-1}; Let us consider again the conversion of butane into methylpropane at 298.15K:

$\Delta G = -2320 + 8.31 \times 298.15 \times \ln 0.667 = -3323\ \text{J mol}^{-1}$

The negative value of ΔG means that the conversion of butane into methylpropane will occur spontaneously as the system moves towards equilibrium (this reaction mixture would be to the left of the minimum in Figure 18.11). In other words, the system will move to the right towards equilibrium.

We could have drawn the same conclusion by comparing the value of Q to the value of the equilibrium constant at this temperature (2.55). Q is smaller than K, so the system moves to the right towards equilibrium.

We know that some butane must be converted into methylpropane to get to equilibrium, so let us look at what happens if 1 mol butane is converted into methylpropane so that the concentrations are now

$[CH_3CH_2CH_2CH_3] = 2.00\ \text{mol dm}^{-3}$

$[(CH_3)_3CH] = 3.00\ \text{mol dm}^{-3}$

$$Q = \frac{3.00}{2.00} = 1.50$$

$\Delta G = -2320 + 8.31 \times 298.15 \times \ln 1.5 = -1315\ \text{J mol}^{-1}$

The value is still negative, so the reaction must proceed further to the right to get to equilibrium. The value is, however, less negative than before, so the system is getting closer to equilibrium. Equilibrium corresponds to the point at which the difference between the Gibbs energy of the quantities of reactants and products that are present is zero, so there is no tendency to go in one direction or the other. If we put $\Delta G = 0$ into the equation $\Delta G = \Delta G^{\ominus} + RT\ln Q$, we get

$0 = -2320 + 8.31 \times 298.15 \times \ln Q$

Solving this, we get $Q = 2.55$, which is the value of the equilibrium constant at this temperature.

Thus, we can see that, when the system is at equilibrium, $\Delta G = 0$ and $Q = K$. If we put these into our original equation,

$\Delta G = \Delta G^{\ominus} + RT\ln Q$

we get $0 = \Delta G^{\ominus} + RT\ln K$

which can be re-arranged to $\Delta G^{\ominus} = -RT\ln K$

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Calculations using $\Delta G^{\ominus} = -RT\ln K$

The equilibrium constant is related to the standard change in Gibbs energy.

KEY POINT

$\Delta G^{\ominus} = -RT\ln K$

where

R is the gas constant (8.31 J K^{-1} mol^{-1})

T is the temperature in kelvin

$\Delta G^{\ominus}$ is the standard change in Gibbs energy in J mol^{-1}.

WORKED EXAMPLE 18.8

Consider the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Given that the value of $\Delta G^{\ominus}$ at 600 K for this reaction is –21.6 kJ mol^{-1}, calculate the value of the equilibrium constant.

Answer

$\Delta G^{\ominus} = -RT\ln K$

Because R has units of J K^{-1} mol^{-1}, the value of $\Delta G^{\ominus}$ must be converted into J mol^{-1}:

$\Delta G^{\ominus} = -21\,600$ J mol^{-1}

Substituting in values, we get:

$-21\,600 = -8.31 \times 600 \times \ln K$

Rearranging this expression, we get:

$$\ln K = \frac{21\,600}{8.31 \times 600} = 4.33$$

The inverse function for $\ln x$ is e^x; therefore, both sides need to be raised as powers of e. Note: use the key combination shift/2nd function + ln on your calculator.

$K = e^{4.33} = 76.1$

The equilibrium constant has a value of 76.1, which is greater than 1, which implies that the position of equilibrium lies closer to the products than the reactants. This is also consistent with the value of $\Delta G^{\ominus}$ being negative.

KEY POINTS

When $K < 1$, the value of $\ln K$ is negative, and so, $\Delta G^{\ominus}$ is positive.

When $K > 1$, the value of $\ln K$ is positive, and so, $\Delta G^{\ominus}$ is negative.

The relationship between $\Delta G^{\ominus}$ and the value of K is summarised in Table 18.4.

$\Delta G^{\ominus}$	K	Position of equilibrium
negative	>1	closer to products than reactants
positive	<1	closer to reactants than products

Table 18.4: The relationship between $\Delta G^{\ominus}$ and K.

KEY POINT

When calculating $\Delta G^{\ominus}$ from a value for K, the units of $\Delta G^{\ominus}$ will come out as J mol^{-1}.

WORKED EXAMPLE 18.9

Consider the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

The value of the equilibrium constant at 926.85 °C is 4.65×10^{-2}. Calculate the value of $\Delta G^{\ominus}$ in kJ mol^{-1}.

Answer

We will use the equation: $\Delta G^{\ominus} = -RT\ln K$

T must be in kelvin; therefore, $T = 926.85 + 273.15 = 1200$ K

Substituting in values, we get

$\Delta G^{\ominus} = -8.31 \times 1200 \times \ln (4.65 \times 10^{-2}) = 30\,600$ J mol^{-1}

Therefore, $\Delta G^{\ominus} = 30.6$ kJ mol^{-1}

A positive value corresponds to the value of the equilibrium constant being less than one. The position of equilibrium will lie towards the reactants (HI) side.

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Link

The equilibrium constant in the equation $\Delta G^{\ominus} = -RT\ln K$ is the standard or thermodynamic equilibrium constant. This has the same value as the equilibrium constants we have calculated in terms of concentrations for reactions in solution; however, for reactions involving gases, the value of K is the same as that of K_p, which is the equilibrium constant in terms of partial pressures (relative to a standard state of 1 bar). If there are different numbers of moles of gas on each side of an equation, the value of K we calculate from concentrations is not the same as the value of K_p or the standard equilibrium constant. The examples in this section, therefore, all involve systems with no change in the number of moles of gas so that the values of the various equilibrium constants are the same.

TEST YOUR UNDERSTANDING

The value of the gas constant is $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$

22 Consider the reaction A(g) ⇌ Z(g), $\Delta G^{\ominus} = -10.0\ \text{kJ mol}^{-1}$, at 500 K

For each of the following sets of concentrations, calculate ΔG.

a $[A] = 0.100\ \text{mol dm}^{-3}$ $[Z] = 0.100\ \text{mol dm}^{-3}$

b $[A] = 0.0900\ \text{mol dm}^{-3}$ $[Z] = 0.110\ \text{mol dm}^{-3}$

c $[A] = 0.0500\ \text{mol dm}^{-3}$ $[Z] = 0.150\ \text{mol dm}^{-3}$

Explain the trend in the values you obtain.

23 Consider the reaction 2X(g) ⇌ A(g) + D(g), $\Delta G^{\ominus} = +25.0\ \text{kJ mol}^{-1}$, at 1000 K

For each of the following sets of concentrations, calculate ΔG and work out in which direction the system will move towards equilibrium:

a $[X] = 0.120\ \text{mol dm}^{-3}$

$[A] = 0.0250\ \text{mol dm}^{-3}$

$[D] = 0.0150\ \text{mol dm}^{-3}$

b $[X] = 0.100\ \text{mol dm}^{-3}$

$[A] = 0.200\ \text{mol dm}^{-3}$

$[D] = 0.100\ \text{mol dm}^{-3}$

24 Calculate the value of $\Delta G^{\ominus}$ (in kJ mol^{-1}) given the following values:

a A(g) ⇌ B(g) $K = 2.78$ $T = 298\ \text{K}$

b C(g) ⇌ D(g) $K = 3.58 \times 10^{5}$ $T = 333\ \text{K}$

c E(g) ⇌ F(g) $K = 7.56 \times 10^{-4}$ $T = 454.85\ ^{\circ}\text{C}$

25 **a** Calculate the value of K given the following values:

i A(g) ⇌ B(g)
$\Delta G^{\ominus} = 50.0\ \text{kJ mol}^{-1}$ $T = 298\ \text{K}$

ii C(g) ⇌ D(g)
$\Delta G^{\ominus} = -25.2\ \text{kJ mol}^{-1}$ $T = 350\ \text{K}$

iii E(g) ⇌ F(g)
$\Delta G^{\ominus} = -154\ \text{kJ mol}^{-1}$ $T = 26.85\ ^{\circ}\text{C}$

b For each of the situations in **a**, state whether the position of equilibrium lies more towards the left (reactants) or towards the right (products).

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain what is meant by the term dynamic equilibrium	18.1			
use Le Chatelier's principle to explain how changes in conditions affect the position of equilibrium	18.2			
write an equilibrium law expression	18.3			
explain the connection between the value of the equilibrium constant and the extent of reaction	18.3			
explain the connection between how a reaction is written and the equilibrium constant expression	18.3			
solve problems involving the equilibrium constant	18.4			
calculate the value of the reaction quotient	18.4			
explain the connection between the change in Gibbs energy, the equilibrium constant and the reaction quotient	18.5			
solve problems involving the change in Gibbs energy, the equilibrium constant and the reaction quotient.	18.5			

REFLECTION

- To what extent do you feel that you understand this topic well enough to answer exam questions?
- Do you feel that you have an active or passive understanding of the topic? Remember, there is a difference between reading through the worked examples (passive understanding) and actually doing them yourself (active understanding). Have you tried doing all the worked examples yourself without looking at the solutions? Could you write out explanations in the exam? This is a bit like the difference between understanding a language and being able to speak it.
- Could you explain Le Chatelier's principle to another student?
- What can you do to further develop your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Unit 6

Mechanisms of chemical change

INTRODUCTION

Now, as we come towards the end of the course, we put together the principles we have learned to study some chemical reactions. Chemistry is all about electrons. What unifies all the reactions in this unit, and in this book, is that they involve the movement of electrons. This may not have been as obvious in the reactions studied so far, but, in this unit, we can see this much more clearly: the reactions of acids and bases involve a pair of electrons being donated to H^+ (or other atoms for Lewis acids/bases); redox reactions involve the transfer of electrons from one atom/ion to another; the reactions of radicals in organic chemistry involve the movement of one electron each time in the making or breaking of a bond; and we use curly arrows in organic reactions to show the movement of pairs of electrons in the breaking of bonds or when nucleophiles react with electrophiles.

If you continue with your study of chemistry beyond this level, be aware that there is a lot more to learn and understand, and we have just touched on the tip of the iceberg here. If we return to the idea of what chemistry is, it is an exciting and ever-growing branch of science, which sometimes is surprisingly simple and elegant, but, at other times, can seem incredibly complex and difficult to understand. Sometimes it will seem like the more you know, the less you actually understand, because you begin to realise just how much there is to understand. The important thing, however, is to keep thinking about it, keep asking questions that further your understanding and enjoy the subject.

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Chapter 19

Proton transfer reactions

LEARNING OBJECTIVES

In this chapter you will:

- understand that acids react with bases in neutralisation reactions
- understand the Brønsted–Lowry definition of acids and bases
- understand what pH is and calculate pH and $[H^+(aq)]$
- understand that water dissociates and relate $[H^+(aq)]$ and $[OH^-(aq)]$ to acidity and basicity
- distinguish between strong and weak acids and bases
- understand the shape of a pH curve for a strong acid–strong base titration

- understand what pOH is and use it in calculations
- understand the connection between the values of K_a, K_b, pK_a and pK_b and the strengths of acids and bases
- solve problems using K_a, K_b, pK_a and pK_b
- understand the connection between K_a and K_b for a conjugate acid–base pair

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CONTINUED

- predict the pH of a salt solution
- sketch and explain pH curves
- understand how acid–base indicators work and predict a suitable indicator for a titration
- understand what a buffer solution is and explain how they work
- solve problems involving buffer solutions.

GUIDING QUESTIONS

- What is an acid?
- How do acids react?
- How can we calculate how acidic/basic a solution is?

Introduction

Acids are substances that are familiar, both in the laboratory and in everyday life, and we regularly eat and drink acidic solutions. A glass of cola (Figure 19.1) will probably have a pH in the range 2.5–3 (although the ice cubes, when they melt, will dilute it and raise the pH). Cola is mostly fizzy water, which is carbonic acid, but will usually also contain phosphoric acid and may contain citric acid. There is a common myth that a tooth will dissolve overnight if left in a glass of cola, but this is not true – there is nothing like enough acid in cola to dissolve a tooth!

Figure 19.1: Cola contains carbonic acid (fizzy water) and phosphoric acid, among other things. Limes owe their sour taste to citric acid.

19.1 Acids, bases and salts

Acids

If we look at the formulas of some acids (Table 19.1), we can see that all acids contain at least one hydrogen atom. It is this hydrogen atom that leads to the characteristic properties of an acid. In the simplest definition of acids, an acid is a substance that produces hydrogen (H^+) ions in solution.

Acid	Formula
hydrochloric	HCl
sulfuric	H_2SO_4
nitric	HNO_3
carbonic	H_2CO_3
ethanoic	CH_3COOH
benzoic	C_6H_5COOH

Table 19.1: The formulas for some common acids, with the H that is lost as H^+ shown in red.

So, when hydrochloric acid is in water, it dissociates to form $H^+(aq)$ and $Cl^-(aq)$ ions:

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

It is the H^+ ions that are responsible for the characteristic reactions of acids.

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Bases

In simple terms, bases can be thought of as the opposite of acids.

KEY POINT

Bases are substances that react with acids in neutralisation reactions.

Bases you are likely to encounter are shown in Table 19.2.

Base	Example, formula
metal oxides	calcium oxide, CaO
metal hydroxides	sodium hydroxide, NaOH
metal carbonates	potassium carbonate, K_2CO_3
metal hydrogencarbonates	sodium hydrogencarbonate, $NaHCO_3$
ammonia	NH_3
amines	methylamine, CH_3NH_2

Table 19.2: Some bases.

Alkalis

Alkalis are solutions containing hydroxide ions that are formed when bases dissolve in water. Common alkalis are the Group 1 hydroxides (e.g. sodium hydroxide solution) and barium hydroxide solution. These are all formed when the base (the metal hydroxide) dissolves in water. Alkalis are also formed when certain bases react with water. For instance, the base sodium oxide (Na_2O) reacts with water:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

to produce the alkali sodium hydroxide, which is fully ionised in solution:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

Most metal hydroxides, however, are insoluble in water, and there are very few metal oxides that react with water, so there are a lot fewer alkalis than bases. Alkaline solutions are also formed when soluble metal carbonates or hydrogencarbonates dissolve in water. The carbonate or hydrogencarbonate ions react with water to form hydroxide ions, for example:

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

The only soluble carbonates you will encounter are the carbonates of the Group 1 metals and ammonium carbonate. Soluble hydrogencarbonates are sodium hydrogencarbonate, potassium hydrogencarbonate and ammonium hydrogencarbonate. The old name for the hydrogencarbonate ions is bicarbonate, so, bicarbonate of soda, which is used in baking is sodium hydrogencarbonate.

Ammonia solution and solutions of amines, such as ethylamine ($CH_3CH_2NH_2$), are also alkaline because hydroxide ions are produced when they react with water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons \underset{\text{ammonium ion}}{NH_4^+(aq)} + OH^-(aq)$$

$$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons \underset{\text{ethylammonium ion}}{CH_3CH_2NH_3^+(aq)} + OH^-(aq)$$

The terms 'alkali' and 'base' are often used interchangeably. 'Base' is the more general term and will be used in all of the discussions in subsequent sections.

SCIENCE IN CONTEXT

What do soap and pretzels (Figure 19.2) have in common?

Figure 19.2: Bars of soap and a pretzel. What do these have in common?

They are both made using sodium hydroxide. Sodium hydroxide, also known as caustic soda or lye, is probably one of the most familiar chemicals from the chemistry laboratory, but it is also one of the most important chemicals in the world. About 80 million tonnes of sodium hydroxide are produced annually by the electrolysis of sodium chloride solution (brine) in what is called the *chlor-alkali industry* because the process is also the major industrial source of chlorine.

If you have ever spilt sodium hydroxide on your hands, you may have noticed that it feels soapy.

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CONTINUED

This is because it reacts with the grease on your hands to make soap. This is also how soap is made industrially – a fat/oil is heated with sodium hydroxide (Figure 19.3) to produce the sodium salt of the fatty acids, soap.

Soap has a non-polar part (the hydrocarbon chain) that dissolves in fat/grease droplets and a polar part (COO^-) that allows the fat droplets to be held in suspension in water. The fat/oil that is used to make soap can be of plant or animal origin. Soap from animal fat will usually be shown as 'sodium tallowate' on the label. The fat for commercial soaps usually comes from cows or sheep, but it is possible to make soap from any fat, and there have been cases where soap has been made from human fat removed by liposuction!

Oh yes, and back to the pretzels… they are dipped in sodium hydroxide solution before baking.

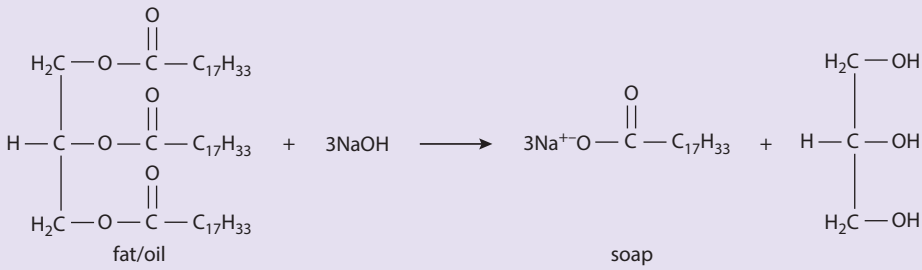

Figure 19.3: A representative reaction showing how soap is made.

Acid	Formula	Name of salt	Example of salt
hydrochloric	HCl	chloride	NaCl
sulfuric	H_2SO_4	sulfate	Na_2SO_4
nitric	HNO_3	nitrate	NH_4NO_3
carbonic	H_2CO_3	carbonate	K_2CO_3
ethanoic	CH_3COOH	ethanoate	$(CH_3COO)_2Ca$
propanoic	CH_3CH_2COOH	propanoate	CH_3CH_2COONa

Table 19.3: The formulas for some common acids and their salts – the hydrogen lost as H^+ is shown in red. The formulas for salts of carboxylic acids are usually written with the metal after the part derived from the acid.

Salts

In each of the reactions of acids we will look at in this section, a **salt** is formed.

KEY POINT

A **salt** is a compound formed when the hydrogen ion (H^+) in an acid is replaced by a metal ion (or ammonium ion).

For example, if the hydrogen ions in sulfuric acid are replaced by sodium ions, a salt called sodium sulfate (Na_2SO_4) is formed. The names of the salts formed by some acids are given in Table 19.3.

It is important to note that not every H in an acid is 'replaceable', and when we are looking at the reactions of carboxylic acids, such as ethanoic acid, it is only the H of the COOH (carboxyl) group that forms H^+ in solution and is therefore replaceable.

The salts formed by ammonia are called ammonium salts and contain the ammonium ion, NH_4^+ ion. The salts of amines are named according to the amine.

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Name of amine	Formula of amine	Name of ion in salt	Formula of ion
methylamine	CH_3NH_2	methylammonium	$CH_3NH_3^+$
ethylamine	$CH_3CH_2NH_2$	ethylammonium	$CH_3CH_2NH_3^+$
dimethylamine	$(CH_3)_2NH$	dimethylammonium	$(CH_3)_2NH_2^+$

Table 19.4: The names of some amines and the ions they form. Note: other ways of naming amines are also used.

The names of some amines and the ions present in their salts are shown in Table 19.4.

19.2 Reactions of acids

Neutralisation reactions

KEY POINT

The reactions between acids and bases or alkalis are called **neutralisation reactions**. Neutralisation reactions produce a salt and water only.

base + acid → salt + water

For example: $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

alkali + acid → salt + water

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

The reactions of acids with ammonia solution are usually written slightly differently:

$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

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

Why do these equations not include water? We saw previously that ammonia reacted with water to form ammonium ions and hydroxide ions, and so, ammonia solution is equivalent to ammonium hydroxide (NH_4OH) – in some laboratories, bottles are labelled 'ammonia solution' and in others they are labelled 'ammonium hydroxide'. The reaction with hydrochloric acid, therefore, could also have been written as:

$NH_4OH(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

which corresponds to the general equation of alkali + acid → salt + water. We, however, almost always, write it in the shorter form.

The ionic equation for a neutralisation reaction

If we look again at the reaction between sodium hydroxide and hydrochloric acid:

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

we can simplify the equation by just concentrating on the species that actually react.

In solution, HCl dissociates to form $H^+(aq)$ and $Cl^-(aq)$, and NaOH is present as separate $Na^+(aq)$ and $OH^-(aq)$ ions, so we can write the following:

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

We can see $Na^+(aq)$ and $Cl^-(aq)$ are present on both sides of the equation, so they do not change during this reaction (they are sometimes called *spectator ions*), and we can leave them out of the equation to produce the ionic equation:

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

All neutralisation reactions, therefore, have the same ionic equation – neutralisation reactions involve H^+ from the acid reacting with OH^- from the alkali to form water.

KEY POINT

Neutralisation reactions are exothermic.

When an acid is mixed with an alkali, the temperature goes up. We have seen this in Section 12.4, and typically the reaction gives out about 50–60 kJ per mole of water formed.

Link

We cannot, however, simply rationalise the fact that this reaction is exothermic in terms of bond enthalpies and a bond being formed between H^+ and OH^- because bond enthalpies only apply to reactions in the gas phase. The

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situation is more complex here because each of the ions is hydrated, so interactions of these ions, and the water that is formed , with solvent molecules (water) have to be taken into account. Also, as we will see in Section 19.4, $H^+(aq)$ is actually better represented by H_3O^+, so a bond will also be broken when it is reacts.

Making salts from acids and bases

In all the neutralisation reactions discussed so far, a salt is formed. Generally, the metal part of the salt comes from a metal oxide or hydroxide and the non-metal part from the acid. So, copper sulfate can be made from the reaction between the base copper oxide and sulfuric acid. Sodium nitrate can be made from the base sodium oxide (or the alkali sodium hydroxide) and nitric acid.

WORKED EXAMPLE 19.1

a State the names of an acid and a base that could be used to make the salt sodium ethanoate.

b Write an equation for the reaction.

Answer

a The name *ethanoate* tells us that this is a salt of ethanoic acid. The metal part comes from the base/alkali, so we could use sodium hydroxide to provide this. Therefore, sodium ethanoate can be made from the reaction between ethanoic acid and sodium hydroxide.

b The word equation for the reaction is

ethanoic acid + sodium hydroxide → sodium ethanoate + water

The symbol equation is

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

EXAM TIP

Unless specifically asked for a word equation, always assume that when asked to write an equation, you are required to write a balanced symbol equation.

WORKED EXAMPLE 19.2

a State the names of an acid and a base that could be used to make the salt ethylammonium chloride.

b Write an equation for the reaction.

Answer

a The chloride part tells us that this is a salt of hydrochloric acid. Ethylammonium comes from the amine ethylamine, so we could make this salt by reacting together hydrochloric acid and ethylamine.

b The equation for the reaction is

$HCl + CH_3CH_2NH_2 \rightarrow CH_3CH_2NH_3Cl$

Remember that we do not include water in the equations for the reactions of ammonia and amines – if you did include water, it would be wrong because the equation would not balance. You may sometimes see $CH_3CH_2NH_3Cl$ written as $CH_3CH_2NH_3^+Cl^-$; this is the same.

If state symbols were required for the reaction, we would have

$HCl(aq) + CH_3CH_2NH_2(aq) \rightarrow CH_3CH_2NH_3Cl(aq)$

Reactions of acids with carbonates and hydrogencarbonates

The reactions of acids with carbonates or hydrogencarbonates are slightly different in that carbon dioxide is formed as well as the salt and water:

$$\text{acid} + \begin{matrix}\text{carbonate/}\\\text{hydrogencarbonate}\end{matrix} \rightarrow \text{salt} + \begin{matrix}\text{carbon}\\\text{dioxide}\end{matrix} + \text{water}$$

For example:

$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$
sodium carbonate

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

$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$
sodium hydrogencarbonate

ionic equation: $HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$

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Reactions of acids with metals

KEY POINT

Unreactive metals, such as copper and silver, do not react with dilute acids.

The general equation for these reactions is as follows:

metal + acid → salt + hydrogen

Acids react with reactive metals, such as magnesium, to produce a salt and hydrogen gas. For example, hydrochloric acid forms magnesium chloride and hydrogen:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

ionic equation: $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

Sulfuric acid forms magnesium sulfate and hydrogen:

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

The ionic equation for this reaction is identical to the one above, so we can see that the reaction of acids with metals is also due to H^+ ions. This is, however, not a neutralisation reaction in the sense we met earlier because water is not formed, and it is better classified as a redox reaction – the metal is oxidised and H^+ is reduced. We will return to this reaction in Chapter 20.

TEST YOUR UNDERSTANDING

1 Complete and balance the following equations:

- **a** $Zn + H_2SO_4 \rightarrow$
- **b** $CuO + HNO_3 \rightarrow$
- **c** $NH_3 + H_2SO_4 \rightarrow$
- **d** $Ca(HCO_3)_2 + HCl \rightarrow$
- **e** $Mg(OH)_2 + H_2SO_4 \rightarrow$
- **f** $Cu + H_2SO_4 \rightarrow$
- **g** $CaO + HCl \rightarrow$
- **h** $K_2CO_3 + CH_3COOH \rightarrow$
- **i** $CH_3NH_2 + HCl \rightarrow$
- **j** $NH_3 + HCOOH \rightarrow$

CONTINUED

2 State the name of an acid and a base that would react together to form each of these salts:

- **a** calcium nitrate
- **b** cobalt(II) sulfate
- **c** copper(II) chloride
- **d** magnesium ethanoate
- **e** ethylammonium sulfate.

19.3 Brønsted–Lowry acids and bases

Hydrogen ions are protons

All the reactions of acids we saw in the previous section involved an H^+ ion, which can be called a *hydrogen ion*, but when we are talking about acids, it is more commonly referred to as a *proton*.

A hydrogen atom consists of one proton and one electron. If this electron is removed to form H^+, then we are left with just a proton, so a hydrogen ion is a proton (Figure 19.4).

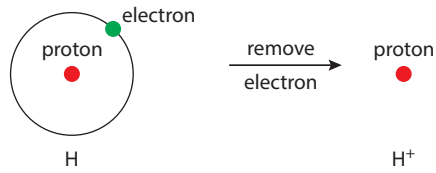

Figure 19.4: An H^+ ion is a proton.

The Brønsted-Lowry definition

So far, we have looked at a simple definition of acids as substances that produce H^+ ions in solution and bases as substances that produce OH^- ions in solutions – this is called the Arrhenius definition of acids and bases. However, it is possible for H^+ ions to be transferred to species other than just OH^-, and so, we now need to widen our definition.

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KEY POINT

The **Brønsted–Lowry** definition:

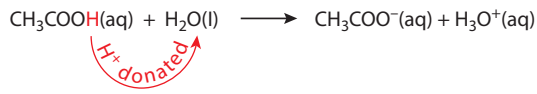
- an acid is a proton (H^+) donor
- a base/alkali is a proton (H^+) acceptor.

According to this definition, all reactions of acids involve the transfer of a proton (H^+) from the acid to the base.

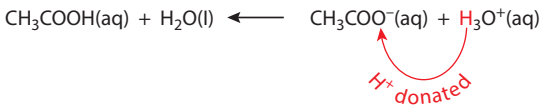
Consider the reaction of ethanoic acid with water:

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

In the forward direction, CH_3COOH donates a proton (H^+) to H_2O, so CH_3COOH is an acid, because it donates a proton. H_2O accepts a proton and, therefore, acts as a base.



In the reverse direction, H_3O^+ donates a proton to CH_3COO^-, so H_3O^+ is an acid and CH_3COO^- is a base:



H_3O^+ (the hydronium ion) has the structure shown in Figure 19.5.

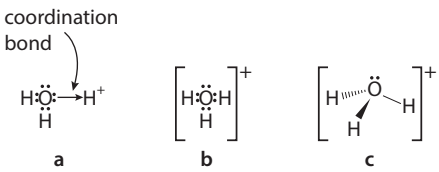


Figure 19.5: Three different representations of the structure of H_3O^+: **a** the formation of a coordination bond, **b** the Lewis formula, **c** the trigonal pyramidal shape.

H^+ does not exist in solution just by itself – it will always be bonded to a water molecule; however, it is often, for simplicity, written as $H^+(aq)$, even though we know that the actual species present in solution is better described as $H_3O^+(aq)$.

Conjugate acid–base pairs

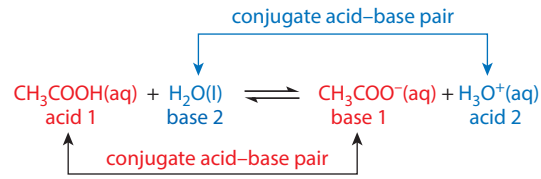
When CH_3COOH acts as an acid and donates a proton, it forms a base, CH_3COO^-. CH_3COO^- is called the conjugate base of CH_3COOH. CH_3COOH and CH_3COO^- are called a **conjugate acid–base pair**.

Similarly, when H_2O acts as a base and accepts a proton, it forms H_3O^+, which acts as an acid in the reverse direction. H_3O^+ is the conjugate acid of H_2O, and H_3O^+ and H_2O are also a conjugate acid–base pair.

KEY POINT

Conjugate acid–base pairs always differ by *one* proton (H^+).

We can label the conjugate acid–base pairs in the equation:



Species with the same number form a conjugate pair. It does not matter which pair you label 1 and which pair 2, as long as the numbers match up from one side to the other.

Other examples of acid–base reactions

Let us look at another example:

$$\underset{\text{base 1}}{NH_3(aq)} + \underset{\text{acid 2}}{H_2O(l)} \rightleftharpoons \underset{\text{acid 1}}{NH_4^+(aq)} + \underset{\text{base 2}}{OH^-(aq)}$$

In the forward direction, H_2O donates a proton to NH_3 (so that it forms NH_4^+). H_2O, therefore, is acting as an acid. And because NH_3 accepts the proton, it is acting as a base.

When H_2O donates the proton, it forms OH^-. OH^- is the conjugate base of H_2O, and H_2O and OH^- are a conjugate acid–base pair. We could also say that H_2O is the conjugate acid of OH^-. OH^- is a base because, in the reverse direction, it accepts H^+ from NH_4^+.

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When NH_3 accepts a proton, it forms NH_4^+. NH_4^+ is the conjugate acid of NH_3, and NH_3 and NH_4^+ are a conjugate acid–base pair. We could also say that NH_3 is the conjugate base of NH_4^+. NH_4^+ is an acid because, in the reverse direction, it donates a proton to OH^-.

General equations for an acid and a base

We can write general equations for the reactions that occur when an acid (HA) or a base (B) reacts with water.

General equation for an acid

$$\underset{\text{acid 1}}{HA(aq)} + \underset{\text{base 2}}{H_2O(l)} \rightleftharpoons \underset{\text{base 1}}{A^-(aq)} + \underset{\text{acid 2}}{H_3O^+(aq)}$$

KEY POINT

When an acid loses a proton (by donating it), it forms its conjugate base.

So, A^- is the conjugate base of HA.

KEY POINT

When a base gains a proton (by accepting it from an acid), it forms its conjugate acid.

HA is formed when A^- accepts a proton, so HA is the conjugate acid of A^-.

HA and A^- are a conjugate acid–base pair.

Similarly, we can say that H_2O and H_3O^+ are a conjugate acid–base pair – H_3O^+ is the conjugate acid of the base H_2O, and H_2O is the conjugate base of the acid H_3O^+.

General equation for a base

$$\underset{\text{base 1}}{B(aq)} + \underset{\text{acid 2}}{H_2O(l)} \rightleftharpoons \underset{\text{acid 1}}{BH^+(aq)} + \underset{\text{base 2}}{OH^-(aq)}$$

B and BH^+ are a conjugate acid–base pair – BH^+ is the conjugate acid of base B, or B is the conjugate base of the acid BH^+.

H_2O and OH^- are a conjugate acid–base pair – H_2O is the conjugate acid of base OH^-, or OH^- is the conjugate base of the acid H_2O.

Species that can act as both Brønsted-Lowry acids and bases

A species that can both donate a proton (acting as a Brønsted–Lowry acid) and accept a proton (acting as a Brønsted–Lowry base) is sometimes called **amphiprotic**. Water is a substance that is amphiprotic, and we have already seen that it acts as a proton donor (to form OH^-) in its reaction with NH_3 but as a proton acceptor (to form H_3O^+) in its reaction with CH_3COOH.

Other common examples of amphiprotic species include the hydrogencarbonate ion (HCO_3^-), the hydrogensulfate ion (HSO_4^-), the dihydrogenphosphate ion ($H_2PO_4^-$) and the monohydrogenphosphate ion (HPO_4^{2-}).

equation 1: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

In **equation 1**, HCO_3^- acts as a base by accepting a proton from H_3O^+.

In **equation 2**, HCO_3^- acts as an acid by donating a proton to H_2O:

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

In **equation 3**, $H_2PO_4^-$ acts as a base by accepting a proton from HCl and, in **equation 4**, $H_2PO_4^-$ acts as an acid donating a proton to OH^-:

equation 3: $H_2PO_4^-(aq) + HCl(aq) \rightleftharpoons H_3PO_4(aq) + Cl^-(aq)$

equation 4: $H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$

NATURE OF SCIENCE

Many common acids (HNO_3, H_2SO_4, etc.) contain oxygen, and in the late 18th and early 19th centuries, it was thought that acids were substances that contained oxygen. However, the discovery, by Humphry Davy, that muriatic acid (hydrochloric acid) did not contain oxygen paved the way for new theories, based on hydrogen, about the nature of acids. The name of oxygen in English (from the Greek: acid former), German (Sauerstoff) and many other languages reflects this mistaken assumption that all acids contain oxygen.

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TEST YOUR UNDERSTANDING

3 Define acids and bases according to the Brønsted–Lowry definition.

4 Classify each species as either an acid or base and indicate the conjugate acid–base pairs.

a $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

b $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

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

d $NH_3(aq) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$

5 Give the formula of the conjugate acid of each of the following:

a NH_3 **b** OH^-

c HSO_4^- **d** Br^-

e HPO_4^{2-}.

6 Give the formula of the conjugate base of each of the following:

a HCO_3^- **b** H_2O

c HCOOH **d** $CH_3NH_3^+$.

7 In each of the following reactions, state whether the species in red is acting as an acid or a base according to the Brønsted–Lowry definition:

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

b $HCO_3^-(aq) + H_2SO_4(aq) \rightleftharpoons H_2CO_3(aq) + HSO_4^-(aq)$

c $CH_3COOH(aq) + H_2SO_4(aq) \rightleftharpoons CH_3COOH_2^+(aq) + HSO_4^-(aq)$

8 Identify which of the following can act as ***both*** Brønsted-Lowry acids and bases (are amphiprotic).

HCO_3^-, NO_3^-, H_2O, $H_2PO_4^-$, NH_4^+, OCl^-

19.4 pH

Measuring pH

The **pH** scale can be used to indicate whether a solution is acidic, alkaline or neutral. At 25 °C, a solution with pH lower than 7 is acidic, a solution with pH 7 is neutral and a solution with pH greater than 7 is alkaline (Figure 19.6).

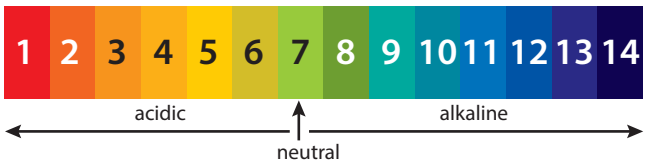

Figure 19.6: The pH scale showing the colours of universal indicator.

The pH of a solution can be determined by using a pH meter/pH probe, which will give a digital readout of the pH, or by using universal indicator solution or paper and comparing the colour to a colour chart. The pH meter/probe will give a more precise reading – for example, using full-range universal indicator, you might be able to say that the pH of a solution is around 3, but, with a pH meter, you could record the value as 2.88.

pH is a measure of the concentration of $H^+(aq)$ ions in a solution

The definition of pH is:

KEY POINT

pH is the negative logarithm to base 10 of the hydrogen ion concentration in an aqueous solution:

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

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When talking about a solution, we could quote the concentration of H^+ ions in mol dm^{-3}, but the use of the $\log_{10}$ function simplifies the numbers involved, so it is much simpler to say the pH of solution is 6, rather than the concentration of hydrogen ions in the solution is 1×10^{-6} mol dm^{-3}.

Note: '10' is often omitted from '$\log_{10}$', giving $pH = -\log[H^+(aq)]$.

Calculating pH from $[H^+(aq)]$

To work out pH, use the 'log' button on a calculator.

If the concentration of H^+ ions in a solution is 1.57×10^{-3} mol dm^{-3}, the pH is worked out as

$pH = -\log_{10}(1.57 \times 10^{-3}) = 2.80$

pH has no units.

Calculating $[H^+(aq)]$ from pH

To calculate $[H^+(aq)]$ from a pH, the inverse function of $\log_{10}$ must be used. So, 10 must be raised to the power of –pH.

KEY POINT

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

This is usually done using the '2nd' (or 'shift') and 'log' key combination on a calculator.

WORKED EXAMPLE 19.3

Calculate the concentration of hydrogen ions in a solution with pH = 3.65.

Answer

$[H^+(aq)] = 10^{-pH} = 10^{-3.65}$

$[H^+(aq)] = 2.24 \times 10^{-4}$ mol dm^{-3}

The relationship between $[H^+(aq)]$ and pH

KEY POINT

The higher the pH, the lower the $[H^+(aq)]$.

KEY POINT

pH is a log scale

pH is a log scale (to base ten), so a one unit change in pH indicates a tenfold change in the H^+ ion concentration. Table 19.5 and Figure 19.7 show how the hydrogen ion concentration relates to pH.

$[H^+(aq)]$ / mol dm^{-3}	pH
1	0
0.1	1
0.01	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8

Table 19.5: pH values and the corresponding concentration of H^+ ions.

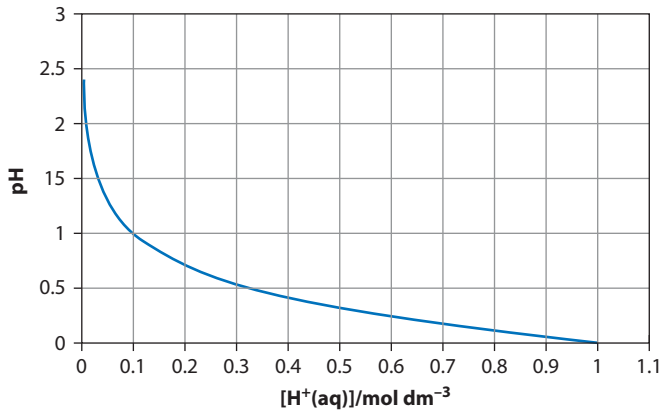

Figure 19.7: There is a logarithmic/exponential relationship between pH and $[H^+(aq)]$.

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KEY POINT

As a general rule, if a solution of a strong acid (see next section) is diluted by a factor of 10^n, the pH increases by n units up to a limit that approaches pH = 7.

WORKED EXAMPLE 19.4

$10.0\ cm^3$ of a solution of hydrochloric acid with pH 2.4 is transferred to a volumetric flask and made up to a total volume of $1.00\ dm^3$. Deduce the pH of the diluted solution.

Answer

$1.00\ dm^3$ is $1000\ cm^3$, so we can see that the solution has been diluted by a factor of $\frac{1000}{10.0}$ $1000/10.0 = 100$, that is 10^2. Because the power of 10 is 2 the pH increases by 2 units to 4.4.

It is not possible to dilute a solution of an acid so that the pH goes above 7, so diluting a solution with pH = 5 by a factor of 1000 (10^3) does not result in a pH of 8 but a pH of about 6.98. Further dilution would just bring the pH closer and closer to seven. If a solution of a strong base is diluted by a factor of 10^n, the pH decreases by n units down to a limit that approaches pH = 7. To understand why this is the case, you must look at the section on the dissociation of water (Section 19.6).

TEST YOUR UNDERSTANDING

9 Complete the table

pH	$[H^+(aq)]$ / mol dm^{-3}	Acidic / alkaline / neutral?
4		
	1.0×10^{-6}	
7		
	1.0×10^{-11}	
13		

CONTINUED

10 Calculate the pH of each solution:

a $[H^+(aq)] = 4.56 \times 10^{-3}$ mol dm^{-3}

b $[H^+(aq)] = 9.83 \times 10^{-13}$ mol dm^{-3}

c $[H^+(aq)] = 7.29 \times 10^{-6}$ mol dm^{-3}

d $[H^+(aq)] = 1.20$ mol dm^{-3}

11 Calculate the hydrogen ion concentration in each solution:

a pH = 11.32 **b** pH = 8.95

c pH = 2.17 **d** pH = –0.14

e pH = 0.00

12 What is the relationship between the $[H^+(aq)]$ of the following solutions? Deduce in each case by what factor the $[H^+(aq)]$ is higher or lower in solution Y compared to solution X.

a Solution X has pH = 2 and solution Y has pH = 3.

b Solution X has pH = 9 and solution Y has pH = 13.

c Solution X has pH = 1 and solution Y has pH = 10.

d Solution X has pH = 12 and solution Y has pH = 7.

13 In each case, deduce the pH of the diluted solution.

a A solution of a strong acid with pH = 2 is diluted by a factor of 1000.

b A solution of a strong acid with pH = 1.2 is diluted by a factor of 100.

c A solution of a strong acid with pH = 4 is diluted by a factor of 10^6.

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19.5 Strong and weak acids and bases

Acids

An acid (HA) in solution will react according to the equation:

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

This can be understood using the Brønsted–Lowry theory – the acid donates a proton to water. Essentially, though, what has happened is that the acid has dissociated or ionised to produce H^+ and A^- ions. This reaction is, therefore, often simplified to

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

KEY POINT

When an acid (HA) reacts with water, it dissociates/ionises to produce $H^+(aq)$ ions and its conjugate base, $A^-(aq)$.

This reaction is the same as the one above, and we still understand that H^+ from the acid has been donated to H_2O, but 'H_2O' has been omitted for simplicity [$H^+(aq)$ is equivalent to $H_3O^+(aq)$]. A^- is the conjugate base of the acid HA.

We can classify acids as strong or weak according to how much they dissociate in aqueous solution.

Strong acids

KEY POINT

Strong acids dissociate completely in aqueous solution. Examples of strong acids are hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), sulfuric acid (H_2SO_4) and nitric acid (HNO_3).

Figure 19.8 shows the complete dissociation of a **strong acid** such as HCl. A 0.1 mol dm^{-3} solution of HCl would contain 0.1 mol dm^{-3} of $H^+(aq)$ ions.

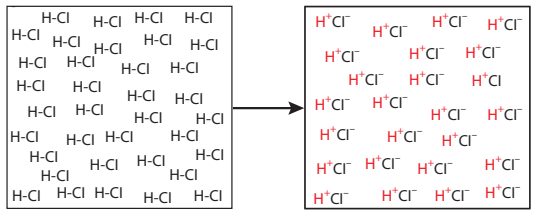

Figure 19.8: HCl dissociates completely in aqueous solution to H^+ and Cl^- ions.

This can be represented as: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

The non-reversible arrow ($\rightarrow$) is used to indicate that dissociation is essentially complete.

HCl is a ***monoprotic* acid** – it dissociates to form one proton per molecule. H_2SO_4 is a ***diprotic* acid** – it can dissociate to form two protons per molecule:

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

or $H_2SO_4(aq) \rightarrow HSO_4^-(aq) + H^+(aq)$

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

or $HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq)$

Sulfuric acid is a strong acid for the first dissociation only and that is why we show a reversible arrow for the second dissociation.

We always show two separate equations for the dissociation of a diprotic acid and would never show it as

$H_2SO_4(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$

This is because each proton has a different tendency to dissociate.

Note that nothing ever dissociates *completely* because all these reactions involve an equilibrium. However, for strong acids, this equilibrium lies a very long way to the right.

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Weak acids

KEY POINTS

Weak acids dissociate only partially in aqueous solution.

Examples of weak acids are carbonic acid (H_2CO_3) and carboxylic acids, such as ethanoic acid (CH_3COOH).

Figure 19.9 shows the dissociation of a **weak acid**, such as ethanoic acid. In a 0.1 mol dm^{-3} solution of ethanoic acid, only about 1% of the molecules are dissociated and the concentration of H^+ ions is about 0.001 mol dm^{-3}.

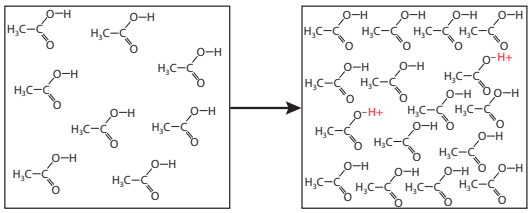

Figure 19.9: Weak acids such as ethanoic acid dissociate only partially in aqueous solution.

The dissociation of a weak acid is represented by

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ or

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

The two-way arrow $\rightleftharpoons$ is essential and indicates that the reaction is reversible and does not go to completion.

The dissociation of ethanoic acid is represented by

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

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

Carbonic acid is formed when carbon dioxide dissolves in water:

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

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

It is a diprotic acid, and its dissociation can be shown as

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

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

HCO_3^-, the hydrogencarbonate ion, is amphiprotic. It accepts a proton in the reverse reaction in the first equation (acts as a base) and donates a proton (acts as an acid) in the second.

Link

The order of acid strength of the hydrogen halides is HF < HCl < HBr < HI

HCl, HBr and HI are all classified as strong acids as they all dissociate essentially completely in aqueous solution, but HF is classified as a weak acid.

The increase in acid strength from HCl to HI can be explained in terms of the decreasing strength of the H–X bond as the halogen atom gets larger. As the H–X bond is weaker, it is more easily broken and so HI dissociates more than HCl.

The situation with HF is, however, much more complicated and HF behaving as a weak acid can be related to a very strong hydrogen bonding interaction between H_3O^+ and F^- and not to the strength of the H–F bond.

The strength of an acid depends on how much it dissociates

Ethanoic acid and methanoic acid are both weak acids, but methanoic acid is a stronger acid than ethanoic acid. In a 0.1 mol dm^{-3} solution of ethanoic acid at 25 °C, about 1% of the molecules are dissociated, but, in a 0.1 mol dm^{-3} solution of methanoic acid, the figure is about 4%. Methanoic acid is described as stronger than ethanoic acid because a larger proportion of the molecules dissociate – the position of the equilibrium:

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

lies more to the right for methanoic acid.

KEY POINT

The more an acid dissociates, the stronger it is.

We should, therefore, be able to distinguish between 0.1 mol dm^{-3} solutions of ethanoic acid and methanoic acid by measuring the pH. Methanoic acid dissociates more, and so, produces a higher concentration of $H^+(aq)$ ions, which means that its pH will be lower (2.38 as

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opposed to 2.88 for ethanoic acid). This measurement would only be possible using a pH meter/probe – universal indicator paper/solution would not give a precise enough value to distinguish between the acids.

KEY POINT

In general, strong acids have a lower pH than weak acids of the same concentration. Strong bases have a higher pH than weak bases of the same concentration.

Other ways of distinguishing between solutions of strong and weak acids of equal concentration include:

- strong acids react more violently with metals or carbonates
- solutions of strong acids conduct electricity better than solutions of weak acids.

These features both rely on the fact that strong acids dissociate more, and so, produce a higher concentration of H^+ ions (or ions in general for conductivity) in solution.

Strength versus concentration

The *concentration* of an acid refers to the amount (in mol) of acid in a certain volume – e.g., in a solution of ethanoic acid of concentration 0.100 mol dm^{-3}, the amount of ethanoic acid before dissociation is 0.100 mol in every cubic decimetre (litre). The *strength* of an acid refers to how much it dissociates in aqueous solution.

1.00 mol dm^{-3} ethanoic acid is a more concentrated solution than 0.100 mol dm^{-3} ethanoic acid, but it is not stronger. No matter how concentrated the solution of ethanoic acid is, it will never become a strong acid because it always dissociates only partially. Similarly, diluting a strong acid, such as hydrochloric acid, does not make it anything other than a strong acid because it always dissociates fully.

KEY POINT

pH is not a measure of acid or base strength.

pH is simply a measure of the concentration of $H^+(aq)$ ions. It is possible for a dilute solution of a strong acid to have a higher pH than a concentrated solution of a weak acid. For example, 0.100 mol dm^{-3} ethanoic acid has a pH of 2.88, but 0.00100 mol dm^{-3} hydrochloric acid has a pH of 3.00. Because the solution of ethanoic acid is much more concentrated, the partial dissociation (about 1.3%) of the weak acid produces a higher concentration of $H^+(aq)$ than the complete dissociation of the strong acid HCl.

KEY POINT

pH can be used to compare acid strength only if equal concentrations of acids are being compared.

Bases

When a base (B) reacts with water, it accepts a proton from water and ionises according to the equation:

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

Bases are classified as strong or weak depending on how much they ionise in aqueous solution.

EXAM TIP

Use the word ionise rather than dissociate when describing the behaviour of bases in solution – they do not dissociate.

Strong bases

Sodium hydroxide is a strong base and ionises completely to produce OH^- ions:

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

Strong bases include the Group 1 hydroxides (LiOH, NaOH, etc.) and $Ba(OH)_2$.

$Ba(OH)_2$ ionises in aqueous solution to give $2OH^-$:

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

So, 0.1 mol dm^{-3} $Ba(OH)_2(aq)$ contains 0.2 mol dm^{-3} OH^-.

KEY POINT

Strong bases ionise completely in aqueous solution.

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Weak bases

KEY POINT

Weak bases ionise only partially in aqueous solution.

Ammonia is a typical **weak base** and ionises according to the equation:

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

In a 0.10 mol dm^{-3} solution of ammonia (at 25 °C), about 1% of the molecules are ionised.

Other weak bases are amines, such as ethylamine ($CH_3CH_2NH_2$). Ethylamine ionises according to the equation:

$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

At 25 °C, a 0.10 mol dm^{-3} solution of ethylamine has about 7% of the molecules ionised – so ethylamine is a stronger base than ammonia – it ionises more.

The relationship between the strength of an acid and the strength of its conjugate base

A strong acid such as HCl dissociates completely in aqueous solution:

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

The conjugate base of HCl is Cl^- – this is a very weak base because it has virtually no tendency to pick up a proton from H_3O^+ to re-form HCl – the above reaction goes essentially to completion.

HCN, on the other hand, is a very weak acid and has very little tendency to dissociate:

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

The position of equilibrium lies a long way to the left – CN^- has a relatively strong tendency to pick up H^+ from H_3O^+, that is, to act as a base.

KEY POINT

The weaker the acid, the stronger its conjugate base.

CN^-, the conjugate base of HCN, is a much stronger base than Cl^- (the conjugate base of HCl), and when it is added to water, it reacts by accepting a proton from water to re-form the parent acid:

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

KEY POINT

The position of equilibrium in the ionisation of an acid or a base lies more towards the weaker conjugate.

Look again at the general acid equilibrium:

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

If HA and its conjugate base have equal strengths, the tendency for HA to donate a proton and A^- to accept a proton are equal, and the equilibrium will be evenly balanced with equal concentrations of HA and A^- present at equilibrium. But, if HA is a stronger acid than A^- is a base, HA will have a greater tendency to donate a proton than A^- has to accept one, and the position of equilibrium lies more towards the right (towards the weaker conjugate) – there will be more A^- than HA present at equilibrium.

KEY POINT

The stronger the base, the weaker its conjugate acid.

A weak base ionises only partially in aqueous solution:

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

The stronger the base, the further the position of this equilibrium lies to the right. The stronger the base, the weaker its conjugate acid (BH^+) and the less tendency it has to donate a proton to re-form B.

If we look again at the equilibria involving ammonia and ethylamine:

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

$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

Ethylamine is described as a stronger base than ammonia because it has a greater tendency to ionise, and the position of equilibrium lies more to the right. This also means that the ethylammonium ion ($CH_3CH_2NH_3^+$) is a weaker acid than the ammonium ion (NH_4^+) – it has a lower tendency to donate a proton to OH^- to re-form the base.

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TEST YOUR UNDERSTANDING

14 Classify the following as strong acid, weak acid, strong base, weak base or salt:

HCl, H_2SO_4, NH_4NO_3, $NaOH$, NH_3, HNO_3, Na_2SO_4, H_2CO_3, $Ba(OH)_2$, KNO_3, CH_3NH_2, $HCOOH$

15 Write equations for the dissociation of the following acids:

a ethanoic acid, $CH_3COOH(aq)$

b nitric acid, $HNO_3(aq)$

c carbonic acid, $H_2CO_3(aq)$.

16 Write equations for the ionisation of the following bases:

a potassium hydroxide, $KOH(aq)$

b ammonia, $NH_3(aq)$

c methylamine, $CH_3NH_2(aq)$

d sodium hydrogencarbonate, $NaHCO_3(aq)$.

17 Arrange the following in order of the pH (lowest first) of 0.100 mol dm^{-3} solutions:

$HCl(aq)$, $NaOH(aq)$, $NH_3(aq)$, $H_2SO_4(aq)$, $Ba(OH)_2(aq)$, $HCN(aq)$.

18 A solution of 0.000100 mol dm^{-3} hydrochloric acid has a pH of 4.00, whereas a solution of 0.100 mol dm^{-3} ethanoic acid has a pH of 2.88. Explain what these values tell you about the usefulness of pH as a measure of acid strength.

19 Explain which is the stronger base:

$NO_3^-(aq)$ or $CH_3COO^-(aq)$

20 Explain which is the stronger acid:

$NH_4^+(aq)$ or $HCl(aq)$

THEORY OF KNOWLEDGE

pH

pH is an artificial scale developed using a mathematical function that converts the concentration of H^+ ions into much simpler numbers. It is definitely easier to say 'the pH of the solution is 6', rather than 'the concentration of hydrogen ions in the solution is 1.0×10^{-6} mol dm^{-3}.

Students of chemistry are introduced to the pH scale at an early age and are usually content to compare 'the acidity of solutions' in terms of pH and work out whether these solutions are acidic, alkaline or neutral. Most students do this without ever really understanding anything about what pH means. The idea of concentration of H^+ ions could not be introduced at such an early age; if it were, far fewer students would be able to work out whether a solution were acidic, alkaline or neutral and would almost certainly not have such a clear picture in their minds about the relative acidities/alkalinities of substances.

So, is it better to have a scale that most people can use but do not understand, or to have a more accurate and in-depth description of the acidity of solutions that most people will not be able to understand? Do we lose or gain understanding by using the pH scale?

19.6 The dissociation of water

Pure water has a pH of 7 at 25 °C. We have already seen that pH is a measure of the concentration of $H^+(aq)$ ions, so this implies that water contains $H^+(aq)$ ions. These come from the ionisation/dissociation of water:

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

We can work out from the pH that the concentration of $H^+(aq)$ ions in pure water at 25 °C, must be 1.0×10^{-7} mol dm^{-3}.

Since, when one H_2O molecule ionises, one $H^+(aq)$ and one $OH^-(aq)$ are formed, the concentration of OH^- ions must also be 1.0×10^{-7} mol dm^{-3}.

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KEY POINT

In pure water, the concentration of $H^+(aq)$ and $OH^-(aq)$ are equal.

An equilibrium constant, K_w, can be written for the ionisation/dissociation of water:

KEY POINT

$K_w = [H^+(aq)][OH^-(aq)]$

K_w is given various names, but on the IB syllabus it is called the **ion product constant of water**. IUPAC calls this term the autoprotolysis constant for water, but it can also be called the ionic product, ionic product constant, the autoionisation constant, the self-ionisation constant, etc. for water.

KEY POINT

K_w has a value of 1.0×10^{-14} at 298.15 K.

The expression for K_w looks different from the equilibrium constants we saw in Chapter 18 because the concentration of water does not appear in the equilibrium constant expression. In general, for reactions occurring in solution, the concentration of water does not appear in the equilibrium constant expression – it is present in such excess that its concentration is essentially constant. Another way of saying this is that water remains essentially a pure liquid during the reaction and its effective concentration (activity) is taken as one.

Note that the ionisation of water could also have been written as

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

for which we write the expression for K_w as

$K_w = [H_3O^+(aq)][OH^-(aq)]$

This is entirely equivalent to the previous expression.

The equilibrium $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ exists in all aqueous solutions and not just in pure water.

KEY POINT

The product of the H^+ and OH^- concentrations in any aqueous solution at 298.15 K is 1.0×10^{-14}.

Consider a 0.10 mol dm^{-3} solution of hydrochloric acid. HCl is a strong acid and dissociates completely in solution, therefore, the concentration of H^+ ions in solution will be 0.10 mol dm^{-3}.

Now, $[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$

so, the concentration of OH^- ions in this solution must be 1.0×10^{-13} mol dm^{-3} because

$0.10 \times (1 \times 10^{-13}) = 1.0 \times 10^{-14}$

So, even a solution of an acid contains some OH^- ions because of the ionisation of water.

Similarly, the concentration of H^+ ions in a 1.0×10^{-3} mol dm^{-3} solution of sodium hydroxide (a strong base) is 1.0×10^{-11} mol dm^{-3}. The presence of H^+ ions from the ionisation of water in all aqueous solutions explains why we can always measure a pH.

KEY POINT

There is an inverse relationship between the concentration of H^+ and OH^- ions in solution (at constant temperature).

If $[H^+(aq)]$ increases, $[OH^-(aq)]$ must decrease and vice versa because they multiply together to give the same number.

In pure water, $[H^+(aq)] = 1.0 \times 10^{-7}$ mol dm^{-3} and $[OH^-(aq)] = 1.0 \times 10^{-7}$ mol dm^{-3} – if we add sodium hydroxide to water, so that the concentration of OH^- ions becomes 2.0×10^{-7} mol dm^{-3}, the concentration of H^+ ions must drop to 5.0×10^{-8} so that $[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$. Since the concentration of H^+ ions has dropped below 1.0×10^{-7} mol dm^{-3}, the pH has increased to above 7 (to 7.3).

Link

We are using Le Chatelier's principle here. If the concentration of one species in a system at equilibrium is increased, the position of equilibrium shifts in order to use up the species added.

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WORKED EXAMPLE 19.5

Calculate $[OH^-(aq)]$ of a solution with pH = 10.44 at 25 °C.

Answer

We know that $[H^+(aq)] = 10^{-pH}$

Therefore, $[H^+(aq)] = 10^{-10.44} = 3.63 \times 10^{-11}$ mol dm^{-3}

$K_w = [H^+(aq)][OH^-(aq)]$

$K_w = 1.00 \times 10^{-14}$ at 25 °C

$1.00 \times 10^{-14} = 3.63 \times 10^{-11} \times [OH^-(aq)]$

Therefore, $[OH^-(aq)] = 2.75 \times 10^{-4}$ mol dm^{-3}

WORKED EXAMPLE 19.6

$K_w = 2.92 \times 10^{-14}$ at 40 °C. Calculate the pH of water at 40 °C.

Answer

Water dissociates according to the equation:

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

$K_w = [H^+(aq)][OH^-(aq)]$

Because one H_2O molecule dissociates to form one H^+ ion and one OH^- ion, in pure water, the concentration of H^+ ions is equal to the concentration of OH^- ions and, therefore

$2.92 \times 10^{-14} = [H^+(aq)]^2$

which gives $[H^+(aq)] = 1.71 \times 10^{-7}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(1.71 \times 10^{-7}) = 6.77$

Therefore, the pH of pure water at 40 °C is 6.77.

The variation of K_w with temperature

Like all other equilibrium constants, the value of K_w varies with temperature. The dissociation of water is endothermic:

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\Delta H^\ominus = +56$ kJ mol^{-1}

Therefore, as the temperature increases, the position of equilibrium shifts in the endothermic direction, to the right, so that more water dissociates.

$K_w = [H^+(aq)][OH^-(aq)]$

Therefore, we can deduce that K_w increases with temperature.

Since water dissociates more as temperature increases, the pH of pure water must also vary with temperature and, for example, the pH of pure water at 40 °C is 6.77.

This does not, however, mean that water is acidic at 40 °C – it is still neutral because $[H^+(aq)] = [OH^-(aq)]$. K_w equals 1.0×10^{-14} only at 25 °C, therefore pH 7 is neutral only at 25 °C!

The idea that pH < 7 is acidic pH = 7 is neutral pH > 7 is alkaline is only true at 25 °C, so we must modify our definitions of acidic, basic and neutral. Instead of looking at what the pH is, we should look at the relative concentrations of H^+ and OH^-.

KEY POINT

A solution is

- neutral if $[H^+(aq)] = [OH^-(aq)]$
- acidic if $[H^+(aq)] > [OH^-(aq)]$
- alkaline if $[OH^-(aq)] > [H^+(aq)]$

TEST YOUR UNDERSTANDING

21 Write an expression for the equilibrium that exists in any aqueous solution and for the ion product constant of water.

22 State the value of K_w at 25 °C.

23 Copy and complete the table for aqueous solutions at 25 °C. The first row has been completed for you.

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CONTINUED

$[H^+(aq)]$ / mol dm^{-3}	$[OH^-(aq)]$ / mol dm^{-3}	pH	Acidic or alkaline?
1.0×10^{-3}	1.0×10^{-11}	3	acidic
1.0×10^{-5}			
	0.01		
		8	
	1.0×10^{-12}		

24 Calculate $[OH^-(aq)]$ in each of the following solutions:

a a solution with $[H^+(aq)] = 2.45 \times 10^{-5}$ mol dm^{-3}

b a solution with $[H^+(aq)] = 9.38 \times 10^{-10}$ mol dm^{-3}

c a solution with pH = 2.78

d a solution with pH = 12.66

e a solution with pH = 5.39.

25 The value of K_w at 80 °C is 2.52×10^{-13}.

Calculate the pH of pure water at 80 °C and deduce whether a solution with pH = 6.8 is acidic, alkaline or neutral at 80 °C.

26 **a** Calculate $[OH^-(aq)]$ in a solution with pH = 11.

b The solution is diluted by a factor of 100, what is the pH of the diluted solution?

19.7 Calculating pH values

For now, we will limit the calculation of pH to solutions of strong acids and bases – calculations involving weak acids and bases will be covered in the Higher Level section.

Calculating the pH of a solution of a strong acid

Because strong acids can be assumed to dissociate fully in aqueous solution, the concentration of H^+ ions is the same as the concentration of the acid (for a monoprotic acid).

WORKED EXAMPLE 19.7

Calculate the pH of a 0.00150 mol dm^{-3} solution of hydrochloric acid.

Answer

The acid is strong, so full dissociation produces an $H^+(aq)$ concentration of 0.00150 mol dm^{-3} (the same as that of the original acid):

$pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.00150] = 2.82$

Calculating the pH of a solution of a strong base

The pH of an alkaline solution can be worked out using the ion product constant, K_w, equal to 1.00×10^{-14} at 25 °C.

WORKED EXAMPLE 19.8

Calculate the pH of a 0.250 mol dm^{-3} solution of potassium hydroxide at 25 °C.

Answer

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

KOH is a strong base, so it is completely ionised in solution, and the OH^- concentration is the same as that of the original base, i.e., 0.250 mol dm^{-3}.

Now, $K_w = [H^+(aq)][OH^-(aq)]$ and, at 25 °C, $K_w = 1.00 \times 10^{-14}$.

Substituting the OH^- concentration and the value of K_w into this expression, we obtain

$1.00 \times 10^{-14} = [H^+(aq)] \times 0.250$

So, $[H^+(aq)] = 4.00 \times 10^{-14}$ mol dm^{-3}

and $pH = -\log_{10}[H^+(aq)] = -\log_{10}(4.00 \times 10^{-14}) = 13.4$

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WORKED EXAMPLE 19.9

Calculate the pH of a 0.0100 mol dm^{-3} solution of barium hydroxide at 25 °C.

Answer

The formula of barium hydroxide is $Ba(OH)_2$, and it is a strong base, so it ionises completely according to the equation:

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

We must be careful here because one $Ba(OH)_2$ unit produces two OH^-; therefore, the concentration of $OH^-(aq)$ is $2 \times 0.0100 = 0.0200$ mol dm^{-3}.

The rest of the question is the same as the previous one.

Substituting the OH^- concentration and the value of K_w into the K_w expression, we obtain

$1.00 \times 10^{-14} = [H^+(aq)] \times 0.0200$

So, $[H^+(aq)] = 5.00 \times 10^{-13}$ mol dm^{-3}

and $pH = -\log_{10}[H^+(aq)] = -\log_{10}(5.00 \times 10^{-13}) = 12.3$

TEST YOUR UNDERSTANDING

27 State whether each of the following statements is TRUE or FALSE:

a The pH of 0.10 mol dm^{-3} HCl is 2.

b The pH of 1.00×10^{-3} mol dm^{-3} NaOH(aq) is 3.00.

c The pH of 5.00×10^{-3} mol dm^{-3} $Ba(OH)_2(aq)$ is 12.0.

d The pH of 0.010 mol dm^{-3} H_2SO_4 is 2.

28 Copy and complete the following table by working out pH values. Solution.

	pH
a solution containing 0.00100 mol dm^{-3} $HNO_3(aq)$	
a solution of 1.00 mol dm^{-3} HCl(aq)	
a solution of 2.00×10^{-4} mol dm^{-3} $HNO_3(aq)$	
a solution of $CH_3COOH(aq)$ of concentration 0.100 mol dm^{-3}, assuming 1.32% dissociation of the acid	
a solution of HCN(aq) of concentration 0.100 mol dm^{-3}, assuming 0.00794% of the acid dissociates	

29 Calculate the pH of these aqueous solutions, assuming that both species ionise completely:

a 0.0150 mol dm^{-3} NaOH

b 0.0500 mol dm^{-3} $Ba(OH)_2$.

30 Calculate the concentration of OH^- ions in

a 0.020 mol dm^{-3} HCl(aq)

b 1.4×10^{-4} mol dm^{-3} $HNO_3(aq)$.

31 **a** Calculate the pH of 0.200 mol dm^{-3} HCl.

b 25.0 cm^3 of the solution from **a** is measured out and made up to a total volume of 250 cm^3 with distilled water in a volumetric flask to form solution X. 10.0 cm^3 of solution X is taken and made up to a total volume of 1.00 dm^3 with distilled water in a volumetric flask; this is solution Y.

Work out the pH value for each solution.

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19.8 Acid–base titrations

We met the use of acid–base titrations in Chapter 16 for determining the concentration of one solution by reacting it with another for which we know the concentration (a standard solution). Here, we will look at how the pH of the reaction mixture varies during the titration of a strong acid with a strong base. The pH can be monitored during a titration by using a pH meter or a pH probe attached to a data logger.

The initial pH is measured and then the pH is again measured after certain volumes of alkali are added. The graph we obtain is called a pH curve or titration curve. The pH curve (titration curve) for adding 0.100 mol dm^{-3} sodium hydroxide solution to 25.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid is shown in Figure 19.10.

The initial pH

The initial pH here is 1.00 because the initial solution is 0.100 mol dm^{-3} hydrochloric acid. Hydrochloric acid is a strong acid and dissociates completely:

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

The concentration of H^+ ions is 0.100 mol dm^{-3} and the $pH = -\log_{10} 0.100$, i.e., 1.00.

The shape of the pH curve

The reaction that occurs as sodium hydroxide is added is

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

The ionic equation for this reaction is

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

Because OH^- from NaOH reacts with H^+ from HCl, $[H^+(aq)]$ decreases and, therefore, the pH increases.

As NaOH is added, the pH initially changes very little. The pH after 20.0 cm^3 of NaOH has been added is 1.95, so adding 20.0 cm^3 of the sodium hydroxide has changed the pH of the solution by less than 1 unit. This is partly a consequence of the fact that the $H^+(aq)$ ion concentration is reasonably high in this region; therefore, the proportionate effect of adding a certain amount of NaOH is reasonably small. However, it also arises from the nature of the log scale for pH; $[H^+(aq)]$ in this region decreases by about 0.09 mol dm^{-3} from 0.100 mol dm^{-3} to 0.010 mol dm^{-3}, but a tenfold change in $[H^+(aq)]$ corresponds to a change in pH of only 1 unit.

The pH then increases much more rapidly, and between a pH of about 3.5 and 10.5 the curve is virtually vertical. In this region (shaded on the graph), the addition of about 0.3 cm^3 of NaOH causes the pH to change by 7 units. When the pH is 3.5, the $[H^+(aq)]$ is about $\frac{1}{300}$ of what it was initially, so adding a certain amount of NaOH has a proportionately larger effect on $[H^+(aq)]$, and hence pH. The fact that this is a log scale, however, magnifies the effect – in this region, $[H^+(aq)]$ actually decreases by only about 0.00031 mol dm^{-3}, but, because it decreases from 3.15×10^{-4} to 3.15×10^{-11} mol dm^{-3}, the pH changes by 7 units.

After this region, the pH changes very little again because $[OH^-(aq)]$ is fairly high, and the proportionate effect of adding more NaOH is relatively small.

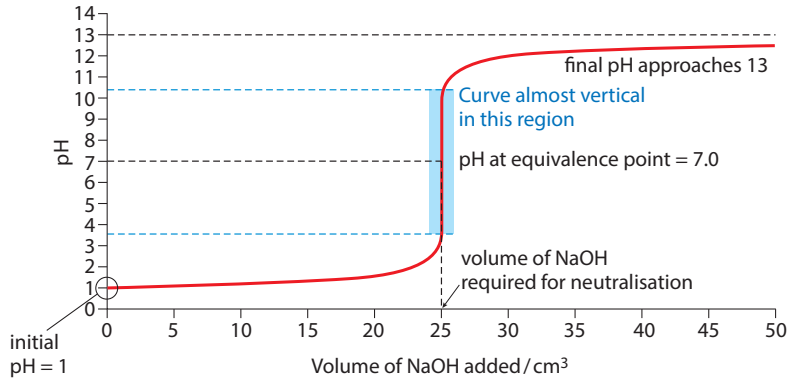

Figure 19.10: A strong acid–strong base pH curve. All pH curves have this general shape – fairly flat at the beginning, a steeper part and then fairly flat again.

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The equivalence point

KEY POINT

The equivalence point in an acid–base titration is the point at which equivalent amounts (in mol) of acid and base have been added.

In this case, because the concentrations of the acid and base are equal, the **equivalence point** occurs when equal volumes of the acid and base have been added. This will not always be the case, and the key point is that the number of moles of acid and alkali used are equivalent.

The word *equivalent* is used rather than *equal* because, if, for instance, 0.100 mol dm^{-3} barium hydroxide ($Ba(OH)_2$) were used instead of 0.100 mol dm^{-3} sodium hydroxide, only 12.5 cm^3 of alkali (half the number of moles) would be required to get to the equivalence point because barium hydroxide and hydrochloric acid react according to the equation:

$$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$$

The equivalence point is sometimes called the *stoichiometric point* – the amounts of acid and alkali are equivalent, according to the stoichiometry of the reaction (the ratio in which substances react).

The volume required to get to the equivalence point can be worked out from a moles calculation.

KEY POINT

The pH at the equivalence point for a strong acid–strong base titration is 7.0.

For the reaction

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

at the equivalence point, the reaction mixture is sodium chloride solution, which is a neutral solution.

The final pH

After the equivalence point, the pH changes only gradually again, and as more and more NaOH is added, the pH gets closer to 13, which is the pH of 0.100 mol dm^{-3} NaOH(aq). Once all the acid has been neutralised, as more NaOH is added, it does not react, and the solution resembles more and more closely the original NaOH solution – a small part has been neutralised, but the rest is just the NaOH solution – the amount that has been neutralised becomes proportionately less as more NaOH is added.

Variations on strong acid–strong base titrations

If, instead of adding 0.100 mol dm^{-3} NaOH to 25 cm^3 of 0.100 mol dm^{-3} HCl, we add 0.200 mol dm^{-3} NaOH, then we would get the pH curve shown in Figure 19.11.

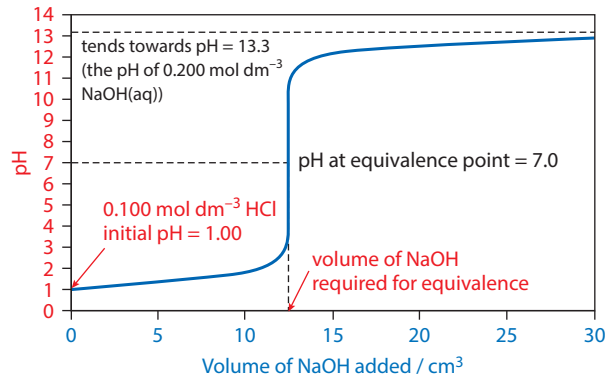

Figure 19.11: The pH curve for adding 0.200 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.100 mol dm^{-3} HCl(aq).

The equivalence point would now occur when 12.5 cm^3 of the alkali has been added. The initial pH would be the same and the pH at the equivalence point still 7.0, but the final pH will tend towards 13.3, the pH of 0.200 mol dm^{-3} NaOH(aq).

If we used 1.00 mol dm^{-3} HCl and 1.00 mol dm^{-3} NaOH for the titration (Figure 19.12):

- the initial pH would be lower (0.00)
- the steep part would be longer (there is more OH^- in one drop of solution)
- the final pH would tend towards 14.0 – the pH of 1.00 mol dm^{-3} NaOH(aq)
- the pH at the equivalence point would still be 7.0.

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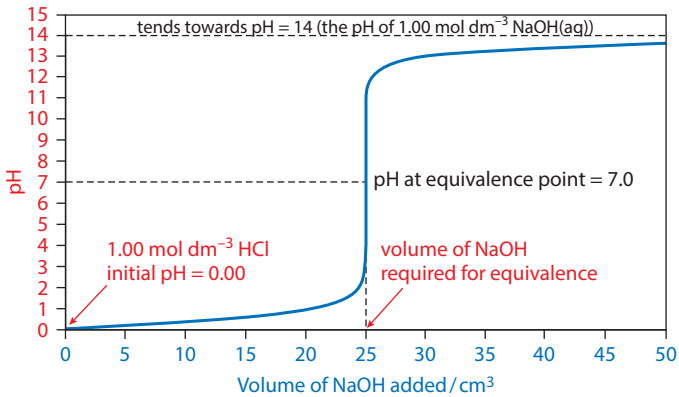

Figure 19.12: The pH curve for adding 1.00 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 1.00 mol dm^{-3} HCl(aq).

If we had performed the original titration the other way round, adding the acid to the alkali, the curve would have been reversed, as shown in Figure 19.13.

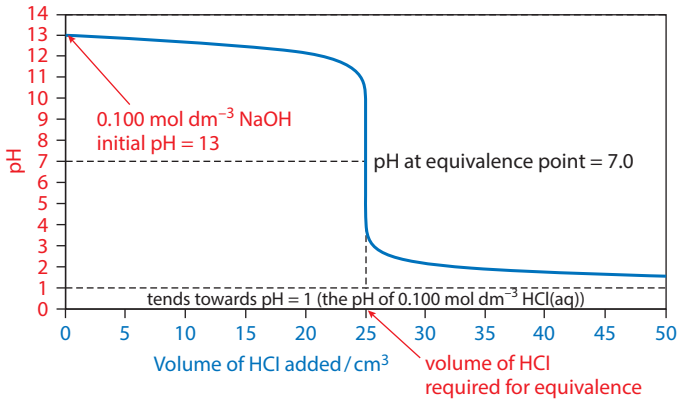

Figure 19.13: The pH curve for adding 0.100 mol dm^{-3} HCl(aq) to 25.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq). The initial pH is 13.0 [the pH of 0.100 mol dm^{-3} NaOH(aq)] and the curve would tend towards 1 [the pH of 0.100 mol dm^{-3} HCl(aq)].

Note: the equivalence point of a titration is not the same as the **end point** – the end point will be discussed in the section on **indicators** (Section 19.11).

Calculating the points on a strong acid–strong base titration curve

Consider again the original titration, i.e., the addition of 0.100 mol dm^{-3} sodium hydroxide solution to 25.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid (Figure 19.10). We will look at how the pH at various points on the pH curve can be calculated.

pH when 5.0 cm^3 of 0.100 mol dm^{-3} NaOH is added to 25.0 cm^3 of 0.100 mol dm^{-3} HCl

HCl is a strong acid, so it completely dissociates.

In 25.0 cm^3 of 0.100 mol dm^{-3} HCl, the amount in mol of H^+ ions is:

amount = concentration × volume in dm^3

$$\text{amount of } H^+(aq) = 0.100 \times \left(\frac{25.0}{1000}\right) = 2.50 \times 10^{-3} \text{ mol}$$

The amount of OH^- ions in 5.0 cm^3 of solution is:

$$\text{amount of } OH^-(aq) = 0.100 \times \left(\frac{5.0}{1000}\right) = 5.0 \times 10^{-4} \text{ mol}$$

These OH^- ions react with H^+ ions in the acid solution:

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

5.0×10^{-4} mol OH^- react with 5.0×10^{-4} mol H^+.
The original amount of H^+ ions was 2.50×10^{-3} mol; therefore, if 5.0×10^{-4} mol react, the amount of H^+ ions left over in the solution is $(2.50 \times 10^{-3}) - (5.0 \times 10^{-4})$ or 2.00×10^{-3} mol.

The total volume of the solution is now 25.0 + 5.0 = 30.0 cm^3 or 0.0300 dm^3.

Therefore, there are 2.00×10^{-3} mol $H^+(aq)$ present in 0.0300 dm^3 of solution.

The concentration of H^+ ions in the solution is given by:

$$[H^+(aq)] = \frac{\text{amount}}{\text{volume in dm}^3} = \frac{2.00 \times 10^{-3}}{0.0300}$$

$$= 6.67 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[H^+(aq)] = -\log_{10}(6.67 \times 10^{-2}) = 1.18$$

This technique can be used to work out the pH of all the solutions, up to the addition of just less than 25.0 cm^3 NaOH.

pH when 25.0 cm^3 of 0.100 mol dm^{-3} NaOH is added to 25.0 cm^3 of 0.100 mol dm^{-3} HCl

If the previous calculation is attempted for 25.0 cm^3 of NaOH added, there is a problem because the amount of H^+ ions in the original solution is 2.50×10^{-3} mol

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and the amount of OH^- that is added is 2.50×10^{-3} mol. These will react together completely so that the amount, and therefore concentration, of H^+ left will be 0, but $-\log_{10}0$ does not exist!

The problem has arisen because, in the previous calculation, we have ignored any H^+ in the solution from the dissociation of water. In most cases, we are totally justified in ignoring this. For instance, at 20.0 cm^3 of NaOH added, the concentration of H^+ ions in the solution from the hydrochloric acid is 0.0111 mol dm^{-3}, whereas that from the dissociation of water is 9.00×10^{-13} mol dm^{-3} – the dissociation of water accounts for only 8.1×10^{-9} % of the H^+ ion concentration of the solution. Even at 24.999 cm^3 of NaOH added, this percentage has only risen to about 0.25%.

However, at 25.0 cm^3 of NaOH added, the H^+ ion concentration of the solution is entirely due to the dissociation of water, and the H^+ ion concentration is 1.00×10^{-7} mol dm^{-3}. So, the pH of the solution is 7.0.

pH when 30.0 cm^3 of 0.100 mol dm^{-3} NaOH is added to 25.0 cm^3 of 0.100 mol dm^{-3} HCl

The original amount of H^+ ions was 2.50×10^{-3} mol. The amount of OH^- ions in 30.0 cm^3 of solution is

$$\text{amount of } OH^-(aq) = \left(\frac{30.0}{1000}\right) \times 0.100 = 3.00 \times 10^{-3} \text{ mol}$$

The amount of OH^- in excess is

$$(3.00 \times 10^{-3}) - (2.50 \times 10^{-3}) = 5.0 \times 10^{-4} \text{ mol}$$

The total volume of the solution is
25.0 + 30.0 = 55.0 cm^3 or 0.0550 dm^3

$$\text{concentration} = \frac{\text{amount}}{\text{volume in dm}^3}$$

$$[OH^-(aq)] = \frac{5.0 \times 10^{-4}}{0.0550} = 9.09 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_w = [H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$$

$$[H^+(aq)] = \frac{(1.0 \times 10^{-14})}{(9.09 \times 10^{-3})} = 1.10 \times 10^{-12} \text{ mol dm}^{-3}$$

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

$$pH = -\log_{10}(1.10 \times 10^{-12}) = 12.0$$

TEST YOUR UNDERSTANDING

32 Sketch a pH curve for adding 0.100 mol dm^{-3} NaOH(aq) to 20.0 cm^3 of 0.200 mol dm^{-3} HCl(aq). On your curve mark the following:

- **a** the initial pH
- **b** the volume required to reach the equivalence point
- **c** the pH at the equivalence point
- **d** the final pH that the curve tends to.

33 For each of these titrations, deduce the following:

- **i** the initial pH
- **ii** the volume required to reach the equivalence point
- **iii** the pH at the equivalence point
- **iv** the final pH that the curve tends to.

a adding 0.200 mol dm^{-3} NaOH(aq) to 30.0 cm^3 of 0.400 mol dm^{-3} HCl(aq)

b adding 0.100 mol dm^{-3} NaOH(aq) to 40.0 cm^3 of 0.0500 mol dm^{-3} HCl(aq)

c adding 0.200 mol dm^{-3} HCl(aq) to 20.0 cm^3 of 0.400 mol dm^{-3} NaOH(aq)

d adding 0.100 mol dm^{-3} HCl(aq) to 25.0 cm^3 of 0.125 mol dm^{-3} NaOH(aq).

34 In each case, calculate the pH of the solution formed:

a 20.0 cm^3 of 0.200 mol dm^{-3} NaOH(aq) is added to 30.0 cm^3 of 0.200 mol dm^{-3} HCl(aq)

b 10.0 cm^3 of 0.150 mol dm^{-3} NaOH(aq) is added to 45.0 cm^3 of 0.100 mol dm^{-3} HCl(aq)

c 50.0 cm^3 of 0.120 mol dm^{-3} NaOH(aq) is added to 25.0 cm^3 of 0.200 mol dm^{-3} HCl(aq)

d 15.0 cm^3 of 0.250 mol dm^{-3} HCl(aq) is added to 40.0 cm^3 of 0.150 mol dm^{-3} NaOH(aq).

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19.9 pOH

We met pH in the previous sections:

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

However, every aqueous solution also contains $OH^-(aq)$ ions, so we can also discuss the acidity/alkalinity of a solution in terms of the concentration of $OH^-(aq)$ ions.

KEY POINT

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

$[OH^-(aq)] = 10^{-pOH}$

These are exactly equivalent expressions to those used when we were introduced to pH, and the equations can be used in the same way.

WORKED EXAMPLE 19.10

Calculate pOH for a 0.100 mol dm^{-3} solution of sodium hydroxide.

Answer

NaOH is a strong base, so it ionises completely in solution, and the concentration of $OH^-(aq)$ ions will be 0.100 mol dm^{-3}.

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}0.100 = 1.00$

Therefore, the pOH of a 0.100 mol dm^{-3} solution of sodium hydroxide is 1.00.

WORKED EXAMPLE 19.11

A solution has a pOH of 9.60. Calculate the hydroxide ion concentration in this solution.

Answer

$[OH^-(aq)] = 10^{-pOH} = 10^{-9.60} = 2.51 \times 10^{-10}$ mol dm^{-3}

Therefore, the concentration of hydroxide ions in a solution with pOH 9.60 is 2.51×10^{-10} mol dm^{-3}.

You will have probably worked out that 'p' means '$-\log_{10}$'. We have already met pH and pOH, and it is convenient to take $-\log_{10}$ of many quantities that we use in calculations involving acids and bases such as, for example, K_w.

KEY POINT

$pK_w = -\log_{10}K_w$

The value of K_w at 25 °C is 1.0×10^{-14}; therefore, the value of pK_w at the same temperature is 14.

The connection between pH and pOH

Consider the expression for the ion product constant for water:

$K_w = [H^+(aq)][OH^-(aq)]$

Working out $-\log_{10}$ for both sides gives

$-\log_{10}K_w = -\log_{10}([H^+(aq)][OH^-(aq)])$

$-\log_{10}K_w = (-\log_{10}[H^+(aq)]) + (-\log_{10}[OH^-(aq)])$

We can rewrite this as

$pK_w = pH + pOH$

$pK_w = 14$ at 25 °C, so we can rewrite this equation as

$pH + pOH = 14$ at 25 °C

This equation gives us a shortcut to working out the pH of a basic solution.

WORKED EXAMPLE 19.12

Calculate the pH of 0.0500 mol dm^{-3} sodium hydroxide solution at 25 °C.

Answer

NaOH is a strong base and ionises completely to form 0.0500 mol dm^{-3} $OH^-(aq)$.

$pOH = -\log_{10}0.0500 = 1.30$

At 25 °C,

$pH + pOH = 14$

$pH + 1.30 = 14$

Therefore, pH = 12.7

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WORKED EXAMPLE 19.13

A solution has pOH = 8.2 at 25 °C. Determine the concentration of H^+ and OH^- ions in the solution and deduce whether the solution is acidic, alkaline or neutral.

Answer

$[OH^-(aq)] = 10^{-pOH}$

$[OH^-(aq)] = 10^{-8.2} = 6.3 \times 10^{-9}$ mol dm^{-3}

At 25 °C, pH + pOH = 14

therefore, pH = 14 – 8.2 = 5.8

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

$[H^+(aq)] = 10^{-5.8} = 1.6 \times 10^{-6}$ mol dm^{-3}

$[H^+(aq)] > [OH^-(aq)]$; therefore, the solution is acidic.

pH, pOH and neutrality

At 25 °C, neutral pH is 7. At that temperature, solutions that have a pH lower than 7 are acidic, and those that have a pH higher than 7 are alkaline.

Using pOH, the situation is reversed – solutions with a pOH lower than 7 are alkaline, and those with a pOH higher than 7 are acidic.

KEY POINT

In general:

- if $[H^+(aq)] = [OH^-(aq)]$, pH = pOH and the solution is neutral (or pure water)
- if $[H^+(aq)] > [OH^-(aq)]$, pH < pOH and the solution is acidic
- if $[OH^-(aq)] > [H^+(aq)]$, pOH < pH and the solution is alkaline.

TEST YOUR UNDERSTANDING

35 Complete the table:

pOH	$[OH^-(aq)]$ / mol dm^{-3}	Acidic/alkaline/neutral?
3		
	1.0×10^{-5}	
7		
	1.0×10^{-9}	
12		

36 Calculate the pOH and pH of each solution:

a $[OH^-(aq)] = 1.27 \times 10^{-9}$ mol dm^{-3} **b** $[OH^-(aq)] = 4.91 \times 10^{-1}$ mol dm^{-3}

c $[OH^-(aq)] = 3.18 \times 10^{-5}$ mol dm^{-3} **d** $[OH^-(aq)] = 2.00$ mol dm^{-3}.

37 Calculate the $OH^-(aq)$ and $H^+(aq)$ concentrations in each solution:

a pOH = 9.60 **b** pOH = 3.78

c pOH = 6.23 **d** pOH = –0.080.

38 Calculate pOH and pH of these aqueous solutions:

a 0.0760 mol dm^{-3} NaOH **b** 0.0250 mol dm^{-3} $Ba(OH)_2$.

39 Calculate the pOH of

a 0.200 mol dm^{-3} HCl(aq) **b** 6.00×10^{-2} mol dm^{-3} HNO_3(aq).

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19.10 Ionisation constants for acids and bases

The acid dissociation constant, K_a

Consider the dissociation of ethanoic acid:

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

We can write an equilibrium constant expression for the dissociation of the acid as:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

The equilibrium constant here is called the **acid dissociation constant** or acid ionisation constant and is given the symbol K_a.

If we write the dissociation of ethanoic acid as

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

we obtain the expression for K_a as

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

This is entirely equivalent to the previous expression. Remember that the concentration of water does not appear in the equilibrium constant expression for reactions in solution because its concentration is essentially constant.

The value of K_a for ethanoic acid at 25 °C is 1.74×10^{-5}.

As with other equilibrium constants, the value of K_a depends on the temperature.

KEY POINT

In general, for the dissociation of an acid, HA:

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

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

The expression for the acid dissociation constant is

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

or $$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Weak acids dissociate only partially, and different weak acids dissociate to different extents. The acid dissociation constant is a measure of the extent to which an acid dissociates.

KEY POINT

The stronger the acid, the more it dissociates and the higher the value of K_a.

If the acid dissociates to a larger extent, the concentrations on the top of the expression are larger and that on the bottom is smaller; therefore, the value of K_a is larger.

pK_a

Acid dissociation constants can be expressed in a more convenient form by taking the negative logarithm to base 10 of K_a.

KEY POINTS

$pK_a = -\log_{10} K_a$

$K_a = 10^{-pK_a}$

The higher the value of K_a, the stronger the acid.

The lower the value of pK_a, the stronger the acid.

You can think about the connection between pK_a and acid strength in the same way as for pH – the lower the pH value, the higher the $[H^+(aq)]$.

Table 19.6 compares the K_a and pK_a values of some acids.

Acid	Formula	K_a	pK_a
hydrofluoric acid	HF	6.31×10^{-4}	3.20
benzoic acid	C_6H_5COOH	6.31×10^{-5}	4.20
propanoic acid	CH_3CH_2COOH	1.35×10^{-5}	4.87
chloric(I) acid	HOCl	3.98×10^{-8}	7.40
hydrocyanic acid	HCN	6.17×10^{-10}	9.21

decreasing strength

Table 19.6: K_a and pK_a values of some acids.

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The acids in Table 19.6 are arranged in order of strength – HF is the strongest acid and dissociates to the greatest extent; HCN is the weakest acid and dissociates to the smallest extent in aqueous solution. These are all, however, weak acids because they all dissociate only partially.

KEY POINT

K_a and pK_a are better measures of acid strength than pH because their values do not depend on the concentration of the acid – K_a and pK_a depend only on temperature.

Calculating K_a and pK_a values

WORKED EXAMPLE 19.14

Calculate the K_a and pK_a values for propanoic acid at 25 °C if a 0.100 mol dm^{-3} solution has a pH of 2.94.

Answer

Propanoic acid dissociates according to the equation:

$CH_3CH_2COOH(aq) \rightleftharpoons CH_3CH_2COO^-(aq) + H^+(aq)$

The pH of the solution is 2.94, so we can work out the concentration of $H^+(aq)$:

$[H^+(aq)] = 10^{-pH} = 10^{-2.94} = 1.15 \times 10^{-3}$ mol dm^{-3}

If we consider the situation before dissociation occurs, we have

	$CH_3CH_2COOH(aq)$	$\rightleftharpoons$	$CH_3CH_2COO^-(aq)$	+	$H^+(aq)$
initial concentration / mol dm^{-3}	0.100		0		0

At equilibrium the concentration of H^+ ions is 1.15×10^{-3} mol dm^{-3}. To produce 1.15×10^{-3} mol dm^{-3} H^+, 1.15×10^{-3} mol dm^{-3} CH_3CH_2COOH must dissociate. The concentration of CH_3CH_2COOH at equilibrium is thus

$0.100 - (1.15 \times 10^{-3}) = 9.89 \times 10^{-2}$ mol dm^{-3}

Because one molecule of CH_3CH_2COOH dissociates to produce one H^+ ion and one $CH_3CH_2COO^-$ ion, the concentration of $CH_3CH_2COO^-$ at equilibrium is the same as that of H^+.

So, the equilibrium concentrations are

	$CH_3CH_2COOH(aq)$	$\rightleftharpoons$	$CH_3CH_2COO^-(aq)$	+	$H^+(aq)$
equilibrium concentration / mol dm^{-3}	9.89×10^{-2}		1.15×10^{-3}		1.15×10^{-3}

These values can be put into the expression for K_a:

$$K_a = \frac{[CH_3CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2COOH(aq)]} = \frac{(1.15 \times 10^{-3}) \times (1.15 \times 10^{-3})}{9.89 \times 10^{-2}} = 1.33 \times 10^{-5}$$

$pK_a = -\log_{10} K_a = -\log_{10}(1.34 \times 10^{-5}) = 4.87$

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The degree of dissociation is very small compared with the concentration of the acid, so the previous calculation may be simplified by assuming that the concentration of CH_3CH_2COOH at equilibrium is the same as the initial concentration (see Chapter 18, section 18.4), that is, 0.100 mol dm^{-3}. This makes the last stage of the calculation:

$$K_a = \frac{[CH_3CH_2COO^-(aq)][H^+(aq)]}{[CH_3CH_2COOH(aq)]}$$

$$= \frac{1.15\times10^{-3}\times1.15\times10^{-3}}{0.100} = 1.32\times10^{-5}$$

$$pK_a = -\log_{10}K_a = -\log_{10}(1.32\times10^{-5}) = 4.88$$

Making the assumption has hardly changed the final answer, and this will generally be true for the calculations you will encounter involving weak acids. This approximation makes very little difference to how difficult the calculation is here but will be much more important in the next section when we have to find pH given a pK_a value, as it will mean that the calculation can be done without solving a quadratic equation.

Calculating the pH of a solution of a weak acid

A weak acid dissociates only partially and, therefore, to calculate the pH, we need to know how much the acid dissociates. This can be worked out using the K_a or pK_a value of the acid.

WORKED EXAMPLE 19.15

Calculate the pH of a 0.100 mol dm^{-3} solution of ethanoic acid at 25 °C. The pK_a of ethanoic acid at 25 °C is 4.76.

Answer

$K_a = 10^{-pK_a} = 10^{-4.76} = 1.74\times10^{-5}$

The equation for the dissociation of ethanoic acid is:

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

and its dissociation constant expression is:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

CONTINUED

Because one molecule of CH_3COOH dissociates to form one CH_3COO^- ion and one H^+ ion, the concentration of CH_3COO^- and H^+ ions in the solution will be equal and we can write

$[H^+(aq)]^2$ instead of $[CH_3COO^-(aq)][H^+(aq)]$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid – so the concentration of the acid at equilibrium is the same as its initial concentration, 0.100 mol dm^{-3} in this case.

These terms, together with the K_a value, are substituted into the K_a expression:

$1.74\times10^{-5} = [H^+(aq)]^2 / 0.100$

$[H^+(aq)]^2 = 1.74\times10^{-5}\times0.100 = 1.74\times10^{-6}$

$[H^+(aq)] = \sqrt{(1.74\times10^{-6})} = 1.32\times10^{-3}$ mol dm^{-3}

Now, $pH = -\log_{10}[H^+(aq)]$

So, $pH = -\log_{10}(1.32\times10^{-3}) = 2.88$

Making the approximation that $[CH_3COOH(aq)]_{equilibrium} \approx [CH_3COOH(aq)]_{initial}$ makes no difference to the value of pH to three significant figures.

EXAM TIP

It is important to remember the assumption we made: the dissociation of the acid is negligible compared with the concentration of the acid.

If c is the concentration of the acid, the hydrogen ion concentration can also be worked out using

$[H^+(aq)] = \sqrt{(c\times K_a)}$

or the pH could be worked out using

$$\text{or } pH = -\tfrac{1}{2}\log_{10}(c\times K_a) = -\tfrac{1}{2}(pK_a - \log_{10}c)$$

If you are given the concentration of the acid as a power of 10, it is possible to work out the pH of the solution without using a calculator.

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WORKED EXAMPLE 19.16

The pK_a of a 0.1 mol dm^{-3} solution of a weak acid, HA, is 5. Calculate the pH of the solution.

Answer

$$pH = \frac{1}{2}(pK_a - \log_{10} c)$$

$c = 0.1$ mol dm^{-3}

$\log_{10} c = -1$

therefore, $pH = \frac{1}{2}[5 - (-1)] = 3$

EXAM TIP

The equation here just summarises the procedure discussed previously, and it is generally better to understand a procedure rather than learning an equation. If you forget the equation in the exam, can you still do the question?

TEST YOUR UNDERSTANDING

40 Write expressions for K_a for each of the acids:

a methanoic acid, HCOOH(aq)

b bromic(I) acid, HOBr(aq)

c nitric(III) acid, HNO_2(aq)

d benzoic acid, C_6H_5COOH(aq).

41 HA to HF are all weak acids.

a Copy and complete the following table:

Acid	Concentration / mol dm^{-3}	[H$^+$] / mol dm^{-3}	pH	K_a	pK_a
HA	0.0100	2.00×10^{-6}			
HB	0.200		4.70		
HC	0.500	2.50×10^{-4}			
HD	2.20×10^{-2}		5.20		
HE	0.250			3.72×10^{-8}	
HF	0.0300			6.31×10^{-6}	

b Use the values in part **a** to arrange the acids in order of acid strength (strongest first).

42 Arrange the following acids in order of decreasing acid strength (strongest first)

Acid	pK_a
ethanoic (CH_3COOH)	4.8
benzoic (C_6H_5COOH)	4.2
ammonium ion (NH_4^+)	9.3

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CONTINUED

43 Calculate the pH for each of the following weak acids. State any assumptions you make.

Acid	pK_a	Concentration / mol dm^{-3}
HA_1	4.60	0.100
HA_2	5.24	0.0250
HA_3	7.40	0.0640

44 Calculate pH values for the following solutions:

a a 0.0200 mol dm^{-3} solution of propanoic acid, given that the pK_a value at 25 °C is 4.87.

b a 0.500 mol dm^{-3} solution of HCN, given that the pK_a value at 25 °C is 9.21.

c a 0.00250 mol dm^{-3} solution of phenol (C_6H_5OH), given that the pK_a value at 25 °C is 9.99.

45 Calculate pH values for each of the following weak acids:

Acid	pK_a	Concentration / mol dm^{-3}
HA_4	5.00	0.100
HA_5	7.42	0.0100
HA_3	4.80	1.00×10^{-3}

46 Arrange the following acids in order of increasing strength (weakest first):

Acid	K_a
HOI	3.0×10^{-11}
HNO_2	4.6×10^{-4}

Acid	pK_a
HOCl	7.4
$HClO_2$	2.0

19.11 The base ionisation constant, K_b

Consider the ionisation of a weak base:

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

We can write an expression for the **base ionisation constant, K_b**:

KEY POINT

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

As discussed in Sections 19.6 and 19.10, the reaction occurs in aqueous solution, so the concentration of water is very much higher than the other concentrations and is essentially constant, so it does not appear in the expression for K_b.

The value of K_b for ammonia is 1.78×10^{-5}. Similar to K_a for acids, K_b for bases provides a measure of the extent to which a base ionises, and hence, the strength of the base.

As for acids, the negative logarithm to base ten of the base ionisation constant can be taken for a more convenient measure.

KEY POINT

$pK_b = -\log_{10} K_b$ $\qquad$ $K_b = 10^{-pK_b}$

The higher the value of K_b, the more the base ionises and the stronger it is.

The lower the value of pK_b, the stronger the base.

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The K_b and pK_b values for some bases are shown in Table 19.7.

Base	Formula	K_b	pK_b
dimethylamine	$(CH_3)_2NH$	5.37×10^{-4}	3.27
methylamine	CH_3NH_2	4.57×10^{-4}	3.34
ammonia	NH_3	1.78×10^{-5}	4.75
phenylamine	$C_6H_5NH_2$	7.41×10^{-10}	9.13

decreasing strength

Table 19.7: K_b and pK_b values for some bases.

They are arranged in order of strength – dimethylamine is the strongest base and ionises to the greatest extent; phenylamine is the weakest base and ionises to the smallest extent in aqueous solution.

The procedure for calculating a value of K_b or pK_b is essentially the same as that discussed previously for calculating K_a and pK_a values.

WORKED EXAMPLE 19.17

The pH of a 0.100 mol dm^{-3} solution of ethylamine at 25 °C is 11.8. Calculate K_b and pK_b values for ethylamine.

Answer

The equation for the ionisation of ethylamine is

$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

At 25 °C, pH + pOH = 14 pOH = 14 – 11.8 = 2.2

$[OH^-(aq)] = 10^{-pOH} = 10^{-2.2} = 6.31 \times 10^{-3}$ mol dm^{-3}

When one molecule of $CH_3CH_2NH_2$ reacts with water, it ionises to form one $CH_3CH_2NH_3^+$ ion and one OH^- ion. This means that, if 6.31×10^{-3} mol dm^{-3} of OH^- are present at equilibrium, they must have come from the ionisation of 6.31×10^{-3} mol dm^{-3} $CH_3CH_2NH_2$. The concentration of $CH_3CH_2NH_2$ at equilibrium is therefore

$0.100 - (6.31 \times 10^{-3}) = 9.37 \times 10^{-2}$ mol dm^{-3}

The concentration of OH^- formed is the same as that of $CH_3CH_2NH_3^+$.

So, at equilibrium, the concentrations are

	$CH_3CH_2NH_2(aq)$	+ $H_2O(l)$	$\rightleftharpoons$	$CH_3CH_2NH_3^+(aq)$	+ $OH^-(aq)$
equilibrium concentration / mol dm^{-3}	9.37×10^{-2}			6.31×10^{-3}	6.31×10^{-3}

The expression for K_b is: $K_b = \dfrac{[CH_3CH_2NH_3^+(aq)][OH^-(aq)]}{[CH_3CH_2NH_2(aq)]}$

The equilibrium concentrations can be substituted into this:

$$K_b = \frac{6.31\times10^{-3} \times 6.31\times10^{-3}}{9.37\times10^{-2}} = 4.25\times10^{-4}$$

$pK_b = -\log_{10}K_b = -\log_{10}(4.25 \times 10^{-4}) = 3.37$

As for the K_a calculation previously, this can be simplified by making the approximation that the amount of ionisation of the base is small compared with its concentration, so the original concentration of the base could be used in the K_b expression. If we do that in this case, the answer for pK_b comes out as 3.40, which is about a 1% difference.

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WORKED EXAMPLE 19.18

Calculate pH and pOH of a 0.120 mol dm^{-3} solution of ammonia, given that its pK_b is 4.75 at 25 °C.

Answer

$K_b = 10^{-pK_b}$ $\quad\quad$ $K_b = 10^{-4.75} = 1.78 \times 10^{-5}$

The ionisation equation for ammonia is: $NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

One NH_3 molecule ionises to produce one NH_4^+ ion and one OH^- ion. This means that the concentration of NH_4^+ is equal to the concentration of OH^- and we can write:

$$K_b = \frac{[OH^-(aq)]^2}{[NH_3(aq)]}$$

We will make the approximation that the concentration of NH_3 at equilibrium is equal to the initial concentration, i.e., that the ionisation of the base is negligible compared with its concentration.

Therefore, we take $[NH_3(aq)]$ as 0.120 mol dm^{-3}. Substituting this value and the value for K_b into the expression for K_b:

$1.78 \times 10^{-5} = [OH^-(aq)]^2 / 0.120$

Therefore, $[OH^-(aq)] = 1.46 \times 10^{-3}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}(1.46 \times 10^{-3}) = 2.84$

At 25 °C, pOH + pH = 14.

Therefore, pH = 14 – 2.84 = 11.16

If c is the concentration of the base, the hydroxide ion concentration can also be worked out using

$[OH^-(aq)] = \sqrt{(c \times K_b)}$

pOH can be worked out using

$$pOH = -\frac{1}{2}\log_{10}(c \times K_b)$$

or $$pOH = \frac{1}{2}(pK_b - \log_{10} c)$$

The pH could be worked out using

$$pH = 14 + \frac{1}{2}\log_{10}(c \times K_b)$$

or $$pH = 14 - \frac{1}{2}(pK_b - \log_{10} c)$$

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WORKED EXAMPLE 19.19

The pK_b for a weak base, B, is 4.8 at 25 °C. Calculate the pOH and pH of a 0.010 mol dm^{-3} solution of B.

Answer

$c = 0.010$ mol dm^{-3} so $\log_{10} c = -2$

$\text{pOH} = -\frac{1}{2}(pK_b - \log_{10} c) = \frac{1}{2}[4.8 - (-2)] = 3.4$

$\text{pH} = 14 - \text{pOH} = 14 - 3.4 = 10.6$

TEST YOUR UNDERSTANDING

47 **a** Write equations for the ionisation of the following weak bases:

i $NH_3(aq)$

ii $CH_3NH_2(aq)$

iii $(CH_3)_2NH(aq)$.

b Write the K_b expression for each of the bases in **a**.

48 B_1, B_2 and B_3 are weak bases.

a Copy and complete the table:

Base	Concentration of base / mol dm^{-3}	[OH$^-$] / mol dm^{-3}	K_b	pK_b
B_1	0.100	1.33×10^{-3}		
B_2	0.250		5.75×10^{-5}	
B_3	0.0200	4.70×10^{-4}		

b Arrange the bases in order of increasing strength (weakest first).

49 Calculate the pOH and pH for each of the weak bases B_4, B_5 and B_6. State any assumptions you make.

Base	pK_b	Concentration / mol dm^{-3}
B_4	4.20	0.120
B_5	6.46	0.0200
B_6	8.80	0.0400

50 Calculate the pOH and pH for each of the following weak bases:

Base	pK_b	Concentration / mol dm^{-3}
B_7	4.00	0.100
B_8	7.60	1.00×10^{-3}
B_9	5.86	0.0100

51 Calculate the pH of:

a a 0.0500 mol dm^{-3} solution of ethylamine ($CH_3CH_2NH_2$) at 25 °C, given that the K_b value is 4.67×10^{-4} at that temperature

b a 0.0100 mol dm^{-3} solution of phenylamine ($C_6H_5NH_2$) at 25 °C, given that the K_b value is 7.41×10^{-10} at that temperature

c a 0.0200 mol dm^{-3} solution of methylamine (CH_3NH_2) at 25 °C, given that the pK_b value is 3.34 at that temperature

d a 0.150 mol dm^{-3} solution of propylamine ($CH_3CH_2CH_2NH_2$) at 25 °C, given that the pK_b value is 3.46 at that temperature.

52 Explain any assumptions that you made in the calculations in questions **50** and **51**.

53 Calculate the pH of each of the following solutions at the given temperature:

a 0.1000 mol dm^{-3} NaOH at 40 °C ($pK_w = 13.53$)

b 0.1000 mol dm^{-3} HCl at 30 °C ($pK_w = 13.83$)

c 0.02000 mol dm^{-3} KOH at 30 °C ($pK_w = 13.83$).

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19.12 The strength of an acid and its conjugate base

The relationship between K_a and K_b

Consider the equilibria for acid HA and its conjugate base A^-:

equation 1: $HA(aq) \rightleftharpoons A^-(aq) + H^+(aq)$

equation 2: $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

We can write the K_a expression for equation 1:

$$K_a = \frac{[A^-(aq)][H^+(aq)]}{[HA(aq)]}$$

and the K_b expression for equation 2:

$$K_b = \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$$

If we multiply K_a by K_b, we get

$$K_a \times K_b = \frac{\cancel{[A^-(aq)]}[H^+(aq)]}{\cancel{[HA(aq)]}} \times \frac{\cancel{[HA(aq)]}[OH^-(aq)]}{\cancel{[A^-(aq)]}}$$

Cancelling like terms, we get

$$K_a \times K_b = [H^+(aq)] \times [OH^-(aq)]$$

But $[H^+(aq)] \times [OH^-(aq)] = K_w$, so we can write

KEY POINT

$$K_a \times K_b = K_w$$

This relationship works only for a conjugate acid–base pair, e.g., for NH_4^+ ($K_a = 5.62 \times 10^{-10}$) and for NH_3 ($K_b = 1.78 \times 10^{-5}$):

$$K_a \times K_b = 5.62 \times 10^{-10} \times 1.78 \times 10^{-5} = 1.00 \times 10^{-14}$$

which is the value for K_w at 25 °C.

If we take negative logarithms to base ten of each side in the expression $K_a \times K_b = K_w$, we get the following relationship:

KEY POINT

$$pK_a + pK_b = pK_w$$

At 25 °C, the value of pK_w is 14, so, at 25 °C, $pK_a + pK_b = 14$.

The pK_a for ethanoic acid (CH_3COOH) is 4.76 and the pK_b for its conjugate base, the ethanoate ion (CH_3COO^-), is 9.24 at 25 °C:

$4.76 + 9.24 = 14$

WORKED EXAMPLE 19.20

Phenol (C_6H_5OH) is a weak acid with $pK_a = 9.99$. It dissociates according to the equation:

$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$

Calculate K_b for the phenoxide ion ($C_6H_5O^-$) at 25 °C.

Answer

The phenoxide ion is the conjugate base of phenol, and so, the pK_a value of phenol and the pK_b value of the phenoxide ion are related by the equation:

$pK_a + pK_b = pK_w$ or, at 25 °C $pK_a + pK_b = 14$

Therefore, pK_b for the phenoxide ion is $14 - 9.99 = 4.01$.

$K_b = 10^{-pK_b} = 10^{-4.01} = 9.77 \times 10^{-5}$

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The stronger the acid, the weaker the conjugate base

For a conjugate acid–base pair, $pK_a + pK_b = pK_w$ (or $K_a \times K_b = K_w$). This means that the lower the value of pK_a for an acid, the higher the value of pK_b for its conjugate base. A lower value of pK_a indicates a stronger acid and a higher value of pK_b indicates a weaker base. This leads to the conclusion that was discussed earlier:

HCN is the weakest acid in Table 19.8 (highest value of pK_a) and has the strongest conjugate base (lowest value of pK_b for CN^-). HCN has very little tendency to dissociate, according to the equation:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

and CN^- has a relatively strong tendency to react with water to re-form the parent acid:

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

KEY POINT

The stronger the acid, the weaker its conjugate base.

decreasing strength ↓

Acid	pK_a	Conjugate base	pK_b
HF	3.20	F^-	10.80
C_6H_5COOH	4.20	$C_6H_5COO^-$	9.80
CH_3CH_2COOH	4.87	$CH_3CH_2COO^-$	9.13
HOCl	7.40	OCl^-	6.60
HCN	9.21	CN^-	4.79

↓ increasing strength

Table 19.8: The relationship between the strength of an acid and its conjugate base.

TEST YOUR UNDERSTANDING

54 State the relationship between K_a and K_b for a conjugate acid–base pair.

55 State the relationship between pK_a and pK_b for a conjugate acid–base pair.

56 Copy and complete the following table, which contains values measured at 25 °C. The first row has been done for you.

Acid	K_a	pK_a	Conjugate base	K_b	pK_b
HCN	6.17×10^{-10}	9.21	CN^-	1.62×10^{-5}	4.79
HF	6.31×10^{-4}				
HIO_3		0.78			
NH_4^+					4.75
			CH_3COO^-	5.75×10^{-10}	
		10.66	CH_3NH_2		

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57 The pK_b values for some bases are given in the table. Arrange the conjugate acids in order of strength, weakest first.

Base	pK_b		pK_b
$CH_3CH_2COO^-$	9.13	$C_6H_5COO^-$	9.80
HCO_3^-	7.65	$CH_3CHClCOO^-$	11.17

NATURE OF SCIENCE

From qualitative models to quantitative ones

We started the chapter with a qualitative discussion of acids and bases and have now considered a mathematical description of acidity. It is the goal of many areas of science to describe natural phenomena mathematically. Depending on the sophistication of the model, more or fewer assumptions/approximations are used. The development of more sophisticated equipment, such as the pH meter, can allow testing and refinement of the models.

19.13 The pH of salt solutions

Solutions of salts can be acidic, neutral or alkaline, e.g., ammonium chloride solution is acidic, sodium nitrate solution is neutral and potassium carbonate solution is alkaline.

A salt will be formed when an acid reacts with a base:

acid + base/alkali → salt + water

e.g. $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

By looking at the whether the acid and base used to make the salt are strong or weak, we can predict whether the salt solution will be acidic, neutral or alkaline. For example, sodium nitrate forms a neutral solution because it is the salt of a strong acid (HNO_3) and a strong base (NaOH).

Salt of a weak acid and a strong base (pH > 7)

Consider the salt sodium ethanoate (CH_3COONa). To predict whether the pH will be equal to, less than or greater than 7, we must consider how it can be made by reacting an acid with an alkali. For the sodium part of a salt, we always choose NaOH [for potassium it would be potassium hydroxide (KOH), etc.]. The other part comes from ethanoic acid (CH_3COOH):

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

Ethanoic acid is a weak acid and sodium hydroxide is a strong base. Because the base is stronger than the acid, the pH will be in the basic/alkaline region, that is, greater than 7. A 0.100 mol dm^{-3} solution of sodium ethanoate has a pH of 8.88.

To understand why the pH is greater than 7, we must look at what happens when the salt dissolves in water.

Sodium ethanoate is an ionic compound, and so, when it dissolves in water, the two ions separate from each other – the solution contains $CH_3COO^-(aq)$ and $Na^+(aq)$ ions.

The CH_3COO^- ion is the conjugate base of ethanoic acid, a weak acid. Remember, the weaker the acid, the stronger the conjugate base. When in aqueous solution, the CH_3COO^- ion acts as a base by accepting a proton from water, according to the following equilibrium:

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

The concentration of OH^- ions in the solution has been increased (it is larger than the concentration of H^+ ions) and, therefore, the solution is alkaline. This process is called *salt hydrolysis*, where a molecule of water is broken apart by reaction with the salt.

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The other ion from CH_3COONa present in this solution, the Na^+ ion, comes from a strong base (NaOH), which is fully ionised. There is, therefore, no tendency for Na^+ to react with the OH^- ions produced.

$Na^+(aq) + OH^-(aq) \not\rightleftharpoons NaOH(aq)$

The discussion here can be extended to the salt of any carboxylic acid, RCOOH, where R is an alkyl group or H. The general equation for the hydrolysis reactions of carboxylate salts is therefore

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

Other salts of weak acids and strong bases that you may come across are sodium and potassium carbonate or hydrogencarbonate.

Sodium hydrogencarbonate

This has the formula $NaHCO_3$ and to get the 'Na part' we could use the strong base NaOH. The 'HCO_3 part' comes from carbonic acid, H_2CO_3, which is a weak acid, so we could imagine making sodium hydrogencarbonate using the reaction:

$NaOH(aq) + H_2CO_3(aq) \rightarrow NaHCO_3(aq) + H_2O(l)$

Since the base (NaOH) is stronger than the acid, the pH > 7. The hydrolysis reaction that occurs in solution is $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$.

The presence of excess $OH^-(aq)$ ions makes the solution alkaline.

Similarly, a solution of sodium carbonate also has a pH > 7 because of the reaction:

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_{3-(aq)} + OH^-(aq)$

Calculation of the pH of a salt solution

WORKED EXAMPLE 19.21

The pK_a of ethanoic acid is 4.76. Calculate the pH of a 0.100 mol dm^{-3} solution of sodium ethanoate at 25 °C.

Answer

Sodium ethanoate has the formula CH_3COONa. It is an ionic salt, so, when it dissolves in water, the ions will separate (it ionises completely), and we will have a solution of $Na^+(aq)$ ions and $CH_3COO^-(aq)$ ions.

The ethanoate ion, $CH_3COO^-(aq)$, is the conjugate base of ethanoic acid, $CH_3COOH(aq)$, and so, the pK_a value of ethanoic acid and the pK_b value of the ethanoate ion are related by the equation:

$pK_a + pK_b = pK_w$ or, at 25 °C, $pK_a + pK_b = 14$

therefore, for the ethanoate ion: $pK_b = 14 - 4.76 = 9.24$

Sodium ethanoate is, therefore, a weak base, and the question now becomes one of calculating the pH of a solution of a weak base. The general equation for a base ionising in water is

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

So, for $CH_3COO^-(aq)$, we have: $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3COOH(aq)][OH^-(aq)]}{[CH_3COO^-(aq)]}$$

$K_b = 10^{-pK_b} = 10^{-9.24} = 5.75 \times 10^{-10}$

$[OH^-(aq)] = [CH_3COOH(aq)]$

Therefore, we have $5.75 \times 10^{-10} = [OH^-(aq)]^2 / [CH_3COO^-(aq)]$

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CH_3COO^- is a weak base, so we will make the approximation that the concentration of CH_3COO^- at equilibrium is equal to the initial concentration, i.e., that the ionisation of the base is negligible compared to its concentration. Substituting in the concentration:

$$5.75 \times 10^{-10} = \frac{[OH^-(aq)]^2}{0.100}$$

Rearranging and solving this we get: $[OH^-(aq)] = 7.59 \times 10^{-6}$ mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}(7.59 \times 10^{-6}) = 5.12$

At 25 °C, pH + pOH = 14 therefore, pH = 14 – 5.12 = 8.88

Therefore, the pH of a 0.100 mol dm^{-3} solution of sodium ethanoate is 8.88.

Salt of a strong acid and a weak base (pH < 7)

Consider ammonium chloride, NH_4Cl. The 'Cl part' of this comes from the strong acid (HCl) and the 'NH_4 part' from the weak base (NH_3), so the salt could be made by the reaction:

$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

Ammonium chloride is, therefore, the salt of a strong acid and a weak base. Because the acid is stronger, ammonium chloride will form an acidic solution.

When NH_4Cl is dissolved in water, the ions separate.

The NH_4^+ ion is the conjugate acid of the weak base NH_3 and will, therefore, dissociate according to the following equation:

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

Extra H^+ is generated, and so, the solution of NH_4Cl is acidic. The pH of a 0.100 mol dm^{-3} solution of NH_4Cl is 5.13.

Cl^- is the conjugate base of the strong acid, HCl. It is, therefore, an extremely weak base (the stronger the acid, the weaker the conjugate base). There is, therefore, virtually no tendency for the following reaction to occur:

$Cl^-(aq) + H_2O(l) \not\rightleftharpoons HCl(aq) + OH^-(aq)$

The pH of a solution of an ammonium chloride solution can be worked out using a similar method to that used to work out the pH of a sodium ethanoate solution previously.

Salt of a strong acid and a strong base (pH = 7)

Consider sodium chloride, NaCl. This is made from the strong acid HCl and the strong base NaOH. These are both fully dissociated in aqueous solution, so a solution of NaCl is neutral (pH = 7 at 25 °C). There is virtually no tendency for either of these reactions to occur:

$Na^+(aq) + OH^-(aq) \not\rightleftharpoons NaOH(aq)$

$Cl^-(aq) + H_2O(l) \not\rightleftharpoons HCl(aq) + OH^-(aq)$

Note: sulfuric acid is only a strong acid for the first dissociation and, therefore, a solution of sodium sulfate will be very slightly alkaline (pH about 7.5 for a 0.100 mol dm^{-3}) solution due to the reaction:

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

Salt of a weak acid and a weak base (pH = ?)

Whether a solution of a salt of a weak acid and a weak base is acidic, neutral or alkaline will depend on the relative strengths of the acid and base it can be made from.

Consider ammonium methanoate, $HCOO^-NH_4^+$. This is the salt of the weak acid, methanoic acid (HCOOH), and the weak base ammonia (NH_3). The pK_a value of methanoic acid is 3.75 and the pK_b value of ammonia is 4.75. A lower value indicates a stronger acid/base; therefore, methanoic acid is stronger and the pH will lie in the acidic region, i.e., the pH of an ammonium methanoate solution will be less than 7.

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The reactions that go on in solution are

$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$
$pK_b = 10.25$

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$
$pK_a = 9.25$

A lower value for $pK_{a/b}$ indicates that the position of equilibrium lies more to the right, so there will be excess $H^+(aq)$ in this solution; therefore, the solution is acidic.

Consider ammonium ethanoate, $CH_3COO^-NH_4^+$. This is the salt of the weak acid CH_3COOH and the weak base NH_3. The pK_a of ethanoic acid is 4.76 and the pK_b of ammonia is 4.75.

The pK_b and pK_a values are virtually identical, and so, the pH of a solution of ammonium ethanoate will be very close to 7.

EXAM TIP

It is worth remembering that ammonium ethanoate has a pH of approximately 7 because it has been asked about in exams.

Ethylammonium ethanoate ($C_2H_5NH_3^+CH_3COO^-$) is the salt of the weak base ethylamine ($pK_b = 3.35$) and the weak acid ethanoic acid ($pK_a = 4.76$). The pK_b value of the base is lower (stronger base) than the pK_a value of the acid; therefore, the pH of a solution of ethylammonium ethanoate will be greater than 7. The reactions that occur are

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
$pK_b = 9.24$

$C_2H_5NH_3^+(aq) \rightleftharpoons C_2H_5NH_2(aq) + H^+(aq)$ $\quad pK_a = 10.73$

The position of the top equilibrium (pK_b lower) lies more to the right, so there is an excess of $OH^-(aq)$ ions.

TEST YOUR UNDERSTANDING

58 **a** Predict whether the pH of each of the following solutions will be equal to, greater than or less than 7.

Solution	pH
0.100 mol dm^{-3} $CH_3CH_2CH_2CH_2COONa$	
0.500 mol dm^{-3} KNO_3	
0.100 mol dm^{-3} Na_2CO_3	
0.100 mol dm^{-3} $CH_3CH_2NH_3^+Cl^-$	

b For each salt solution for which the pH ≠ 7, write an equation to explain this.

59 In each case, use the data given to deduce whether the pH of a 0.100 mol dm^{-3} solution of the salt will be < 7, = 7 or > 7.

a NH_4CN: pK_a of HCN is 9.21, pK_b of NH_3 is 4.75

b $CH_3NH_3^+HCOO^-$: pK_a of HCOOH is 3.75, pK_b of CH_3NH_2 is 3.34.

60 The pK_a for methanoic acid, HCOOH(aq), is 3.75.

a Calculate the pH of a solution that contains 0.100 mol dm^{-3} HCOOH(aq).

b Calculate the pH of 0.100 mol dm^{-3} HCOONa(aq).

61 The pK_b for ammonia, NH_3(aq), is 4.75.

a Calculate the pH of a solution that contains 0.200 mol dm^{-3} NH_3(aq).

b Calculate the pH of 0.200 mol dm^{-3} NH_4Cl(aq).

62 Calculate pH values for the following salt solutions:

a 0.100 mol dm^{-3} solution of potassium cyanide (KCN), given that the pK_a for hydrocyanic acid (HCN) is 9.21.

b 0.200 mol dm^{-3} solution of sodium propanoate (CH_3CH_2COONa), given that the pK_a for propanoic acid is 4.87.

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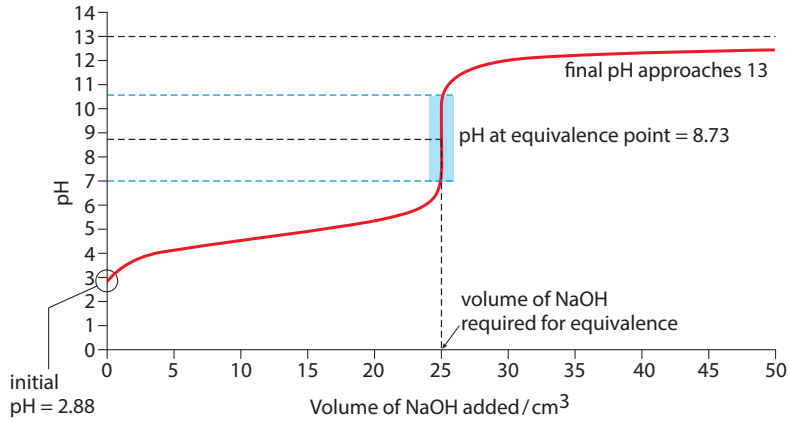

Figure 19.14: A pH curve for adding 0.100 mol dm^{-3} NaOH to 25 cm^3 of 0.100 mol dm^{-3} CH_3COOH.

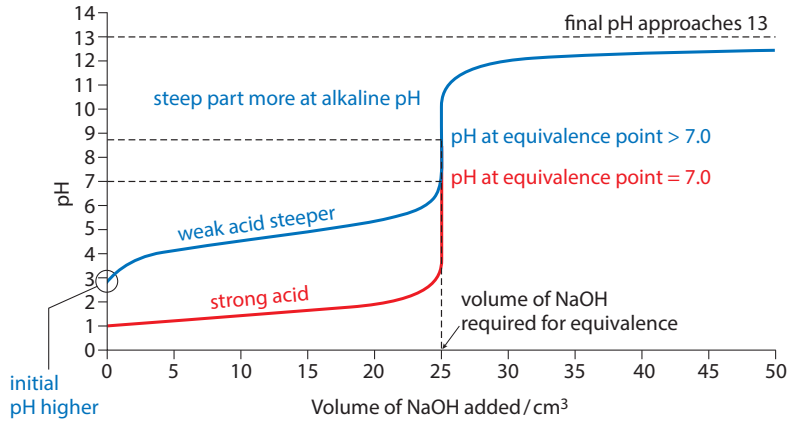

Figure 19.15: Comparison of a weak acid–strong base titration curve (blue) with a strong acid–strong base titration curve (red).

19.14 More pH curves

We looked at the pH (titration) curve for a strong acid–strong base titration in Section 19.9, and here we will consider other possible pH curves.

Weak acid–strong base pH curve

Let us consider adding 0.100 mol dm^{-3} NaOH to 25 cm^3 of 0.100 mol dm^{-3} CH_3COOH (ethanoic acid) ($pK_a = 4.76$). The pH curve is shown in Figure 19.14.

The initial pH can be calculated using the pK_a value for ethanoic acid and the method given in Section 19.10.

The equivalence point is reached when equal numbers of moles of acid and alkali have been added. As the concentrations of the acid and bases are the same, this occurs when the same volumes have been added (that is, when 25.0 cm^3 of sodium hydroxide has been added).

The pH at the equivalence point is not 7; it is greater than 7.

The equation for the reaction is

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

When equivalent amounts of ethanoic acid and sodium hydroxide have been added, a solution of sodium ethanoate, $CH_3COONa(aq)$, has been formed. We saw in the previous section that this had a pH > 7 because of the reaction:

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

This reaction increases the concentration of OH^- ions in the solution and the pH at the equivalence point is, therefore, higher than 7.

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As more and more NaOH is added, the pH approaches 13 – the pH of 0.100 mol dm^{-3} NaOH.

In Figure 19.15, a weak acid–strong base titration curve is compared with a strong acid–strong base titration curve. In the weak acid–strong base titration, 0.100 mol dm^{-3} NaOH(aq) is added to 25.00 cm^3 of 0.100 mol dm^{-3} ethanoic acid, and in the strong acid–strong base titration, 0.100 mol dm^{-3} NaOH(aq) is added to 25.00 cm^3 of 0.100 mol dm^{-3} hydrochloric acid.

Features that are the same

- The same volume of sodium hydroxide is required to get to the equivalence point. The volume of alkali required to reach the equivalence point depends only on the original volume of acid used and the concentrations of the acid and alkali, and not on the strength of the acid.
- The curves tend to the same final pH – in both cases, the curves approach a final pH of 13, which is the pH of the alkali used [0.100 mol dm^{-3} NaOH(aq)].

Differences between the curves

- The initial pH is higher for the weak acid–strong base titration. The strong acid is completely dissociated (higher concentration of H^+ ions), but the weak acid is only partially dissociated (lower concentration of H^+ ions).
- The initial part of the curve, up to a volume of about 24 cm^3 NaOH added, is steeper for the weak acid–strong base titration. Because the weak acid is only partially dissociated, the concentration of H^+ ions in the solution is lower and adding a certain volume of NaOH has a greater relative effect on the pH than that for a strong acid, in which the concentration of H^+ ions is higher.
- The steep (near vertical) part of the curve is more in the alkaline region for the weak acid–strong base titration, but, for the strong acid–strong base titration, it is symmetrical about pH 7.
- The pH at the equivalence point is higher than 7 for the weak acid–strong base titration but equal to 7 for the strong acid–strong base titration.

Determination of pK_a from a pH curve

The pK_a value for a weak acid can be determined experimentally from a weak acid–strong base pH curve.

In the previous example of the titration of 0.100 mol dm^{-3} ethanoic acid with 0.100 mol dm^{-3} NaOH, 25.0 cm^3 of NaOH is required to reach the equivalence point. Here, we will consider the point in the titration when half this volume of NaOH has been added, i.e., 12.5 cm^3. This is called the *half-equivalence point*.

The equation for the reaction is

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

which can be written as an ionic equation:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

When 12.5 cm^3 of NaOH has been added, half of the CH_3COOH has been converted into CH_3COO^- and, therefore, the concentrations of CH_3COOH and CH_3COO^- are equal.

The ethanoic acid in the solution is in equilibrium with the ethanoate ion:

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

The expression for K_a for ethanoic acid is

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

Because the concentration of CH_3COO^- is equal to the concentration of CH_3COOH, we can cancel their concentrations:

$$K_a = \frac{\cancel{[CH_3COO^-(aq)]}[H^+(aq)]}{\cancel{[CH_3COOH(aq)]}}$$

so, $K_a = [H^+(aq)]$

and if we take $-\log_{10}$ of both sides, we get

$$pK_a = pH$$

KEY POINT

The pH at the half-equivalence point in a weak acid–strong base titration is equal to pK_a of the weak acid.

The pK_a value for ethanoic acid can, therefore, be read off the graph, as shown in Figure 19.16.

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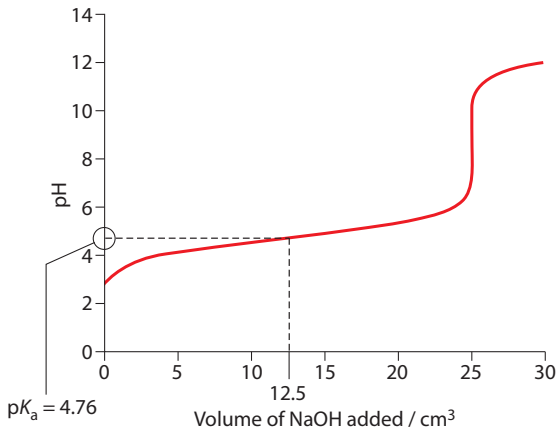

Figure 19.16: The pK_a value of the acid is equal to the pH at the half-equivalence point.

Strong acid–weak base pH curve

The pH curve for adding 0.100 mol dm^{-3} NH_3(aq) to 25 cm^3 0.100 mol dm^{-3} HCl(aq) is shown in Figure 19.17.

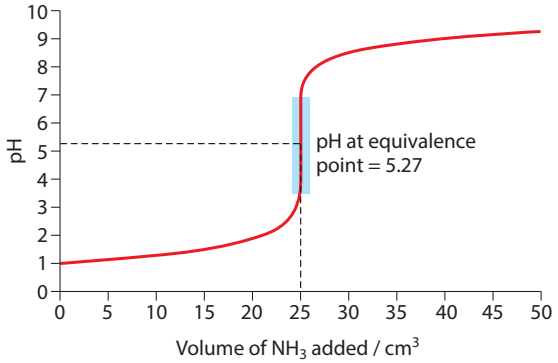

Figure 19.17: A strong acid–weak base pH curve.

Key features:

- initial pH is the pH of the strong acid (1.00 in this case)
- pH at the equivalence point <7
- the steep portion of the curve is more in the acidic region (below pH 7) than in the alkaline region
- the curve approaches a final pH of 11.1 [the pH of 0.100 mol dm^{-3} NH_3(aq)].

The equation for the reaction is

$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

At the equivalence point, we therefore have a solution of NH_4Cl.

We saw previously that, because the ammonium ion is the conjugate acid of a weak base, it dissociates to a certain extent in aqueous solution, according to the equation:

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

So, the concentration of H^+ ions in the solution is increased, and the pH is lower than 7.

Determination of pK_b from a pH curve

The previous titration could also have been performed the other way around, that is, by adding hydrochloric acid to the ammonia solution. The pH curve obtained is shown in Figure 19.18.

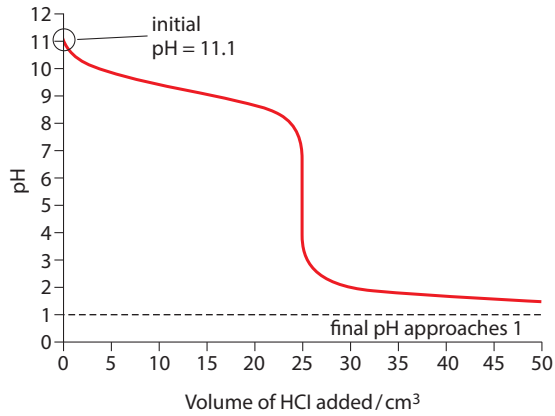

Figure 19.18: pH curve for adding a strong acid to a weak base.

This curve can be used to determine the pK_b of ammonia. Again, we will be looking at the half-equivalence point, when enough HCl has been added to react with half of the ammonia.

Ammonia is in equilibrium with the ammonium ion in this solution:

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

The expression for K_b is

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

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When 12.5 cm^3 of HCl has been added, half of the NH_3 will have been converted into NH_4^+, and so

$[NH_3(aq)] = [NH_4^+(aq)]$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

Therefore, at the half-equivalence point: $K_b = [OH^-]$

Taking $-\log_{10}$ of both sides, we get $pK_b = pOH$

KEY POINT

$pK_b = pOH$ at the half-equivalence point when a strong acid is added to a weak base.

At 25 °C, pH + pOH = 14 so, when $pK_b = pOH$, $pK_b = 14 - pH$

KEY POINT

$pK_b = 14 - pH$ at the half-equivalence point when a strong acid is added to a weak base.

So, we can thus work out pK_b for ammonia from the graph in Figure 19.19.

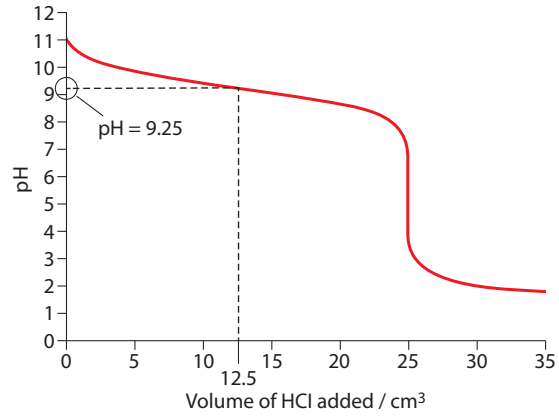

Figure 19.19: pK_b can be obtained from a strong acid–weak base titration curve.

The pH at the half-equivalence point is 9.25, so the pK_b of ammonia is given by

$14 - 9.25 = pK_b$

Therefore, pK_b for ammonia is 4.75.

Weak acid–weak base pH curve

An example of titration of a weak acid and a weak base is the addition of 0.100 mol dm^{-3} $NH_3(aq)$ to 25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH (Figure 19.20).

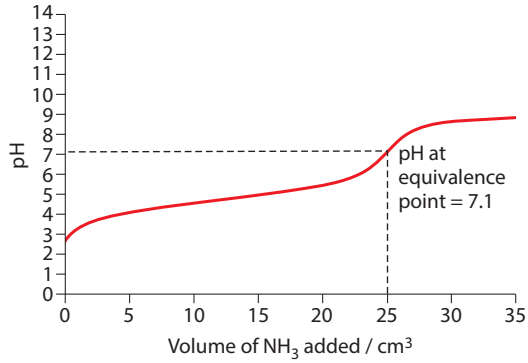

Figure 19.20: A weak acid–weak base pH curve.

The key feature to notice here is that there is no very steep (almost vertical) part in this pH curve.

The pH at the equivalence point may be lower than 7 or higher than 7, depending on the relative strength of the acid and the base.

In this case, ethanoic acid ($pK_a = 4.76$) is very similar in strength to ammonia ($pK_b = 4.75$), and the pH at the equivalence point is very close to 7.0 (it is just slightly higher than 7.0 because the base is very slightly stronger than the acid). If we had used a different acid, such as methanoic acid ($pK_a = 3.75$), the pH at the equivalence point would have been lower than 7 because the acid is stronger than the base.

Indicators

Acid–base titrations are carried out to establish the equivalent amounts of acid and base that react with each other, and hence, the concentration of the acid or the alkali. We need some way of determining when equivalent amounts of acid and base have been mixed, and this can be done either using a pH meter and looking for the point of inflexion in the pH curve or, more usually and more conveniently, by using an acid–base indicator.

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Indicators are often weak acids (they can also be weak bases) and can be represented by HInd. The indicator dissociates according to the equation:

$$\underset{\text{colour I}}{HInd(aq)} \rightleftharpoons \underset{\text{colour II}}{H^+(aq) + Ind^-(aq)}$$

The ionised (Ind^-) and un-ionised (HInd) forms must have different colours for the substance to function as an indicator. In this case, we will take the colours as red and blue, as shown in the equation.

If we add some indicator to a solution and the colour is blue, this indicates that the position of the above equilibrium lies mostly to the right – there is so much more of the blue form than the red form that the solution appears blue to our eyes.

If we now add some acid to the solution, the colour of the indicator changes to red (Figure 19.21).

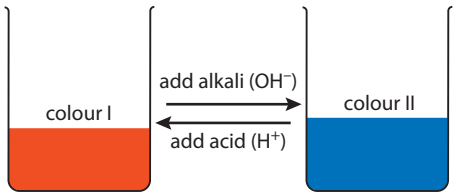

Figure 19.21: The indicator changes from colour II to colour I as acid is added and from colour I to colour II as alkali is added.

This can be understood in terms of Le Chatelier's principle (Chapter 18, section 18.2). If acid (H^+) is added to the system at equilibrium, the position of equilibrium will shift to the left to use up (reduce the concentration of) H^+ that has been added. Because the position of equilibrium shifts to the left, there is now significantly more HInd (red) than Ind^- (blue) and the colour of the indicator appears red.

If we now add some alkali base to this solution, the colour changes to blue (Figure 19.21).

When we add alkali, the OH^- ions from the alkali react with the H^+ ions on the right-hand side of the equation to produce water. The position of equilibrium shifts to the right to replace the H^+ as far as possible and, because there is now a significantly higher concentration of Ind^-, the solution appears blue.

The pH range of an indicator

If we imagine a different indicator, for which the colours of the un-ionised and ionised forms are yellow and blue, respectively:

$$\underset{\text{colour I}}{HInd(aq)} \rightleftharpoons \underset{\text{colour II}}{H^+(aq) + Ind^-(aq)}$$

Let us consider increasing the pH gradually from 1. The indicator will change colour as shown in Figure 19.22.

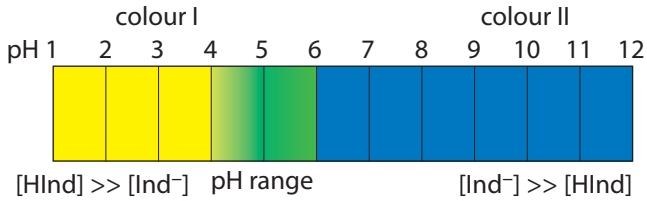

Figure 19.22: The variation of colour with pH for an indicator that is yellow in acidic solutions and blue in alkaline solution.

Up to pH 4, the concentration of HInd (yellow) is so much greater than the concentration of Ind^- (blue) that the indicator appears yellow. From pH 6 onwards, the concentration of Ind^- is so much greater than the concentration of HInd that the colour appears blue. Between pH 4 and 6, the concentrations of HInd and Ind^- are fairly evenly balanced, and the indicator is various shades of green (green is a mixture of yellow and blue). In this region, if we gradually change the pH, we can see the indicator changing colour, and this is called the **pH range of the indicator**. In this case, the pH range of the indicator would be quoted as 4–6.

KEY POINT

The pH range of an indicator is the pH values between which the indicator has intermediate colours because comparable amounts of the un-ionised and ionised forms are present.

EXAM TIP

The pH range is also called the end point range on the IB syllabus.

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Indicator	pH range	Acid colour	Alkali colour	pK_a
methyl orange	3.1–4.4	red	yellow	3.7
bromophenol blue	3.0–4.6	yellow	blue	4.2
bromocresol green	4.0–5.6	yellow	blue	4.7
methyl red	4.4–6.2	red	yellow	5.1
bromothymol blue	6.0–7.6	yellow	blue	7.0
phenol red	6.4–8.0	yellow	red	7.9
phenolphthalein	8.0–10.0	colourless	pink	9.6

Table 19.9: The pH ranges and colours of some indicators. pK_a values are discussed in the next section.

The pH ranges of various indicators are given in Table 19.9.

Universal indicator solution and pH paper change colour over a very wide range of pH because they contain a mixture of indicators that change colour over different pH ranges.

The pK_a value of an indicator

Consider the dissociation of an indicator that is a weak acid:

$HInd(aq) \rightleftharpoons H^+(aq) + Ind^-(aq)$

The K_a expression for the indicator is

$$K_a = \frac{[Ind^-(aq)][H^+(aq)]}{[HInd(aq)]}$$

At the midpoint of the pH range, half of HInd will have dissociated, and the concentrations of HInd and Ind^- will be equal:

$[HInd(aq)] = [Ind^-(aq)]$

$$K_a = \frac{\cancel{[Ind^-(aq)]}[H^+(aq)]}{\cancel{[HInd(aq)]}} = [H^+(aq)]$$

Taking $-\log_{10}$ of each side, we get $pK_a = pH$

Therefore, the pK_a of the indicator is equal to the pH at the midpoint of its pH range.

The midpoint of the pH range means that there will be equal amounts of both colours, so the indicator is exactly halfway between its two colours. As a rough rule of thumb, we can take the pH range of an indicator to be $pK_a \pm 1$. This is a theoretical derivation of the pH range of an indicator. In practice, due to our ability to detect various colours and colour changes, the midpoint of the working pH range of an indicator may not correspond exactly to the pK_a of the indicator. The pK_a values of some indicators are shown in Table 19.9.

We can now decide on the best indicator to use for a titration using the pH range and the pK_a value for the indicator. The indicator will be suitable if its pK_a value is close to the pH at the equivalence point of the titration.

Choosing an indicator for a titration

We saw in the section on pH curves that the pH at the equivalence point varies, depending on what combination of strong/weak acid/bases we use, and we saw in the section above that different indicators have different pK_a values and pH ranges (different end points), so we need to use different indicators for different titrations.

KEY POINT

The *equivalence point of a titration* is the point at which equivalent numbers of moles of acid and alkali have been added.

The *end point of a titration* is the point at which the indicator changes colour.

These are not necessarily the same.

We are generally using the indicator to determine the equivalence point as closely as possible, so, for an indicator to be suitable for a particular titration, we need the end point (where the indicator changes colour) to be as close as possible to the equivalence point of the titration (what we are trying to find). The most precisely we can know the equivalence point is to within one drop – ideally, we want the addition of one drop of

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acid/alkali to cause the indicator to change completely between its two colours and the equivalence point to have been reached/passed within this one drop.

KEY POINT

For an indicator to be suitable for a titration, the pK_a of the indicator should be as close as possible to the pH at the equivalence point of a titration *and* the pH range of the indicator should occur entirely within the steep part of the pH curve around the equivalence point.

An indicator is no good for a titration if it can be seen to change colour gradually – it would be very difficult to judge when the colour change was complete – the end point of the titration would not be clear. We know that the pH range of the indicator covers about two pH units, so we need one drop of alkali to cause a pH change of at least two units – this only occurs in the steep part of the pH curve around the equivalence point.

Indicator for a strong acid–strong base titration

Consider a strong acid–strong base titration, as shown in Figure 19.23. In the vertical region of the curve, approximately one drop of alkali causes the pH to change by about 6–7 units. Therefore, if an indicator has its range in this part of the curve, adding one drop of alkali will cause the indicator to change from the acid colour (colour of HInd) to the alkali colour (colour of Ind^-) and the end point and the equivalence point will coincide (occur at the same volume, to within one drop).

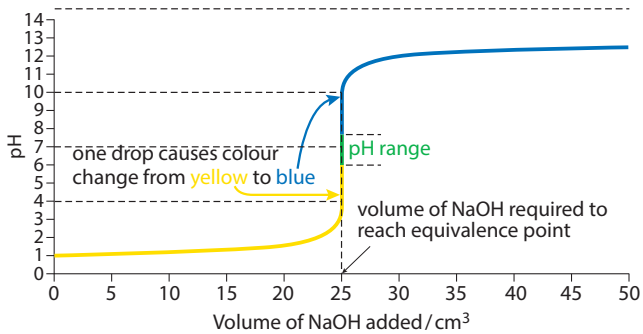

Figure 19.23: The colour changes of bromothymol blue during a strong acid–strong base titration.

Let us consider what happens if we use bromothymol blue (pH range 6.0–7.6) for this titration (Figure 19.23). Before any alkali has been added, the colour of the indicator is yellow. As alkali is added, the colour remains yellow until the volume of alkali added is just less than 25.0 cm^3 and the pH of the mixture is about 4. At this point, adding one drop of alkali causes the pH to change from about 4 to 10 and the indicator changes colour from yellow to blue – this is the end point of the titration. We know that the equivalence point of the titration occurs somewhere within that one drop of alkali (pH at the equivalence point = 7), and so we know the equivalence point to a good degree of precision. Therefore, bromothymol blue is a suitable indicator for the titration because it has allowed us to find the equivalence point to within one drop.

If we do the same titration with an indicator that changes colour from red to yellow and has a pH range of 1.2–2.8, we get the colour changes shown in Figure 19.24.

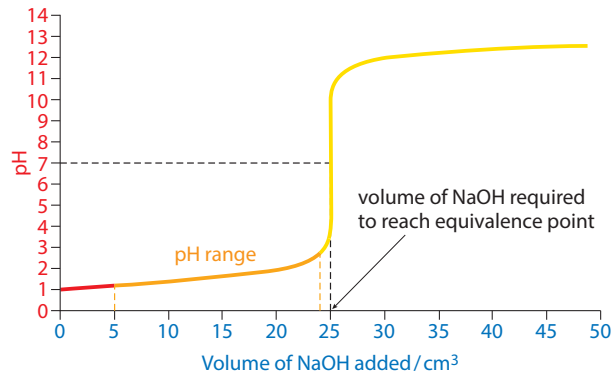

Figure 19.24: The colour changes during a strong acid–strong base titration using an indicator with a pH range of 1.2–2.8.

The indicator is initially red, but, as we add alkali, we see the indicator begin to change colour when we have added 5 cm^3 of alkali. The colour then changes gradually from red, through orange, to yellow as we add more alkali. It has completely changed colour to yellow before the equivalence point, so the end point does not coincide with the equivalence point, and we are not able to determine the equivalence point using this indicator.

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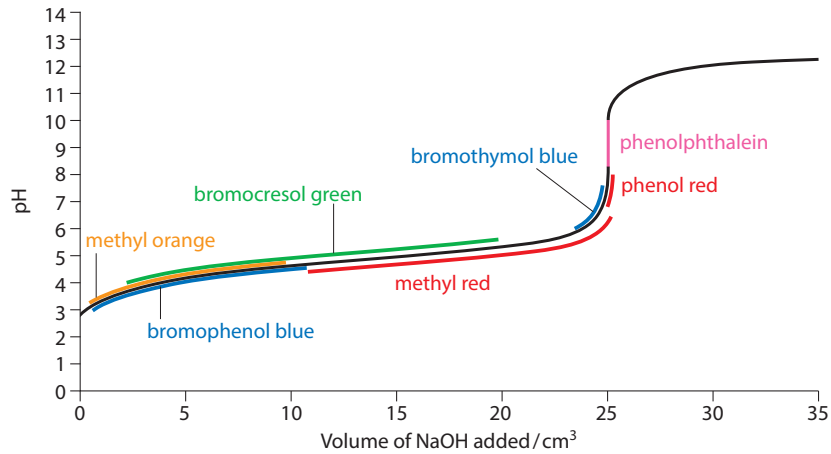

Figure 19.25: The pH ranges of various indicators superimposed on a weak acid–strong base pH curve.

EXAM TIP

Depending on the concentrations of the solutions used, all the indicators in Table 19.9 are suitable for a strong acid–strong base titration, but the best choice in an exam would be bromothymol blue ($pK_a = 7.0$), which has pK_a equal to the pH at the equivalence point.

Indicator for a weak acid–strong base titration

Let us now consider the weak acid–strong base titration shown in Figure 19.25. The pH at the equivalence point is greater than 7.

Phenolphthalein is the most suitable indicator for this type of titration – its pK_a value is 9.6 (greater than 7) and its pH range occurs entirely within the steep part of the curve. Phenol red ($pK_a = 7.9$) may also be suitable, depending on the particular acid/alkali used.

KEY POINT

Only strong acid–strong base titrations have pH = 7.0 at the equivalence point; therefore, an indicator is being used to determine the point at which equivalent numbers of moles of acid and alkali have been added and not the point at which pH = 7.

Indicator for a weak base–strong acid titration

The pH at the equivalence point is less than 7, so we need to choose an indicator that has a pK_a below 7. Methyl red ($pK_a = 5.1$) would generally be a good choice, but bromocresol green, methyl orange or bromophenol blue may also be suitable, depending on the weak base used and the concentration of the acid.

Indicator for a weak acid–weak base titration

Because the change in pH is gradual for titrating a weak acid with a weak base (no very steep part in the curve), it is not generally possible to carry out this titration with an indicator and obtain a good estimate of the equivalence point. It would be difficult to judge the end point of the titration because the indicator would change colour gradually around the equivalence point.

KEY POINT

Universal indicator is not a suitable indicator for any of these titrations.

Universal indicator changes colour gradually over a wide pH range and would not show a sharp end point.

KEY POINT

Titration using an indicator cannot be used to distinguish between a weak and a strong acid – if they have the same concentration, they will require the same amount of alkali to reach the equivalence point.

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TEST YOUR UNDERSTANDING

63 For each of the following combinations sketch the pH curve and:

- calculate the initial pH
- deduce the volume of alkali required to reach the equivalence point
- state whether the pH at the equivalence point is less than, equal to, or greater than 7
- calculate the pH that the curve tends to as excess alkali is added

a starting with 25.0 cm^3 0.100 mol dm^{-3} HCl and adding 0.100 mol dm^{-3} NaOH

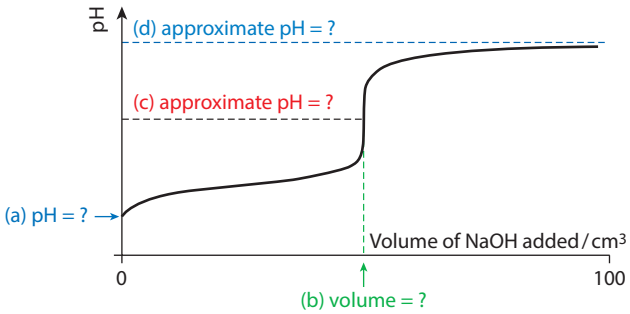
b starting with 20.0 cm^3 0.100 mol dm^{-3} HCl and adding 0.200 mol dm^{-3} NH_3 ($pK_b = 4.75$)

c starting with 10.0 cm^3 0.200 mol dm^{-3} CH_3COOH ($pK_a = 4.76$) and adding 0.100 mol dm^{-3} NaOH

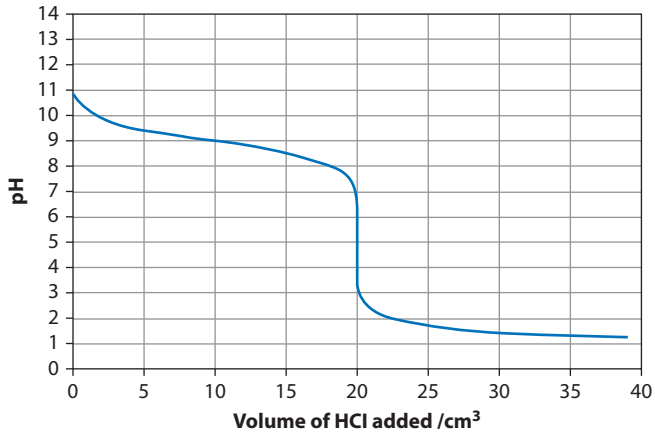
d starting with 25.0 cm^3 0.100 mol dm^{-3} CH_3COOH ($pK_a = 4.76$) and adding 0.100 mol dm^{-3} NH_3 ($pK_b = 4.75$).

64 For the titration in **63c**, deduce the pH of the solution when 10.0 cm^3 of NaOH has been added.

65 30.0 cm^3 of an acid, HA ($pK_a = 4.20$), of concentration 0.0800 mol dm^{-3} is put into a beaker with a pH probe and 0.100 mol dm^{-3} NaOH added. The pH curve (not to scale) is shown. Calculate the quantities marked on the graph.



66 The pH curve shown is for adding 0.125 mol dm^{-3} hydrochloric acid to 25.00 cm^3 of a solution of a weak base, B.



a Deduce the concentration of B.

b Deduce the pK_b of B.

67 Use data in Table 19.9 to deduce the colour of the following indicators at the stated pH:

a methyl orange at pH = 2.0

b bromophenol blue at pH = 6.2

c methyl red at pH = 5.0

d phenolphthalein at pH = 7.0.

68 Select the most suitable indicator, from the list given, for each of the following titrations in which the alkali is added to 25.0 cm^3 of acid.

phenolphthalein $pK_a = 9.6$

bromocresol green $pK_a = 4.7$

bromothymol blue $pK_a = 7.0$

	Acid	Alkali	Indicator
a	0.100 mol dm^{-3} CH_3COOH	0.100 mol dm^{-3} NaOH	
b	0.010 mol dm^{-3} HNO_3	0.020 mol dm^{-3} KOH	
c	0.010 mol dm^{-3} HCl	0.010 mol dm^{-3} NH_3	

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19.15 Buffer solutions

The blue line on the graph in Figure 19.26 shows the result of adding 10 cm^3 of 0.100 mol dm^{-3} hydrochloric acid in stages to 100 cm^3 of water.

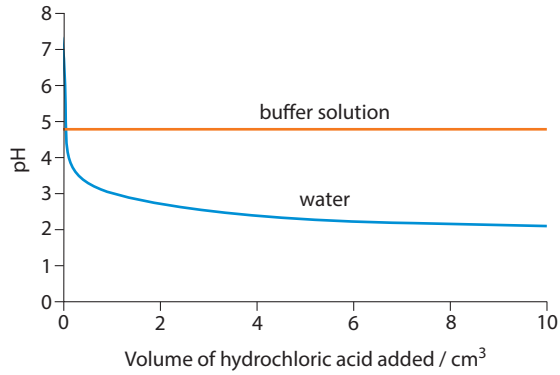

Figure 19.26: The pH of a buffer solution changes very little when hydrochloric acid is added. Water is not a good buffer.

The orange line shows the effect of adding hydrochloric acid to 100 cm^3 of a **buffer solution** formed by mixing 50 cm^3 of 1.00 mol dm^{-3} ethanoic acid and 50 cm^3 of 1.00 mol dm^{-3} sodium ethanoate. The pH of water changes from 7.00 to 2.04 when 10 cm^3 of hydrochloric acid is added, but the pH of the buffer solution only changes from 4.76 to 4.74. When 10 cm^3 of 0.100 mol dm^{-3} sodium hydroxide is added to 100 cm^3 of the ethanoic acid/sodium ethanoate buffer solution, the pH changes from 4.76 to 4.78. The pH of the buffer solution remains virtually constant when an acid or a base is added.

KEY POINT

A **buffer solution** is a solution that resists changes in pH when *small* amounts of acid or alkali are added.

The 'small amount' in this definition is important. If, for instance, 33.3 cm^3 of 2.00 mol dm^{-3} hydrochloric acid is added to 100 cm^3 of the ethanoic acid/sodium ethanoate buffer solution we have just considered, the pH will change by about 4.5 units!

A buffer solution consists of two components and must always contain something to react with any acid added and something to react with any base added. In other words, a buffer solution always contains an acid and a base.

Acid buffer solutions

KEY POINT

An acid buffer solution consists of a weak acid (e.g. ethanoic acid) and the conjugate base/salt of that weak acid (e.g. the ethanoate ion).

We say *conjugate base or salt* because, although it is only the conjugate base (e.g. the ethanoate ion) that is essential for the buffer, it is not possible to have a bottle just containing ethanoate ions – we have to add sodium ethanoate or potassium ethanoate to ethanoic acid to make the buffer.

The equilibrium that exists in an acidic buffer solution is between the acid and its conjugate base, for example:

equilibrium 1:

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

If some hydrochloric acid is added to this solution, CH_3COO^- reacts with H^+:

$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$

If some sodium hydroxide is added to the solution, CH_3COOH in the solution reacts with OH^-:

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

For the solution to function as a buffer, the concentration of $CH_3COO^-(aq)$ and $CH_3COOH(aq)$ must be large so that any changes in their concentrations that occur when an acid or a base are added are small (negligible) compared with these concentrations. This means that the position of **equilibrium 1** changes very little when acid or alkali are added and the $H^+(aq)$ concentration (and pH) changes very little.

We can also understand how a buffer works in terms of the K_a expression for **equilibrium 1**:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

This can be rearranged to

$$[H^+(aq)] = \frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} \times K_a$$

Because K_a is a constant, this means that the H^+ concentration in the solution is proportional to the ratio of the ethanoic acid concentration to the ethanoate ion concentration. If both $[CH_3COO^-(aq)]$ and $[CH_3COOH(aq)]$ are large, any small changes in their concentrations that occur when an acid or a

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	$\frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$	K_a	$\frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} \times K_a$	$[H^+(aq)]$ / mol dm^{-3}	pH
Before adding HCl	1.000	1.738×10^{-5}	1.738×10^{-5}	1.738×10^{-5}	4.760
After adding HCl	1.004	1.738×10^{-5}	1.745×10^{-5}	1.745×10^{-5}	4.758

Table 19.10: Comparing the [acid] to [base] ratio in a buffer solution.

	$\frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$	K_a	$\frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} \times K_a$	$[H^+(aq)]$ / mol dm^{-3}	pH
Before adding HCl	169	1.738×10^{-5}	2.93×10^{-3}	2.93×10^{-3}	2.53
After adding HCl	257	1.738×10^{-5}	4.47×10^{-3}	4.47×10^{-3}	2.35

Table 19.11 Comparing the [acid] to [base] ratio in a non-buffer solution.

base are added have very little effect on the ratio of $[CH_3COOH(aq)]$ to $[CH_3COO^-(aq)]$ and, therefore, very little effect on $[H^+(aq)]$ and pH.

This can be illustrated by looking at an example: let us consider what happens when 1.00 cm^3 of 0.100 mol dm^{-3} HCl is added to 100.0 cm^3 of a buffer solution in which the concentrations of ethanoic acid and sodium ethanoate are both 0.500 mol dm^{-3}. The CH_3COO^- ion in the buffer reacts with H^+ from HCl to form CH_3COOH:

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

Therefore, the concentration of CH_3COOH increases slightly and that of CH_3COO^- decreases. However, because the concentrations of both CH_3COOH and CH_3COO^- are large compared with the amount of acid added, the addition of the HCl only changes the concentration of each one by about 1%. This means that the $[CH_3COOH(aq)]$ to $[CH_3COO^-(aq)]$ ratio hardly changes at all (from 1.000 to 1.004), and, to three significant figures, the pH does not change. The relevant values are given in Table 19.10.

Now consider what happens if we add the same amount of hydrochloric acid to 100 cm^3 of 0.500 mol dm^{-3} ethanoic acid. Ethanoic acid is a weak acid, and so, dissociates very little, meaning that the initial concentration of ethanoate ions in this solution is very low, at 2.94×10^{-3} mol dm^{-3}. Adding 1 cm^3 of hydrochloric acid causes this to change to 1.92×10^{-3} mol dm^{-3} – a change of about 35%. This has a significant effect on the $[CH_3COOH(aq)]$ to $[CH_3COO^-(aq)]$ ratio, and hence, on the pH, which changes by about 100 times as much as that for the buffer solution (Table 19.11).

An analogy for a buffer solution

Consider Mr A and Ms B, both of whom have $1,000,000. If Mr A gives $10 to Ms B, they both still have essentially $1,000,000 and it will make very little difference to their lifestyles (large initial amounts = very little change). Now, suppose Mr A comes across a child, C, who only has $5. If Mr A gives C $10, the amount of money C has goes up by 200%, and it will make a great deal of difference to what they can buy (small initial amount = a large change). Large concentrations of each component in a buffer solution are, therefore, essential for it to be effective at resisting changes in pH.

Link

A solution of a strong acid and its conjugate base does not make an effective buffer because the conjugate base is very weak and has no tendency to react with any acid added (see Section 19.5).

Basic buffer solutions

KEY POINT

A basic buffer solution consists of a weak base (e.g. ammonia) and the conjugate acid/salt of that weak base (e.g. the ammonium ion or an ammonium salt: ammonium chloride, ammonium nitrate, etc.).

The equilibrium in this solution is:

equilibrium 2: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

If some hydrochloric acid is added to this solution, the added H^+ reacts with NH_3 in the solution:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

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If some sodium hydroxide is added to the solution, the added OH^- reacts with NH_4^+ in the solution:

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

As discussed previously, if the concentrations of NH_3 and NH_4^+ in the solution are both high, any small change in their concentrations has very little effect on **equilibrium 2**, so the position of this equilibrium shifts very little and the value of the OH^- concentration, and hence, the pH, changes very little.

Some key points about buffer solutions

- A buffer solution does not have to contain equal amounts of the weak acid/base and its conjugate base/acid (although the buffer is most effective when the concentrations are equal).
- The pH of a buffer solution depends on the relative concentrations of the weak acid/base and its conjugate base/acid. For an acidic buffer, the relationship between pH and relative concentration is given by

  $pH = pK_a + \log_{10}([salt]/[acid])$ or
  $pH = pK_a + \log_{10}([conjugate\ base]/[acid])$

  These equations will be discussed in more detail below.
- When [conjugate base] = [acid], the pH of an acid buffer is equal to the pK_a of the weak acid.
- The pH of a buffer solution is not affected by diluting it because the ratio of [conjugate base] to [acid] stays the same.
- Diluting a buffer reduces its capacity to resist changes in pH – if the concentrations of the individual components are lower, then any slight changes in concentration will have a larger relative effect on them, and hence, on the position of equilibrium and the pH.

Let's look at this last point in a bit more detail by considering the acid buffer system with ethanoic acid and the ethanoate ion, which is governed by the following equilibrium:

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

Consider two different buffer solutions:

buffer 1: $[CH_3COOH(aq)] = [CH_3COO^-(aq)] = 0.100\ mol\ dm^{-3}$

buffer 2: $[CH_3COOH(aq)] = [CH_3COO^-(aq)] = 0.0100\ mol\ dm^{-3}$

Using the equation $pH = pK_a + \log_{10}([conjugate\ base]/[acid])$, the pH of each solution will be 4.76.

If 1.00 cm^3 of 0.100 mol dm^{-3} hydrochloric acid is added to 100 cm^3 of each solution, then the pH of **buffer 1** goes down to 4.75 but that of **buffer 2** goes down to 4.67. Adding HCl caused about a 2% change in the concentration of the components in **buffer 1** but a 9% change in the concentration of the components in **buffer 2** because the initial concentrations were lower.

How this calculation could be carried out will be shown below.

Making buffer solutions by partial neutralisation of a weak acid/base

A buffer solution can be made by partial neutralisation of a weak acid with a strong base, for example, by adding sodium hydroxide to ethanoic acid. The reaction that occurs is:

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O$

When 10 cm^3 of 0.100 mol dm^{-3} NaOH is added to 25 cm^3 of 0.100 mol dm^{-3} CH_3COOH, some of the ethanoic acid will be converted into sodium ethanoate, but there will still be some ethanoic acid left. So, the solution contains both ethanoic acid and sodium ethanoate, which are the components of a buffer system. As long as the amount in mol of sodium hydroxide added is lower than the amount of ethanoic acid present in the original solution, the solution will contain both ethanoic acid and sodium ethanoate and act as a buffer.

A buffer solution can also be made by partial neutralisation of a weak base with a strong acid, for example, when hydrochloric acid is added to ammonia solution. The reaction that occurs is:

$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

As long as the amount in mol of hydrochloric acid added is lower than the amount of ammonia in the solution, the solution will contain some NH_3 and some NH_4Cl and will act as a buffer.

WORKED EXAMPLE 19.22

Which of the following combinations would produce a buffer solution?

a 25.0 cm^3 of 0.100 mol dm^{-3} $CH_3NH_2(aq)$ and 50.0 cm^3 of 0.100 mol dm^{-3} $CH_3NH_3^+NO_3^-(aq)$

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b 25.0 cm^3 of 0.100 mol dm^{-3} HCOOH(aq) and 50.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq)

c 50.0 cm^3 of 0.100 mol dm^{-3} NH_3(aq) and 30.0 cm^3 of 0.100 mol dm^{-3} HNO_3(aq)

d 25.0 cm^3 of 0.100 mol dm^{-3} CH_3NH_2(aq) and 25.0 cm^3 of 0.100 mol dm^{-3} HCl(aq)

Answer

a would be a buffer solution because it contains a weak base (CH_3NH_2) and its salt ($CH_3NH_3^+NO_3^-$). The concentrations of each component in the buffer solution do not have to be equal.

b would not be a buffer solution. Methanoic acid (HCOOH) and sodium hydroxide react together according to the equation:

$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$

Looking at the volumes and concentrations, we can deduce that the amount in mol of NaOH added is twice the amount of methanoic acid. Because the amount of NaOH added is greater than the amount of HCOOH, all the HCOOH will react. There is no weak acid present in the solution, so it will not be a buffer solution.

c will be a buffer solution. NH_3 and HNO_3 react together according to the equation:

$NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$

The amount of HNO_3 (3.00×10^{-3} mol) that has been added is less than the amount of NH_3 (5.00×10^{-3} mol), so some of the NH_3 has been converted into its salt, but there will be some NH_3 left. The solution, therefore, contains a weak base and its salt and is a buffer solution.

d will not be a buffer solution. Methylamine and hydrochloric acid react according to the equation:

$CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3Cl(aq)$

The amount of HCl added is equal to the amount of CH_3NH_2, so all the CH_3NH_2 will react. Because there is no weak base left, the solution will not be a buffer solution.

The buffer region in pH curves

KEY POINT

The pH curves of a weak acid–strong base titration and a weak base–strong acid titration show buffer regions.

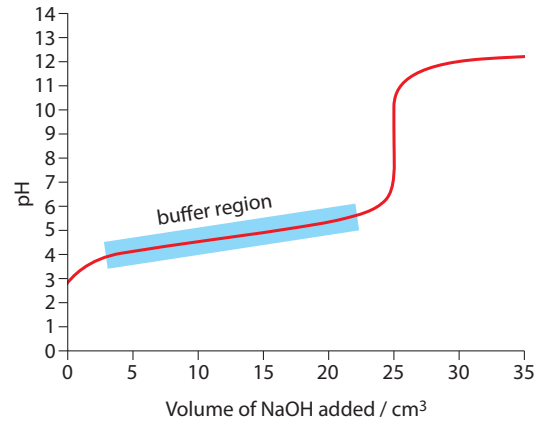

Figure 19.27: The buffer region in a weak acid–strong base titration curve.

Figure 19.27 shows the pH curve obtained when a strong base (NaOH) is added to a weak acid (ethanoic acid).

The shaded region in Figure 19.30 is called the *buffer region*. In this region, adding sodium hydroxide does not cause the pH to change very much (the curve is fairly flat) – addition of a 5 cm^3 portion of 0.10 mol dm^{-3} NaOH causes the pH to change by only about 0.4 units (adding the same volume to water would cause the pH to change by over 5 units).

As sodium hydroxide is added to ethanoic acid in the titration, some of the ethanoic acid is converted into sodium ethanoate:

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O$

Therefore, in the buffer region, significant amounts of both ethanoic acid and sodium ethanoate are present in the solution; these are the components of a buffer solution.

A buffer solution can also be made by partial neutralisation of a weak base with a strong acid, for example, when hydrochloric acid is added to ammonia solution (Figure 19.28).

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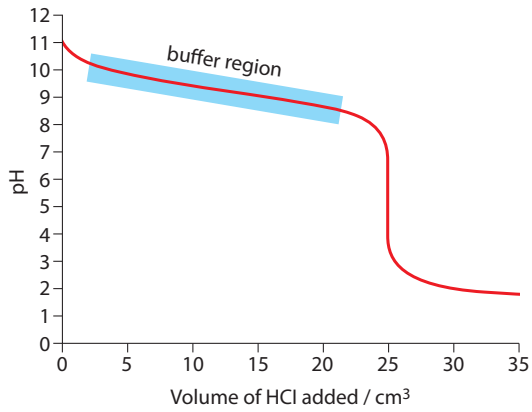

Figure 19.28: The buffering region in a strong acid–weak base titration curve.

The reaction that occurs is:

$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

As long as the amount of hydrochloric acid added is lower than the amount of ammonia in the solution, the solution will contain some NH_3 and some NH_4Cl and will act as a buffer. When the amount of HCl added gets very close to the amount of NH_3 originally present (close to the equivalence point), there will be very little NH_3 left in the solution, and it will lose its effectiveness as a buffer (the curve becomes steeper).

How to calculate the pH of a buffer solution

WORKED EXAMPLE 19.23

Calculate the pH of a solution containing 0.200 mol dm^{-3} ethanoic acid ($pK_a = 4.76$) and 0.250 mol dm^{-3} sodium ethanoate.

Answer

This is an acid buffer and the equilibrium that exists in this solution is just the acid dissociation equilibrium:

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

K_a for this equilibrium is given by: $K_a = \dfrac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$

Sodium ethanoate is a salt and, therefore, breaks apart completely into its ions in aqueous solution. The concentration of ethanoate ions is, therefore, the same as that of sodium ethanoate, that is, 0.250 mol dm^{-3}.

We will make the approximation that the equilibrium concentrations of ethanoic acid and the ethanoate ion are the same as their initial concentrations. This is a reasonable assumption, as the dissociation of ethanoic acid in pure water is very low and, therefore, the dissociation is going to be even lower if some CH_3COO^- is already present (Le Chatelier's principle – the position of the dissociation equilibrium shifts even more to the left if CH_3COO^- is added).

$K_a = 10^{-pK_a}$ therefore $K_a = 10^{-4.76} = 1.74 \times 10^{-5}$

We can now substitute values into the K_a expression: $1.74 \times 10^{-5} = \dfrac{0.250 \times [H^+(aq)]}{0.200}$

Rearranging this we get: $[H^+(aq)] = 1.39 \times 10^{-5}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(1.39 \times 10^{-5}) = 4.86$

Therefore, the pH of this buffer solution is 4.86.

The calculation here uses the same method as we used in Worked Example 19.15 to determine the pH of ethanoic acid. The only difference here is that $[CH_3COO^-(aq)] \neq [H^+(aq)]$.

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The Henderson–Hasselbalch equation

The pH of a buffer can also be worked out by using the Henderson–Hasselbalch equation:

$pH = pK_a + \log_{10}([salt]/[acid])$ or
$pH = pK_a + \log_{10}([conjugate\ base]/[acid])$

Remember that the salt provides the conjugate base, and, therefore, [salt] ≡ [conjugate base].

The Henderson–Hasselbalch equation is derived from the K_a expression for a weak acid.

EXAM TIP

The equation is a quick and easy way of solving problems involving buffers but must be remembered correctly!

If you are ever unsure which is the conjugate base and which is the acid, the acid will be the one with one more H (actually H^+). For example, in a buffer made from $H_2PO_4^-$ and HPO_4^{2-}, $H_2PO_4^-$ is the acid as it has an extra H.

WORKED EXAMPLE 19.24

Calculate the pH of a buffer solution containing 0.550 mol dm^{-3} propanoic acid and 0.450 mol dm^{-3} sodium propanoate. The pK_a for propanoic acid is 4.87.

Answer

[salt] = 0.450 mol dm^{-3}, [acid] = 0.550 mol dm^{-3}

$pH = pK_a + \log_{10}([salt]/[acid])$

$pH = 4.87 + \log_{10}(0.450/0.550) = 4.87 + \log_{10}0.818 = 4.78$

Therefore, the pH of this buffer solution is 4.78.

Calculating the pH of a basic buffer solution

WORKED EXAMPLE 19.25

Calculate the pH of a solution containing 0.400 mol dm^{-3} ammonia ($pK_b = 4.75$) and 0.200 mol dm^{-3} ammonium chloride.

Answer

We will follow the same procedure as that for working out the pH of a weak base, B, described in Worked Example 19.18, except $[OH^-(aq)] \neq [BH^+(aq)]$.

$K_b = 10^{-4.75} = 1.78 \times 10^{-5}$

The expression for the ionisation of the base is: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

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Again, making the approximation that the ionisation of the base does not cause any change in the concentration of the base or the conjugate acid, we can put values into the K_b expression:

$$1.75 \times 10^{-5} = \frac{0.200 \times [OH^-(aq)]}{0.400}$$

Rearranging, we get $[OH^-(aq)] = 3.56 \times 10^{-5}$ mol dm^{-3}

$pOH = -\log_{10} [OH^-(aq)] = 4.45$

At 25 °C: pH + pOH = 14 i.e., pH = 9.55.

This can also be worked out using an equation similar to the Henderson–Hasselbalch equation:

$pH = pK_w - pK_b + \log_{10}([base]/[salt])$

or $pH = pK_w - pK_b + \log_{10}([base]/[conjugate\ acid])$

Calculating the pH of a buffer solution when volumes rather than overall concentrations are given

WORKED EXAMPLE 19.26

A buffer solution is formed when 30.0 cm^3 of 1.00 mol dm^{-3} ethanoic acid ($pK_a = 4.76$) is added to 40.0 cm^3 of 1.10 mol dm^{-3} sodium ethanoate. Calculate the pH of the buffer solution.

Answer

We cannot simply put the concentrations we have been given into the K_a expression because mixing together the solutions causes their concentrations to change. To calculate the concentration of ethanoic acid in the buffer:

30.0 cm^3 of 1.00 mol dm^{-3} ethanoic acid contains $\frac{30.0}{1000} \times 1.00 = 0.0300$ mol.

This amount is now present in 70.0 cm^3 instead of 30.0 cm^3, so the concentration is

$$\frac{0.0300}{(70.0 / 1000)} = 0.429 \text{ mol dm}^{-3}$$

The concentrations can also be worked out using the equation for dilutions that we met in Chapter 4:

$$C_{dil} = \frac{V_{und}}{V_{dil}} \times C_{und}$$

So, for sodium ethanoate we have:

$$\text{concentration of sodium ethanoate} = \frac{40.0}{70.0} \times 1.10 = 0.629 \text{ mol dm}^{-3}$$

The rest of the process for working out the pH of the buffer is exactly the same as above, i.e.,

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

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

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CONTINUED

$K_a = 10^{-pK_a} = 1.74 \times 10^{-5}$

Substituting into the K_a expression:

$$1.74 \times 10^{-5} = \frac{0.629 \times [H^+(aq)]}{0.429}$$

Rearranging this, we get:

$[H^+(aq)] = 1.19 \times 10^{-5}$ mol dm^{-3}

$pH = -\log_{10}[H^+(aq)] = -\log_{10}(1.19 \times 10^{-5}) = 4.93$

Therefore, the pH of this buffer solution is 4.93.

Determining the composition of a buffer solution given its pH

WORKED EXAMPLE 19.27

Determine the ratio of the concentration of ammonium chloride to ammonia in a buffer of pH 9.00 at 25 °C. pK_b for ammonia is 4.75.

Answer

The expression for the ionisation of the base is: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

$K_b = 10^{-4.75} = 1.78 \times 10^{-5}$

pH = 9.00 so, at 25 °C, pOH = 14 – 9.00 = 5.00

$[OH^-(aq)] = 10^{-pOH}$ so, $[OH^-(aq)] = 1.00 \times 10^{-5}$ mol dm^{-3}

Substituting the known values into the expression for K_b, we get

$$1.78 \times 10^{-5} = \frac{[NH_4^+(aq)] \times 1.00 \times 10^{-5}}{[NH_3(aq)]}$$

Rearranging, we get

$$\frac{[NH_4^+(aq)]}{[NH_3(aq)]} = \frac{1.78 \times 10^{-5}}{1.00 \times 10^{-5}} = 1.78$$

Therefore, to produce a buffer of pH 9.00, the ratio of the ammonium chloride concentration to the ammonia concentration must be 1.78 : 1.00.

If we were mixing solutions of equal concentrations, then we would use 1.78 cm^3 of ammonium chloride solution for every 1.00 cm^3 of ammonia solution to achieve this ratio. If the solutions were not of equal concentrations, you would have to do a calculation (working out numbers of moles) to determine how much of each solution to add.

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CONTINUED

The last calculation could have been carried out more rapidly using the equation:

$pH = pK_w - pK_b + \log_{10}([base]/[salt])$

$[salt] = [NH_4Cl] \quad [base] = [NH_3]$

$9.00 = 14 - 4.75 - \log_{10}([NH_3]/[NH_4Cl])$

Rearranging this, we get

$\log_{10}([NH_3]/[NH_4Cl]) = 0.25$

therefore, $\frac{[NH_3]}{[NH_4Cl]} = -10^{-0.25} = 0.562$

Therefore,

$\frac{[NH_4Cl]}{[NH_3]} = \frac{1}{0.562} = 1.78$

WORKED EXAMPLE 19.28

What mass of solid sodium ethanoate must be dissolved in 100.0 cm^3 of 0.200 mol dm^{-3} ethanoic acid to produce a buffer of pH = 4.00? Assume there is no change in volume when sodium ethanoate is added. The pK_a for ethanoic acid is 4.76.

Answer

$[H^+(aq)] = 10^{-pH} = 10^{-4.00} = 1.00 \times 10^{-4}$ mol dm^{-3}

$K_a = 10^{-pK_a} = 10^{-4.76} = 1.74 \times 10^{-5}$

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

$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$

$1.74 \times 10^{-5} = \frac{[CH_3COO^-] \times 1.00 \times 10^{-4}}{0.200}$

Rearranging this, we get

$[CH_3COO^-(aq)] = 0.0348$ mol dm^{-3}

Therefore, the concentration of sodium ethanoate in the solution must be 0.0348 mol dm^{-3}.

We are making up 100 cm^3 of buffer solution; therefore, the amount of sodium ethanoate that must be used is given by

amount = concentration × volume (in dm^3) $= 0.0348 \times \frac{100.0}{1000} = 0.00348$ mol

The molar mass of sodium ethanoate is 82.04 g mol^{-1}.

Therefore, the mass of 0.00348 mol is

mass = amount × molar mass = 0.00348 × 82.04 = 0.285 g

Therefore, 0.285 g of sodium ethanoate must be dissolved in ethanoic acid to produce a buffer of pH = 4.00.

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CONTINUED

The first part could also have been done using the Henderson–Hasselbalch equation:

$pH = pK_a + \log_{10}([salt]/[acid])$

Substituting in the known values, we get

$4.00 = 4.76 + \log_{10}([CH_3COONa(aq)]/0.200)$

$\log_{10}([CH_3COONa(aq)]/0.200) = -0.76$

$[CH_3COONa(aq)]/0.200 = 10^{-0.76} = 0.174$

$[CH_3COONa(aq)] = 0.0348 \text{ mol dm}^{-3}$

Calculating the change in pH of a buffer solution when acid or alkali are added

WORKED EXAMPLE 19.29

a Calculate the pH of a buffer solution containing 0.750 mol dm^{-3} ethanoic acid ($pK_a = 4.76$) and 0.750 mol dm^{-3} sodium ethanoate.

b By how much does the pH change when 10.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid is added to 50.0 cm^3 of the buffer solution in **a**?

Answer

a The Henderson–Hasselbalch equation is

$pH = pK_a + \log_{10}([salt]/[acid])$

When [salt] = [acid], $pH = pK_a$, so we can see here that the pH of the solution is 4.76.

b When acid is added to the buffer, the following reaction occurs:

$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$

This means that the concentration of ethanoate ions decreases and the concentration of ethanoic acid increases. To work out by how much they change, we need to calculate the initial amount in mol of CH_3COO^- and CH_3COOH and what amount of acid was added.

The amount of ethanoic acid in 50.0 cm^3 of 0.750 mol dm^{-3} solution is given by

amount = concentration × volume in dm^3

$$\text{amount} = 0.750 \times \left(\frac{50.0}{1000}\right) = 0.0375 \text{ mol}$$

This is the same as the amount in mol of ethanoate ions.

The amount of hydrochloric acid in 10.0 cm^3 of 0.100 mol dm^{-3} solution is

$$\text{amount} = 0.100 \times \left(\frac{10.0}{1000}\right) = 1.00 \times 10^{-3} \text{ mol}$$

We will assume that H^+ from hydrochloric acid reacts with the equivalent amount of CH_3COO^- and that there is no further change in the amounts as equilibrium is established.

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The amount of CH_3COO^- thus decreases by 1.00×10^{-3} mol and the amount of CH_3COOH increases by 1.00×10^{-3} mol.

	$CH_3COO^-(aq)$	$CH_3COOH(aq)$
initial amount / mol	0.0375	0.0375
amount after HCl added / mol	$0.0375 - 1.00 \times 10^{-3}$	$0.0375 + 1.00 \times 10^{-3}$
amount / mol	0.0365	0.0385

The concentration of each species can now be worked out by dividing the amounts by the total volume in dm^3. Total volume = 50.0 + 10.0 = 60.0 cm^3 = 0.0600 dm^3

	$CH_3COO^-(aq)$	$CH_3COOH(aq)$
concentration after HCl added / mol dm^{-3}	0.0365 / 0.0600	0.385 / 0.0600
concentration / mol dm^{-3}	0.608	0.642

$pH = pK_a + \log_{10}([\text{conjugate base}]/[\text{acid}]) = 4.76 + \log_{10}(0.608/0.642) = 4.74$

The original pH was 4.76, therefore, upon addition of 10.0 cm^3 of the hydrochloric acid, the pH of the solution drops by 0.02 to 4.74.

EXAM TIP

When [conjugate base (salt)] = [acid], the pH of an acidic buffer is equal to the pK_a of the acid.

TEST YOUR UNDERSTANDING

69 State whether or not each of the following mixtures would constitute a buffer solution:

- **a** 50 cm^3 0.100 mol dm^{-3} $CH_3COOH(aq)$ and 25 cm^3 0.100 mol dm^{-3} $CH_3COONa(aq)$
- **b** 50 cm^3 0.100 mol dm^{-3} $CH_3CH_2COOH(aq)$ and 50 cm^3 0.100 mol dm^{-3} NaOH(aq)
- **c** 50 cm^3 0.100 mol dm^{-3} HCOOH(aq) and 75 cm^3 0.100 mol dm^{-3} NaOH(aq)
- **d** 25 cm^3 0.010 mol dm^{-3} NaOH(aq) and 25 cm^3 0.020 mol dm^{-3} $CH_3COOH(aq)$
- **e** 50 cm^3 0.200 mol dm^{-3} HCl(aq) and 25 cm^3 0.400 mol dm^{-3} NaCl(aq)
- **f** 50 cm^3 0.100 mol dm^{-3} $NH_3(aq)$ and 50 cm^3 0.100 mol dm^{-3} $NH_4NO_3(aq)$
- **g** 50 cm^3 0.100 mol dm^{-3} $NH_3(aq)$ and 25 cm^3 0.100 mol dm^{-3} HCl(aq).

70 Calculate the pH of buffers made from propanoic acid (pK_a = 4.87), $CH_3CH_2COOH(aq)$, and sodium propanoate, $CH_3CH_2COONa(aq)$.

- **a** $[CH_3CH_2COOH(aq)] = 0.800$ mol dm^{-3}
  $[CH_3CH_2COONa(aq)] = 0.800$ mol dm^{-3}
- **b** $[CH_3CH_2COOH(aq)] = 0.500$ mol dm^{-3}
  $[CH_3CH_2COONa(aq)] = 0.600$ mol dm^{-3}
- **c** $[CH_3CH_2COOH(aq)] = 1.00$ mol dm^{-3}
  $[CH_3CH_2COONa(aq)] = 0.700$ mol dm^{-3}

71 Calculate the pH of buffers made from methylamine (pK_b = 3.34), $CH_3NH_2(aq)$, and methylammonium chloride, $CH_3NH_3Cl(aq)$.

- **a** $[CH_3NH_2(aq)] = 0.500$ mol dm^{-3}
  $[CH_3NH_3Cl(aq)] = 0.500$ mol dm^{-3}

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CONTINUED

b $[CH_3NH_2(aq)] = 0.400$ mol dm^{-3}

$[CH_3NH_3Cl(aq)] = 0.600$ mol dm^{-3}

c $[CH_3NH_2(aq)] = 0.750$ mol dm^{-3}

$[CH_3NH_3Cl(aq)] = 0.500$ mol dm^{-3}

72 HA is a weak acid and NaA is its salt. Calculate the pH of the buffer formed when the following solutions are mixed:

a 50.0 cm^3 of 1.00 mol dm^{-3} HA ($pK_a = 5.00$) and 50.0 cm^3 of 1.00 mol dm^{-3} NaA

b 50.0 cm^3 of 1.00 mol dm^{-3} HA ($pK_a = 5.00$) and 50.0 cm^3 of 0.900 mol dm^{-3} NaA

c 25.0 cm^3 of 0.500 mol dm^{-3} HA ($pK_a = 4.60$) and 40.0 cm^3 of 0.800 mol dm^{-3} NaA

d 100.0 cm^3 of 0.645 mol dm^{-3} HA ($pK_a = 6.32$) and 80.0 cm^3 of 0.560 mol dm^{-3} NaA.

73 B is a weak base and BHCl is its salt. Calculate the pH of the buffer formed when the following solutions are mixed:

a 40.0 cm^3 of 1.00 mol dm^{-3} B ($pK_b = 4.00$) and 60.0 cm^3 of 1.00 mol dm^{-3} BHCl

b 60.0 cm^3 of 1.00 mol dm^{-3} B ($pK_b = 4.00$) and 40.0 cm^3 of 1.00 mol dm^{-3} BHCl

c 30.0 cm^3 of 0.728 mol dm^{-3} B ($pK_b = 3.80$) and 50.0 cm^3 of 0.640 mol dm^{-3} BHCl

d 200.0 cm^3 of 0.510 mol dm^{-3} B ($pK_b = 5.27$) and 150.0 cm^3 of 0.420 mol dm^{-3} BHCl.

74 HA is a weak acid and NaA is its salt. Calculate the ratio of NaA(aq) : HA(aq) in each of the buffers:

a HA $pK_a = 5.00$, pH of buffer = 5.00

b HA $pK_a = 4.60$, pH of buffer = 5.00

c HA $pK_a = 5.20$, pH of buffer = 4.80.

75 B is a weak base and BHCl is its salt. Calculate the volume of 0.100 mol dm^{-3} BHCl(aq) that must be mixed with 100.0 cm^3 of 0.100 mol dm^{-3} B(aq) to produce a buffer with the stated concentration.

a B $pK_b = 4.20$, pH of buffer = 9.80

b B $pK_b = 4.80$, pH of buffer = 9.50

c B $pK_b = 4.50$, pH of buffer = 9.10

76 Calculate the mass of sodium methanoate (HCOONa) that must be dissolved in 100.0 cm^3 of 0.500 mol dm^{-3} methanoic acid ($pK_a = 3.75$) to produce a buffer of the required pH.

a pH of buffer = 3.75

b pH of buffer = 4.00

c pH of buffer = 3.65

77 Calculate the mass of ammonium chloride that must be dissolved in 50.0 cm^3 of 0.200 mol dm^{-3} ammonia solution ($pK_b = 4.75$) to produce a buffer of the required pH.

a pH of buffer = 9.25

b pH of buffer = 10.00

c pH of buffer = 9.00

78 100.0 cm^3 of distilled water is added to 100.0 cm^3 of an ethanoic acid/sodium ethanoate buffer of pH = 5.00. What is the pH of the solution obtained?

79 A buffer contains 0.500 mol dm^{-3} ethanoic acid ($pK_a = 4.76$) and 0.500 mol dm^{-3} sodium ethanoate.

In each case, work out by how much the pH of the buffer changes when acid or alkali is added to 100.0 cm^3 of the buffer.

a 10.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid is added

b 20.0 cm^3 of 0.200 mol dm^{-3} hydrochloric acid is added

c 10.0 cm^3 of 0.100 mol dm^{-3} sodium hydroxide solution is added

d 5.0 cm^3 of 0.500 mol dm^{-3} sodium hydroxide solution is added

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain that acids react with bases in neutralisation reactions	19.2			
explain the Brønsted–Lowry definition of acids and bases	19.3			
explain what pH is and calculate pH and $[H^+(aq)]$	19.4			
explain that water dissociates and relate $[H^+(aq)]$ and $[OH^-(aq)]$ to acidity and basicity	19.6			
distinguish between strong and weak acids and bases	19.5			
explain the form of a pH curve for a strong acid–strong base titration	19.8			
explain what pOH is and use it in calculations	19.9			
explain the connection between the values of K_a, K_b, pK_a and pK_b and the strengths of acids and bases	19.10			
solve problems using K_a, K_b, pK_a and pK_b	19.10			
explain the connection between K_a and K_b for a conjugate acid–base pair	19.10			
predict the pH of a salt solution	19.11			
sketch and explain pH curves	19.11			
explain how acid–base indicators work and predict a suitable indicator for a titration	19.11			
explain what a buffer solution is and how they work	19.12			
solve problems involving buffer solutions.	19.12			

REFLECTION

- How well do you understand the concepts in this topic?
- pH is referred to in everyday life; do you feel you could explain it to someone with little scientific knowledge?
- Do you feel confident with all the different types of calculation?
- Could you write some questions, with answers, for another student and get them to do the same for you?
- Do you find writing questions a useful learning tool?
- Do you need to go through any sections again?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 20

Electron transfer reactions

LEARNING OBJECTIVES

In this chapter you will:

- understand redox reactions in terms of electron transfer and changes in oxidation state
- write half-equations for oxidation and reduction reactions
- construct equations for redox reactions
- interpret data regarding displacement reactions
- understand the reactions that occur in a voltaic cell
- understand how rechargeable batteries work
- understand electrolysis of molten salts
- describe the oxidation of alcohols and aldehydes
- describe the reduction of aldehydes, ketones and carboxylic acids
- describe the reduction of unsaturated compounds

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- understand what a standard electrode potential is
- use standard electrode potentials to calculate cell potentials
- understand the connection between the standard Gibbs energy change and standard electrode potentials
- solve problems involving $\Delta G^{\ominus}$ and $E^{\ominus}$
- understand the reactions that occur when aqueous solutions are electrolysed.
- understand how electroplating works

GUIDING QUESTIONS

- What is a redox reaction?
- What happens when electrons are transferred between substances?

Introduction

Redox reactions are ones that involve oxidation and reduction. These are extremely common reactions and, as you read this text, they are occurring all around you and inside you. Redox reactions are fundamental to life – these are the reactions of many energy conversions on Earth. It all starts with the redox reactions of photosynthesis, by which plants convert energy from the sun to chemical energy. This energy can then be released again by the redox reactions that occur in our bodies as food is processed. Combustion reactions are redox reactions and, when we burn fossil fuels, such as coal, oil and gas, we are releasing the energy that was stored during photosynthesis millions of years ago. This energy can then be converted into electrical energy and used to charge our laptops and mobile phones, where the reactions in the batteries also involve redox (Figure 20.1)

Figure 20.1: Redox reactions power your phones – in the batteries, a redox reaction occurs as chemical energy is converted into electrical energy.

20.1 Redox reactions

KEY POINT

A redox reaction is one that involves both oxidation and reduction.

Definitions of oxidation and reduction

Oxidation and reduction may be defined in various ways.

Oxidation and reduction in terms of loss/gain of hydrogen/oxygen

KEY POINTS

Oxidation is the loss of hydrogen or the gain of oxygen.

Reduction is the gain of hydrogen or the loss of oxygen.

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For instance, in the equation:
$CuO + Mg \rightarrow MgO + Cu$

EXAM TIP

Be careful with the wording of your answers. You could also state that the Cu in CuO is reduced, but do not just state that 'Cu is reduced', because Cu is one of the products.

CuO is reduced in this reaction because it loses oxygen, and Mg is oxidised because it gains oxygen.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

NH_3 is oxidised because it loses hydrogen and gains oxygen, whereas O_2 gets reduced because it gains hydrogen.

These definitions are, however, only useful in a limited number of reactions and can cause confusion, for example, the reaction between sodium hydroxide and hydrochloric acid:

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

is not a redox reaction, despite the fact that HCl has lost H and OH has gained H.

Oxidation and reduction in terms of electron transfer

KEY POINTS

Oxidation is loss of electrons.

Reduction is gain of electrons.

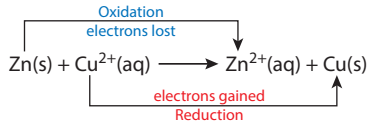
This can be remembered using the mnemonic:

O xidation
I s
L oss of electrons
R eduction
I s
G ain of electrons

The reaction between zinc and copper(II) sulfate is a redox reaction:

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

The loss/gain of electrons is more easily seen if the reaction is written as an ionic equation:



Zn has been oxidised to Zn^{2+}, because it has lost electrons, and Cu^{2+} has been reduced to Cu, because it has gained electrons.

If something loses electrons, something else must gain them, so oxidation and reduction always occur together – if something is oxidised, something else must be reduced.

Although it is fairly easy to understand which species has been oxidised and which reduced in ionic equations such as this, it is more difficult to see where electrons are being transferred in redox reactions, such as $PCl_3 + Cl_2 \rightarrow PCl_5$. To discuss reactions such as these in terms of oxidation and reduction, we use oxidation states (oxidation numbers).

Oxidation and reduction in terms of oxidation states

How to work out oxidation states was explained in Chapter 10, but if you are unsure about whether you understand how to assign these, have a go at the first of the Test Your Understanding questions at the end of this section before proceeding.

If an atom gains electrons, its oxidation state becomes more negative. If an atom loses electrons, its oxidation state increases (becomes more positive).

KEY POINTS

Reduction is a decrease in oxidation state.

Oxidation is an increase in oxidation state.

We can work out which species is oxidised or reduced in a redox reaction by analysing the oxidation states of the substances involved in the reaction. Let us look again at:

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

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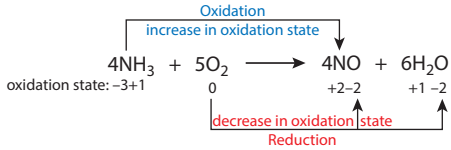
Remember that the oxidation state of atoms in an element is zero and, in most compounds, we can assume that the oxidation state of O is –2 and that of H is +1, so we can assign oxidation states:



Ammonia is oxidised because the oxidation state of nitrogen increases (from –3 to +2) and oxygen is reduced because the oxidation state decreases (from 0 to –2).

EXAM TIP

Remember, oxidation states are written with the sign first, e.g., –2, but a charge is written with the number first, e.g., 2–.

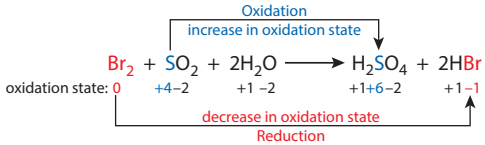
WORKED EXAMPLE 20.1

Deduce which species is oxidised and which is reduced in the equation:

$Br_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$

Answer

The first step is to assign oxidation states according to the set of rules in Section 10.5:



Br_2 is reduced because its oxidation state decreases from 0 to –1. The sulfur in SO_2 is oxidised because its oxidation state increases from +4 to +6. We would usually just say that SO_2 is oxidised.

WORKED EXAMPLE 20.2

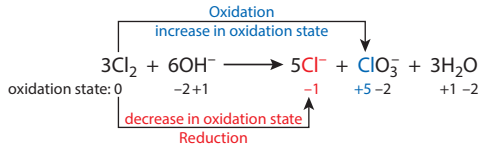
Deduce which species is oxidised and which is reduced in the following equation:

$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

CONTINUED

Answer

Again, we start by assigning oxidation states. Remember that the oxidation state of an ion, such as Cl^-, is just the charge but with the sign and number written the other way round, that is, –1. The sum of the oxidation states in an ion must add up to the overall charge; therefore, in ClO_3^-, we have $+5 + (3 \times -2) = 1-$.



In this reaction, five chlorine atoms have been reduced (oxidation state changes from 0 to –1), but one has been oxidised (oxidation state changes from 0 to +5). Therefore, Cl_2 has been oxidised and reduced. This type of reaction, in which the same species has been both oxidised and reduced, is called a *disproportionation reaction*.

EXAM TIP

You do not need to know the word *disproportionation* but should be aware that the same species can be oxidised and reduced in a redox reaction.

WORKED EXAMPLE 20.3

Deduce whether the following reaction is a redox reaction:

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$

Answer

If we assign oxidation states, we get

	$Cr_2O_7^{2-}$	H_2O	CrO_4^{2-}	H^+
oxidation states	+6 –2	+1 –2	+6 –2	+1

The oxidation state of Cr on both sides of the equation is +6, and no other atom undergoes a change in oxidation state. This reaction is, therefore, not a redox reaction, because no atoms undergo a change in oxidation state.

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KEY POINT

For a reaction to be a redox reaction, it must involve a change in oxidation states.

Variable oxidation states and names

We have already met (Chapter 10) the concept that most main group non-metals and transition metals show variable oxidation states, and the previous examples illustrate this. Because of this variation, we often include the oxidation state in Roman numerals to distinguish between different compounds (Table 20.1).

Molecule/ion	Oxidation state of 'central atom'	Name
SO_2	+4	sulfur(IV) oxide
H_2SO_4	+6	sulfuric(VI) acid
$Cr_2O_7^{2-}$	+6	dichromate(VI) ion
Cr^{3+}	+3	chromium(III) ion

Table 20.1: Main group non-metals and transition metals show variable oxidation states and are named using the oxidation state. The 'central atom', in this case, means the atom that is not oxygen or hydrogen in the molecule/ion.

EXAM TIP

Although you need to know how to name substances using oxidation states, it is still acceptable to use their more common names – like sulfur dioxide for SO_2 and sulfuric acid for H_2SO_4.

Link

Oxidation states are extremely useful for keeping track of the movement of electrons between atoms in redox reactions, but it must be remembered that it is a purely formal concept, which assumes that all compounds are ionic and assigns charges accordingly. In covalently bonded compounds, the oxidation states do not represent the actual charges on atoms, for example, the charge on the S atom in H_2SO_4 is definitely not 6+!

NATURE OF SCIENCE

Defining oxidation and reduction

Scientific knowledge is constantly changing and evolving and, wherever possible, scientists aim to make models/theories as fundamental and all-encompassing as possible. The original idea of defining oxidation and reduction in terms of oxygen and hydrogen has been broadened to include other reactions. The model of oxidation and reduction in terms of electrons is more fundamental than that in terms of oxygen/hydrogen loss/gain.

Oxidising and reducing agents

All redox reactions involve an oxidising agent reacting with a reducing agent.

KEY POINTS

Oxidising agents (oxidants) oxidise other species and, in the process, are themselves reduced. An oxidising agent takes electrons away from something.

Reducing agents (reductants) reduce other species and, in the process, are themselves oxidised. A reducing agent gives electrons to something.

Consider again the ionic equation for the reaction between zinc and copper(II) sulfate:

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

In this reaction, two electrons are transferred from Zn as it gets oxidised:

$$Zn(s) \longrightarrow Zn^{2+}(aq) \quad \text{Oxidation}$$
$$2e^- \text{ transferred}$$
$$Cu^{2+}(aq) \longrightarrow Cu(s) \quad \text{Reduction}$$

The two electrons cause the Cu^{2+} ion to be reduced. Zn is, therefore, the reducing agent – it reduces Cu^{2+} by donating electrons to it. In the process, Zn has lost electrons and has, therefore, been oxidised.

Cu^{2+} is the oxidising agent because it takes two electrons from Zn, thus oxidising it. In the process, Cu^{2+} gains electrons and has, therefore, been reduced.

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WORKED EXAMPLE 20.4

Deduce which is the oxidising agent and which is the reducing agent in the reaction:

$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$

Answer

Cl_2 is the oxidising agent because it oxidises Br^- to Br_2. In terms of electrons, Cl_2 removes electrons from the bromide ions, oxidising them. In the process, Cl_2 has gained electrons and has been reduced – the oxidising agent is always the species that gets reduced.

Br^- in this reaction causes Cl_2 to be reduced by giving electrons to it to form Cl^- – Br^- acts as a reducing agent in this reaction. The Br^- ions have lost electrons and been oxidised – the reducing agent is always the species that gets oxidised.

Link

We met this reaction in Chapter 10. The solution would become orange as bromine is formed.

WORKED EXAMPLE 20.5

Deduce which is the oxidising agent and which is the reducing agent in the reaction:

$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

If we put in the key oxidation states:

$$\underset{+6}{Cr_2O_7^{2-}}(aq) + \underset{+2}{6Fe^{2+}}(aq) + 14H^+(aq) \rightarrow \underset{+3}{2Cr^{3+}}(aq) + \underset{+3}{6Fe^{3+}}(aq) + 7H_2O(l)$$

Fe^{2+} is oxidised in the reaction; therefore, Fe^{2+} is the reducing agent – the reducing agent always gets oxidised. $Cr_2O_7^{2-}$ is the oxidising agent because it has been reduced in the reaction – the oxidising agent always gets reduced. In terms of electrons, $Cr_2O_7^{2-}$ oxidises the Fe^{2+} ions by taking an electron away from each one and the Fe^{2+} ions reduce the $Cr_2O_7^{2-}$ ion by donating electrons to it.

EXAM TIP

You must state the complete species when describing oxidising or reducing agents. For example, the oxidising agent here is $Cr_2O_7^{2-}$, not Cr.

TEST YOUR UNDERSTANDING

1 Determine the oxidation states of all elements in the following species:

N_2	CO_2	Cl_2O	PO_4^{3-}	HCl	$HClO_3$	ClO_4^-	C_2H_3Cl	$C_6H_{12}O_6$
Ca	Na_2CrO_4	$K_2Cr_2O_7$	Na_2O_2	Na_2SO_4	LiH	$LiAlH_4$	$(NH_4)_2SO_4$	NH_4NO_3

2 Name the following molecules/ions/compounds using oxidation states:

SO_2	SO_3	$Cr_2O_7^{2-}$	$FeCl_2$	$CuSO_4$	$KMnO_4$	$NaClO_4$	Cu_2O	$Fe_2(SO_4)_3$

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CONTINUED

3 State which of the following reactions are redox reactions. For each redox reaction, identify the species that has been oxidised and the species that has been reduced.

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

b $2ZnS + 3O_2 \rightarrow 2ZnO + SO_2$

c $Na + 2H_2O \rightarrow 2NaOH + H_2$

d $SO_3 + H_2O \rightarrow H_2SO_4$

e $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

f $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

g $2KNO_3 \rightarrow 2KNO_2 + O_2$

h $2I^- + H^+ + HOCl \rightarrow I_2 + H_2O + Cl^-$

4 In each of the following redox reactions, identify the oxidising agent and the reducing agent:

a $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

b $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

c $I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$

d $S + 6HNO_3 \rightarrow 2H_2O + H_2SO_4 + 6NO_2$

e $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

f $2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 10CO_2 + K_2SO_4 + 5Na_2SO_4 + 8H_2O$

g $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$

20.2 Redox equations

Half-equations

A redox equation may be broken down into two half-equations. These half-equations show the oxidation and reduction processes separately. The overall redox equation never contains electrons, but half-equations always show the electrons that are lost or gained in the redox reaction. For instance, from the following redox equation:

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

we get the two half-equations:

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

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

For the reaction:

$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

we get

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

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

The redox equation

$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

separates into half-equations as:

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

oxidation: $6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$

This second half-equation can be simplified to

oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

It can be seen that all these half-equations balance, both in terms of number of atoms on both sides and the total charge on both sides. This must be true for all half-equations.

Balancing half-equations in neutral solution

Half-equations must balance in terms of the number of atoms on both sides and in terms of the total charge on both sides. In some cases, it is very straightforward to balance half-equations, and electrons can simply be added to one side or the other.

For example, consider the unbalanced half-equation:

$Ni^{2+} \rightarrow Ni$

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Although the number of nickel atoms on each side is the same, the total charge on the left-hand side is 2+, but the total charge on the right-hand side is 0. To balance the charges, we must add $2e^-$ to the left-hand side:

$Ni^{2+} + 2e^- \rightarrow Ni$

Now the number of atoms and the charges balance on each side and the half-equation is balanced.

Now, let us look at another unbalanced half-equation:

$Br_2 \rightarrow Br^-$

In this example, neither the number of atoms nor the total charge balance. Firstly, we balance the atoms, to get:

$Br_2 \rightarrow 2Br^-$

The total charge on the left-hand side is 0, but that on the right-hand side is 2–. To balance the charges, we need to add $2e^-$ to the left-hand side so that the charge is equal on both sides:

$Br_2 + 2e^- \rightarrow 2Br^-$

This is now balanced.

These were fairly straightforward examples, but the process becomes a bit more difficult in some cases – we will now consider balancing more complex half-equations for reactions in acidic solution.

Balancing half-equations in acidic solution

The following procedure should be followed for balancing half–equations.

1. Balance all atoms except H and O.
2. Add H_2O to the side deficient in O to balance O.
3. Add H^+ to the side deficient in H to balance H.
4. Add e^- to the side deficient in negative charge to balance charge.

WORKED EXAMPLE 20.6

Balance the following half-equation, which occurs in acidic solution:

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Answer

1. Balance all atoms, except H and O – the Cr atoms must be balanced:

   $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

2. Add H_2O to the side deficient in O to balance O – there are 7 O atoms on the left-hand side and none on the right-hand side, so $7H_2O$ must be added to the right-hand side:

   $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

3. Add H^+ to the side deficient in H to balance H – there are 14 H atoms on the right-hand side but none on the left-hand side, so $14H^+$ must be added to the left-hand side:

   $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

4. Add e^- to the side deficient in negative charge to balance the charge.

   The total charge on the left-hand side is 2– + 14+ = 12+, and the total charge on the right-hand side is $2 \times 3+ = 6+$, so $6e^-$ must be added to the left-hand side to balance the charges:

   $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

   The total charge on the left-hand side is now 2– + 14+ + 6– = 6+, which is equal to the total charge on the right-hand side.

   As a final check, you should make sure that the total number of atoms and total charge on each side are, indeed, equal.

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WORKED EXAMPLE 20.7

Balance the following half-equation, which occurs in acidic solution:

$S_4O_6^{2-} + H_2O \rightarrow H_2SO_3 + H^+ + e^-$

Answer

In this case, H_2O, H^+ and e^- have already been included on their correct sides. However, the overall process of balancing the equation is the same.

1 There are four S atoms on the left-hand side but only one on the right-hand side, so H_2SO_3 must be multiplied by 4:

$S_4O_6^{2-} + H_2O \rightarrow 4H_2SO_3 + H^+ + e^-$

There are now 4 S atoms on each side.

2 There are 7 O atoms on the left-hand side and 12 on the right-hand side, so another 5 H_2O must be added to the left-hand side:

$S_4O_6^{2-} + 6H_2O \rightarrow 4H_2SO_3 + H^+ + e^-$

There are now 12 O atoms on each side.

3 There are 12 H atoms on the left-hand side but only 9 on the right-hand side, so another 3 H^+ must be added to the right-hand side:

$S_4O_6^{2-} + 6H_2O \rightarrow 4H_2SO_3 + 4H^+ + e^-$

There are now 12 H atoms on each side.

4 The total charge on the left-hand side is 2– and the total charge on the right-hand side is $(4 \times 1+) + 1- = 3+$, so 5 more e^- must be added to the right-hand side to balance the charges:

$S_4O_6^{2-} + 6H_2O \rightarrow 4H_2SO_3 + 4H^+ + 6e^-$

The total charge on both sides is now 2–.

Combining half-equations to produce an overall redox equation

An oxidation half-equation may be combined with a reduction half-equation to produce an overall redox equation. When the half-equations are combined, the number of electrons lost in the oxidation reaction must be the same as the number gained in the reduction reaction.

Let us consider two half-equations:

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

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

Two electrons are produced in the oxidation process, but only one electron is required to reduce each Ag^+ ion. Electrons cannot simply disappear, so one Cu must combine with two Ag^+ ions, donating one electron to each. We can show this by multiplying the reduction half-equation by 2 to give:

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

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Now that the electrons balance, the half-equations can be added together:

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

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

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

The overall redox equation is therefore:

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

This balances both in terms of the number of each atom on each side, and also in terms of the total charge on each side.

WORKED EXAMPLE 20.8

Deduce the overall redox equation when the following two half-equations are combined:

reduction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Answer

5 electrons are gained in the reduction half-equation, but only 1 is lost in the oxidation half-equation. The oxidation half-equation must, therefore, be multiplied by 5:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$

The number of electrons now balance, and, if the two half-equations are added together and electrons cancelled from each side, the overall redox equation is obtained:

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$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

A final check could be done to see that this is, indeed, balanced by checking that the number of atoms of each type is the same on both sides and that the total charge is the same on both sides.

EXAM TIP

Overall redox equations never contain electrons – only half-equations have electrons. If you have electrons in an overall redox equation, it is wrong, and you will almost certainly not get any marks for the question.

INTERNATIONAL MINDEDNESS

Corrosion is a general term to describe the oxidation of materials (usually metals) that results in a deterioration of its properties. The most famous type of corrosion is rusting. Rusting occurs when iron/steel is exposed to air(oxygen) and water. When iron/steel rusts the iron atoms are oxidised and a orange-brown flaky substance is formed. The exact formula of rust is variable and complex. Rusting significantly weakens the strength of steel structures and it is estimated that rusting and other forms of corrosion costs World economies trillions of US dollars each year.

WORKED EXAMPLE 20.9

Deduce the overall redox equation when the following two half-equations are combined.

reduction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

oxidation: $Re^{3+}(aq) + 4H_2O(l) \rightarrow ReO_4^{2-}(aq) + 8H^+(aq) + 3e^-$

Answer

5 electrons are gained in the reduction half-equation, but only 3 are lost in the oxidation half-equation. Therefore, to balance the number of electrons lost with the number of electrons gained, the oxidation half-equation must be multiplied by 5 and the reduction half-equation by 3:

$3MnO_4^-(aq) + 24H^+(aq) + 15e^- \rightarrow 3Mn^{2+}(aq) + 12H_2O(l)$

$5Re^{3+}(aq) + 20H_2O(l) \rightarrow 5ReO_4^{2-}(aq) + 40H^+(aq) + 15e^-$

The numbers of electrons now balance, and the two half-equations can be added together and electrons cancelled:

$5Re^{3+}(aq) + 20H_2O(l) + 3MnO_4^-(aq) + 24H^+(aq) \rightarrow 3Mn^{2+}(aq) + 12H_2O(l) + 5ReO_4^{2-}(aq) + 40H^+(aq)$

There are H_2O molecules and H^+ ions on both sides:

$5Re^{3+}(aq) + 20H_2O(l) + 3MnO_4^-(aq) + 24H^+(aq) \rightarrow 3Mn^{2+}(aq) + 12H_2O(l) + 5ReO_4^{2-}(aq) + 40H^+(aq)$

These can also be cancelled to give:

$5Re^{3+}(aq) + 8H_2O(l) + 3MnO_4^-(aq) \rightarrow 3Mn^{2+}(aq) + 5ReO_4^{2-}(aq) + 16H^+(aq)$

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Balancing redox equations for reactions in acidic or neutral solution

We can combine the above techniques to balance overall redox equations. The equation is first split up into two half-equations, which are balanced separately and then combined to give the overall redox equation.

The procedure for doing this is:

1. Separate the reaction equation into oxidation and reduction half-equations.
2. Balance each half-equation separately.
3. Multiply the half-equations by the appropriate numbers to balance the electrons in each.
4. Add the two half-equations.
5. Subtract any duplications on left- and right-hand sides.

WORKED EXAMPLE 20.10

Balance the following redox equation:

$HAsO_2(aq) + BrO_3^-(aq) + H_2O(l) + H^+(aq) \rightarrow Br_2(aq) + H_3AsO_4(aq)$

Answer

We ignore H_2O and H^+ when splitting this up into half-equations, so the two half-equations are

Reduction		Oxidation
$BrO_3^-(aq) \rightarrow Br_2(aq)$		$HAsO_2(aq) \rightarrow H_3AsO_4(aq)$
balance all atoms except H and O:		
$2BrO_3^-(aq) \rightarrow Br_2(aq)$		$HAsO_2(aq) \rightarrow H_3AsO_4(aq)$
add H_2O to side deficient in O to balance O:		
$2BrO_3^-(aq) \rightarrow Br_2(aq) + 6H_2O(l)$		$HAsO_2(aq) + 2H_2O(l) \rightarrow H_3AsO_4(aq)$
add H^+ to side deficient in H to balance H:		
$2BrO_3^-(aq) + 12H^+(aq) \rightarrow Br_2(aq) + 6H_2O(l)$		$HAsO_2(aq) + 2H_2O(l) \rightarrow H_3AsO_4(aq) + 2H^+(aq)$
add e^- to the side deficient in negative charge to balance charge:		
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow Br_2(aq) + 6H_2O(l)$		$HAsO_2(aq) + 2H_2O(l) \rightarrow H_3AsO_4(aq) + 2H^+(aq) + 2e^-$
balance electrons between the half-equations (multiply the oxidation half-equation by 5 here):		
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow Br_2(aq) + 6H_2O(l)$		$5HAsO_2(aq) + 10H_2O(l) \rightarrow 5H_3AsO_4(aq) + 10H^+(aq) + 10e^-$

The two half-equations can now be added together, and the electrons cancelled:

$2BrO_3^-(aq) + 12H^+(aq) + \cancel{10e^-} \rightarrow Br_2(aq) + 6H_2O(l)$

$5HAsO_2(aq) + 10H_2O(l) \rightarrow 5H_3AsO_4(aq) + 10H^+(aq) + \cancel{10e^-}$

$2BrO_3^-(aq) + 12H^+(aq) + 5HAsO_2(aq) + 10H_2O(l) \rightarrow Br_2(aq) + 6H_2O(l) + 5H_3AsO_4(aq) + 10H^+(aq)$

There are H_2O molecules and H^+ ions on both sides, and these can be cancelled to give the overall equation:

$2BrO_3^-(aq) + 2H^+(aq) + 5HAsO_2(aq) + 4H_2O(l) \rightarrow Br_2(aq) + 5H_3AsO_4(aq)$

A final check can be done to see that this is, indeed, balanced by checking that the number of atoms of each type is the same on both sides and that the total charge is the same on both sides.

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TEST YOUR UNDERSTANDING

5 State whether each of the following half-equations involves oxidation or reduction:

a $Cl_2 + 2e^- \rightarrow 2Cl^-$

b $Mn^{3+} + e^- \rightarrow Mn^{2+}$

c $Cu^+ \rightarrow Cu^{2+} + e^-$

d $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$

e $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+} + 7H_2O(l)$

6 Balance the following half-equations for reactions that occur in neutral solution:

a $Fe^{3+} \rightarrow Fe$

b $Pb^{2+} \rightarrow Pb^{4+}$

c $I_2 \rightarrow I^-$

d $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

e $C_2O_4^{2-} \rightarrow CO_2$

7 Balance the following half-equations for reactions that occur in acidic solution:

a $I_2 + H_2O \rightarrow OI^- + H^+ + e^-$

b $MnO_4^-(aq) + H^+(aq) + e^- \rightarrow Mn^{2+}(aq) + H_2O(l)$

c $IO_3^- + H^+ + e^- \rightarrow I_2 + H_2O$

d $N_2 + H_2O \rightarrow NO_3^- + H^+ + e^-$

e $SO_4^{2-} + H^+ + e^- \rightarrow H_2SO_3 + H_2O$

8 Balance the following half-equations for reactions that occur in acidic solution:

a $VO^{2+} \rightarrow V^{3+}$

b $Xe \rightarrow XeO_3$

c $NO_3^- \rightarrow NO$

d $NO_3^- \rightarrow N_2O$

e $VO_2^+ \rightarrow VO^{2+}$

9 Write balanced redox reactions from each pair of half-equations and identify the oxidising and reducing agent in each case

a $Eu^{2+} \rightarrow Eu^{3+} + e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

b $2HCN \rightarrow (CN)_2 + 2H^+ + 2e^-$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

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

$2I^-(aq) \rightarrow I_2(aq) + 2e^-$

d $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$

10 In each case balance the individual half-equations and combine them to produce the overall redox equation.

a $Au(OH)_3 + H^+ + e^- \rightarrow Au + H_2O$
$Br^- + H_2O \rightarrow HBrO + H^+ + 2e^-$

b $IO_3^- + H^+ + e^- \rightarrow I_2 + H_2O$
$NO + H_2O \rightarrow NO_3^- + H^+ + e^-$

c $ReO_4^- + H^+ + e^- \rightarrow Re + H_2O$
$P + H_2O \rightarrow H_3PO_3 + H^+ + e^-$

11 Balance the following redox equations for reactions that occur in neutral solution:

a $Cl_2 + Br^- \rightarrow Cl^- + Br_2$

b $Zn + Ag^+ \rightarrow Zn^{2+} + Ag$

c $Fe^{3+} + I^- \rightarrow Fe^{2+} + I_2$

12 Balance the following redox equations for reactions that occur in acidic solution and in each case identify the oxidising agent and reducing agent:

a $Fe^{2+} + Cr_2O_7^{2-} + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$

b $Br^- + Cr_2O_7^{2-} + H^+ \rightarrow Br_2 + Cr^{3+} + H_2O$

c $Zn + VO^{2+} + H^+ \rightarrow V^{3+} + H_2O + Zn^{2+}$

d $BrO_3^- + I^- \rightarrow Br_2 + I_2$

e $NpO_2^{2+} + U^{4+} \rightarrow NpO_2^+ + UO_2^+$

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Link

We discussed acid-base titrations in Chapter 16, and titrations involving redox reactions are also routinely used in analytical work.

The two most commonly encountered redox titrations are:

1 **Manganate(VII)/iron(II) titration**

A solution of potassium manganate(VII) is added from a burette to an acidified solution of iron(II). $KMnO_4(aq)$ is dark purple and turns colourless as it enters the flask and the purple MnO_4^- ion is reduced to colourless $Mn^{2+}(aq)$. The end point is detected when one drop of $KMnO_4$ turns the solution in the flask pale pink – within that one drop, we added excess $KMnO_4$, so we know the equivalence point to within one drop. This reaction, therefore, does not need a separate indicator, it is self-indicating.

The reaction that occurs is:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

2 **Thiosulfate/iodine titration**

The titration is carried out by adding the colourless solution of sodium thiosulfate to the brown solution of iodine. The iodine colour fades through orange to yellow to colourless as the redox reaction occurs and iodine is reduced to colourless iodide ions. Starch indicator is often added near the end point, and so, the colour change at the end point is from blue-black to colourless, which is easier to see than a pale yellow solution becoming colourless.

The reaction that occurs is:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The thiosulfate ion ($S_2O_3^{2-}$) is oxidised as it reduces iodine to iodide ions, and the average oxidation state of sulfur changes from +2 in the thiosulfate ion to +2.5 in the tetrathionate ion ($S_4O_6^{2-}$). Sulfur has a fractional oxidation state here because not all the sulfur atoms have the same oxidation state; +2.5 is an average (see Section 10.7).

20.3 Arranging metals in order of reactivity

When metals react, they form positive ions and so we can talk about the reactivity of metals in terms of how readily they form positive ions – the more readily a metal forms a positive ion, the more reactive it is. Formation of positive ions involves loss of electrons, which is oxidation, so, when a metal reacts it is oxidised and we can say that a metal is more reactive if it is oxidised more easily.

When a piece of zinc is put in a solution containing copper(II) ions, the zinc becomes coated with copper; the blue colour of the solution fades and the solution gets warmer (Figure 20.3).

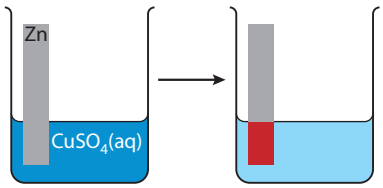

Figure 20.3 Zinc displaces copper from solution.

The reaction that occurs is:

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

We say that zinc displaces copper from solution and call this a **displacement** or **single replacement** reaction.

The ionic equation for the reaction that occurs is

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

In this reaction, the Zinc is more readily oxidised than copper and we can say that zinc is more reactive than copper. Zinc transfers electrons to the copper ion and, therefore, acts as a reducing agent; it reduces copper ions to copper. Zinc is therefore a stronger reducing agent than copper.

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KEY POINTS

A more reactive metal is more readily oxidised than a less reactive metal.

A more reactive metal is a stronger reducing agent than a less reactive metal.

If we added a piece of copper to a solution of zinc sulfate, we would see no reaction

$Cu(s) + Zn^{2+}(aq) \rightarrow$ No Reaction

Copper is less readily oxidised than: and therefore, copper is a weaker reducing agent than zinc and not able to reduce zinc ions to zinc.

If we put a piece of magnesium into a solution of zinc sulfate, we see the piece of magnesium getting smaller and zinc metal forming. The reaction that occurs is:

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

Magnesium is more readily oxidised to its aqueous ions than zinc is and we can say that magnesium is more reactive than zinc, or that magnesium is a stronger reducing agent than zinc.

WORKED EXAMPLE 20.11

The table gives details about a series of reactions between some metals X, Y, Q, Z and solutions of their nitrates.

Salt solution / Metal	$X(NO_3)_2(aq)$	$Y(NO_3)_2(aq)$	$Q(NO_3)_2(aq)$	$Z(NO_3)_2(aq)$
X		No Reaction	No Reaction	No Reaction
Y	Reaction		Reaction	Reaction
Q	Reaction	No Reaction		No Reaction
Z	Reaction	No Reaction	Reaction	

a Arrange the metals in order of reactivity from least reactive to most reactive.

b Arrange the metals in order from the strongest reducing agent to the weakest.

c Arrange the metal ions in order from the strongest oxidising agent to the weakest.

Answer

a We can see that Y displaces all the other metals from solution, therefore it must be the most reactive metal (most readily oxidised to its aqueous ion).

Z displaces X and Q, therefore Z must be more reactive than X and Q (more readily oxidised to its aqueous ion than X and Q).

Q displaces X, therefore Q must be more reactive than X (more readily oxidised to its aqueous ion than X)

The order of reactivity is: X(least reactive) < Q < Z < Y(most reactive)

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CONTINUED

b The more reactive a metal is, the greater tendency it has to get oxidised and therefore act as a reducing agent, therefore Y is able to reduce the ions of all the other metals, e.g.

$Y(s) + Z^{2+}(aq) \rightarrow Y^{2+}(aq) + Z(s)$

and is the strongest reducing agent.

The order of strength of reducing agents is: Y(strongest reducing agent) > Z > Q > X(weakest reducing agent)

c A solution containing $X^{2+}(aq)$ oxidises all the other metals, therefore $X^{2+}(aq)$ is the strongest oxidising agent. The order of strength of oxidising agents for the metal ions is therefore opposite to that of the strength of reducing agents for the metals.

$X^{2+}(aq)$ (strongest oxidising agent) > $Q^{2+}(aq)$ > $Z^{2+}(aq)$ > $Y^{2+}(aq)$ (weakest oxidising agent)

The Electrochemical Series

We can use displacement reactions to arrange metals (and hydrogen) in an **electrochemical series** (reactivity series) based on their tendency to be oxidised to aqueous ions (Figure 20.4).

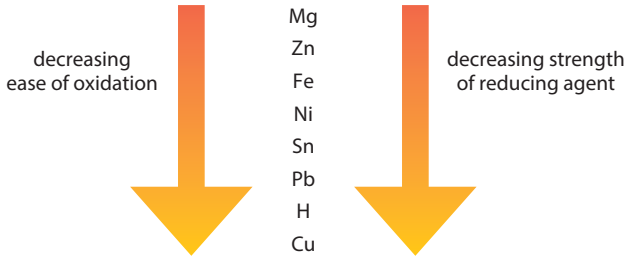

Figure 20.4 The metals in the electrochemical series are arranged in order of how easily they are oxidised to form aqueous positive ions.

The metals higher in the electrochemical series will displace those lower in the series from solutions of their salts, so zinc will displace nickel from solution but there will be no reaction between a piece of copper and a solution of lead(II) nitrate.

EXAM TIP

The electrochemical series is shown as a table of standard reduction potentials in the IB data booklet.

Reaction of metals with acids

Metals above hydrogen in the electrochemical series are stronger reducing agents than hydrogen and should reduce hydrogen ions to hydrogen gas. The reaction between magnesium and hydrogen ions is

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

Solutions of acids contain hydrogen ions, so we can predict that metals above hydrogen in the series should liberate hydrogen gas when mixed with an acid, for example:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

or

$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

The general equation for these reactions is

metal + acid → salt + hydrogen

Metals lower than hydrogen in the electrochemical series will not react with acids, so copper does not react with hydrochloric or sulfuric acids.

The relation between reactivity of metals and position in the periodic table

Because the reactions of metals involve the loss of electrons, we can relate the reactivity of metals, at least in part, to the ionisation energy of the metal and the position in the periodic table.

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KEY POINT

Ionisation energy decreases down a group in the periodic table because the outer electron is further from the nucleus and, therefore, less strongly attracted to it.

We would, therefore, expect reactivity (the metals form positive ions more easily) to increase down a group in the periodic table and, indeed, find that reactivity increases from Na to Cs down Group 1 and from Be to Ba down Group 2. Another way of saying this is:

KEY POINT

Metals become stronger reducing agents down Group 1 from Na to Cs and down Group 2 from Be to Ba.

The same trend does not hold down Group 13 or Group 14 (lead is below tin in the periodic table and also below it in the electrochemical series).

Reactivity of some non-metals

The reactivity of the halogens

We have already looked at the reactions between halogens and halide ions in Chapter 10.

The reactions that occur are

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

The more reactive halogen displaces the less reactive halogen from solution. Chlorine is more reactive than bromine and iodine and, therefore, displaces bromine and iodine from solution. Bromine is more reactive than iodine, and so, displaces iodine from solution. Bromine is, however, not able to displace chlorine from solution:

$Br_2(aq) + 2Cl^-(aq) \rightarrow$ no reaction

These reactions between halogens and halide ions are all redox reactions.

KEY POINT

Going down Group 17, the tendency of a halogen to be reduced decreases.

For example, in the reaction between chlorine and bromide ions, Cl_2 has a greater tendency to undergo reduction than bromine and, therefore, takes the electrons from Br^-, oxidising it. Cl_2 is the oxidising agent and Br^- is the reducing agent – Br^- gives electrons to Cl_2 molecules and, therefore, reduces them.

KEY POINT

The halogens become weaker oxidising agents down Group 17.

Chlorine can oxidise bromide ions to bromine and iodide ions to iodine, but bromine is only able to oxidise iodide ions to iodine, and iodine cannot oxidise any of the halide ions. Therefore, chlorine is a stronger oxidising agent than bromine, and bromine is a stronger oxidising agent than iodine. In terms of electrons, chlorine has the strongest affinity for electrons and will remove electrons from bromide ions and iodide ions.

Link

The trend in the tendency to be reduced to the X^- ion can be related, in part, to the electron affinity of the halogen. Electron affinity is the energy released in the following process:

$X(g) + e^- \rightarrow X^-(g)$

Going down Group 17, from Cl to I, this process becomes less exothermic and, therefore, less favourable, as the halogen atoms get bigger and the electron is brought into a shell further from the nucleus.

F, however, has a less exothermic electron affinity than Cl (see Chapter 10, section 10.2) but a much greater tendency to be reduced. The reaction we need to consider though is $X_2(aq) + 2e^- \rightarrow 2X^-(aq)$, which does not just involve the atom gaining an electron. The F—F bond energy is much lower than the Cl—Cl bond energy, and the fluoride ion has a much more exothermic enthalpy of hydration – these two terms more than compensate for the less exothermic electron affinity.

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TEST YOUR UNDERSTANDING

13 a Complete the following table by predicting whether a 'reaction' or 'no reaction' will occur:

	$ZnSO_4(aq)$	$MgCl_2(aq)$	$CuSO_4(aq)$
zinc			
magnesium			
copper			

Write ionic equations for the reactions that occur and identify the oxidising and reducing agents.

b For the reactions that occur, write half-equations for the oxidation and reduction processes.

14 Astatine, At, is the element below iodine in the periodic table. Predict whether a reaction would occur if

a a solution of iodine were added to a solution of potassium astatide

b a solution of astatine were added to a solution of potassium iodide.

If a reaction occurs, identify the oxidising and reducing agents and write an overall redox equation.

20.4 Electrochemical cells

There are two broad classes of **electrochemical cells** that interconvert chemical energy and electrical energy.

We will consider each type of cell in turn.

KEY POINTS

In a voltaic cell, chemical energy is converted into electrical energy – a chemical reaction produces electricity.

In an electrolytic cell, electrical energy is converted into chemical energy – electricity is used to bring about a chemical reaction.

Voltaic cells?

Voltaic cells (galvanic cells) provide us with a way of harnessing spontaneous redox reactions to generate electricity. This is the basis of batteries (primary cells) that power the technology we use.

EXAM TIP

Voltaic cells are called primary cells in the IB syllabus.

When a piece of zinc is put into a solution of copper(II) sulfate, an exothermic reaction occurs – the zinc becomes coated with copper, and the blue colour of the copper sulfate solution fades (Figure 20.3).

The overall reaction is

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

The half-equations are

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

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

When zinc metal is added to a solution containing Cu^{2+} ions, electrons are transferred directly from zinc to Cu^{2+} – Cu^{2+} is reduced and zinc is oxidised. The reaction is exothermic – chemical energy is converted into heat.

However, if the oxidation and reduction reactions are separated, as in Figure 20.5, the same reaction occurs, except that, instead of the electrons being transferred directly from Zn to Cu^{2+}, they are transferred via the external circuit, and chemical energy is converted into electrical energy instead of heat.

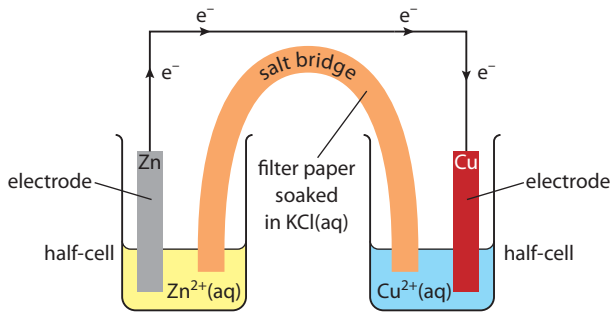

Figure 20.5: A voltaic cell. If we put a bulb in the circuit, it lights up because current flows.

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In the left-hand beaker (the Zn/Zn^{2+} *half-cell*), zinc atoms are oxidised to Zn^{2+} ions, and the electrons that are lost flow around the external circuit (the wire joining the two electrodes) to the other beaker, where they are gained by Cu^{2+} ions to form copper. If the reaction were allowed to keep going, we would see

- the zinc electrode getting smaller – zinc goes into solution as Zn^{2+}
- the Cu electrode getting larger – it is coated with copper, formed from Cu^{2+} in the solution
- the colour of the solution in the right-hand beaker becoming paler – the blue colour of the solution is due to the presence of $Cu^{2+}(aq)$ ions and, as copper ions are converted into copper atoms, the concentration of $Cu^{2+}(aq)$ decreases.

The salt bridge

KEY POINTS

The **salt bridge** in a voltaic cell completes the circuit. It allows ions to flow into or out of the half-cells to balance out the charges in the half-cells.

A salt bridge can be made by soaking a strip of filter paper in a concentrated solution of an ionic salt, such as KCl.

In the cell shown in Figure 20.5, current will not flow unless the salt bridge is present. If the **salt bridge** were not present and the reaction were to proceed, there would be a build-up of Zn^{2+} ions in the left-hand beaker, the solution would become positively charged overall and any further oxidation of zinc atoms to Zn^{2+} would be opposed. Similarly, there would be a decrease in the concentration of Cu^{2+} ions in the right-hand beaker, which would mean that this solution would have a negative charge (remember that there are also negative ions in the beaker). Negatively charged electrons will not flow from a positively charged half-cell to a negatively charged half-cell.

The salt bridge contains ions that can flow out of the salt bridge into the individual half-cells to prevent any build-up of charge. Similarly, any excess ions in the individual half-cells can flow into the salt bridge to prevent any build-up of charge (see Figure 20.6).

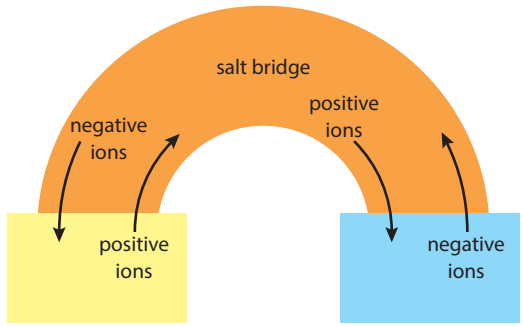

Figure 20.6: Ions flow through the salt bridge. Negative ions and positive ions flow in opposite direction.

The direction of charge flow

KEY POINT

Electrons flow through the external circuit, but ions flow through the salt bridge.

Negative charge always flows in the same continuous direction around a complete circuit. Figure 20.7 shows the direction the electrons flow through the external circuit and negative ions flow through the salt bridge in this cell. In this case, the electrons and the negative ions are all travelling clockwise around the circuit.

Negative ions travelling in one direction through the salt bridge is equivalent to positive ions flowing in the opposite direction (Figure 20.6).

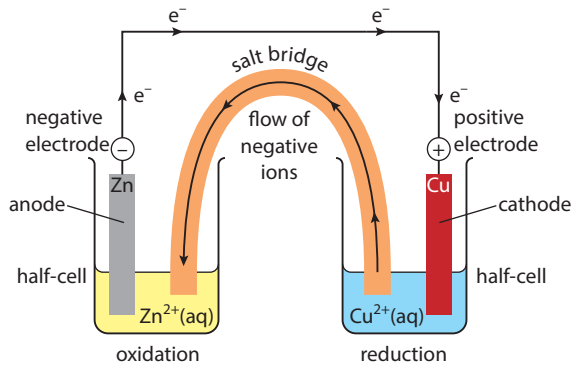

Figure 20.7: Direction of flow of charge. Positive ions flow in the opposite direction through the salt bridge.

The electrodes

The electrodes in an electrochemical cell are named according to the reaction that occurs at each one.

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KEY POINT

The **anode** is the electrode at which oxidation occurs.

So, in the cell shown in Figures 20.5 and 20.7, the zinc electrode is the **anode**. The reaction that occurs at that electrode is oxidation:

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

Because electrons are released at the zinc electrode, this is the negative electrode.

KEY POINT

In a voltaic cell, the anode is always the negative electrode.

We will see later in this chapter that, in an electrolytic cell, the anode is positive – the electrodes are named depending on whether oxidation or reduction occurs and not whether they are positive or negative.

KEY POINT

The **cathode** is the electrode at which reduction occurs.

Copper ions are reduced to copper atoms at the copper electrode:

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

Therefore, this is the **cathode** in the cell.

KEY POINT

In a voltaic cell, the cathode is the positive electrode.

Cell notation for voltaic cells

Chemists often use a shorthand notation (cell-diagram convention) for describing the reactions that go on in a voltaic cell. The cell discussed in the last section can be written as

$$Zn(s)|Zn^{2+}(aq) \parallel Cu^{2+}(aq)|Cu(s)$$
$$\text{oxidation} \qquad \text{reduction}$$

A *single vertical line* represents a phase boundary (between solid and aqueous solution here), and the *double line* indicates the salt bridge. Reading from left to right, we can see that Zn is oxidised to Zn^{2+} and that Cu^{2+} is reduced to Cu. The reaction at the anode is shown by convention on the left and that at the cathode on the right.

The size of the voltage

If a voltmeter is inserted across the $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell described above, it will read a voltage of just over 1 volt (Figure 20.8a). However, if the zinc electrode is replaced by a magnesium electrode, the voltage is much higher (Figure 20.8b). This is because there is a bigger difference in reactivity between magnesium and copper than between zinc and copper – magnesium and copper are further apart in the electrochemical series than magnesium and zinc. Magnesium has a greater tendency than zinc to donate electrons to copper ions.

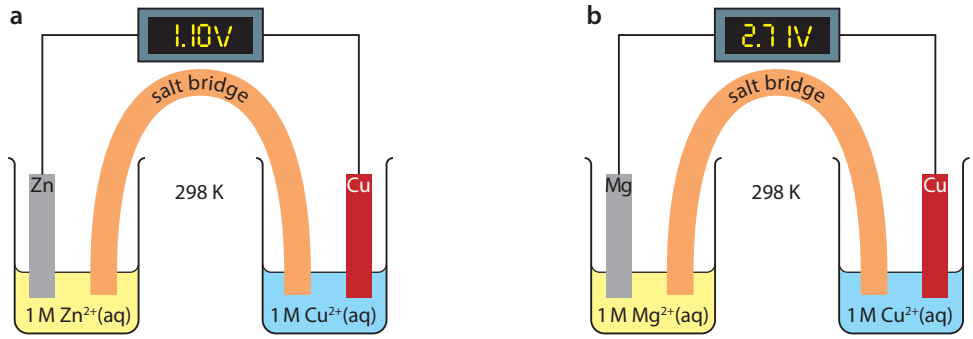

Figure 20.8 The voltage **a** in a $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell is less than that **b** in an $Mg|Mg^{2+}||Cu^{2+}|Cu$ cell. Note: 1 M = 1 mol dm^{-3}.

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KEY POINT

The bigger the difference in reactivity between the metal electrodes, the higher the voltage of the cell.

KEY POINT

The metal higher in the electrochemical series will have the greater tendency to be oxidised and will be the negative electrode (anode) in a voltaic cell.

The reactions that occur in each cell are equivalent to the displacement reactions that were described in Section 20.3.

$Zn|Zn^{2+}||Cu^{2+}|Cu$ cell:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$Mg|Mg^{2+}||Cu^{2+}|Cu$ cell:
$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

Things to note in these cells:

- Electrons will always flow around the external circuit from the more reactive metal to the less reactive one.
- Negative ions will flow through the salt bridge from the half-cell containing the less reactive metal to the half-cell containing the more reactive metal. Positive ions will flow in the opposite direction through the salt bridge.

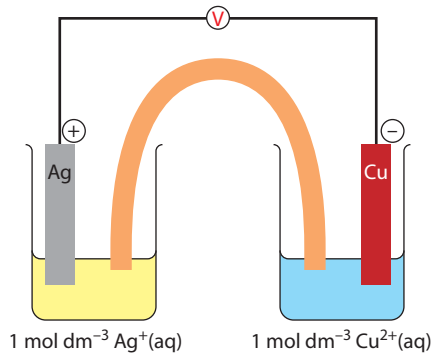
WORKED EXAMPLE 20.16

a In the voltaic cell shown

i state which electrode will be the anode

ii mark on the diagram the direction of electron flow through the external circuit

iii mark on the diagram the direction of flow of positive ions through the salt bridge.



b Write the half-equations for the reactions in each half-cell and, hence, the equation for the overall redox reaction that occurs in the cell.

c If the Cu/Cu^{2+} half-cell is replaced by a Ni/Ni^{2+} half-cell, predict whether the voltage will be higher or lower than in the cell in **a**.

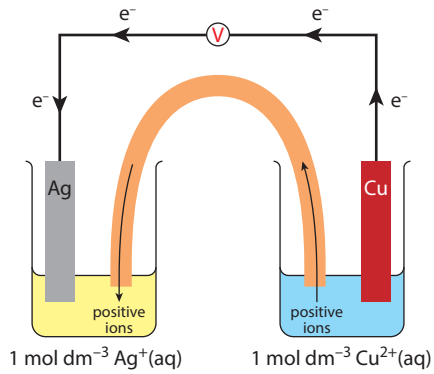
Answer

a **i** Copper is the negative electrode, so electrons are being produced there as copper atoms are oxidised to copper ions:

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

The electrode at which oxidation occurs is the anode, therefore, the copper electrode is the anode.

ii Electrons flow through the external circuit from the electrode at which oxidation occurs, so, in this case, they flow from copper to silver. Or, alternatively, electrons flow around the external circuit from the negative electrode to the positive electrode.



iii There is always the same continuous direction of flow of negative or positive charge around the circuit. Negative charge flows anti-clockwise around this circuit, so positive ions must flow in the opposite direction through the salt bridge.

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CONTINUED

b Cu is oxidised to Cu^{2+}: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Ag^+ ions are reduced to Ag: $Ag^+(aq) + e^- \rightarrow Ag(s)$

To combine these two half-equations, the second one must be multiplied by 2 so that there are the same number of electrons in both half-equations. The overall reaction is: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

c Nickel is higher in the electrochemical series than copper, so there is a bigger difference in reactivity between silver and nickel than there is between silver and copper; therefore, the voltage for the $Ni|Ni^{2+}||Ag^+|Ag$ cell will be larger.

TEST YOUR UNDERSTANDING

15 Consider four imaginary metals X, Z, A and Q.

a On the basis of the following data, arrange the metals X, Z and Q in order of reactivity (most reactive first):

- Z reduces Q^{2+} to Q
- X reduces Z^{2+} to Z.

b The following reactions also occur:

$A(s) + Q^{2+}(aq) \rightarrow A^{2+}(aq) + Q(s)$

$Z(s) + A^{2+}(aq) \rightarrow Z^{2+}(aq) + A(s)$

i Explain whether A is a stronger or weaker reducing agent than Q.

ii Arrange all four metals in order of reducing ability (strongest reducing agent first).

iii Which of the species, A, A^{2+}, Z, Z^{2+}, Q, Q^{2+}, X or X^{2+}, is the strongest oxidising agent?

c A voltaic cell is set up with a piece of A dipping into a solution of $A(NO_3)_2$ in one half-cell and a piece of X dipping into a solution of XSO_4 in the other half-cell.

i Draw a labelled diagram showing this cell. Mark on your diagram the following:

- the positive and negative electrodes
- the anode and cathode
- the direction of electron flow through the external circuit
- the direction that negative ions flow through the salt bridge.

ii Write half-equations for the reactions occurring in each half-cell.

iii The $X|XSO_4$ half-cell is replaced by a $Z|ZSO_4$ half-cell. Will the voltage be higher or lower than that in the original cell?

20.5 Rechargeable batteries

Modern life is powered by rechargeable batteries in our phones, tablets and laptops. These are also called **secondary cells**. The chemical reactions in a rechargeable battery are reversible and can be reversed by connecting them to an electricity supply.

The 'ordinary' batteries that we might use to power a torch or a radio, and that cannot be re-charged, are called **primary cells**. Primary cells cannot usually be recharged by connecting to an electricity supply because the reaction in the cell is non-reversible.

Common types of rechargeable battery that you may encounter are lithium-ion batteries used in phones and laptops; lead–acid batteries found in car engines; and nickel–cadmium batteries used for powering small

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electronic devices, such as clocks, calculators, remote controls and toys.

Although the components and chemicals used to make each type of cell are different, the basic form of all secondary cells is the same (Figure 20.9).

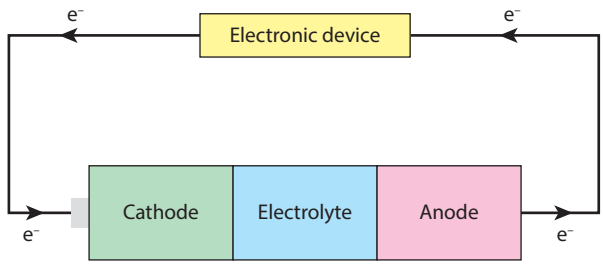

Figure 20.9: A schematic diagram showing the features of a secondary cell during discharge.

They all contain

- an anode, where an oxidation reaction occurs during discharge (when the cell is supplying current) – electrons are produced at the anode;
- a cathode, where reduction occurs – electrons flow to the cathode during discharge;
- an **electrolyte** – this is equivalent to the salt bridge in the cells we saw previously. The electrolyte keeps the anode and cathode separate so that electrons cannot be transferred directly. Ions (not electrons) flow through the electrolyte to complete the circuit.

KEY POINT

An **electrolyte** is a solution or a molten compound that will conduct electricity, due to the presence of ions that are free to move towards the electrodes.

Nickel–cadmium battery

We will consider the reactions in a nickel–cadmium (NiCad) battery to illustrate the concepts of discharging and charging a secondary cell. NiCad batteries use a nickel oxide hydroxide [NiO(OH)] cathode and a metallic cadmium anode separated by a potassium hydroxide electrolyte.

When the cell is producing a current (discharge), electrons are produced at the anode as cadmium is oxidised:

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

The anode is the negative electrode because electrons are being produced there. The electrons travel around the external circuit to reduce NiO(OH) (nickel in oxidation state +3) to $Ni(OH)_2$ (nickel in oxidation state +2).

cathode (reduction):
$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

The cathode is the positive electrode because electrons are being used up there.

To produce the overall redox equation, the second half-equation must be multiplied by two, so that the number of electrons matches in the oxidation and reduction half-equations. The two half-equations are then added together and like terms [$2OH^-(aq)$] cancelled from each side:

overall reaction:
$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

During discharge, Cd is, therefore, converted into $Cd(OH)_2$ and NiO(OH) is converted into $Ni(OH)_2$, so, once all the Cd or NiO(OH) has been used up, the reaction will stop – the battery has run out.

KEY POINT

The reactions during discharge and charging of a secondary cell are the same, just in opposite directions.

To recharge the battery, it must be connected to a direct current (DC) power supply (current only flows in one direction). The negative pole of the power supply is attached to what *was* the anode (we need to put electrons back into the anode) when the cell was delivering current, and electrons from the power supply reduce $Cd(OH)_2$ back to Cd. As a reduction reaction is now occurring, this is now the cathode:

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

During charging, the cathode is the negative electrode (see the section on electrolysis).

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The positive pole of the power supply is attached to what *was* the cathode. Electrons are removed from $Ni(OH)_2$. Since the reaction here is oxidation, this is now the anode:

anode (oxidation):
$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + H_2O(l) + e^-$

During charging, the anode is the positive electrode.

Overall reaction during charging:
$Cd(OH)_2(s) + 2Ni(OH)_2(s) \rightarrow Cd(s) + 2NiO(OH)(s) + 2H_2O(l)$

EXAM TIP

The syllabus states that you should be able to deduce the electrode reactions for charging/discharging from given half-equations for the reverse process; therefore, you do not need to learn the electrode reactions here but just need to remember that the reactions are the opposite way round during discharging and charging.

What makes a redox reaction suitable for use in a secondary cell? First of all, the reactions must be exactly reversible (there must be no other reactions possible on charging). The substances produced during oxidation/reduction should be solids that become part of the existing electrodes – if the substances produced go into solution or flake off the electrodes, then charging to restore the electrodes will not generally be possible.

We will always get less electrical energy out of battery than we put in as there will always be losses as heat during both charging and discharging. For example, during discharge, the battery will heat up due to the internal resistance.

Rechargeable vs non-rechargeable batteries

Both rechargeable batteries (secondary cells) and non-rechargeable batteries (primary cells) are portable and convenient sources of energy. The most common primary cells are the AA and AAA batteries alkaline batteries used to power small devices such as a TV remote control. Billions of these batteries are produced each year.

The main difference between a primary cell and a secondary one is that the primary cell cannot be recharged and so must be disposed of after use. There are advantages and disadvantages here – when a primary cell runs out it can be easily and quickly replaced with another one, but the battery must be then disposed of – most batteries go to landfill. A secondary cell can be recharged over and over again, but this takes time and therefore can be inconvenient.

Other advantages and disadvantages of primary versus secondary cells include:

- Primary cells are generally cheaper than secondary cells
- Primary cells have higher specific energy (energy supplied per unit mass).
- Primary cells generally have higher internal resistance and so cannot deliver as high a current as secondary cells.
- Primary cells have better shelf life (how long they can be kept without losing charge) than secondary cells.
- Secondary cells often contain toxic heavy metals, such as lead and cadmium that are hazardous to the environment, so they must be recycled after use. Alkaline batteries contain less hazardous chemicals.

Fuel cells vs rechargeable batteries

We have already discussed fuel cells in Chapter 14, as another type of device that converts chemical energy into electrical energy, and here, we will discuss some of the advantages and disadvantages of fuel cells versus rechargeable batteries. First, let's look at some of the differences between them.

Differences between fuel cells and rechargeable batteries

Differences between fuel cells and rechargeable batteries include the following:

- Fuel cells require an external source of chemical energy (fuel), but rechargeable batteries have their chemical energy source within them.
- Fuel cells work continuously, as long as there is a constant supply of fuel from an external source; rechargeable batteries run out and then have to be recharged periodically by connecting to an electricity supply.

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- Hydrogen fuel cells produce water as a by-product, direct methanol fuel cells produce water and carbon dioxide; there is no by-product of rechargeable batteries.
- Rechargeable batteries can only be recharged so many times – they have a finite life and must be replaced eventually; fuel cells have much better longevity.

Advantages and disadvantages of using fuel cells or rechargeable batteries

Some of the differences between fuel cells and rechargeable batteries can be seen as advantages or disadvantages of each, depending on the circumstances. For example, it is generally much more convenient not to have to carry around an external fuel supply for your laptop but rather to re-charge it periodically from the mains electricity supply; however, in remote areas, having a replaceable fuel cartridge could be a distinct advantage. Similarly, powering a device with a hydrogen fuel cell might be inconvenient if you have a constant trickle of water coming out of the fuel cell or have to empty a water storage tank every so often, but hydrogen fuel cells have been used on a spacecraft to produce drinkable water as well as electricity. We will, therefore, look at the advantages and disadvantages of fuels cells for a particular use – electric vehicles.

Electric vehicles

With targets being set to reduce the carbon dioxide emissions from transport, there has been a rise in the production and use of electric cars in recent years (Figure 20.11). Different countries and companies have approached the problem differently, with the development of two main types of technology – lithium-ion batteries, as in the Nissan Leaf or the Tesla Model S, which are called battery electric vehicles (BEVs); or hydrogen fuel cells, as in the Toyota Mirai (a fuel cell electric vehicle (FCEV)).

Figure 20.10: Electric vehicles are becoming more common. Will we see the day when there are no more vehicles with internal combustion engines on the roads?

Both technologies have advantages and disadvantages, which include the following:

- Lithium-ion batteries are more efficient than fuel cells.
- Hydrogen is an explosive gas, so storage can be difficult and there is a risk of explosions.
- BEVs are cheaper to run than FCEVs.
- FCEVs have a much shorter re-fuelling time (5 minutes) compared to BEVs (hours).
- Fuel cell systems used to power vehicles have a higher energy-to-mass ratio – the vehicles can travel further for the same mass of a battery/fuel cell plus fuel. The advantage of using fuel cells to power vehicles increases with the distance between stops that is required because this can be increased by simply having a larger fuel tank, which will not add significantly to the overall mass of the vehicle (hydrogen is a very light gas). With rechargeable batteries, the distance between stops can only be improved by adding extra rechargeable batteries, which contribute significantly to the overall mass of the vehicle and take up a lot of space.

INTERNATIONAL MINDEDNESS

How environmentally friendly are electric vehicles?

The environmental impact of both types of vehicle, compared to each other and to conventional cars with gasoline-powered internal combustion engines (ICEVs), depends significantly on how the electricity is generated to produce electricity for the rechargeable batteries and how the hydrogen for the FCEV is produced. This will vary from country to country, and, if the primary source of the energy for these processes is from burning coal, then the overall environmental impact of electric vehicles could be worse than that of ICEVs.

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CONTINUED

The environmental issues do not just concern the vehicles in operation but also their manufacture and disposal. A major contributor to the environmental impact of BEVs comes from the manufacture of the batteries, and more carbon dioxide is generated in making a BEV than a similar ICEV.

SCIENCE IN CONTEXT

Lithium-ion batteries (Figure 20.11) are an essential part of modern life, being in our phones, laptops and now increasingly in electric vehicles.

Figure 20.12 shows the basic structure of a lithium-ion cell. Typically, the anode is made of graphite with lithium atoms inserted in the lattice, and the cathode is a metal oxide, such as manganese(IV) oxide or cobalt(IV) oxide, with Li^+ ions inserted in the lattice. The electrolyte is a complex lithium salt, such as lithium hexafluorophosphate ($LiPF_6$), dissolved in an organic solvent.

During discharge, lithium ions are oxidised at the anode and electrons are released to the external circuit:

$Li \rightarrow Li^+ + e^-$

Figure 20.11: Lithium-ion batteries power modern life.

The lithium ions move through the electrolyte to the cathode, where they become inserted into the lattice of the transition metal oxide as cobalt(IV) ions are reduced to cobalt(III) ions. The reaction that occurs each time a cobalt ion is reduced is

$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

We use these batteries every day, but how do we assess their environmental impact? One factor to consider is the energy and greenhouse gases involved in the manufacturing process. Life cycle analysis is the term given to the method of assessing the environmental impact of a product or process. Many studies have been carried out on lithium-ion batteries, but the analysis is extremely difficult and the figures produced vary widely. All aspects of the production process have to be taken into account, from mining and processing of the materials for the individual parts, to transportation to where cells are made, and construction of the cells, but it is clear that the manufacturing process has a significant environmental impact. A major contributor to this is the production of the materials for the cathode, such as cobalt, but even just producing the aluminium casing also requires a lot of energy (and generates a lot of greenhouse gases). But there is more to the story of a lithium-ion battery than just energy use and greenhouse gas emissions. For example, much of the cobalt used in batteries comes from the Democratic Republic of Congo, and there have been concerns about the conditions that workers, including children, have to endure in the mining process. There are also worries about the extraction of lithium compounds in South America and the impact it has on local communities through affecting the availability of water and the pollution of water supplies.

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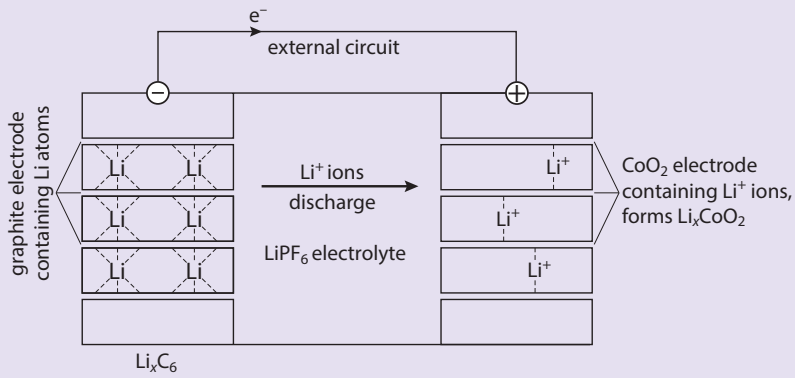

Figure 20.12: The structure of a lithium-ion battery. Li_x indicates that the anode and cathode contain varying numbers of lithium atoms/ions.

TEST YOUR UNDERSTANDING

16 The half-equations for the reaction that occurs in a lead–acid cell during discharge are

I $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

II $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

a Identify which reaction occurs at the anode and which at the cathode.

b Write the overall equation for the reaction that occurs during discharge.

c Write the half-equation for the reaction that occurs at the electrode attached to the negative pole of the power supply during charging.

d Write the half-equation for the reaction that occurs at the anode during charging.

20.6 Electrolysis

KEY POINT

Electrolysis is the process of breaking down a substance (in molten state or solution) by the passage of electricity through it.

Electrolytic cells

An electrolytic cell is a type of electrochemical cell in which **electrolysis** is carried out. The reaction in an electrolytic cell does not happen by itself – it requires the continuous flow of electricity to occur – it is non-spontaneous.

Link

The term *spontaneous* is discussed in Chapter 15. A spontaneous reaction is one that will occur without any outside influence – it will happen by itself – we do not have to supply energy.

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Electrolysis of molten salts

The experimental set-up for the electrolysis of molten lead bromide is shown in Figure 20.13.

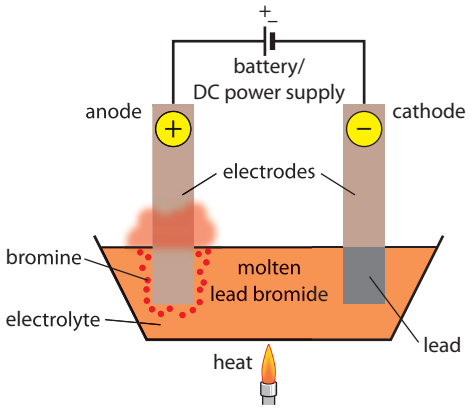

Figure 20.13: The electrolysis of molten lead bromide.

The electrodes are usually made of graphite, a fairly inert non-metal that conducts electricity, but could also be made of, for example, platinum. The power supply must produce direct current (DC) – where electricity only flows in one direction – for electrolysis to work.

No reactions occur and electricity does not flow until lead bromide becomes molten. Molten lead bromide is an electrolyte.

During operation, bromine (brown gas) is produced at the positive electrode, and the negative electrode becomes coated with lead, which sinks to the bottom as molten lead.

The overall reaction is

$$PbBr_2(l) \xrightarrow{\text{electrical energy}} Pb(l) + Br_2(g)$$

Lead bromide is broken down into its elements, lead and bromine, by the passage of electricity.

Positive electrode

Br^- ions are negative and are attracted to the positive electrode, where they lose electrons (are oxidised) to form bromine:

oxidation: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

Because oxidation occurs at this electrode, the positive electrode is the anode in an electrolytic cell.

Remember, the anode is the electrode at which oxidation occurs.

Negative electrode

Pb^{2+} ions are attracted to the negative electrode, where they gain electrons and are, therefore, reduced:

reduction: $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$

Because reduction occurs at this electrode, the negative electrode is the cathode in an electrolytic cell.

Remember, the cathode is the electrode at which reduction occurs.

Conduction of electricity in an electrolytic cell

The movement of electrons and ions is shown in Figure 20.14.

KEY POINT

In the external circuit, the current is carried by electrons (delocalised electrons in the metal wire), but, in the molten salt (electrolyte), conduction involves the movement of ions.

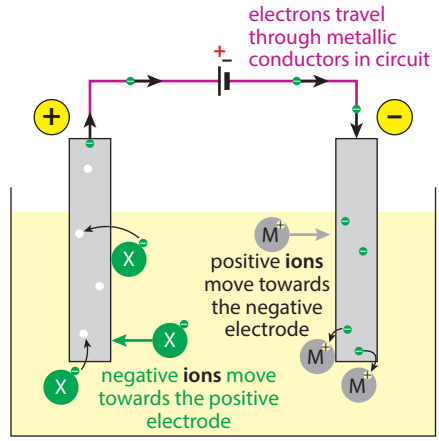

Figure 20.14: Conduction of electricity in an electrolytic cell.

Electrons travel from the negative pole of the battery to the negative electrode. The positive ions in the electrolyte move towards the negative electrode. At the negative electrode, electrons are transferred to the positive ions. The negative ions move towards the positive electrode.

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At the positive electrode, the extra electron(s) from the negative ion is (are) transferred to the electrode. The electrons released from the negative ions travel through the external circuit to the positive pole of the battery.

Electrons are taken from the external circuit at the negative electrode (by the positive ions) and given back to the external circuit at the positive electrode (by the negative ions). The circuit is completed, but the electrons that flow into the positive side of the battery are not the ones that flowed out of the negative side of the battery. No electrons travel through the electrolyte.

KEY POINT

The salt must be molten for electricity to flow.

Ionic salts will not conduct electricity when solid because the ions are held tightly in the lattice structure and are, therefore, not free to move (Figure 20.15).

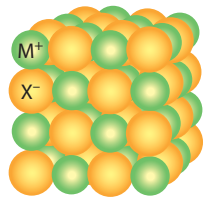

Figure 20.15: An ionic lattice.

When the salt is molten, the ions become free to move towards the electrodes and so current flows.

The products of electrolysis of a molten salt

When a molten salt is electrolysed, the products at the electrodes are the elements of which that salt is made up.

KEY POINTS

A metal is formed at the negative electrode because metals form positive ions, which are attracted towards the negative electrode.

A non-metal is formed at the positive electrode because non-metals form negative ions, which are attracted towards the positive electrode.

Electrolysis of molten aluminium oxide (Al_2O_3)

A metal is formed at the negative electrode (cathode) – in this case, aluminium:

reduction: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

A non-metal is formed at the positive electrode – in this case, oxygen:

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

overall reaction: $2Al_2O_3(l) \rightarrow 4Al(l) + 3O_2(g)$

Electrolysis of molten potassium chloride

Potassium is formed at the negative electrode (cathode):

reduction: $K^+(l) + e^- \rightarrow K(l)$

Chlorine is formed at the positive electrode (anode):

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

The differences between an electrolytic cell and a voltaic cell

The differences between a voltaic and an electrolytic cell are summarised in Table 20.2.

Voltaic cell	Electrolytic cell
spontaneous redox reaction generates electricity	non-spontaneous redox reaction (one that would not happen by itself) is brought about by the passage of an electric current
conversion of chemical energy into electrical energy	conversion of electrical energy into chemical energy
the anode is the negative electrode, and the cathode is the positive electrode	the anode is the positive electrode, and the cathode is the negative electrode

Table 20.2: Comparison of voltaic and electrolytic cells.

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TEST YOUR UNDERSTANDING

17 Sketch a labelled diagram of an electrolytic cell for electrolysis of molten sodium bromide. Identify on your diagram

- the positive and negative electrodes
- the anode and cathode.

18 For electrolysis of the following molten salts:

a potassium bromide

b copper(II) chloride

c nickel(II) oxide

d calcium chloride

e sodium chloride

f iron(III) oxide

g magnesium bromide,

i state the products at the anode and cathode

ii write half-equations for the reactions at the electrodes.

20.7 Redox reactions in organic chemistry

Redox reactions are very important in organic chemistry, and functional groups are sometimes classified in terms of their oxidation level (based on the oxidation state of the C atom). If we look at the following series:

	CH_4	CH_3OH	HCHO	HCOOH	CO_2
oxidation state of C	–4	–2	0	+2	+4

Carbon has the lowest oxidation state when it is part of an alkyl group (or methane in this case). To go to the right in this series, we need to use an oxidising agent and to go to the left, a reducing agent.

When we consider oxidation in organic chemistry, we are usually talking about chemical oxidation and do not mean combustion, but combustion is a redox reaction, where the organic compound is oxidised to produce carbon dioxide and water. This is the most complete form of oxidation and the carbon in the organic compound is oxidised to oxidation state +4, its highest oxidation state.

Oxidation of alcohols

Combustion of alcohols

In a plentiful supply of oxygen, alcohols burn to produce carbon dioxide and water:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$$

EXAM TIP

When balancing these equations, do not forget the oxygen in the alcohol!

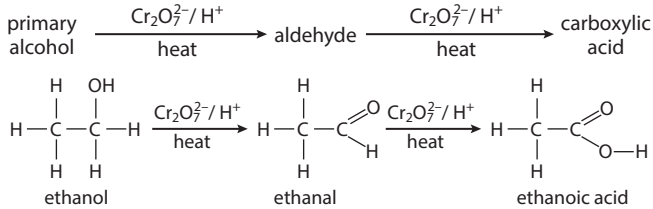
Chemical oxidation of alcohols

We have already met the idea of classifying alcohols as primary, secondary or tertiary, according to the number of carbon atoms joined to the carbon attached to the OH group, in Section 11.5. A primary alcohol contains the —CH_2OH group, a secondary alcohol has 2 C atoms joined to the carbon attached to the OH group and a tertiary alcohol has 3 C atoms attached to the C of the COH group.

Primary and secondary alcohols can be oxidised using an oxidising agent such as acidified potassium dichromate(VI) ($K_2Cr_2O_7/H^+$) or acidified potassium manganate(VII) ($KMnO_4/H^+$).The potassium ions are not important in these formulas – the $Cr_2O_7^{2-}$ and MnO_4^- ions are the important parts – sodium salts would work equally well.

Primary alcohols

Primary alcohols are oxidised first to an aldehyde (partial oxidation). Then the aldehyde is oxidised further to a carboxylic acid (complete oxidation).



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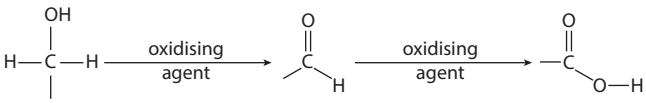
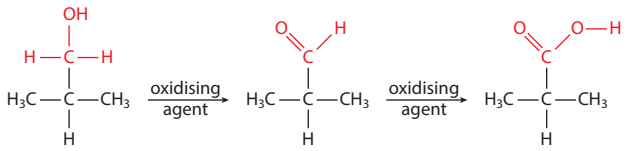
Remember that aldehydes and carboxylic acids contain the following groups:

Aldehydes Carboxylic acids

If we look at the oxidation of primary alcohols in terms of changes to the functional groups, it is easier to generalise the reaction to other compounds:



Consider the oxidation of 2-methylpropan-1-ol:



2-methylpropan-1-ol 2-methylpropanal 2-methylpropanoic acid

The only changes involve the groups highlighted in red – the rest of the molecule is unchanged. In organic chemistry, it is important to focus on only the changes to a particular functional group – the rest of the molecule (the carbon skeleton) should remain unchanged.

We can also show the reactions using condensed formulas:

$(CH_3)_2CHCH_2OH \xrightarrow{\text{oxidising agent}} (CH_3)_2CHCHO \xrightarrow{\text{oxidising agent}} (CH_3)_2CHCOOH$

Choosing the conditions to get the aldehyde or the carboxylic acid

Reaction mixtures in organic chemistry are usually heated using the apparatus set-up as shown in Figure 20.18a. This is called heating under **reflux**. Many organic compounds are volatile (evaporate easily) and flammable; they may also be toxic. If we heat the reaction mixture just in an open beaker, then there is a good chance that most of it would just evaporate, and we also run the risk of filling the laboratory with flammable and toxic fumes. When the reaction mixture is heated under reflux, the vapour from the reaction mixture rises up into the condenser (which has cold

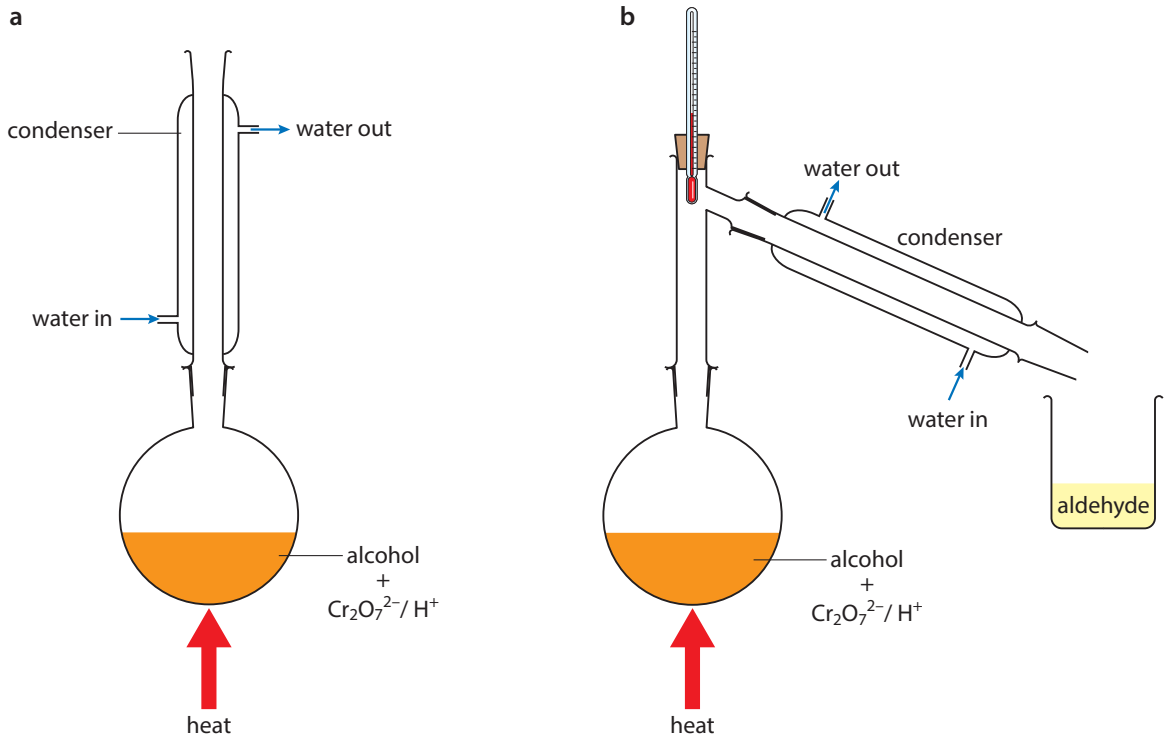


Figure 20.18 a Apparatus for reflux – this produces a carboxylic acid (complete oxidation). **b** Apparatus for distillation – this produces an aldehyde (partial oxidation). Acidified dichromate(VI) is orange, and, as it oxidises the alcohol/aldehyde, it gets reduced to a green solution containing the $Cr^{3+}(aq)$ ion.

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water running through it), condenses and runs back into the flask – very little should escape from the top of the condenser.

If a reaction mixture containing a primary alcohol and acidified potassium dichromate(VI) is heated under reflux, the alcohol is first oxidised to the aldehyde, but, because this is also readily oxidised, it undergoes further oxidation to the carboxylic acid. This is sometimes called *complete oxidation*. For example, when a mixture of ethanol and acidified potassium dichromate(VI) is heated under reflux, ethanoic acid is the main product.

KEY POINT

Complete oxidation of a primary alcohol to a carboxylic acid is brought about by heating the reaction mixture under reflux.

However, it is possible to set up the apparatus for distillation (Figure 20.18b) so that the aldehyde boils off as soon as it is formed and before it can be oxidised further. This is sometimes called *partial oxidation* of the primary alcohol. This technique works because aldehydes have lower boiling points than the equivalent alcohols (and all other components of the reaction mixture) because they do not have a hydrogen atom attached directly to an oxygen atom, so there is no hydrogen bonding between molecules. Therefore, when a mixture of ethanol and acidified potassium dichromate(VI) is heated with the apparatus set-up for distillation, we get partial oxidation and ethanal as the main product.

KEY POINTS

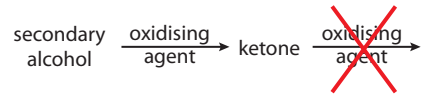
Partial oxidation of a primary alcohol to an aldehyde is brought about by heating the reaction mixture in apparatus set-up for distillation.

To make a carboxylic acid, excess of the oxidising agent is used, to ensure complete conversion.

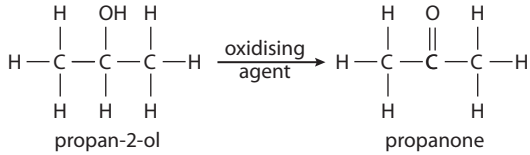
To make an aldehyde, the stoichiometric amount (for an exact reaction) of the oxidising agent is used, to reduce the chance of further oxidation.

Secondary alcohols

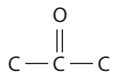
Secondary alcohols are also oxidised by heating with acidified potassium dichromate(VI) or acidified potassium manganate(VII). They are oxidised to ketones, which cannot be oxidised any further.



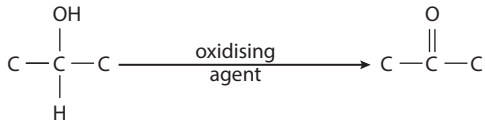
For example,



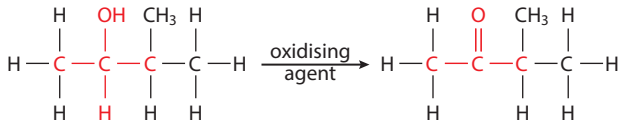
Remember that ketones contain the group:



In terms of changes to the functional group, the reaction can be represented as



Looking at the reaction of another secondary alcohol:

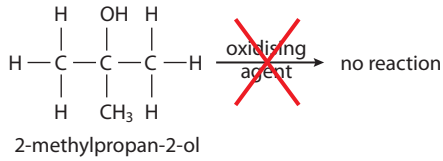


3-methylbutan-2-ol 3-methylbutanone

The only change is to the group highlighted in red – the rest of the molecule is unchanged.

Tertiary alcohols

Tertiary alcohols are resistant to oxidation.



2-methylpropan-2-ol

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Writing balanced equations for the oxidation of alcohols

Oxidation reactions in organic chemistry are often balanced simply by using [O] to represent oxygen from the oxidising agent, for example:

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

$CH_3CHO + [O] \rightarrow CH_3COOH$

The general equation for oxidation of a primary alcohol (where R represents an alkyl group or H) can therefore be written as

$RCH_2OH + [O] \rightarrow RCHO + H_2O$

And that for oxidation of an aldehyde to a carboxylic acid as

$RCHO + [O] \rightarrow RCOOH$

The complete oxidation of a primary alcohol to a carboxylic acid is therefore:

$RCH_2OH + 2[O] \rightarrow RCOOH + H_2O$

The general equation for the oxidation of a secondary alcohol to a ketone can be shown as

$R_1CH(OH)R_2 + [O] \rightarrow R_1COR_2 + H_2O$

However, if a fully balanced equation for the oxidation of an alcohol is required, we must consider the half-equations involved. The half-equation for the oxidation of ethanol to ethanal can be deduced using the procedure in Section 20.2.

$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-$

We can see that this is indeed an oxidation reaction by working out the average oxidation state of C in the reactant and product. If H and O are taken as having oxidation states of +1 and –2, respectively, we can calculate that the average oxidation state of C increases from –2 in CH_3CH_2OH to –1 in CH_3CHO. An increase in oxidation state indicates an oxidation reaction.

During the reaction, the oxidising agent gets reduced, and reduction half-equations for the oxidising agents we have mentioned previously are

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

EXAM TIP

The half-equations for the reduction of $Cr_2O_7^{2-}/H^+$ and MnO_4^-/H^+ are given in the IB Chemistry data booklet.

The overall reaction for the oxidation of ethanol to ethanal by acidified dichromate(VI) can be obtained by multiplying the ethanol half-equation by three to balance the electrons, adding the equations together and cancelling like terms ($6e^-$ and $6H^+$ from each side):

$$3CH_3CH_2OH \rightarrow 3CH_3CHO + 6H^+ + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$3CH_3CH_2OH + Cr_2O_7^{2-} + 14H^+ \rightarrow 3CH_3CHO + 6H^+ + 2Cr^{3+} + 7H_2O$$

overall equation:

$$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

The half-equation for the oxidation of ethanal to ethanoic acid is:

$CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$

To get the overall redox equation for the oxidation of ethanal by acidified manganate(VII), we need to balance the electrons – so the oxidation half-equation is multiplied by 5 and the reduction half-equation by 2:

$$5CH_3CHO + 5H_2O \rightarrow 5CH_3COOH + 10H^+ + 10e^-$$

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

$$5CH_3CHO + 5H_2O + 2MnO_4^- + 16H^+ \rightarrow 5CH_3COOH + 10H^+ + 2Mn^{2+} + 8H_2O$$

overall equation:

$$5CH_3CHO + 2MnO_4^- + 6H^+ \rightarrow 5CH_3COOH + 2Mn^{2+} + 3H_2O$$

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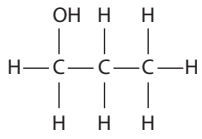
Link

The oxidising agents we are using here contain transition metal ions. In both cases, the change in oxidation state results in a change in colour for the transition metal ion – orange to green for the dichromate(VI) reaction and purple to colourless for the manganate(VII) reaction. The colours of transition metal ions result from a rearrangement of d electrons as light of certain frequencies is absorbed, and if the number of d electrons changes, a different frequency of light will be absorbed (see Chapter 10).

TEST YOUR UNDERSTANDING

19 Write a balanced equation for the complete combustion of butan-1-ol.

20 Name the following alcohols and classify each as primary, secondary or tertiary:



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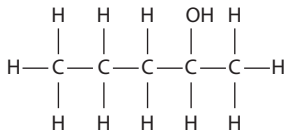

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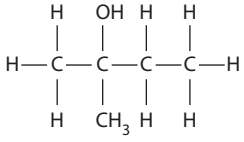

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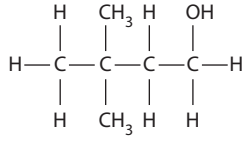


d

21 For each of the alcohols in question 20, give the structural formula of the product (if any) of complete oxidation when they are heated with an oxidising agent, such as acidified potassium dichromate(VI).

22 Give the structure of the organic product formed when each of the following alcohols is heated with an oxidising agent, such as acidified potassium dichromate(VI), with the apparatus set-up for distillation:

- **a** 3-methylbutan-1-ol
- **b** 2-methylpentan-3-ol
- **c** 2,3-dimethylpentan-1-ol.

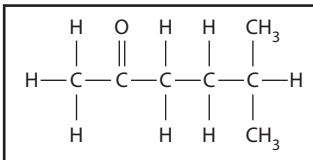
23 Deduce half-equations for the following processes:

- **a** the oxidation of methanol to methanal
- **b** the oxidation of methanol to methanoic acid
- **c** the oxidation of butan-2-ol to butanone
- **d** the oxidation of pentan-1-ol to pentanal.

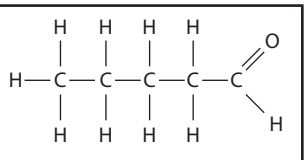
24 Write balanced redox equations for the following processes:

- **a** the oxidation of ethanol to ethanal using acidified manganate(VII)
- **b** the oxidation of ethanal to ethanoic acid using acidified dichromate(VI)
- **c** the oxidation of propan-2-ol to propanone using acidified dichromate(VI).

25 Identify which of the following will be oxidised when they are heated with an oxidising agent such as acidified potassium dichromate(VI). For those that can be oxidised, give the structural formula of the product of oxidation.



a



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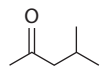

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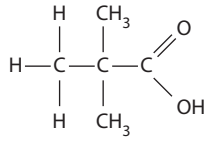

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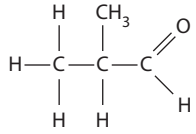

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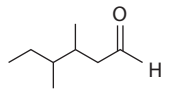

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20.8 Reduction reactions

Reduction of aldehydes, ketones and carboxylic acids

Just as alcohols, aldehydes and ketones can be oxidised using an oxidising agent, the products of the reactions can be reduced again using a reducing agent. Common reducing agents are hydrides – lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$).

Aldehydes

The basic reaction is:

aldehyde $\xrightarrow{\text{reducing agent}}$ primary alcohol

Figure 20.19 shows the reduction of ethanal.

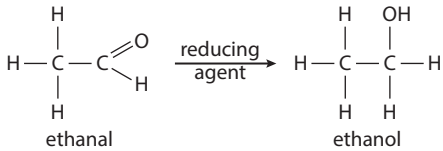

Figure 20.19: Reduction of ethanal to ethanol.

A balanced equation for the reaction can be written using [H] to represent hydrogen from the reducing agent:

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$

Ketones

The basic reaction is:

ketone $\xrightarrow{\text{reducing agent}}$ secondary alcohol

Figure 20.20 shows the reduction of propanone.

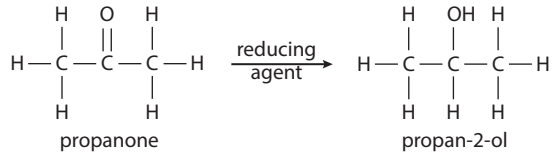

Figure 20.20: Reduction of propanone to propan-2-ol.

Carboxylic acids

Carboxylic acids are reduced to aldehydes and then to primary alcohols. It can be very difficult to stop the reaction at the aldehyde stage, but it is possible with some reagents. The reaction is

carboxylic acid $\xrightarrow{\text{reducing agent}}$ aldehyde $\xrightarrow{\text{reducing agent}}$ primary alcohol

Figure 20.21 shows the reduction of ethanoic acid.

The overall reaction can also be written as a balanced equation using [H] to represent hydrogen from the reducing agent:

$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$

The role of hydride ions

If $LiAlH_4$ and $NaBH_4$ are used as reducing agents, the reduction reactions described in the previous sections can be regarded as involving the transfer of a hydride ion (H^-) from the reducing agent to the organic

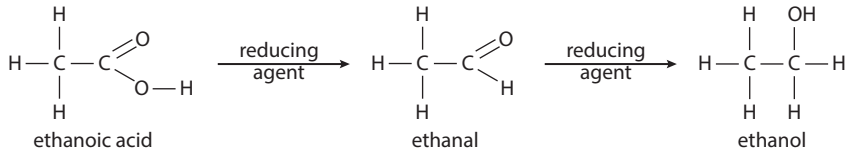

Figure 20.21 Reduction of ethanoic acid to ethanol via ethanal.

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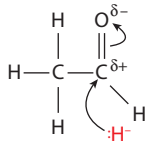
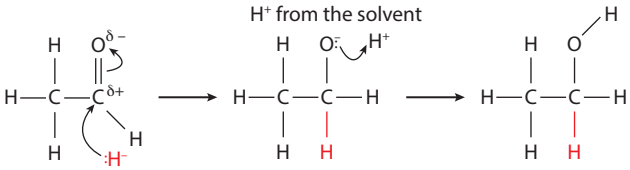
compound – a hydride transfer reaction. This can be shown as:



With the hydride ion donating its lone pair of electrons to C of the C=O group and the electrons being used to form a bond between C and H. In this way, the hydride ion can be regarded as acting as a nucleophile (see Chapter 22). C can only form four bonds, so, as a new C—H bond forms, one of the C=O bonds (the π component) must break (the weakest bond). The reaction mechanism can then be shown in simplified form as

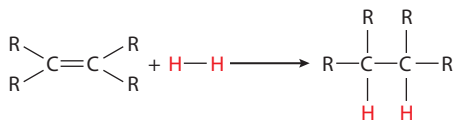


The curly arrows represent movement of a pair of electrons and will be discussed in Chapter 22.

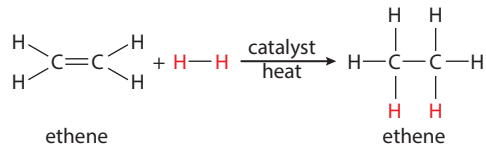
Reduction of alkenes and alkynes

Alkenes and alkynes are called unsaturated compounds because they contain C=C bonds or C≡C bonds. Alkanes, and other compounds not containing multiple C—C bonds, are described as saturated. The addition of hydrogen to alkenes and alkynes in a reduction reaction can convert them into saturated compounds or, if they contain multiple C=C or C≡C bonds, decrease the degree of unsaturation (the number of C—C double/triple bonds present).

The general reaction for an alkene reacting with hydrogen is:

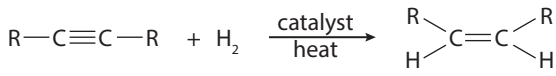


The reaction, which is also called **hydrogenation**, occurs when the alkene is heated in the presence of a catalyst (e.g. nickel) and involves hydrogen adding across the C=C double bond to produce a C—C single bond. We can understand hydrogenation as a reduction reaction from the definition of reduction as the addition of hydrogen but also by looking at oxidation states. If we look at the reaction of ethene with hydrogen:

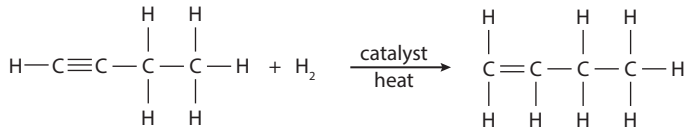


Remembering that H has an oxidation state of +1 in virtually all compounds, we can calculate the oxidation state of C in ethene as –2 but that of C in ethane as –3. Since the oxidation state of C has decreased, it has been reduced. The reducing agent is H_2 – the oxidation state of H increases from 0 to +1 – reducing agents get oxidised in a redox reaction.

Alkynes can be reduced to alkenes. The general reaction is



For example, but-1-yne can be reduced to but-1-ene:



It can be difficult to stop the alkene being reduced further to the alkane, but this can be achieved with certain catalysts.

The equation for the reduction of ethyne to ethane is:

$$H-C\equiv C-H+2H_2 \xrightarrow[\text{heat}]{\text{catalyst}} H_3C-CH_3$$

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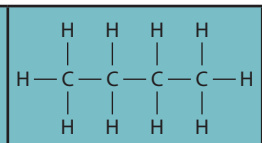
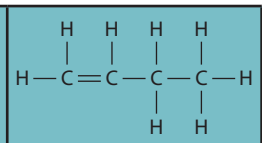
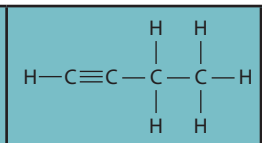
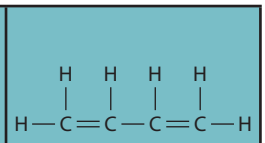
Molecule				
Name	butane	but-1-ene	but-1-yne	buta-1,3-diene
Molecular formula	C_4H_{10}	C_4H_8	C_4H_6	C_4H_6
Double bond equivalents	0	1	2	2
Degree of unsaturation	0	1	2	2

Table 20.3: Formulas and number of double bonds. A triple bond counts as 2 double bonds.

INTERNATIONAL MINDEDNESS

Unsaturated fats (C=C bonds present) from vegetable sources tend to be liquids at room temperature and are called oils. Saturated fats (no C=C bonds) from animal sources are solids at room temperature. A polyunsaturated oil containing many C=C bonds is shown in Figure 20.23. The double bonds are all shown as *cis* (groups either side of the C=C bond are on the same side of the carbon chain – see Section 11.7).

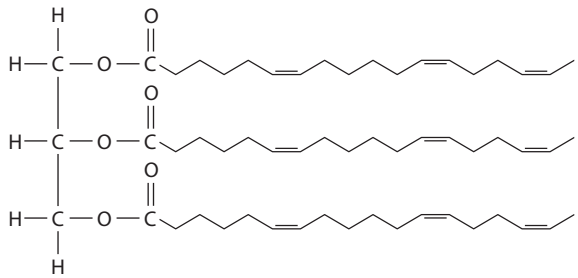


Figure 20.23: The basic structure of a polyunsaturated oil.

It is the presence of *cis*-double bonds that gives an oil its low boiling point – they introduce kinks into the chains, which means that molecules cannot pack together as closely, and so, London forces are weaker.

Hydrogenation of alkenes is used in the manufacture of margarine and in the processing of vegetable oils to produce solid fats, which are more suitable for certain purposes (e.g. pastry making). Partial hydrogenation can be carried out to convert some of the C=C bonds into C—C single bonds. This increases the melting point of the fat so that it is a solid at room temperature. However, the process can produce *trans-fats* (groups either side of the C=C bond are on opposite sides of the carbon chain), which are bad for health. The World Health Organisation believes that artificially produced *trans*-fats could be responsible for 500 000 deaths each year through heart disease. Industrially produced *trans*-fats have been banned in some countries, and other countries have introduced limits on the amount of *trans*-fat that can be in food and/or labelling showing the amount of trans fats (Figure 20.24).

Figure 20.24: Some countries have labelling that shows how much *trans*-fat is in food.

However, there are a great number of countries around the world with no regulations at all. How do you know if there are *trans*-fats in your food? If *partially hydrogenated vegetable oil* appears on a food label, it almost certainly contains industrially produced *trans*-fats.

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The degree of unsaturation

If we compare the molecular formulas of some non-cyclic (not containing rings of atoms) organic compounds (Table 20.3), we can see the relationship between the formula and the number of multiple bonds.

It can be seen that, for every two hydrogen atoms fewer than in the alkane with the same number of carbon atoms, there is one double bond equivalent.

So, a molecule with the formula C_4H_8 has two hydrogen atoms fewer than the parent alkane (C_4H_{10}) and contains one double bond. C_4H_6 has four hydrogens fewer than in the alkane and since four divided by two is two, it has two double bond equivalents – which could mean that there are two double bonds or one triple bond – the reduction in the number of hydrogens caused by a triple bond is equivalent to two double bonds.

The number of double bond equivalents is sometimes called the *degree of unsaturation* or the *index of hydrogen deficiency (IHD)*.

If we look at a more complicated hydrocarbon with formula $C_{18}H_{28}$, we can work out the degree of unsaturation as follows. The general formula for an alkane is C_nH_{2n+2}, so the formula of the alkane with 18 C atoms would be $C_{18}H_{38}$. We see that our hydrocarbon has ten fewer H atoms than the parent alkane. $10 \div 2 = 5$; therefore, the degree of unsaturation is 5 and there are 5 double bond equivalents, e.g., 5 C=C, 3 C=C and 1 C≡C or 1 C=C and 2 C≡C.

If this hydrocarbon is reacted with hydrogen, we could have the following equation:

$$C_{18}H_{28} + 3H_2 \rightarrow C_{18}H_{34}$$

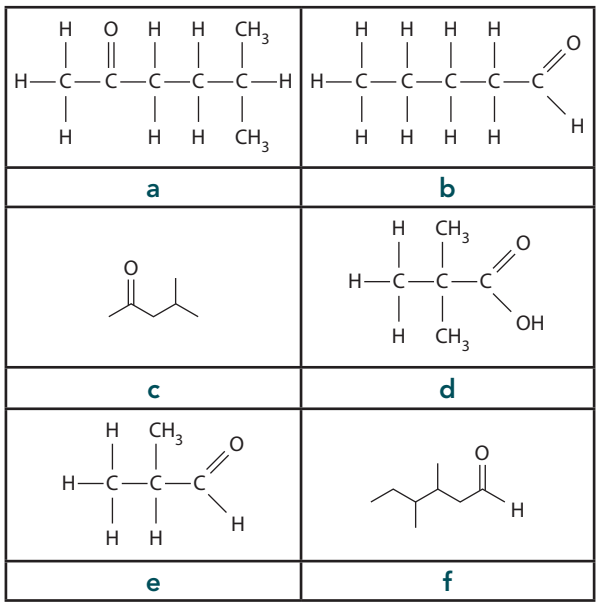
The degree of unsaturation of $C_{18}H_{34}$ is given by $(38 - 34) \div 2 = 2$. Therefore, the degree of unsaturation has decreased. If the original molecule contained five C=C, the product of the reaction would only contain two C=C. Of course, we could have also known this from the fact that $C_{18}H_{28}$ reacted with three hydrogen molecules – each H_2 reacts with one C=C (or one part of a triple bond).

KEY POINT

A ring is also a double bond equivalent, so $C_{18}H_{28}$ could have contained one ring and four C=C, two rings and three C=C, etc.

TEST YOUR UNDERSTANDING

26 Draw the structure of the products formed when each of the following is reacted with a reducing agent, such as $LiAlH_4$.



27 Give the name of the organic product formed when each of the following is reduced using a reducing agent, such as lithium aluminium hydride:

a propanoic acid

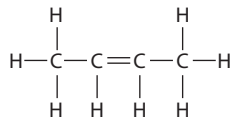
b 2-methylpentanal

c pentan-3-one

d 3-methylbutanoic acid.

28 Draw the structure of the product formed when the following molecules react with hydrogen.

a



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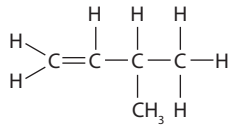

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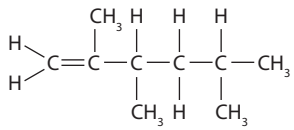
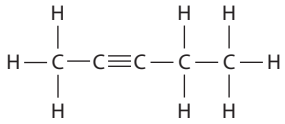
c

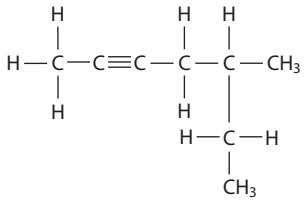


29 Deduce the structural formula of the compound formed when 1 mol of each of the following compounds reacts with 1 mol hydrogen.

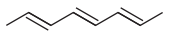
a

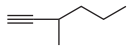


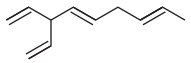
b



30 Deduce the molecular formula of the compound formed when 1 mol of each of the following compounds reacts with the stated amount of hydrogen.

a  + 2 mol H_2

b  + 2 mol H_2

c  + 3 mol H_2

31 Calculate the maximum number of C=C that could be present in each of the following.

a $C_{10}H_{18}$ **b** $C_{15}H_{22}$ **c** $C_{37}H_{60}$

32 Deduce by how much the degree of unsaturation changes in each reaction:

a $C_8H_{14} + nH_2 \rightarrow C_8H_{18}$

b $C_{18}H_{30} + nH_2 \rightarrow C_{18}H_{38}$

c $C_{30}H_{50} + nH_2 \rightarrow C_{30}H_{60}$

20.9 Standard electrode potentials

Cell potentials

We saw earlier in the chapter that the voltage of a voltaic cell depended on the metals/ions in the half-cell. When all concentrations are 1 mol dm^{-3} and the temperature is 298 K, the voltmeter in the $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell reads 1.10 V and that in the $Mg|Mg^{2+}||Cu^{2+}|Cu$ reads 2.71 V (Figure 20.25). Each value is called a **standard cell potential** and give us some idea of the favourability of the redox reactions involved.

KEY POINT

A standard cell potential is the electromotive force [EMF (voltage)] produced when two half-cells are connected under standard conditions (all concentrations 1 mol dm^{-3} and pressure 100 kPa).

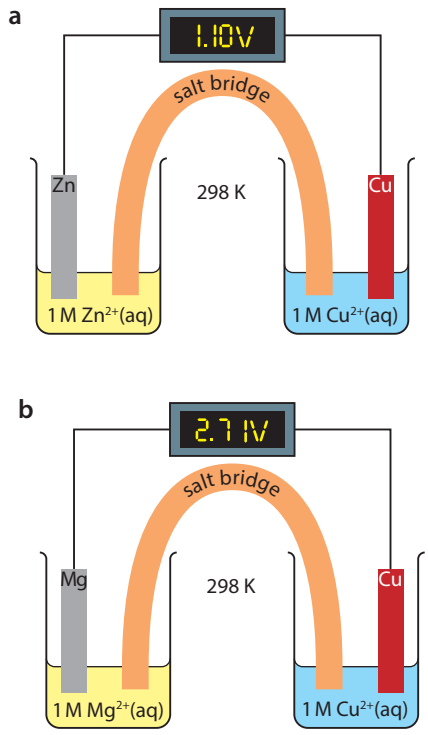


Figure 20.25: The standard cell potentials of **a** $Zn|Zn^{2+}||Cu^{2+}|Cu$ and **b** $Mg|Mg^{2+}||Cu^{2+}|Cu$ cells.

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The standard cell potential ($E^{\ominus}_{cell}$) is related to the value of $\Delta G^{\ominus}$ and K (the equilibrium constant) for the reaction. The higher (more positive) the value of the standard cell potential, the more favourable the reaction, so $\Delta G^{\ominus}$ is more negative, and the value of K is larger, indicating that the position of equilibrium lies more to the right. The reactions that go on in these cells are

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $\quad E^{\ominus}_{cell} = 1.10$ V

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$ $\quad E^{\ominus}_{cell} = 2.71$ V

So, we can say that Mg has a greater tendency to donate electrons to copper ions than zinc does, or magnesium has a greater potential to be oxidised, relative to copper, than zinc does. The voltage (potential difference) in each cell represents the potential for Mg or Zn to be oxidised relative to the potential for Cu^{2+} ions to be reduced. This is related to the energy an electron being transferred has in an Mg or a Zn atom, when compared to the energy it has in a Cu atom and, therefore, to the energy given out when an electron is transferred (Figure 20.26).

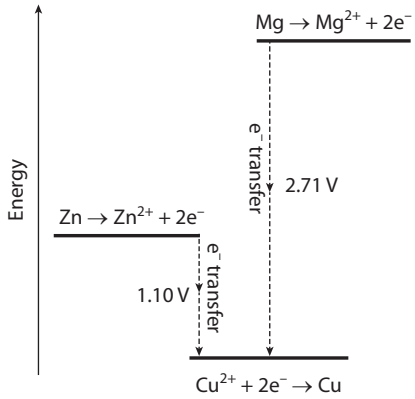

Figure 20.26: Schematic diagram showing the transfer of electrons from zinc or magnesium to Cu^{2+} ions.

We can see that Mg has a higher tendency to donate electrons/be oxidised than zinc, and since we know the tendency of magnesium and zinc to donate electrons relative to copper, we can work out the tendency for magnesium to donate electrons to Zn^{2+} ions as 2.71 – 1.10 = 1.61 V and predict that the following reaction:

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

will be spontaneous with a standard cell potential of 1.61 V, which, indeed, is what we find when the $Mg|Mg^{2+}||Zn^{2+}|Zn$ cell is set up.

It is not possible to measure the tendency for reactions such as

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

to occur in isolation, because if something is reduced then something else must be oxidised – the tendency for redox reactions to occur can be measured only by connecting one half-cell to another half-cell and measuring the cell potential. However, we can see from the above discussion that, if we know the value of two quantities relative to the same baseline, we know them relative to each other. This is a bit like saying, if Rosalie is 15 cm taller than Molly and Steve is 25 cm taller than Molly, we can deduce that Steve must be 10 cm taller than Rosalie.

We have seen here that, if we always choose one particular half-cell as a reference half-cell (Cu^{2+}/Cu in this case), then by measuring the cell potentials of different half-cells relative to this, we will be able to build up a set of values that enable us to judge the relative oxidising and reducing abilities of various species. The reference half-cell that we choose is not, however, the Cu^{2+}/Cu half-cell but rather the **standard hydrogen electrode**.

The standard hydrogen electrode

Individual half-cell electrode potentials cannot be measured in isolation, and so, they are measured relative to a standard. The standard that is chosen is the standard hydrogen electrode (Figure 20.27).

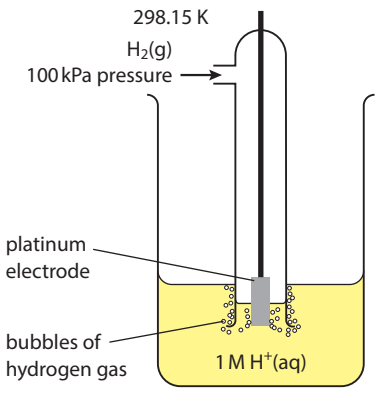

Figure 20.27: The standard hydrogen electrode. Note: 1 M = 1 mol dm^{-3}.

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In the standard hydrogen electrode, hydrogen gas at 100 kPa (1 bar) pressure is bubbled around a platinum electrode of very high surface area in a solution of H^+ ions of concentration 1 mol dm^{-3}. Platinum is chosen because it is an inert metal – it has very little tendency to be oxidised and does not react with acids. The reaction occurring in this half-cell is:

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

and this is arbitrarily assigned a **standard electrode potential** ($E^\ominus$) of 0.00 V.

Note: the reaction could also have been written as

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g) \qquad E^\ominus = 0.00\ V$

A temperature is not included in the definition of standard conditions, but all measurements with the standard hydrogen electrode are usually taken at 298.15 K.

Measuring standard electrode potentials

Figure 20.28 shows a cell that is constructed by joining a standard hydrogen electrode to a Cu^{2+}/Cu half-cell.

A very high resistance voltmeter is used so that the current is as low as possible. If current flows, the concentrations of the species in the half-cells will change, and the system will no longer be under standard conditions.

The overall reaction is

$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s) \qquad E^\ominus_{cell} = 0.34\ V$

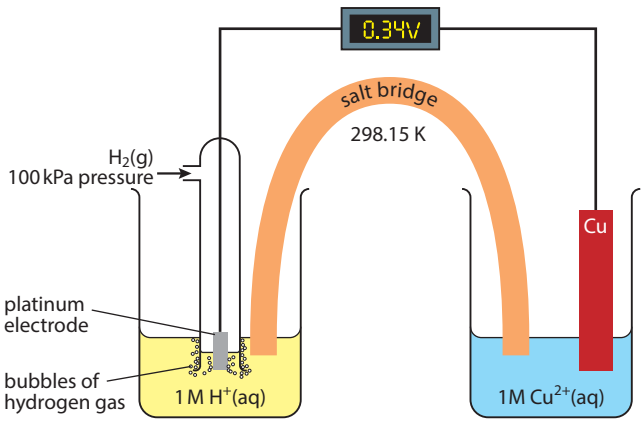

Figure 20.28 Measuring the standard electrode potential of the Cu^{2+}/Cu half-cell. Note: 1 M = 1 mol dm^{-3}.

The half-equations for the reactions that occur in the half-cells are

oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

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

Hydrogen is oxidised and the copper(II) ions are reduced.

Since the standard cell potential when copper is attached to a standard hydrogen electrode is 0.34 V, we can write

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\ V$

where $E^\ominus$ is called the standard electrode potential and shows the tendency for the *reduction* of $Cu^{2+}(aq)$ to Cu(s) to occur relative to the standard hydrogen electrode.

KEY POINT

A standard electrode potential is always quoted for the reduction reaction.

The half-equations for standard electrode potentials are always written as reduction reactions and, because the reduction of Cu^{2+} occurs when it is attached to a standard hydrogen electrode, the standard electrode potential has a positive sign, which indicates that the reduction of copper(II) ions is favourable compared with the reduction of H^+ in the standard hydrogen electrode.

Figure 20.29 shows a cell in which a standard zinc half-cell is connected to a standard hydrogen electrode.

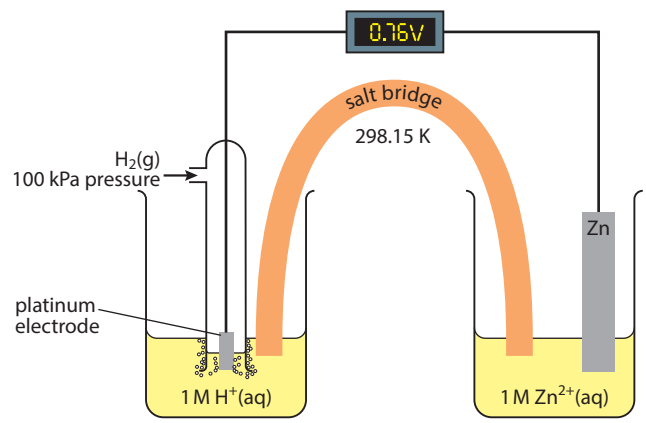

Figure 20.29: Measuring the standard electrode potential of the Zn^{2+}/Zn half-cell. Note: 1 M = 1 mol dm^{-3}.

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The overall reaction is

$2H^+(aq) + Zn(s) \rightarrow H_2(g) + Zn^{2+}(aq) \quad E^\ominus_{cell} = 0.76\ V$

The half-equations for the reactions in the half-cells are

reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

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

Zinc is oxidised when attached to the standard hydrogen electrode, but, because a standard electrode potential is always written in terms of a reduction reaction, we must write

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\ V$

The negative sign indicates that it is the reverse reaction (oxidation) that is favourable when the zinc half-cell is connected to a standard hydrogen electrode.

KEY POINT

The standard electrode potential is the potential of a reduction reaction relative to a standard hydrogen electrode and measured under standard conditions. All solutions must be of concentration 1 mol dm^{-3} and gases at a pressure of 100 kPa.

Some standard electrode potentials are given in Table 20.4.

This makes absolutely no difference to the value of the standard electrode potential.

Half-equation	$E^\ominus$/V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.37
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.45
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.26
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51

Table 20.4: Some standard electrode potentials. Note that the values do change slightly, depending on the state of the element, so, for instance, the electrode potential for $Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ is +1.09 V, and that for $Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ is +1.40 V, but these slight differences should not be relevant to exam questions.

EXAM TIP

Standard electrode potentials are called *standard reduction potentials* in the IB data booklet.

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Note: in some tables of standard electrode potentials, the half-equation for the Cl_2/Cl^- reaction, for example, is written as

$$\frac{1}{2}Cl_2\,(g) + e^- \rightleftharpoons Cl^-\,(aq)$$

A positive value for the standard electrode potential indicates that the reduction reaction occurs (is favourable) when a particular half-cell is attached to a standard hydrogen electrode.

Therefore, we would predict that the reaction:

$$H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s) \quad E^\ominus_{cell} = 0.80\ V$$

would occur spontaneously. Note that multiplying the Ag^+/Ag half-equation by two makes no difference to the cell potential – these potential values give a measure of the tendency of the reaction to occur (the energy per coulomb of charge transferred) and not the total amount of energy released.

A negative value for a standard electrode potential indicates that the oxidation reaction is favourable relative to the standard hydrogen electrode. Therefore, the reaction:

$$2H^+(aq) + Mg(s) \rightarrow H_2(g) + Mg^{2+}(aq) \quad E^\ominus_{cell} = 2.71\ V$$

occurs spontaneously.

Calculating cell potentials

We can use standard electrode potentials to work out the cell potential of the $Zn|Zn^{2+}||Ni^{2+}|Ni$ cell (Figure 20.30).

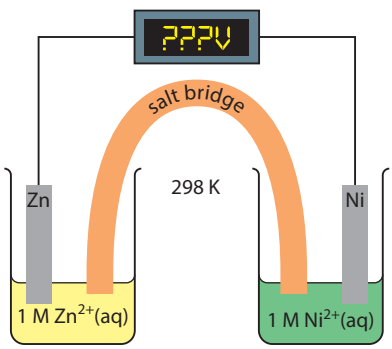

Figure 20.30: A zinc–nickel cell.

The standard electrode potentials are:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\ V$$

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^\ominus = -0.26\ V$$

However, both of these are written as reduction reactions, and, in any cell, there must be a reduction reaction and an oxidation reaction. One of the reactions must occur in the reverse direction.

Because the value of the standard electrode potential is more negative for the Zn^{2+}/Zn reaction, this means that the oxidation (reverse) reaction is more favourable for zinc than that for nickel. We, therefore, reverse the zinc half-equation:

$$\text{oxidation: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^\ominus_{ox} = +0.76\ V$$

$$\text{reduction: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \quad E^\ominus = -0.26\ V$$

here, $E^\ominus_{ox}$ indicates the potential for oxidation, rather than reduction.

The cell potential is just the sum of these electrode potentials:

$$E^\ominus_{cell} = 0.76 - 0.26 = +0.50\ V$$

An overall positive value indicates a spontaneous reaction.

The overall equation for the redox reaction is obtained by adding together the two half-equations (checking first that the numbers of electrons balance):

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

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

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

When calculating a cell potential, we are always looking for a cell potential that is positive overall, as a positive value indicates a spontaneous reaction.

In general, the procedure for calculating a standard cell potential is:

1. Write down the half-equations and standard electrode potentials for the two reactions involved.
2. Change the sign of the more negative (less positive) standard electrode potential and add it to the other electrode potential.

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The polarity of the electrodes and the direction of electron flow in the external circuit

In the previous discussion, we worked out that Zn is oxidised. Since oxidation produces electrons, Zn must be the negative electrode. These electrons will flow around the external circuit from the negative electrode to the positive electrode, where they are gained; therefore, the nickel electrode is the positive electrode (Figure 20.31).

In Figure 20.31, negative charge flows clockwise through the external circuit; therefore, negative ions will also flow clockwise through the salt bridge.

A shortcut to determine which are the negative and positive electrodes is just to look at the original electrode potentials before we have turned one around:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\ V$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^\ominus = -0.2\ 6\ V$

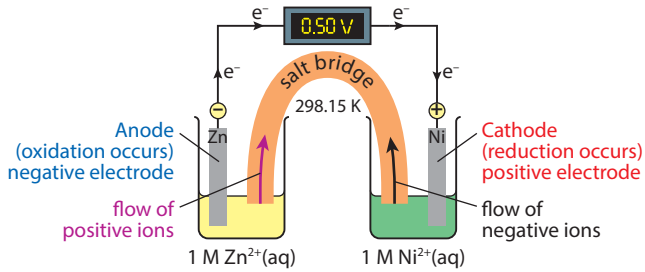


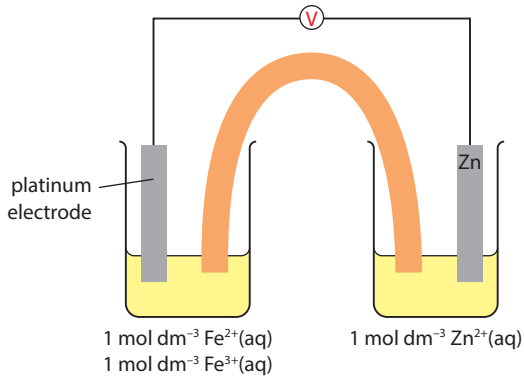
Figure 20.31: Negative charge always flows in the same continuous direction around the circuit.

The more negative value indicates which will be the negative electrode, so here Zn will be the negative electrode.

Oxidation occurs at the zinc electrode; therefore, this is the anode, and reduction occurs at the nickel electrode; therefore, this is the cathode. The negative electrode is always the anode in a voltaic cell.

WORKED EXAMPLE 20.12

A voltaic cell is shown in the diagram.



a Calculate the cell potential.

b Deduce the equation for the overall redox reaction that occurs.

c Explain which is the negative electrode in the cell.

d Deduce the direction of flow of negative ions in the salt bridge.

Answer

This looks different from the cells we have seen previously because there is a platinum electrode in one of the half-cells. Some cells are set up using gases or metal ions but no solid metal. In this case, we do not have anything that we can physically connect a wire to, and so, use platinum (a very inert metal) as the electrode.

a In Table 20.4, there are two electrode potentials involving $Fe^{2+}(aq)$, so which one do we use? It is important to always look at the oxidised and reduced forms in the half-cell (you will always be given these). Here, we are given $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$, and so, we select the standard electrode potential that involves both of those.

The two half-equations are:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76\ V$

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \quad E^\ominus = +0.77\ V$

The more negative value is –0.76 V, and this half-equation is reversed (Zn has a greater tendency to be oxidised than Fe^{2+}):

oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^\ominus_{ox} = +0.76\ V$

reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^\ominus = +0.77\ V$

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CONTINUED

The electrode potential values are added together to give the cell potential:

$E^{\ominus}_{cell} = 0.76 + 0.77 = +1.53$ V

A positive cell potential indicates a spontaneous reaction.

b To combine the two half-equations to produce the overall redox equation, the Fe^{3+}/Fe^{2+} half-equation must be multiplied by 2 so that the number of electrons is the same in the two half-equations.

The two half-equations are then added together to give the overall redox equation:

overall redox reaction: $Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$ $\quad E^{\ominus}_{cell} = +1.53$ V

Remember: although the Fe^{3+}/Fe^{2+} half-equation is multiplied by 2, the standard electrode potential is not. A standard electrode potential indicates the potential for a reaction to occur (energy per coulomb of charge that is transferred) – it is never multiplied by anything when working out a standard cell potential.

c Zn is oxidised, so electrons are produced at this electrode, and it is therefore the negative electrode. Remember, the negative electrode is always the one with the more negative standard electrode potential.

d Electrons travel around the external circuit from the Zn/Zn^{2+} half-cell to the Fe^{3+}/Fe^{2+} half-cell; therefore, negative ions must flow through the salt bridge from the Fe^{3+}/Fe^{2+} half-cell to the Zn/Zn^{2+} half-cell in order for negative charge to flow in the same continuous direction around the entire circuit.

EXAM TIP

In the IB Chemistry data booklet, the electrode potentials are arranged from negative to positive. The half-equation higher up the table is, therefore, the one that is reversed to give the overall spontaneous reaction.

TEST YOUR UNDERSTANDING

33 Use data in Table 20.4 to answer these questions. For each of the cells listed here:

i calculate the cell potential

ii deduce which is the positive and which is the negative electrode

iii deduce which electrode is the anode and which is the cathode

iv deduce the direction of electron flow in the external circuit

v deduce the direction of flow of negative ions in the salt bridge

vi write an overall equation for the reaction that occurs.

a $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $\quad Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$

b $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $\quad Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

c $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

d $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

e $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $\quad Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

f $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

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Using standard electrode potentials to predict the feasibility of a redox reaction

In chemistry, rather than being concerned with generating electricity and voltaic cells, we usually use standard electrode potentials to predict whether or not a particular redox reaction is likely to occur. For example, what happens when we add a solution of iron(III) chloride to a solution of potassium iodide? Will Fe^{3+} oxidise I^- to I_2, so that the following reaction occurs?

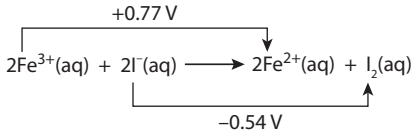
$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

The relevant half-equations are:

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $\quad E^\ominus = +0.54$ V

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^\ominus = +0.77$ V

If we show these in the equation:



The value for $2I^-$ to I_2 is –0.54 V because this is the potential for oxidation – the reverse of the standard electrode potential reaction.

We can see that, overall, the cell potential will be positive (+0.23 V), and we predict, therefore, that this reaction will be spontaneous.

We can test our prediction by seeing what happens when we add iron(III) chloride to a potassium iodide solution – in this case, the solution becomes orange due to the production of iodine. However, even if we could not see any visible reaction, that does not mean our prediction is wrong – as with using $\Delta G^\ominus$ to predict the spontaneity of a reaction, the fact that a reaction is spontaneous does not tell us anything about the speed of the reaction. Although this reaction occurs relatively rapidly at room temperature, this will not always be the case and some reaction mixtures will need heating for the reaction to occur at a significant rate.

Predictions using standard electrode potentials are also valid only under standard conditions – that is, with 1 mol dm^{-3} solutions (and 100 kPa) and usually at 298.15 K. However, as long as the standard cell potential values are not too close to zero, the predictions are likely to be useful, even when a reaction is carried out under non-standard conditions.

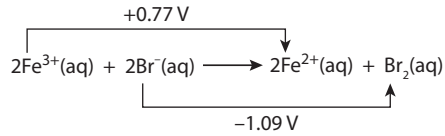
What happens when we add a solution of iron(III) chloride to a solution of potassium bromide? Will the following reaction occur?

$2Fe^{3+}(aq) + 2Br^-(aq) \rightarrow 2Fe^{2+}(aq) + Br_2(aq)$

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^\ominus = +0.77$ V

$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ $\quad E^\ominus = +1.09$ V

Again, if we show these values on the equation, with the value for Br_2/Br^- reversed:



we can see that the overall cell potential is negative (–0.32 V), so the reaction will not be spontaneous, and Fe^{3+} cannot oxidise Br^- to Br_2.

WORKED EXAMPLE 20.13

Predict, using standard electrode potentials, whether or not acidified potassium dichromate(VI) will oxidise Br^- to Br_2.

The half-equations are:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E^\ominus = +1.36$ V

$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ $\quad E^\ominus = +1.09$ V

We are looking at the possibility of Br^- ions being oxidised and must, therefore, reverse that half-equation:

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E^\ominus = +1.36$ V

oxidation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$ $\quad E^\ominus_{ox} = -1.09$V

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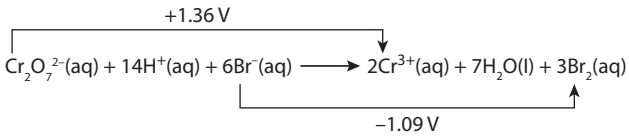
CONTINUED

When the electrode potentials are added together, we get $E^{\ominus}_{cell} = 1.36 - 1.09 = +0.27$ V

The value is positive, which indicates that the reaction will be spontaneous under standard conditions, and acidified dichromate(VI) should oxidise Br^- to Br_2.

We can also see this in the overall equation:



EXAM TIP

We have switched to a single direction arrow here because we know the direction in which the reaction goes. Once you have determined in which direction the reaction proceeds, you should generally switch to single-headed arrows for half-equations and redox equations in the exam.

Oxidising and reducing agents

A very positive value for $E^{\ominus}$, for example:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$
$E^{\ominus} = +1.36$ V

indicates that the reduction reaction is very favourable (relative to the standard hydrogen electrode), and the substance has a very strong tendency to pick up electrons from other species and, therefore, oxidise them.

KEY POINT

The more positive the standard electrode potential, the stronger the oxidising agent.

Remember that, because oxidising agents oxidise substances by taking electrons from them, they gain electrons and, therefore, get reduced in the process.

A very negative value of the standard electrode potential, for example:

$Na^+(aq) + e^- \rightleftharpoons Na(s) \quad E^{\ominus} = -2.71$ V

indicates that the reverse reaction is very favourable:

$Na(s) \rightarrow Na^+(aq) + e^- \quad E^{\ominus}_{ox} = +2.71$ V

So, sodium has a very strong tendency to give electrons to other species, that is, to reduce them. So, Na is a very good reducing agent.

KEY POINTS

The more negative the standard electrode potential, the stronger the reducing agent.

In general, a substance with a more positive standard electrode potential will oxidise (the reduced form of) a substance with a less positive electrode potential

OR

a substance with a more negative standard electrode potential will reduce (the oxidised form of) a substance with a less negative standard electrode potential.

Example

Consider the following half-equations:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $E^{\ominus} = +1.36$ V

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^{\ominus} = +0.54$ V

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$Cr_2O_7^{2-}$ has a more positive standard electrode potential than I_2 and, therefore, $Cr_2O_7^{2-}$ is a stronger oxidising agent than I_2. $Cr_2O_7^{2-}$ will, therefore, oxidise I^- to I_2. Note that it will oxidise the reduced form of I_2, which is I^-, and not I_2 itself.

The overall reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

$$E^\ominus_{cell} = 1.36 - 0.54 = +0.82V$$

In this reaction, $Cr_2O_7^{2-}$ is the oxidising agent and I^- is the reducing agent.

Example

Consider the half-equations:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^\ominus = -2.37\ V$$

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

The standard electrode potential for Mg/Mg^{2+} is more negative than that for the Pb/Pb^{2+} half-cell, which indicates that Mg is a stronger reducing agent than Pb. Mg will, therefore, reduce Pb^{2+} (the oxidised form) to Pb.

The overall equation is

$$Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s) \qquad E^\ominus_{cell} = +2.24\ V$$

In this reaction, Mg is the reducing agent and Pb^{2+} is the oxidising agent.

If we look at Table 20.5, we can see that it is arranged in order of strength of oxidising and reducing agents. K is the strongest reducing agent (most negative $E^\ominus$ value) and F_2 is the strongest oxidising agent (most positive $E^\ominus$ value) in this table.

Species on the right of the reversible arrow higher in the table reduce those on the left of the reversible arrow lower in the table. So, Mg will reduce Zn^{2+} ions, and Zn will reduce Fe^{2+} ions:

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

reduces

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

reduces

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$$

Species on the left of the reversible arrow lower in the table oxidise those on the right of the reversible arrow higher in the table – MnO_4^- will oxidise Cl^- and Cl_2 will oxidise Br^-:

$$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$$

oxidises

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

oxidises

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

It is important to realise here which species are reducing agents and which ones are oxidising agents in Table 20.5. For example, K is the reducing agent and not K^+. K^+ cannot be a reducing agent. For K^+ to be a reducing agent, it would have to be possible to oxidise it to, e.g., K^{2+}, which does not happen. Similarly, F_2 is the oxidising agent – F^- is not an oxidising agent. For F^- to be an oxidising agent, it would have to be possible to reduce it, e.g., to F^{2-}, which does not happen.

Metal reactivity and electrode potentials – the electrochemical series

We saw earlier in this chapter that a more reactive metal would displace a less reactive metal from solution. For example, zinc is more reactive than copper and displaces copper(II) ions from solution:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad E^\ominus_{cell} = +1.10\ V$$

In terms of standard electrode potentials, the more reactive a metal, the more negative its standard electrode potential. The more negative standard electrode potential indicates that the reduction reaction of the metal ion is very unfavourable and, therefore, that the oxidation of the metal is very favourable. More reactive metals have a greater tendency to be oxidised and, thus, give electrons to (reduce) other species.

In Table 20.6, Mg is the most reactive metal and Ag the least reactive. Table 20.6 (and Table 20.5) represents an electrochemical series - the metals are arranged from the most reactive (greatest tendency to be oxidised) at the top to the least reactive metal at the bottom.

Metals above hydrogen in the electrochemical series are stronger reducing agents than hydrogen and should displace hydrogen from a solution of its ions, that is, from acids:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad E^\ominus_{cell} = +2.37\ V$$

Metals lower than hydrogen in the electrochemical series will not react with acids – so copper and silver do not react with hydrochloric acid. In terms of standard electrode potentials, any metal with a negative standard electrode potential is a stronger reducing agent than

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Oxidised form (oxidising agent)		Reduced form (reducing agent)	$E^\ominus$ / V
$K^+(aq) + e^-$	⇌	$K(s)$	−2.92
$Na^+(aq) + e^-$	⇌	$Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$	−2.37
$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$	−0.26
$Pb^{2+}(aq) + 2e^-$	⇌	$Pb(s)$	−0.13
$2H^+(aq) + 2e^-$	⇌	$H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+0.34
$I_2(s) + 2e^-$	⇌	$2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+0.80
$Br_2(l) + 2e^-$	⇌	$2Br^-(aq)$	+1.07
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⇌	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$Cl_2(g) + 2e^-$	⇌	$2Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$F_2(g) + 2e^-$	⇌	$2F^-(aq)$	+2.87

strongest reducing agent

increasing strength of reducing agent

increasing strength of oxidising agent

strongest oxidising agent

Table 20.5: The connection between standard electrode potentials and oxidising/reducing ability.

	$E^\ominus$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

metals will react with acids to produce hydrogen

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ 0.00

metals will not react with acids to produce hydrogen

Table 20.6: The electrochemical series and standard electrode potentials.

hydrogen ($E^\ominus = 0.00$ V) and will reduce hydrogen ions to hydrogen gas. In other words, metals with negative standard electrode potentials should liberate hydrogen from acids.

The reactivity of the halogens

We can consider the reactivity of the halogens in terms of their oxidising ability. Chlorine is a stronger oxidising agent than bromine and iodine, and will oxidise bromide ions to bromine and iodide ions to iodine. Bromine is a stronger oxidising agent than iodine, and will oxidise iodide ions to iodine. In terms of electrons, chlorine has the strongest affinity for electrons and will remove electrons from bromide ions and iodide ions.

Let us consider the standard electrode potentials in Table 20.7. Chlorine has the most positive standard electrode potential and is, therefore, the strongest oxidising agent.

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	$E^{\ominus}$/V
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.40

Table 20.7: Standard potentials for halogens in aqueous solutions. **Note:** some of these values are different to those in Tables 20.4 and 20.5 because the halogen is in aqueous solution here.

$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq) \quad E^{\ominus}_{cell} = +0.31\ V$

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq) \quad E^{\ominus}_{cell} = +0.86\ V$

$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq) \quad E^{\ominus}_{cell} = +0.55\ V$

All these reactions have a positive cell potential and are, therefore, spontaneous. All other possible reactions between the halogens and the halide ions would have a negative electrode potential and are, therefore, not spontaneous, for example:

$Br_2(aq) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(aq) \quad E^{\ominus}_{cell} = -0.31\ V$

TEST YOUR UNDERSTANDING

34 Use the standard electrode potentials in Table 20.5 to predict whether the following reactions will be spontaneous. If the reaction is spontaneous, state the identities of the oxidising agent and the reducing agent.

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

b $Ag^+(aq) + Fe^{2+}(aq) \rightarrow Ag(s) + Fe^{3+}(aq)$

c $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Br^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(l)$

d $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6F^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3F_2(g)$

e $5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \rightarrow 5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq)$

35 Consider the following standard electrode potentials:

	$E^{\ominus}$/V
$U^{4+}(aq) + e^- \rightleftharpoons U^{3+}(aq)$	–0.61
$U^{3+}(aq) + 3e^- \rightleftharpoons U(s)$	–1.79
$Sm^{3+}(aq) + e^- \rightleftharpoons Sm^{2+}(aq)$	–1.15
$Np^{3+}(aq) + 3e^- \rightleftharpoons Np(s)$	–1.86
$Np^{4+}(aq) + e^- \rightleftharpoons Np^{3+}(aq)$	+0.15
$Eu^{3+}(aq) + e^- \rightleftharpoons Eu^{2+}(aq)$	–0.43
$Po^{2+}(aq) + 2e^- \rightleftharpoons Po(s)$	+0.65
$In^{3+}(aq) + 3e^- \rightleftharpoons In(s)$	–0.34

a Select from this list:

i the strongest oxidising agent

ii the strongest reducing agent.

b Use the standard electrode potentials in the table to work out whether the following statements are TRUE or FALSE:

i Eu^{2+} will reduce In^{3+} to In

ii Sm^{3+} will oxidise Np to Np^{3+}

iii Po will reduce Sm^{3+} to Sm^{2+}

iv Np^{3+} is a stronger reducing agent than Po

v U is a stronger reducing agent than Np

vi Np^{3+} will reduce Po^{2+} to Po but will not oxidise Eu^{2+} to Eu^{3+}

vii Sm^{2+} will reduce U^{4+} to U^{3+} but will not reduce U^{3+} to U.

c Predict whether or not the following reactions will be spontaneous:

i $3Eu^{3+}(aq) + In(s) \rightarrow 3Eu^{2+}(aq) + In^{3+}(aq)$

ii $2Eu^{2+}(aq) + Po^{2+}(aq) \rightarrow 2Eu^{3+}(aq) + Po(s)$

iii $3Np^{3+}(aq) + In(s) \rightarrow 3Np^{4+}(aq) + In^{3+}(aq)$

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Standard cell potentials and $\Delta G^{\ominus}$

The standard cell potential and the standard Gibbs energy change ($\Delta G^{\ominus}$) tell us whether a reaction is spontaneous or not. The two quantities are related by the equation:

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

where n is the number of electrons transferred in a redox reaction and F is the Faraday constant, which is equal to the charge on one mole of electrons and has a value of approximately 96 500 C mol^{-1}.

The units of $\Delta G^{\ominus}$ in this equation are J mol^{-1}.

The connection between the signs of $E^{\ominus}$ and $\Delta G^{\ominus}$ is summarised in Table 20.8.

$E^{\ominus}_{cell}$	$\Delta G^{\ominus}$	Spontaneous?
positive	negative	spontaneous
negative	positive	non-spontaneous

Table 20.8: The relationship between $E^{\ominus}_{cell}$, $\Delta G^{\ominus}$ and spontaneity.

EXAM TIP

Remember that the units of $\Delta G^{\ominus}$ in the equation $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ are J mol^{-1}.

WORKED EXAMPLE 20.14

Calculate $\Delta G^{\ominus}$ for the reaction:

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

Answer

The standard electrode potentials are

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s) \quad E^{\ominus} = -0.76$ V

$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(aq) \quad E^{\ominus} = +0.80$ V

The Zn^{2+}/Zn half-equation must be reversed and, therefore, the cell potential can be worked out as

$E^{\ominus}_{cell} = 0.76 + 0.80 = 1.56$V

If the overall equation is split into its two half-equations:

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

it can be seen that two electrons are transferred from the zinc to the silver ions; therefore, $n = 2$.

Using $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$\Delta G^{\ominus} = -2 \times 96\,500 \times 1.56 = -301\,000$ J mol^{-1}

We normally quote $\Delta G^{\ominus}$ values in kJ mol^{-1}; therefore,

$\Delta G^{\ominus} = -301$ kJ mol^{-1}

A negative value of $\Delta G^{\ominus}$ indicates that the reaction is spontaneous.

WORKED EXAMPLE 20.15

Use the half-equations and standard electrode potentials shown to

a calculate the cell potential for the reaction between manganate(VII) ions and iodide ions

b write an equation for the overall redox reaction that occurs

c calculate the value of $\Delta G^{\ominus}$ for the reaction in **b**

d predict whether the reaction will be spontaneous or not.

$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad E^{\ominus} = +1.51$ V

$\frac{1}{2}I_2(aq) + e^{-} \rightleftharpoons I^{-}(aq) \quad E^{\ominus} = +0.54$ V

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CONTINUED

Answer

a We are required to find the cell potential for the reaction of iodide ions, therefore the second half equation is reversed:

$I^-(aq) \rightarrow \frac{1}{2}I_2(aq) + e^-$ $\quad E^\ominus_{ox} = -0.54$ V

The electrode potential is now added to that for the reduction of manganate(VII) ions:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $\quad E^\ominus = +1.51$ V

$E^\ominus_{cell} = +1.51 - 0.54 = +0.97$ V

b There are two equations we could write here. If we multiply the MnO_4^-/Mn^{2+} equation by 2 and the I^-/I_2 equation by 10, we get 10 e^- in each half-equation and the half-equations can be added together:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	$\times 2$	$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$
$I^-(aq) \rightarrow \frac{1}{2}I_2(aq) + e^-$	$\times 10$	$10I^-(aq) \rightarrow 5I_2(aq) + 10e^-$

Overall: $2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(aq)$

However, we could also have just multiplied the I^-/I_2 half–equation by five to give

$MnO_4^-(aq) + 8H^+(aq) + 5I^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + \frac{5}{2}I_2(aq)$

Both equations are correct and would be accepted in the exam. At this stage, however, we must be careful as, although how you write the equation makes no difference to the cell potential, it does affect the value of $\Delta G^\ominus$ because twice as many electrons are transferred in the first equation.

c If we use the first equation from **b**, we can see from the half-equations that 10 electrons are transferred; therefore, $n = 10$.

$\Delta G^\ominus = -nFE^\ominus_{cell}$

Substituting in values, we get $\Delta G^\ominus = -10 \times 96\,500 \times 0.97 = -936\,000$ J mol^{-1} i.e., $\Delta G^\ominus = -936$ kJ mol^{-1}

If we use the second equation from **b**, the half-equations are:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ and $5I^-(aq) \rightarrow \frac{5}{2}I_2(aq) + 5e^-$

Therefore, $n = 5$

$\Delta G^\ominus = -5 \times 96\,500 \times 0.97 = -468\,000$ J mol^{-1} i.e., $\Delta G^\ominus = -468$ kJ mol^{-1}

which is half the value from the previous calculation. Both answers are correct, but your answer must correspond to the equation you wrote in **b**.

d We can see from either the standard cell potential being positive, or the change in Gibbs energy being negative, that the reaction is spontaneous.

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TEST YOUR UNDERSTANDING

36 Use the standard electrode potentials in Table 20.5 to work out the cell potential and hence calculate $\Delta G^{\ominus}$ for each of the following and predict whether the reaction will be spontaneous or not:

a $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

b $Pb^{2+}(aq) + Cu(s) \rightarrow Pb(s) + Cu^{2+}(aq)$

c $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(s)$

d $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

e $\frac{1}{2}Br_2(l) + Fe^{2+}(aq) \rightarrow Br^-(aq) + Fe^{3+}(aq)$

f $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$

g $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

h $2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$

20.10 Electrolysis of aqueous solutions

Electrolysis was introduced earlier in this chapter, where we looked at the electrolysis of molten salts. Here, we will look at the electrolysis of aqueous solutions.

Ionic salts conduct electricity when dissolved in water because the ions are free to move. These solutions can be electrolysed, but the products are not as straightforward as in the electrolysis of molten salts due to the possibility of oxidising or reducing water at the electrodes as well as the ions of the salt. The general rule for the products formed at the electrodes when aqueous solutions are electrolysed is:

Electrode	Product
positive (anode)	oxygen or halogen (not fluorine)
negative (cathode)	metal or hydrogen

We can use standard electrode potentials to rationalise the formation of the products shown here.

Using standard electrode potentials to predict the products of electrolysis

Products at the cathode

When sodium chloride solution is electrolysed, a reduction reaction occurs at the cathode. The two possible species that are present in the solution that could be reduced are Na^+ and H_2O. Let us consider the standard electrode potentials for the reduction of Na^+ and water:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^{\ominus} = -2.71\ V$$

$$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq) \qquad E^{\ominus} = -0.83\ V$$

The standard electrode potential for the reduction of water is much more positive than that for the reduction of Na^+. Therefore, the reduction of water is more favourable than the reduction of Na^+, and hydrogen will be formed from the reduction of water rather than sodium metal from the reduction of Na^+.

If we then compare this with the electrolysis of copper(II) sulfate solution, the electrode potentials for the possible reduction reactions are:

$$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq) \qquad E^{\ominus} = -0.83\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^{\ominus} = +0.34\ V$$

It is more favourable to reduce Cu^{2+} ions than to reduce water and, therefore, copper, from the reduction of Cu^{2+}, will be formed at the cathode rather than hydrogen.

The cut-off point for whether we get hydrogen or the metal would, therefore, seem to be a standard electrode potential of –0.83 V – the standard electrode potential for the reduction of water to hydrogen. However, the situation is a little more complicated than this, and, in general, we can divide metals into three groups:

1 Very reactive metals with standard electrode potentials more negative than –0.83 V. These are metals such as sodium, potassium and magnesium, that is, metals above zinc in the electrochemical series. Hydrogen is produced at the cathode when aqueous solutions of their ions are electrolysed. It is more favourable (less negative standard electrode potential) to reduce water to hydrogen than to reduce the metal ion.

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2 Unreactive metals with positive standard electrode potentials. These are metals such as copper and silver. These produce the metal when aqueous solutions of their ions are electrolysed. It is more favourable to reduce the metal ion (more positive standard electrode potential) than to reduce water.

3 Metals of intermediate reactivity with standard electrode potentials between –0.83 and 0.00 V. These are metals such as zinc, nickel and lead. For these metals, it is much more difficult to make predictions, and we can get either the metal, a mixture of the metal and hydrogen, or hydrogen, depending on the metal and the conditions used (e.g. concentration of the solution and the material of the electrodes). In general, you can assume that the metal will be obtained at the cathode when concentrated solutions are electrolysed, and hydrogen will be obtained from dilute solutions.

We can see that it is possible, to a certain extent, to predict the products of electrolysis of aqueous solutions based on the reactivity of the metals and their standard electrode potentials. It must, however, be remembered that standard electrode potentials refer to standard conditions (1 mol dm^{-3} concentrations) and that there are many factors (concentration, nature of the electrodes, pH, temperature, etc.) that can affect the products of electrolysis.

Products at the anode

Formation of halogens during electrolysis of aqueous solutions

When a solution of sodium iodide is electrolysed, iodine is produced at the anode, but when a solution of sodium fluoride is electrolysed, oxygen (from the oxidation of water) is produced at the anode. This can be explained in terms of how easy it is to oxidise the halide ions to the element, compared to the oxidation of water. Standard electrode potentials can be used as a guide to this.

Consider these standard electrode potentials:

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

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $\quad E^\ominus = +1.23$ V

$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ $\quad E^\ominus = +2.87$ V

At the anode, oxidation occurs and, therefore, we can reverse all these half-equations to get the oxidation reactions:

$2I^-(aq) \rightarrow I_2(s) + 2e^-$ $\quad E^\ominus_{ox} = -0.54$ V

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E^\ominus_{ox} = -1.23$ V

$2F^-(aq) \rightarrow F_2(g) + 2e^-$ $\quad E^\ominus_{ox} = -2.87$ V

At the anode, two oxidation reactions are possible – either the halide ion can be oxidised to produce the halogen, or water can be oxidised to produce oxygen. From these values, it can be seen that it is more favourable to oxidise I^- ions (more positive potential for oxidation) than to oxidise water, but it is less favourable to oxidise F^- ions (more negative potential for oxidation). So, when NaI(aq) is electrolysed, iodide ions will be oxidised at the anode to produce iodine, but when NaF(aq) is electrolysed, water will be oxidised in preference to fluoride ions to produce oxygen gas at the anode. From this discussion, we would also expect to get bromine ($E^\ominus_{ox} = -1.09$ V) when a 1 mol dm^{-3} solution of sodium bromide is electrolysed. With chloride ions, however, the situation is a little more complicated and the product at the anode depends on the concentration of the solution.

At very low chloride concentrations, the product of electrolysis of a solution containing chloride ions is mainly oxygen, but, with more concentrated solutions, chlorine is the major product.

If we compare the potential for oxidation of water and chloride ions:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E^\ominus_{ox} = -1.23$ V

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\quad E^\ominus_{ox} = -1.36$ V

it can be seen that it is slightly more favourable ($E^\ominus_{ox}$ more positive) to oxidise H_2O to form oxygen than to oxidise Cl^- to form chlorine. If a very dilute solution of sodium chloride is electrolysed, the product at the anode is oxygen. However, these values are very close together and, at higher concentrations of sodium chloride, chlorine becomes the major product.

The exact reasons for this are complex, but it can be explained in terms of the difficulty in transferring electrons from water across the electrode–solution interface – a higher voltage is required. The voltage in excess of the expected voltage is known as the overvoltage.

Electrolysis of solutions of sulfates and nitrates

Electrolysis of sulfates and nitrates always produces oxygen gas at the anode. This comes from the oxidation of water:

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

Sulfates and nitrates contain sulfur and nitrogen in their highest oxidation state and, therefore, are not susceptible to oxidation.

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Electrolysis of hydroxides

This produces oxygen at the anode from the oxidation of hydroxide ions:

$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^- \quad E^{\ominus}_{ox} = -0.40\ V$

Electrolysis of water

Distilled water is a very poor conductor of electricity, and so, the electrolysis of water is usually carried out on water to which a small amount of sulfuric acid has been added ('acidified water'). Universal indicator has also been added to the water in Figure 20.32.

The reaction that occurs at the anode (+) is the oxidation of water:

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

The product at the anode is oxygen gas. H^+ ions are also produced in this reaction, and the universal indicator goes redder around the anode.

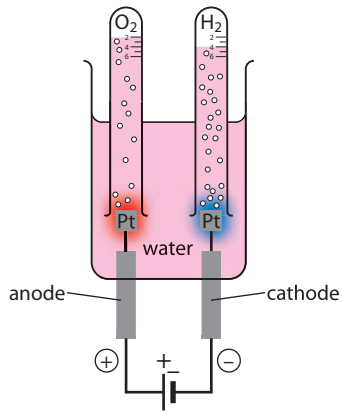

Figure 20.32: Electrolysis of acidified water to which some universal indicator has been added.

The reaction that occurs at the cathode (–) is the reduction of water:

$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$

The product at the cathode is hydrogen gas. OH^- ions are also produced at the cathode, and the universal indicator goes blue around the cathode.

The H^+ ions produced at the anode combine with the OH^- ions formed at the cathode to re-form water. The overall reaction when water is electrolysed is therefore:

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

It can be seen from this equation that twice as much hydrogen as oxygen should be collected. Why this occurs can be understood by looking at the half-equations, which have been written here so that the number of electrons is the same in each:

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

cathode: $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

When four electrons are lost at the anode, one molecule of O_2 is formed, but, when four electrons are gained at the cathode, two molecules of H_2 are formed. Electrons must be lost from the anode at the same rate at which they are gained at the cathode (continuous flow of electrons in the external circuit), so two molecules of H_2 are formed for every molecule of O_2 formed.

The effect of the nature of the Electrodes on the products of electrolysis

When copper(II) sulfate solution is electrolysed, the products at the anode depend on what the anode is made of.

Electrolysis of copper(II) sulfate solution using inert electrodes (graphite or platinum)

The electrolysis of copper(II) sulfate solution using platinum electrodes is shown in Figure 20.33. The products and half-equations at each electrode are shown in Table 20.10.

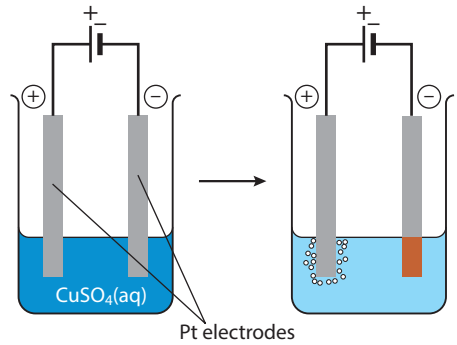

Figure 20.33: Electrolysis of copper(II) sulfate solution using platinum electrodes.

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Electrode	Product	Half-equation
anode (+)	oxygen	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode (–)	copper	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Table 20.10: Electrolysis of copper(II) sulfate solution with platinum electrodes.

Observations that we can make during the experiment include:

- the cathode (–) becomes coated in a pink–brown metal (copper)
- bubbles of a colourless gas (oxygen) are given off at the anode (+)
- the blue colour of the solution fades
- the solution becomes more acidic (test with a pH meter or pH paper) – the pH decreases.

The blue colour of the solution is due to the presence of $Cu^{2+}(aq)$ ions. The colour of the solution becomes paler as the Cu^{2+} ions are removed from the solution by reduction at the cathode.

The oxidation of water at the anode produces H^+ ions as well as O_2. This means that the solution becomes acidic.

The sulfate ions remain unchanged in the solution, and, because H^+ ions are also produced, the remaining solution after all the copper ions have been removed is sulfuric acid (H_2SO_4).

Electrolysis of copper(II) sulfate solution using copper electrodes

The electrolysis of copper(II) sulfate solution using copper electrodes is shown in Figure **20.34**.

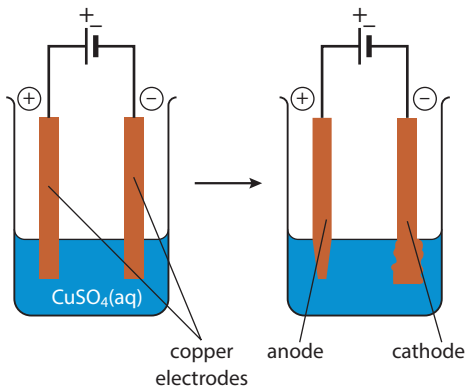

Figure 20.34: Electrolysis of copper(II) sulfate solution using copper electrodes.

Observations that we can make during the experiment include:

- the positive electrode (anode) becomes smaller
- the negative electrode (cathode) becomes coated with a brown metal (copper)
- the solution remains the same colour
- the pH of the solution remains constant

The reaction at the cathode is exactly the same as when inert electrodes are used. However, at the anode the reaction is different and no oxygen is given off. The reaction at the anode is oxidation and two reactions are possible:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\qquad E^{\ominus}_{ox} = -0.34$ V

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\qquad E^{\ominus}_{ox} = -1.23$ V

The potential for oxidation of copper is more positive than that for the oxidation of water, and therefore the oxidation of copper is more favourable than the oxidation of water. So copper ions pass into solution from the anode and oxygen is not produced. The oxidation of copper at the anode was not possible when inert electrodes were used.

The overall processes that occur are summarised in Table 20.11.

Electrode	Product	Half-equation
anode (+)	copper ions pass into solution	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode (–)	copper	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Table 20.11: Electrolysis of copper(II) sulfate solution with copper electrodes.

The net process is therefore a transfer of copper from the anode to the cathode. If pure copper electrodes are used, the mass of copper lost from the anode is equal to the mass of copper deposited on the cathode.

Because one Cu^{2+} ion is removed from the solution at the cathode for every Cu^{2+} ion added to the solution at the anode, the overall concentration of Cu^{2+} ions in the electrolyte does not change and the blue colour of the solution remains constant. There is no change in the concentration of $H^+(aq)$ ions, so the pH of the solution does not change.

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Summary of the products of electrolysis of aqueous solutions

The products obtained from the electrolysis of various solutions using platinum electrodes are given in Table 20.12.

Table 20.13 shows some differences between the products formed when molten salts and (reasonably concentrated) aqueous solutions are electrolysed using inert electrodes.

Solution	Product at anode (+)	Product at cathode (–)
$CuCl_2$	chlorine gas	copper metal
$CuSO_4$	oxygen gas	copper metal
NaCl – very dilute	oxygen gas	hydrogen gas
NaCl – concentrated	chlorine gas	hydrogen gas
HCl	chlorine gas	hydrogen gas
H_2O (acidified)	oxygen gas	hydrogen gas
NaF	oxygen gas	hydrogen gas

Table 20.12: Electrolysis products of aqueous solutions using platinum electrodes. Pure water is not technically a solution, but here the results are for 'acidified water', which is water with a small amount of sulfuric acid added so that it conducts electricity better.

Electroplating

KEY POINT

Electroplating is the process of coating an object with a thin layer of a metal using electrolysis.

For example, steel objects can be electroplated with chromium to prevent rusting and to provide a decorative finish (Figure 20.16).

Figure 20.16: Plating with chromium is usually called 'chrome plating' and can be used on motorcycle engines.

Figure 20.17 shows the experimental set-up for coating a key with copper.

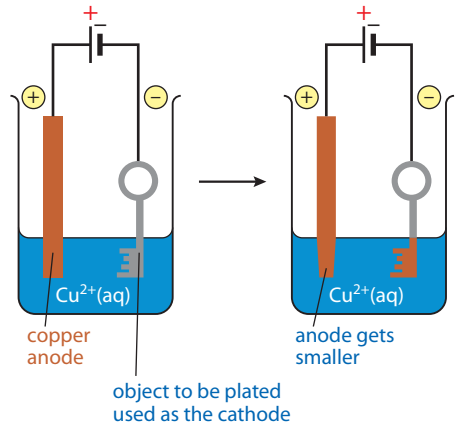

Figure 20.17: Experimental set-up for electroplating a key with copper.

Key features of the experimental set-up are:

- the object to be coated should be used as the cathode
- the anode should be made of the metal with which the object is to be plated

	Copper chloride		Sodium chloride		Sodium fluoride	
	anode(+)	cathode(–)	anode(+)	cathode(–)	anode(+)	cathode(–)
molten	chlorine	copper	chlorine	sodium	fluorine	sodium
aqueous	chlorine	copper	chlorine	hydrogen	oxygen	hydrogen

Table 20.13: Differences between electrolysis of molten salts and aqueous solutions are highlighted in red.

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- the electrolyte will normally be a solution containing the ions of the coating metal.

The object to be plated must be the cathode (–) because metal ions are positively charged and will be attracted to the cathode. The object to be plated must be thoroughly cleaned before electroplating; otherwise, the coating will not stick properly to the surface. The reactions involved are:

Electrode	Product	Half-equation
anode (+)	copper ions pass into solution	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode (–)	copper deposited on cathode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Copper metal is oxidised to copper ions at the anode, so the copper anode gets smaller. Copper ions are reduced to copper metal at the cathode, and so, a layer of copper builds up on the cathode. The net process is, therefore, a transfer of copper from the anode to the cathode. If pure copper electrodes are used, the mass of copper lost from the anode is equal to the mass of copper deposited on the cathode.

Because one Cu^{2+} ion is removed from the solution at the cathode for every Cu^{2+} ion added to the solution at the anode, the overall concentration of Cu^{2+} ions in the electrolyte does not change, and the blue colour of the solution remains constant.

EXAM TIP

The electrolyte must be a solution containing ions of the plating metal. To select a suitable solution, remember that all nitrates are soluble in water.

	Anode(+)	Cathode (-)	Electrolyte
composition	silver	object	$Ag^+(aq)$, e.g., $AgNO_3(aq)$
reaction	$Ag(s) \rightarrow Ag^+(aq) + e^-$	$Ag^+(aq) + e^- \rightarrow Ag(s)$	

Table 20.14: Electroplating an object with silver. A different electrolyte is used commercially to silver plate objects, but details of the actual process are not required.

Details of how to plate an object with silver are given in Table 20.14.

Electrolysis and $\Delta G^{\ominus}$

Remember that all the electrolysis reactions we have looked at here are non-spontaneous ($\Delta G^{\ominus}$ for the process is positive) – a constant supply of electricity must be supplied to cause them to occur. As soon as the supply is turned off, the reaction stops. This can be contrasted with a voltaic cell, in which a spontaneous reaction can be used to generate electricity ($\Delta G^{\ominus}$ negative).

TEST YOUR UNDERSTANDING

37 When the following aqueous solutions are electrolysed using platinum electrodes:

i predict the products at the anode and cathode

ii write equations for the reactions at the anode and cathode.

a potassium iodide solution

b calcium nitrate solution

c concentrated potassium chloride solution

d magnesium sulfate solution

e silver nitrate solution

f sodium sulfate solution

g copper(II) fluoride solution

h magnesium nitrate solution

38 Metal objects can be plated with nickel.

a Draw a labelled diagram to show how a metal object could be plated with nickel. On your diagram identify the positive and negative electrodes.

b Suggest the name of an electrolyte that could be used.

c Write half-equations to show the reactions at the anode and cathode (nickel forms a 2+ ion).

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain redox reactions in terms of electron transfer and changes in oxidation state	20.1			
write half-equations for oxidation and reduction reactions	20.2			
construct equations for redox reactions	20.2			
interpret data regarding displacement reaction	20.3			
explain the reactions that occur in a voltaic cell	20.4			
work out the reactions that occur in a rechargeable battery	20.5			
explain electrolysis of molten salts	20.6			
describe the oxidation of alcohols and aldehydes	20.7			
describe the reduction of aldehydes, ketones and carboxylic acids	20.8			
describe the reduction of unsaturated compounds	20.8			
explain what a standard electrode potential is	20.9			
use standard electrode potentials to calculate cell potentials	20.9			
explain the connection between the standard Gibbs energy change and standard electrode potentials	20.9			
solve problems involving $\Delta G^{\ominus}$ and $E^{\ominus}$	20.9			
explain the products formed when aqueous solutions are electrolysed.	20.10			
explain how electroplating works	20.6			

REFLECTION

- This is a large topic, which involves many aspects of other topics. To what extent do you feel that your understanding of this topic would be enhanced by revising other chapters?
- Which parts of this topic are you most unsure about? How can you improve your understanding in these areas?
- Try explaining the terms oxidising agent and reducing agent to another student – are you sure that you understand what these terms mean?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 21

Electron sharing reactions

LEARNING OBJECTIVES

In this chapter you will:

- understand what a radical is
- understand the radical substitution reactions of alkanes with halogens.

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GUIDING QUESTIONS

- What is a radical?
- How do radicals react?

Introduction

Radicals are reactive species that are important in organic chemistry, atmospheric chemistry and our bodies. They are often called *free radicals* and have become well known in recent years due to perceived health risks associated with them. When too many radicals are produced in the body, this can cause oxidative stress in cells, which has been linked with ageing and various diseases such as cancer. The link between radicals and ageing/cancer has created a great deal of interest in antioxidants, which scavenge radicals in the body, and a huge rise in the sale of food supplements containing antioxidants. The debate is still ongoing as to whether taking antioxidant food supplements has any effect at all.

21.1 Radicals

KEY POINT

A radical is a molecular entity containing an unpaired electron.

Radicals can be atoms, molecules or ions. Examples of some radicals are shown in Figure 21.1.

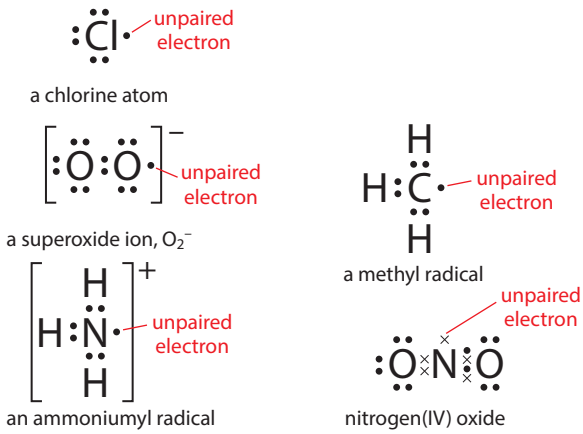

Figure 21.1: Lewis formulas for some radicals.

The term *molecular entity* seems confusing in the definition of a radical as radicals can be atoms, ions or molecules. However, the official, IUPAC, definition of a molecular entity encompasses atoms, molecules and ions.

Radicals are usually represented with a dot to show the **unpaired electron**, for example:

$Cl\cdot$ chlorine radical $H_3C\cdot$ methyl radical

KEY POINT

If a molecular entity contains an odd number of electrons, it will be a radical.

For example, we can tell that NO is a radical by adding up the total number of electrons. There are 7 electrons in a nitrogen atom and 8 in an oxygen atom: $7 + 8 = 15$, which is an odd number, so NO must contain an unpaired electron. Similarly, NO_2 is a radical because it contains $7 + 2 \times 8 = 23$ electrons.

TEST YOUR UNDERSTANDING

1 Identify which of the following are radicals:

a	NH_3	**b**	Br
c	OH	**d**	OH^-
e	C_2H_5	**f**	CO
g	ClO_2	**h**	NO_2
i	SO_2	**j**	O_2^-
k	CH_3^+	**l**	CH_4^+
m	NH_4^+	**n**	O_2^+
o	O_3^-		

Reactions of radicals

Radicals are usually highly reactive, with the reactions involving the pairing up of the unpaired electron to form a covalent bond. For instance, the reaction

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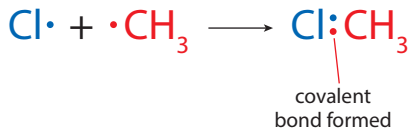
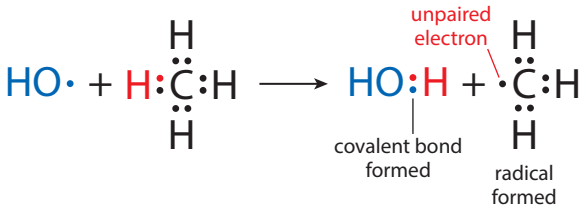
between a chlorine radical (chlorine atom) and a methyl radical is:



This process, where two radicals come together to form a covalent bond is called *colligation*.

When two NO_2 radicals react N_2O_4 is formed, which does not contain any unpaired electrons:

If a radical reacts with a molecular species that does not have an unpaired electron, a covalent bond will again be formed to pair up the unpaired electron, but a bond will also be broken to form another radical, e.g.



Unreactivity of alkanes

We met alkanes, saturated hydrocarbons with the general formula C_nH_{2n+2}, in Chapter 11. Alkanes are obtained from crude oil and are important in everyday life because of their combustion reaction – they are fuels. However, apart from combustion, alkanes are generally fairly unreactive. The reasons for this are:

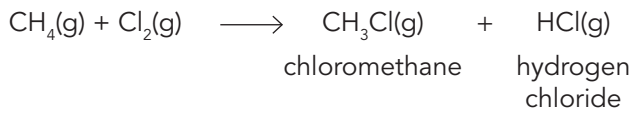
- the high strengths of C—C and C—H bonds mean that it is generally energetically unfavourable to break them in a reaction
- alkanes are essentially non-polar, and so, are unlikely to attract polar molecules or ions.

Link

Alkanes are thermodynamically unstable with respect to the products of combustion – the reaction is highly exothermic and, therefore, the products have less energy than the reactants (see Chapter 12). They can, however, be described as *kinetically stable* – the activation energy is relatively high, and the reaction does not occur at a significant rate unless we do something to start it, e.g., light a match (see Chapter 17).

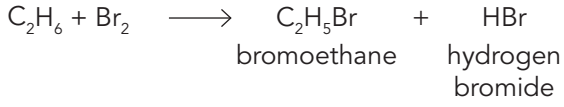
Reaction of alkanes with halogens

Alkanes react with halogens when heated or in the presence of ultraviolet (UV) light. There is no reaction in the dark at room temperature. The equation for the reaction between methane and chlorine in the presence of UV light or heat is



Note that it is *hydrogen chloride* and not hydrochloric acid that is formed. Hydrochloric acid is formed when hydrogen chloride gas is dissolved in water.

The equation for the reaction between ethane and bromine is



If we look at this reaction in terms of full structural formulas (Figure 21.4), we can see what is happening more clearly.

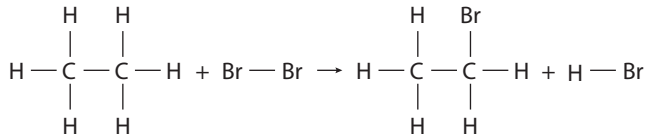


Figure 21.4: The reaction between ethane and bromine.

This type of reaction is called a **substitution reaction**.

KEY POINT

A substitution reaction is one in which an atom or a group is replaced by a different atom or group.

In Figure 21.4, a hydrogen atom in ethane is replaced by a bromine atom.

The reactions shown involve *mono*-substitution – the replacement of *one* hydrogen atom in the molecule by *one* halogen atom. However, because the reaction involves highly reactive radicals, it is difficult to control and a

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mixture of products, some of which involve multiple substitutions, is formed. For example, in the reaction between methane and chlorine, dichloromethane, trichloromethane and tetrachloromethane can all be formed by stepwise substitution of H atoms:

$$CH_4 + Cl_2 \rightarrow HCl + \underset{\text{chloromethane}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \rightarrow HCl + \underset{\text{dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \rightarrow HCl + \underset{\text{trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \rightarrow HCl + \underset{\text{tetrachloromethane}}{CCl_4}$$

Other alkanes

These reactions do not just occur with methane and ethane – all alkanes react in a similar way. Figure 21.5 shows what happens when butane reacts with chlorine in the presence of UV light; there are two possible mono-chlorinated products.

There are, of course, many multi-substituted products as well.

21.2 The radical substitution mechanism

KEY POINT

The mechanism for the reactions between alkanes and halogens is called radical substitution.

The reaction proceeds in a series of steps.
Consider the reaction between methane and chlorine:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

Initiation

This first step in the reaction mechanism involves breaking apart chlorine molecules into two chlorine radicals (chlorine atoms):

$$Cl_2 \xrightarrow{UV} 2Cl\bullet$$

This is called the **initiation step** – it starts off the reaction and involves an increase in the number of radicals. The energy needed to break the Cl—Cl bond is provided by UV light or heat. The Cl—Cl bond (242 kJ mol^{-1}) is substantially weaker than the C—H bond (412 kJ mol^{-1}) and, therefore, the Cl—Cl bond is more easily broken.

The bond-breaking process is called **homolytic fission**.

KEY POINT

Homolytic fission is the breaking of a covalent bond (made up of two electrons) so that one electron goes to each atom that made up the original bond.

When the Cl—Cl bond breaks, two identical Cl atoms are formed, hence the name *homo*lytic – the 'homo' part coming from the Greek word 'homos' meaning 'same'. This movement of one electron in a chemical reaction can be shown with single-headed curly arrows ('fish hooks') – Figure 21.6.

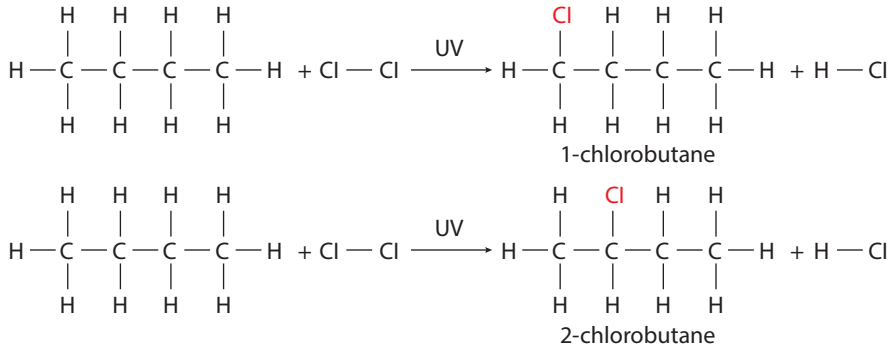

Figure 21.5: The formation of more than one mono-substituted product when butane reacts with chlorine.

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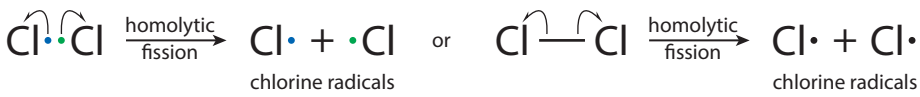

Figure 21.6: The single-headed arrows show one electron going to each atom as the bond breaks.

Propagation

There are two **propagation steps** in the radical substitution mechanism.

A chlorine radical is a very reactive species – when it collides with a methane molecule in the reaction mixture, it will combine with a hydrogen atom to pair up its unpaired electron:

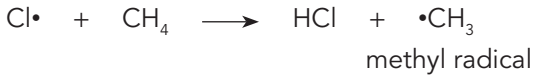

Figure 21.7 shows more detail of what happens to the electrons in this step.

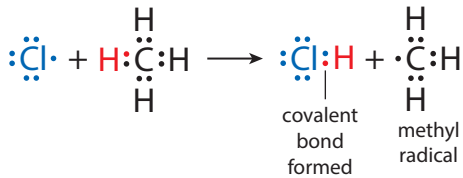

Figure 21.7: The first propagation step showing the making and breaking of bonds.

This step can also be shown using fish hooks, as in Figure 21.8.

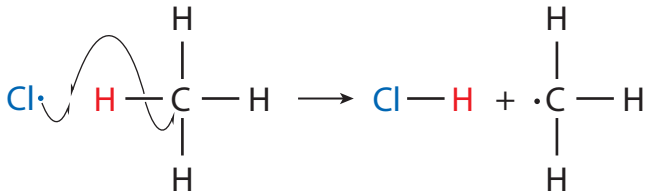

Figure 21.8: The first propagation step shown using fish hooks. You do not usually need to show fish hooks in exams for propagation and termination (see below) steps.

A highly reactive methyl radical is generated in this step, and this will react with a Cl_2 molecule to form a C—Cl bond:

$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

Figure 21.9 shows what happens to the electrons in this step.

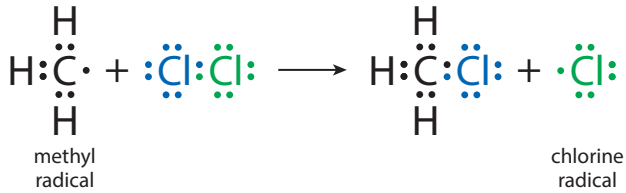

Figure 21.9: The second propagation step showing the making and breaking of bonds.

Cl• generated in this step can go on to react with another methane molecule, so that the reaction keeps going (Figure 21.10).

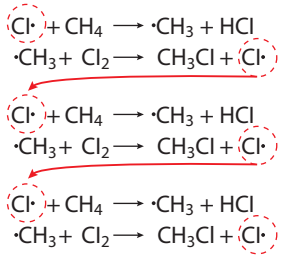

Figure 21.10: The propagation steps are repeated over and over again.

This is an example of a **chain reaction** because one initial event (the breaking of the Cl—Cl bond) causes a large number of subsequent reactions, with the reactive species being regenerated in each cycle of reactions.

Termination

In this reaction mixture, the radicals are always present in very low concentrations, so the chance of two colliding is very low. However, they do collide sometimes and this brings the chain reaction to an end. There are several possible **termination steps**:

$Cl\bullet + Cl\bullet \rightarrow Cl_2$

$Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

$\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$

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The formation of a bond between two radicals can also be shown using fish hooks (Figure 21.11).

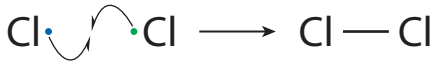

Figure 21.11: The formation of a bond in a termination step, using fish hooks.

The overall mechanism

We can show the overall mechanism as:

initiation: $Cl_2 \xrightarrow{UV} 2Cl\bullet$

propagation: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

propagation: $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

termination: $Cl\bullet + Cl\bullet \rightarrow Cl_2$

termination: $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

termination: $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$

We can see how the number of radicals changes in each step:

- Initiation: increase in the number of radicals.
- Propagation: no change in the number of radicals.
- Termination: decrease in the number of radicals.

Formation of other products

Formation of multi-substituted products occurs when a chlorine radical collides with a different molecule in the first propagation step. So, dichloromethane is formed when a chlorine radical collides with a chloromethane molecule rather than a methane molecule:

propagation: $Cl\bullet + CH_3Cl \rightarrow \bullet CH_2Cl + HCl$

propagation: $\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$

Trichloromethane is formed when a chlorine radical collides with a dichloromethane molecule:

propagation: $Cl\bullet + CH_2Cl_2 \rightarrow \bullet CHCl_2 + HCl$

propagation: $\bullet CHCl_2 + Cl_2 \rightarrow CHCl_3 + Cl\bullet$

Tetrachloromethane is formed when a chlorine radical collides with a trichloromethane molecule:

propagation: $Cl\bullet + CHCl_3 \rightarrow \bullet CCl_3 + HCl$

propagation: $\bullet CCl_3 + Cl_2 \rightarrow CCl_4 + Cl\bullet$

Ethane and bromine

The radical substitution mechanism is basically the same, irrespective of the halogen or the alkane, so the reaction of ethane with bromine can be shown as:

initiation: $Br_2 \xrightarrow{UV} 2Br\bullet$

propagation: $C_2H_6 + Br\bullet \rightarrow \bullet CH_2CH_3 + HBr$

propagation: $\bullet CH_2CH_3 + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$

termination: $Br\bullet + Br\bullet \rightarrow Br_2$

termination: $Br\bullet + \bullet CH_2CH_3 \rightarrow CH_3CH_2Br$

termination: $\bullet CH_2CH_3 + \bullet CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3$

TEST YOUR UNDERSTANDING

2 Write an equation for the reaction of ethane with chlorine in the presence of UV light.

3 How many mono-substituted products are possible when chlorine reacts with each of the following molecules in the presence of UV light?

- **a** hexane
- **b** 2-methylpropane
- **c** 2,2-dimethylpropane

4 Draw out the structures of all possible di-substituted products when propane reacts with bromine.

5 Write the mechanism for the reaction between chlorine and ethane in the presence of UV light.

6 Draw two propagation steps to show the formation of 1,1,1-trichloroethane from a suitable starting material.

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SCIENCE IN CONTEXT

Chlorofluorocarbons (CFCs), also called Freons, are non-toxic, non-flammable substances developed in the first half of the 20th century. Examples are CCl_3F (CFC-11, trichlorofluoromethane) and CCl_2F_2 (CFC-12, dichlorodifluoromethane). CFCs were used extensively as refrigerants, aerosol propellants, in fire extinguishers as foaming agents for plastics and as solvents. However, in the early 1970s, two scientists, F Sherwood Rowland and Mario Molina, realised that CFCs were destroying the ozone layer.

The 'ozone layer' is a region in the stratosphere where there is a higher concentration of ozone. About 90% of the ozone in the atmosphere is found in this region. The ozone layer is essential for protecting the surface of the Earth from the harmful effects of UV radiation. Ozone does this by absorbing UV, which causes it to break apart:

$$O_3 \xrightarrow{UV} O_2 + O\bullet$$

Ozone will also be reformed in the atmosphere, and as long the rate at which ozone is destroyed is balanced by the rate at which it is formed, there is a steady concentration of ozone and the Earth is safe. However, if something is introduced into this system that can destroy ozone, this steady state is disturbed and the concentration of ozone in the atmosphere decreases, leading to an increase in UV reaching the Earth, which can result in increased incidences of cataracts and skin cancer.

The main reason for using CFCs was that they were unreactive, but this is also the reason why they are so dangerous. CFCs are so unreactive they can pass through the troposphere (the lower level of the atmosphere where we live) and up into the stratosphere (where the ozone layer is) without reacting.

In the stratosphere, UV light causes the C—Cl bond to break (it is weaker than the C—F bond) to produce chlorine radicals, which catalyse the depletion of ozone:

$$\bullet Cl + O_3 \rightarrow ClO\bullet + O_2$$

$$ClO\bullet + O\bullet \rightarrow O_2 + \underset{\text{chlorine radical reformed}}{Cl\bullet}$$

The net effect of these reactions is: $O_3 + O \rightarrow 2O_2$

One chlorine radical can destroy thousands of ozone molecules.

Molina and Rowland met a great deal of opposition from chemical companies when they first made their findings public, but eventually the world came together to reduce the production of ozone-depleting substances with the 1987 Montreal Protocol – the only UN treaty to be ratified by all 197 UN states. This resulted in a significant reduction in the atmospheric concentration of CFCs, and the ozone layer seems to be recovering. Molina and Rowland were awarded the Nobel Prize for Chemistry in 1995 (together with Paul Crutzen who discovered that NO catalysed the destruction of ozone).

Figure 21.12: CFCs were used in refrigerators. Incorrect disposal led to the CFCs going into the atmosphere and destroying the ozone layer.

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Link

Why do chlorine radicals catalyse the destruction of O_3 but not O_2?

If we look at the first step in the destruction of ozone by chlorine radicals and compare it with a possible reaction of dioxygen with chlorine radicals, we have:

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ $\quad \Delta H = -162\ kJ\ mol^{-1}$ $\quad \Delta G = -170\ kJ\ mol^{-1}$

$Cl\bullet + O_2 \rightarrow ClO\bullet + O\bullet$ $\quad \Delta H = +230\ kJ\ mol^{-1}$ $\quad \Delta G = +225\ kJ\ mol^{-1}$

The enthalpy and Gibbs energy change for these reactions are very different. The first reaction is spontaneous but the second one is very much not. The entropy change in each case is going to be quite small because both reactions involve no change in the number of moles of gas, therefore the main contribution to the Gibbs energy change is from the enthalpy change. Why are these so different? In both cases a Cl—O bond is made, so the difference between the reactions is due to the O—O bonds. In the first reaction we break a relatively weaker O—O bond in ozone (bond order 1.5) and make a stronger bond (bond order 2) in O_2, but in the second reaction we just break an O=O bond; the first reaction is this exothermic but the second is endothermic.

SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain what a radical is	21.1			
explain the radical substitution reactions of alkanes with halogens.	21.2			

REFLECTION

- Did you find understanding what a radical is a difficult concept?
- Do you feel that you would be able to recognise a species with an unpaired electron?
- To what extent do you feel that you understand what is happening in the radical substitution reaction?
- Do you feel that this is something that you will just have to learn or could you explain it to someone else?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Chapter 22

Electron-pair sharing reactions

LEARNING OBJECTIVES

In this chapter you will:

- understand the term nucleophile
- describe nucleophilic substitution reactions
- understand the term heterolytic fission
- understand the term electrophile
- understand why alkenes are more reactive than alkanes
- construct equations for the reaction of alkenes

- understand the Lewis definition of acids and bases
- understand the mechanism for nucleophilic substitution reactions

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CONTINUED

- explain how the nature of the leaving group affects the rate of nucleophilic substitution reactions
- understand the mechanism for electrophilic addition reactions
- understand the reactions of unsymmetrical alkenes with hydrogen halides
- understand the mechanism for electrophilic substitution reactions.

GUIDING QUESTIONS

- How are bonds made and broken in reactions?
- How can organic reactions be understood using mechanisms?
- How can substances be classified as Lewis acids or bases?

Introduction

Ernest Rutherford (Nobel Prize for Chemistry, 1908) is often quoted as having said 'all science is either physics or stamp collecting' (Figure 22.1). To a certain extent, if organic chemistry is just regarded as a series of reactions that need to be learned, then perhaps there are some elements of truth in the description. However, there is much more to organic chemistry than this, and the idea of reaction mechanisms and using curly arrows to show the movement of electron pairs is now fundamental to our understanding of organic reactions.

Figure 22.1: It is not certain that Rutherford made the comment about stamp collecting, but he has appeared on stamps! The colours on the stamp are due to organic chemicals.

22.1 Nucleophilic substitution reactions

Halogenoalkanes were introduced in Chapter 11. They are organic compounds containing a halogen atom as the functional group. They usually undergo substitution reactions.

KEY POINT

In a substitution reaction one atom or group is replaced by another atom or group.

Figure 22.2 shows what happens when, for example, bromoethane is heated with aqueous sodium hydroxide – the Br atom is replaced by an OH group to form ethanol.

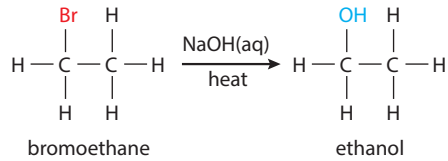

Figure 22.2: A nucleophilic substitution reaction. This sort of diagram is often called a reaction scheme and is used in organic chemistry to show how one organic molecule is converted into another; it is not a balanced equation but just focuses on the organic compounds. Reagents and conditions are usually shown on the reaction arrow.

The balanced equation for this reaction is

$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

or, as an ionic equation:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

This reaction is also known as **hydrolysis** because it is essentially equivalent to breaking a molecule apart

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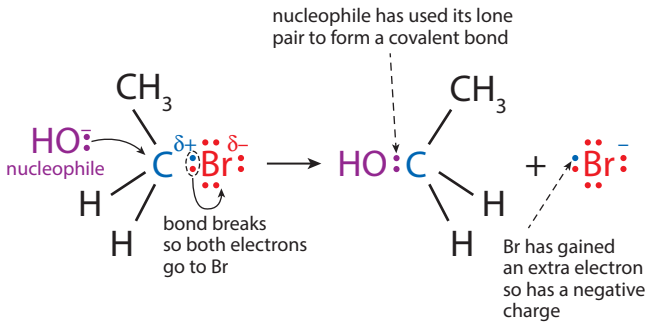
using water. There are a large number of reactions that are classified as hydrolysis. Hydrolysis reactions can occur with water, acid or alkali. The reaction here could be referred to as *hydrolysis or alkaline hydrolysis*.

The type of *mechanism* by which this reaction occurs is **nucleophilic substitution** – the halogenoalkane is attacked by a **nucleophile** and the nucleophile replaces the halogen atom.

KEY POINT

A nucleophile is a molecule or negatively charged ion that has a lone pair of electrons – it is attracted to a more positively charged region in a molecule (a region with lower electron density) and donates a lone pair of electrons to an electrophile to form a covalent bond (coordination bond).

In the reaction between bromoethane and sodium hydroxide, the nucleophile is the hydroxide ion, OH^-:



The C—Br bond is polar because Br is more electronegative than C. The negatively charged nucleophile is, therefore, attracted to the δ+ C. The nucleophile donates a pair of electrons to form a covalent bond (coordination bond) to carbon. At the same time, the C—Br bond breaks and both electrons go to Br. Because Br has gained an extra electron (instead of just sharing it), it now has a negative charge.

The O no longer has a negative charge because it has essentially donated its extra electron to C to replace the one it lost when the C—Br bond broke.

When the C—Br bond breaks, both electrons in the bond go to one of the atoms. This type of bond breaking is called **heterolytic fission**, and we can compare it to homolytic fission, which we met in Chapter 21. Figure 22.3 shows the movement of electrons that occurs in each process.

KEY POINTS

Heterolytic fission of a bond occurs in nucleophilic substitution reactions.

Heterolytic fission is the breaking of a covalent bond (made up of two electrons) so that *both* electrons go to one of the atoms that made up the original bond.

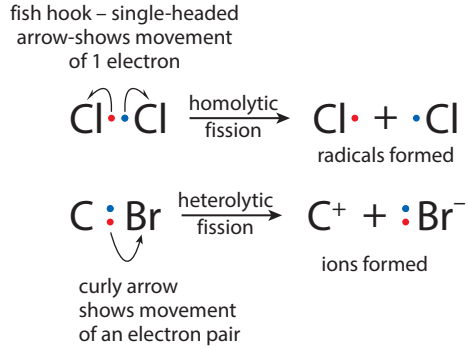


Figure 22.3: A comparison of homolytic and heterolytic fission. The C formed in the nucleophilic substitution reaction shown in Figure 22.2 does not have a positive charge because it gets another electron from OH^-.

Curly arrows are used extensively in organic chemistry to show the movement of pairs of electrons in reaction mechanisms. Figure 22.4 shows the reaction between OH^- and bromoethane but with bonds and curly arrows.

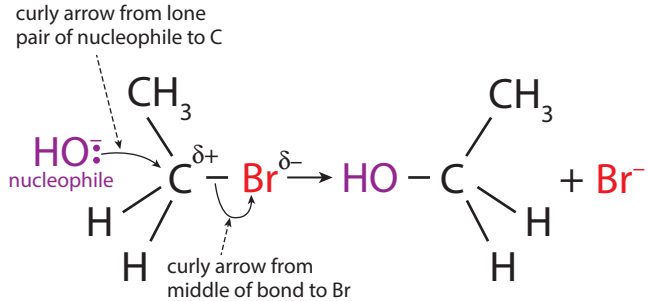


Figure 22.4: Using curly arrows to show a reaction mechanism.

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Some terms you should know

- In this reaction, the C_2H_5Br can be described as the **substrate**.
- C_2H_5Br can also be described as the **electrophile** in this reaction. We will define an electrophile more fully in Section 22.2, but, for the moment, an electrophile is what a nucleophile reacts with.
- Br^- can be described as a **leaving group**.

KEY POINTS

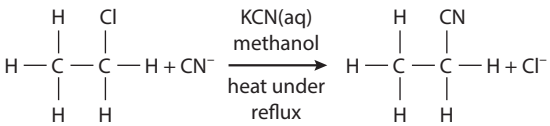
A **substrate** is the main chemical species that undergoes a reaction and is transformed into something else.

A **leaving group** is an atom/ion/group of atoms that is lost from the substrate when a bond is broken in a reaction.

Nucleophilic substitution with other nucleophiles

Another negative ion that can act as a nucleophile is the cyanide ion, CN^-.

Chloroethane reacts with potassium cyanide to form a nitrile:



propanenitrile

The nitrile contains the —C≡N functional group. The longest continuous carbon chain in the molecule is now three carbon atoms, and so, the name is propanenitrile. This reaction is useful because it provides a way of increasing the length of the carbon chain.

The mechanism (Figure 22.5) is essentially the same as that for OH^- (Figure 22.4). Here, Cl^- is the leaving group.

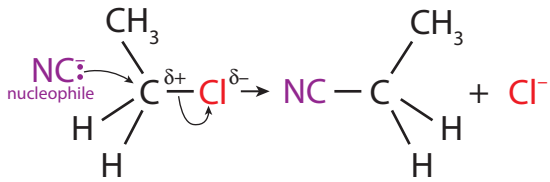
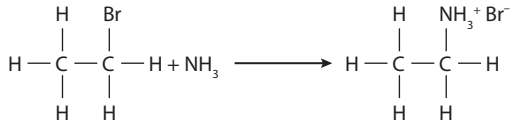


Figure 22.5: The nucleophilic substitution reaction of the cyanide ion with a halogenoalkane.

KEY POINT

Nucleophiles can be negative ions or neutral molecules.

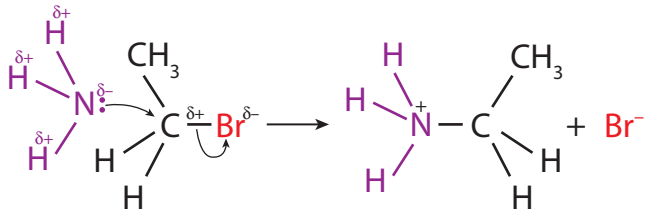
Neutral molecules that can act as nucleophiles include water and ammonia, both of which have at least one lone pair on the central atom. The equation for the reaction of ammonia with bromoethane is



ethylammonium bromide

The product of the reaction is the salt of an amine.

Here, the mechanism is slightly different because the nucleophile does not have a charge:



The nitrogen atom in the product has a positive charge because it has essentially given an electron to carbon in the formation of the coordination bond. The formation of the ultimate product, the amine, then occurs when H^+ is removed from N by another molecule of ammonia in the reaction mixture or by adding sodium hydroxide:

$CH_3CH_2NH_3^+ + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4^+$ or

$CH_3CH_2NH_3^+ + OH^- \rightarrow CH_3CH_2NH_2 + H_2O$

OH^- and NH_3 are acting as bases (proton acceptors) in these reactions.

Water, like the hydroxide ion, reacts with halogenoalkanes to form an alcohol, for example:

$CH_3CHClCH_3 + H_2O \rightarrow CH_3CH(OH)CH_3 + HCl$

KEY POINT

Halogenoalkanes are more reactive than alkanes.

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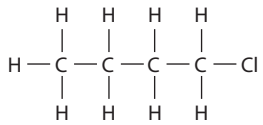
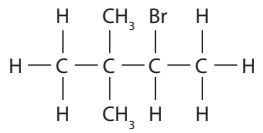
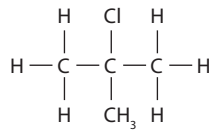
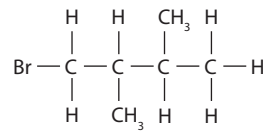
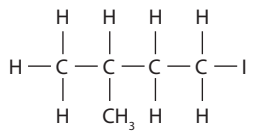
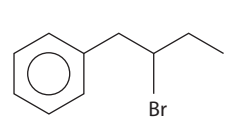
We have seen in this section that halogenoalkanes are more reactive than alkanes – this is due to the presence of the halogen atom. If a chlorine atom, for example, is present in a molecule, the C—Cl bond will be polar (Cl more electronegative than C) , and a nucleophile will be attracted to the δ+ carbon atom. Another factor is that Cl^- is classified as a 'good leaving group' – the C—Cl bond is weaker than a C—C bond or a C—H bond and Cl^- is stable in many solvents.

TEST YOUR UNDERSTANDING

1 Draw the structures of the products formed when each of the halogenoalkanes reacts with the nucleophile shown.

a		OH^-
b		OH^-
c		CN^-
d		NH_3
e		H_2O
f		OH^-

22.2 Addition reactions

Alkenes are hydrocarbons with C=C double bonds as the functional group. Alkanes undergo **addition reactions**.

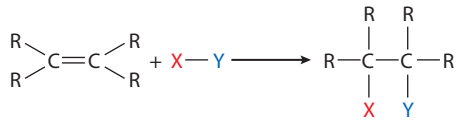
KEY POINT

An addition reaction is one in which a molecule is added to another molecule to form just one product. No other molecules/ions are formed in the reaction.

Alkenes are more reactive than alkanes. There are two reasons for this:

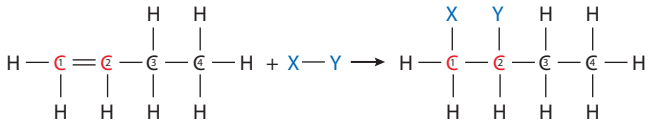
- The double bond (614 kJ mol^{-1}) is less than twice as strong as a single bond (346 kJ mol^{-1}). The reactions of alkenes usually involve the C=C bond breaking to form a C—C bond. Because the second component (π bond) of the C=C bond is weaker than a C—C single bond (σ bond), it is more easily broken.
- The double bond (four electrons) represents a region of high electron density and, therefore, it attracts electrophiles.

A general equation for an addition reaction of an alkene is:



'R' represents either an alkyl group or hydrogen.

The molecule X—Y is added across the double bond, which leaves a single bond between the carbon atoms. It is only the C=C that reacts, so, if but-1-ene reacts, X and Y add across carbons 1 and 2:



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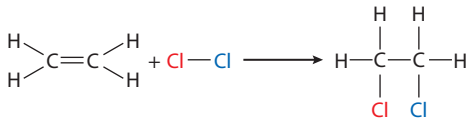
Reactions of alkenes

Alkenes and halogens

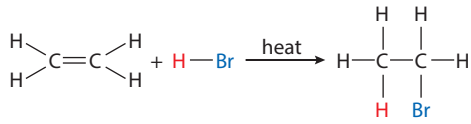
Alkenes react with halogens at room temperature:



1,2-dichloroethane

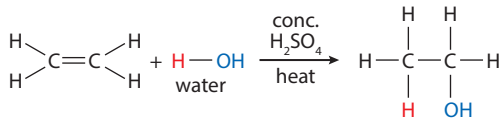
Alkenes and hydrogen halides

Alkenes react with hydrogen halides, such as hydrogen bromide:



bromoethane

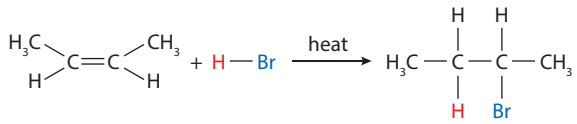
Alkenes and water



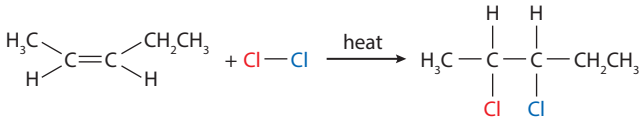
ethanol

In the laboratory, this reaction can be carried out by passing ethene through concentrated sulfuric acid at room temperature and then warming the product with water.

Although all these reactions have been shown with ethene, they are applicable to all alkenes. So, but-2-ene would react with HBr:



and pent-2-ene would react with chlorine:



EXAM TIP

In organic chemistry, we are learning about the reactions of functional groups, not individual molecules. The reactions here are of the C=C functional group, and it makes little difference what the rest of the molecule is like.

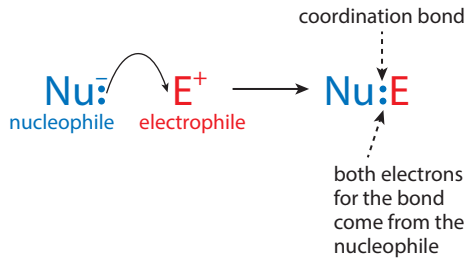
Electrophilic addition

The mechanism of each of these reactions is **electrophilic addition**. These are addition reactions where the initial attack on the organic molecule is by an electrophile.

KEY POINT

An electrophile is a reagent that is attracted to regions of high electron density and forms a covalent bond to a nucleophile by accepting a pair of electrons from it.

The reaction between an electrophile and a nucleophile involves the formation of a coordination bond:



In each of the reactions above, the reagent that reacts with the alkene is the electrophile (Cl_2, HBr, H_2O) and the alkene is the nucleophile. The electrophile is attracted to the alkene because C=C contains four electrons and, therefore, the electron density (negative charge) is very concentrated in this region and, for example, the $H^{\delta+}$ of the HBr molecule will be attracted. The first stage in the reaction between ethene and HBr is shown in Figure 22.6. A pair of electrons from C=C is donated from the nucleophile (C_2H_4) to the electrophile (HBr) to form a bond to the H of HBr. The full mechanism will be considered in Higher Level Section 22.4 that follows.

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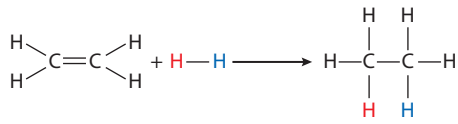
All of the electrophiles shown above are neutral molecules, but electrophiles can also be positively charged. Examples of positively charged electrophiles are H^+ or NO_2^+.

Link

We saw the reaction between an alkene and hydrogen in Chapter 20. The reaction also involves addition across the C=C but the mechanism is different and does not involve initial attack by an electrophile:



The reaction is better classified as a *reduction reaction* – one of the definitions of reduction we met in Chapter 20 was addition of hydrogen. We can also see that the oxidation state of C decreases from −2 in ethene to −3 in ethane.

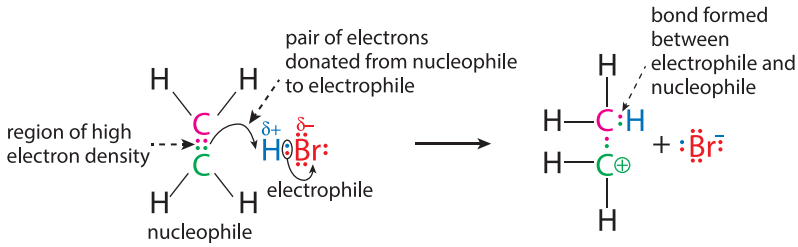
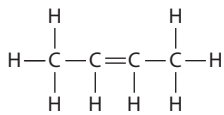
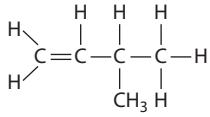
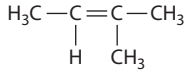
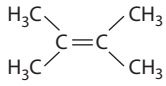
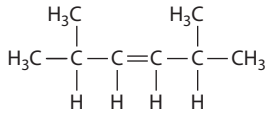
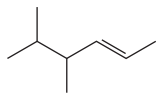


Figure 22.6: The reaction of an alkene with HBr involves an electrophile reacting with a nucleophile.

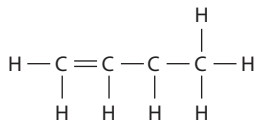
TEST YOUR UNDERSTANDING

2 Draw the structure and name the product formed when the alkenes react with the electrophile shown.

a		HCl
b		Br_2
c		Cl_2
d		HBr
e		H_2O
f		Cl_2

3 More than one product is possible when each of the following alkenes react with hydrogen chloride. In each case, draw out the structures of both possible products.

a



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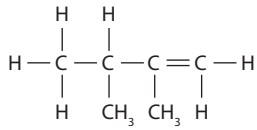
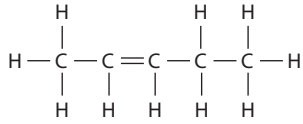


c



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CONTINUED

4 Draw the structures of the products of the following reactions:

a but-1-ene + hydrogen

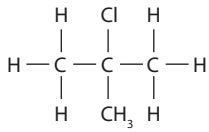
b hex-3-ene + hydrogen bromide

c pent-2-ene + chlorine

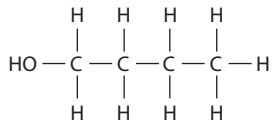
d but-2-ene + water.

5 Write equations, using structural formulas, for the formation of the following compounds from appropriately chosen alkenes:

a



b



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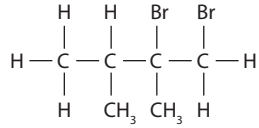

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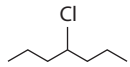

SCIENCE IN CONTEXT

Organic chemistry and colour

Why is tomato ketchup red (Figure 22.7)? The simplest answer to this is that it absorbs certain wavelength/colours of white light and reflects others – in the case of tomato ketchup then, it absorbs light at the green/blue end of the electromagnetic spectrum but reflects red light, and so, appears red. But what is there in tomato ketchup that makes it absorb green/blue light? The molecule responsible for this is lycopene.

Figure 22.7: Tomato ketchup on chips.

The key feature of lycopene that allows it to absorb light in the visible region of the spectrum is the system of 11 double bonds alternating with single bonds, highlighted in Figure 22.8. This is called a conjugated (or delocalised) system. But why should this allow it to absorb light? Well, colour is actually all about electrons, and light is absorbed when an electron is promoted from a lower to a higher energy level.

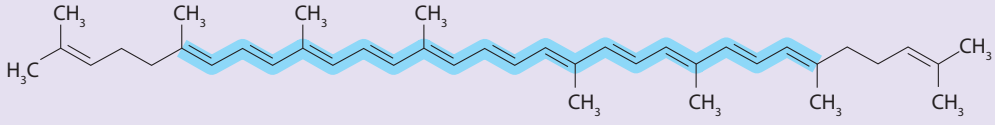

Figure 22.8: Lycopene showing the conjugated system.

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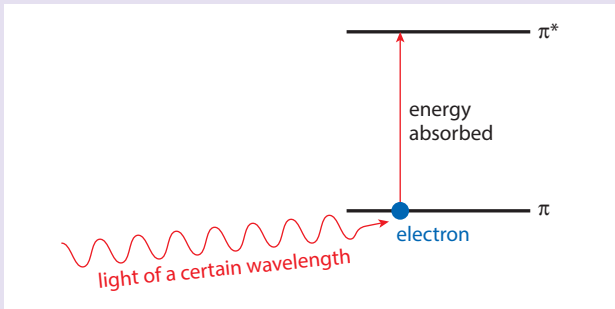
But where do these energy levels come from? To understand this, we have to delve a bit more deeply into theories of bonding and look at molecular orbital theory. When a bond is formed, atomic orbitals overlap to form molecular orbitals, but each time a bonding molecular orbital is formed, an antibonding molecular orbital is also formed. Therefore, when a double bond forms between the two C atoms in ethene, a π bonding (lower energy) and a π* antibonding (higher energy) molecular orbital are generated. Ethene absorbs electromagnetic radiation of wavelength 162 nm to promote an electron from the π (full) to the π* (empty) molecular orbital.



This wavelength is, however, in the UV region of the spectrum, and so, ethene is colourless. If the double bond is conjugated with other double bonds (alternating single and double bonds), the energy gap between the highest occupied π and lowest unoccupied π* molecular orbitals decreases. The longer the conjugated system, the smaller the energy gap between these π and π* molecular orbitals and the longer the wavelength of radiation absorbed. If a conjugated system involves more than about eight double bonds (as in lycopene), the molecule should absorb in the visible region of the spectrum and be coloured.

Most of the things we see around us are coloured because of conjugated systems. A phenyl group contributes the equivalent of three alternating double and single bonds, and so, many dyes/pigments will contain this unit (Figure 22.9).

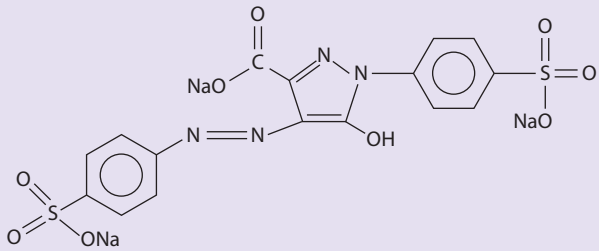


Figure 22.9: The structure of tartrazine, a yellow dye used widely in food and drinks. The lone pair on the nitrogen atom in the 5-membered ring allows the conjugated system to continue over the whole structure. Some people believe that there are health risks associated with tartrazine and its use has been banned or restricted in some countries.

Some dyes are natural, but most of the ones used in our clothes are artificial and have been made using organic chemistry. The production of dyes and pigments is an important part of the organic chemical industry, which began over 150 years ago with an accidental discovery by an 18 year old. At the age of 18, William Henry Perkin was already involved in chemical research. He was given the task of making quinine (an antimalarial drug) from phenylamine ($C_6H_5NH_2$) and attempted to oxidise it using acidified potassium dichromate(VI). He ended up with a black sludge at the bottom of the flask (like in many organic preparations!). However, when he washed out the flask with ethanol, he noticed a purple colour (later named mauveine or aniline purple) and had discovered, by accident, one of the first artificial organic dyes, which was to become the basis of a huge industry. There are now thousands of synthetic dyes, and well over half a million tonnes of dyes and pigments are produced each year. However, there are enormous environmental problems associated with the use of dyes, and the textile industry releases hundreds of thousands of tonnes of dyes into the environment every year in wastewater.

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22.3 Lewis acids and bases

We met the Brønsted–Lowry definition of acids and bases in Chapter 19.

KEY POINT

Brønsted–Lowry definition:

- An acid is a proton (H^+) donor.
- A base/alkali is a proton (H^+) acceptor.

Although this is very useful for describing reactions in aqueous solution, it is not more widely applicable. The **Lewis definition** is more general than the Brønsted–Lowry definition and can be applied to reactions that do not involve the transfer of protons. It is also useful when considering acid–base reactions in solvents other than water.

KEY POINT

Lewis definition:

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

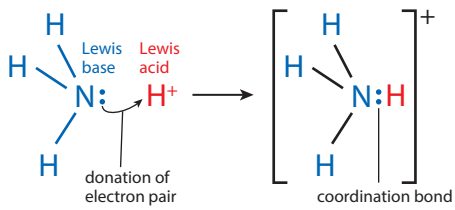
In Chapter 19 we described reactions such as:

$NH_3 + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+$

in terms of the Brønsted–Lowry definition. The NH_3 is a Brønsted–Lowry base because it accepts a proton (H^+) and the CH_3COOH is a Brønsted–Lowry acid because it donates a proton.

The Lewis definition of acids and bases covers all Brønsted–Lowry reactions, because the acceptance of a proton by a base must involve the donation of an electron pair to the proton. Consider the protonation of ammonia in the reaction above:

$NH_3 + H^+ \rightarrow NH_4^+$



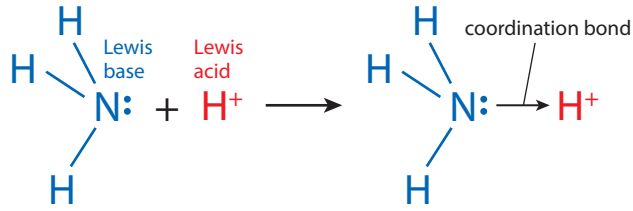
KEY POINTS

In all Brønsted–Lowry acid–base reactions, H^+ is the Lewis acid.

A coordination bond is always formed in a Lewis acid–base reaction.

NH_3 is the Lewis base, because it donates an electron pair to H^+, which is the electron-pair acceptor, i.e., Lewis acid.

Sometimes a coordination bond is shown with an arrow, and the reaction between NH_3 and H^+ can be shown as

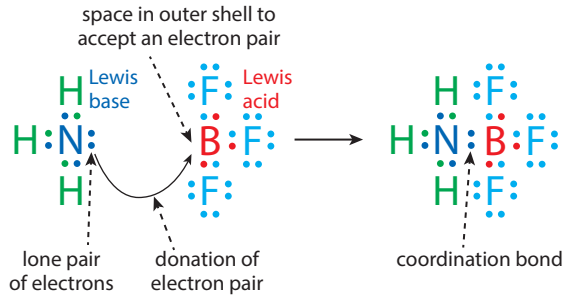


EXAM TIP

The arrow is used here to illustrate formation of a coordination bond, however, when asked for a Lewis formula in the exam, do not use arrows, just use an ordinary line (or a pair of dots) to show a coordination bond.

Remember: once a coordination bond has been formed, it is identical to an 'ordinary' covalent bond – it is just a shared pair of electrons.

The reaction between BF_3 and NH_3 is a Lewis acid–base reaction that does not involve the transfer of a proton:



NH_3 donates a pair of electrons (Lewis base) and BF_3 accepts a pair of electrons (Lewis acid). Because no proton is transferred, this would not be classified as an acid–base reaction under the Brønsted–Lowry definition.

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KEY POINTS

For a substance to act as a Lewis base, it must have a lone pair of electrons.

For a substance to act as a Lewis acid, it must have space to accept a pair of electrons in its outer shell.

For example, NH_3 can act as a Lewis base, because it has a lone pair of electrons. H^+ and BX_3 (where X is a halogen) can act as Lewis acids because they have space in their outer shells to accept a pair of electrons.

The formation of a complex ion by a transition metal ion (Figure 22.10) is another example of a Lewis acid–base reaction. The transition metal ion is the Lewis acid, and the ligands are Lewis bases. The ligands bond to the transition metal ion through the formation of coordination bonds.

$$Fe^{2+} + 6H_2O \rightleftharpoons [Fe(H_2O)_6]^{2+}$$

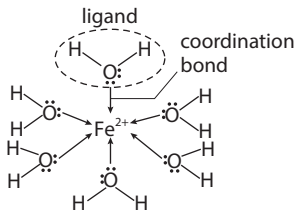

Figure 22.10: Formation of a transition metal complex ion.

Again, this reaction would not be described as an acid–base reaction according to the Brønsted–Lowry theory because there is no transfer of a proton.

The overall charge on the complex ion formed is 2+ because the charge on the metal ion was 2+ and all the ligands are neutral.

Ligands can also be negative ions and, for example, in the reaction:

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

the Cl^- ion is the Lewis base and the Co^{2+} ion is the Lewis acid. The overall charge on the complex ion formed is 2− because it consists of a Co^{2+} ion and 4 Cl^- ligands: $2+ + (4 \times 1-) = 2-$.

This reaction is reversible, and so, in the reverse direction, H_2O would be the Lewis base.

Link

How to work out the overall charge on a complex ion given the charges on the ligands has already been discussed in Chapter 10.

THEORY OF KNOWLEDGE

The relationship between depth and simplicity

There are various theories of acids and bases. We have met the Brønsted–Lowry and Lewis theories. The Lewis theory is more sophisticated and extends the Brønsted–Lowry theory, which is limited to describing the acid–base behaviour of species in aqueous solution. The Lewis theory can be used to describe the acid–base reactions of substances, including those not containing hydrogen atoms, in a variety of different solvents. The Lewis theory can be applied to reactions in organic chemistry – a nucleophile is a Lewis base, and the reaction between an electrophile and a nucleophile is a Lewis acid–base reaction. The reaction of a transition metal with a ligand such as CO is a Lewis acid–base reaction.

Before we knew about the Lewis theory, we probably had a fairly good picture in our minds as to what an acid is. Have we got a more sophisticated theory at the expense of losing an understanding of what an acid is?

TEST YOUR UNDERSTANDING

6 Define acids and bases according to the Brønsted–Lowry and Lewis definitions.

7 State what type of bond is formed when a Lewis acid reacts with a Lewis base.

8 Classify each of the following as a substance that can act as a Lewis acid or as a Lewis base:

H_2O, BF_3, HCO_3^-, H^+, NH_3, CO, Fe^{2+}, CN^-.

9 Explain whether $AlCl_3$ is a Lewis acid or Lewis base in the following reaction:

$AlCl_3 + Cl^- \rightarrow AlCl_4^-$

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10 Identify the Lewis acid and Lewis base in each of the following reactions:

a $CH_3COO^- + H^+ \rightarrow CH_3COOH$

b $OH^- + H^+ \rightarrow H_2O$

c $(CH_3)_3C^+ + Br^- \rightarrow (CH_3)_3CBr$

d $[Cu(H_2O)_6]^{2+} + NH_3 \rightarrow [Cu(H_2O)_5NH_3]^{2+} + H_2O$

11 Deduce the charge on the following complexes

a $[Co(H_2O)_6]^?$ contains cobalt(III)

b $[NiCl_4]^?$ contains nickel(II)

c $[Ni(CO)_4]^?$ contains nickel(0)

d $[Mn(CN)_6]^?$ contains manganese(III)

e $[Cr(OH)(H_2O)_5]^?$ contains chromium(III)

12 Classify the following as involving an acid–base reaction according to

I the Lewis definition only

II the Brønsted–Lowry definition only

III both Lewis and Brønsted–Lowry definitions.

a $NH_3 + BCl_3 \rightleftharpoons H_3NBCl_3$

b $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

c $Ni^{2+} + 6H_2O \rightleftharpoons [Ni(H_2O)_6]^{2+}$

d $[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+} + H_3O^+$

22.4 Nucleophilic substitution mechanisms

We first met nucleophilic substitution reactions earlier in the chapter. These can also be described in terms of Lewis acids and bases.

KEY POINT

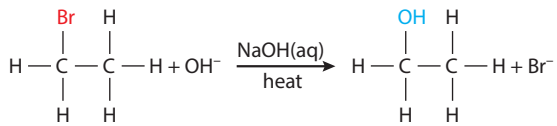
In organic reactions:

- nucleophiles donate electron pairs and are Lewis bases
- electrophiles accept electron pairs and are Lewis acids.

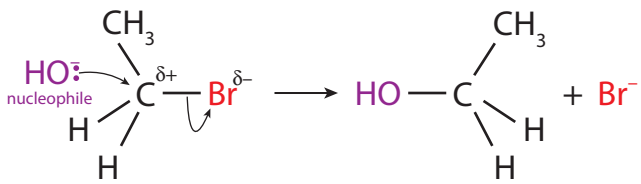
In Section 22.1, we looked at these reactions in general terms with the nucleophile donating a pair of electrons to the electrophile (the halogenoalkane) to form a coordination bond and the halide ion being the leaving group. Here, we will look in more depth at the mechanisms. The exact nature of a nucleophilic substitution reaction depends on which type of halogenoalkane is involved in the reaction – primary, secondary or tertiary.

Primary halogenoalkanes – the S_N2 mechanism

Consider the reaction of bromoethane with sodium hydroxide:



Br is more electronegative than C, so the carbon atom is slightly positive (δ+) and the OH^- ion is attracted to it. The hydroxide ion is a nucleophile and donates a lone pair of electrons to the carbon atom to form a covalent bond (it acts as a Lewis base):



EXAM TIP

The curly arrow must come from the lone pair on oxygen and not from the hydrogen of OH^-.

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The first curly arrow shows the lone pair on OH^- becoming a bonding pair of electrons between oxygen and carbon (a coordination bond is formed). A carbon atom can have a maximum of eight electrons in its outer shell and, therefore, as the C—O bond forms, the C—Br bond must break. The C—Br bond breaks such that both electrons from the C—Br bond go back to the bromine atom (heterolytic fission) to form a bromide ion – shown by the curly arrow from the C—Br bond to Br.

Partway through this nucleophilic substitution process, both OH and bromine are partially joined to the carbon (Figure 22.11), and this is often shown in the mechanism. This is not an intermediate in the reaction but is the highest point on the energy profile – the transition state. The difference between an intermediate and a transition state is discussed in Chapter 17.

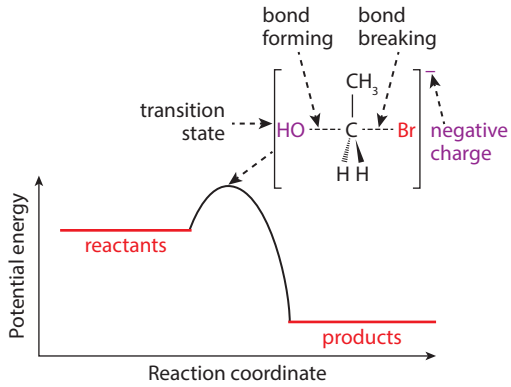


Figure 22.11: Energy profile for the S_N2 mechanism.

Figure 22.12 shows the full mechanism for the reaction of bromoethane with aqueous sodium hydroxide.

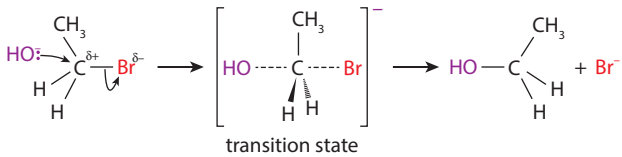


Figure 22.12: The S_N2 mechanism showing the transition state (activated complex). Remember that *curly arrows* show the movement of electron pairs.

It is important to remember that this is a single-step (concerted) mechanism – bond breaking and bond making occur at the same time, and the formation of the transition state is just part of the way along this step. The mechanism could be shown just as well without including the transition state.

EXAM TIP

It is usually required to show the transition state in an exam answer. In the transition state, you must show that the oxygen of OH is joined to the carbon (OH-C is not correct) and do not forget the negative charge.

The type of nucleophilic substitution described above is called an S_N2 reaction and is the main mechanism by which primary halogenoalkanes undergo nucleophilic substitution. The 'S' and 'N' stand for substitution and nucleophilic, respectively. The '2' indicates that this is a bimolecular reaction, that is, the molecularity is 2. Molecularity was introduced in Chapter 17 and refers to the number of molecules (or ions) that take part in a particular step in a mechanism.

The rate equation for the above reaction is

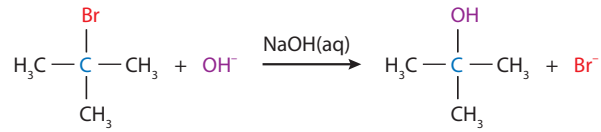
$$\text{rate} = k[CH_3CH_2Br][OH^-]$$

This means that if the concentration of either bromoethane or sodium hydroxide is doubled, the rate of reaction is doubled.

Remember that molecularity and order are not the same thing. 'Order' is an experimentally determined quantity that relates the concentrations of reactants to the rate. 'Molecularity' refers to the number of molecules (or ions) that take part in a particular step in a mechanism.

Tertiary halogenoalkanes – the S_N1 mechanism

2-bromo-2-methylpropane is a tertiary halogenoalkane because there are three alkyl groups joined to the C (in blue) that is attached to the Br atom. 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide at room temperature:



2-bromo-2-methylpropane 2-methylpropan-2-ol

Studies of the rate of this reaction have determined that the rate does not depend on the concentration of sodium hydroxide. This reaction must, therefore, have a different mechanism to the S_N2 mechanism discussed previously.

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In the first step, the C—Br bond breaks to form a positively charged carbocation (Figure 22.13).

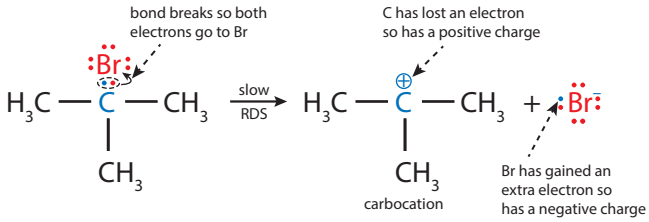


Figure 22.13: An intermediate carbocation is formed. RDS is rate-determining step.

This is again heterolytic fission – when the bond breaks, both electrons from the C—Br bond go to Br to form Br^-. Because both electrons from the C—Br bond go to Br, C has lost an electron and, therefore, has a positive charge and the intermediate is called a **carbocation**. A carbocation is an organic molecular species with a positive charge on a C atom.

Once formed, the carbocation intermediate is rapidly attacked by nucleophiles, such as the OH^- ion (Figure 22.14).

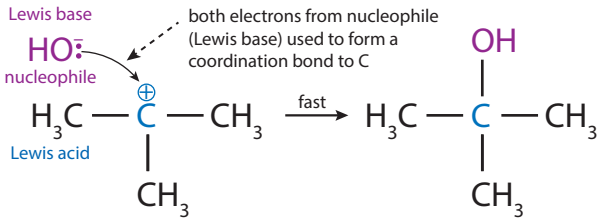
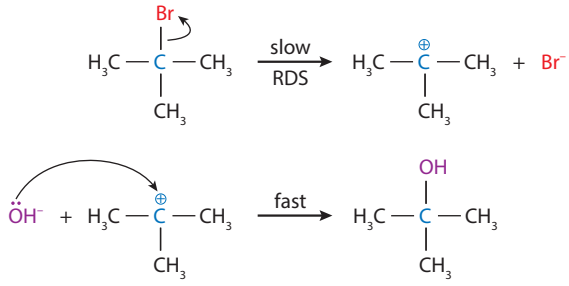


Figure 22.14: The second step of the S_N1 mechanism.

We usually show the overall mechanism as:



This is a two-step process (S_N2 was one step), and this can be seen on the energy profile in Figure 22.15.

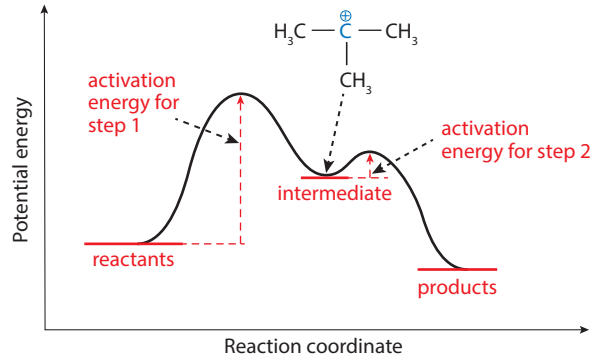


Figure 22.15: Energy profile for an S_N1 reaction, showing the formation of the intermediate (local minimum in the profile).

It can be seen from the energy profile that the first step is the rate-determining step (higher activation energy). The first step is unimolecular, involving only one molecule (the halogenoalkane), but the second step is bimolecular, involving the carbocation and the nucleophile. However, this mechanism is described as **S_N1** – 'substitution nucleophilic unimolecular' because the rate-determining step is unimolecular.

The nucleophile is only involved in the mechanism in a fast step that happens after the rate-determining step, and so, does not appear in the rate equation. The rate equation for this reaction is:

$$\text{rate} = k[(CH_3)_3CBr]$$

The effects of changing the concentration of a nucleophile on the rate of S_N1 and S_N2 mechanisms are summarised in Table 22.1.

Which mechanism?

The main mechanism by which different types of halogenoalkane undergo nucleophilic substitution are:

- primary halogenoalkanes – S_N2
- secondary halogenoalkanes – S_N1 and S_N2
- tertiary halogenoalkanes – S_N1.

Secondary halogenoalkanes undergo nucleophilic substitution via a mixture of the two mechanisms – the dominant mechanism will depend on the halogenoalkane, the nucleophile and the specific conditions of the reaction.

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Mechanism	Rate equation	Effect of doubling the concentration of the nucleophile
S_N1	rate = *k*[halogenoalkane]	no effect – nucleophile is only involved in a fast step after the rate-determining step
S_N2	rate = *k*[halogenoalkane][nucleophile]	rate doubles – nucleophile is involved in the rate-determining step

Table 22.1: The effect of changing the concentration of the nucleophile on the rate of S_N1 and S_N2 mechanism reactions.

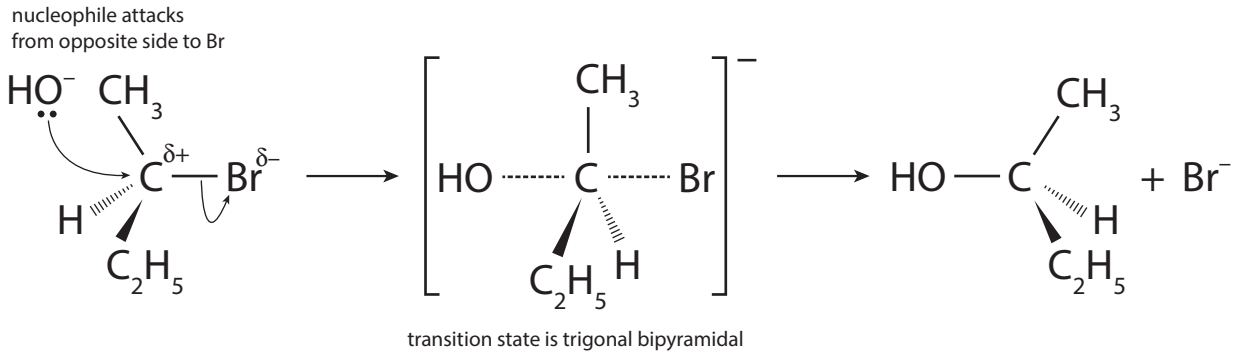


Figure 22.17: One enantiomer produces just one enantiomer in the S_N2 mechanism.

Stereochemistry of nucleophilic substitution reactions

We met the idea of chiral molecules in Chapter 11. For example, the secondary halogenoalkane 2-bromobutane has a chirality centre (chiral centre) – a carbon atom with four different groups attached, and two enantiomers exist that are mirror images of each other (Figure 22.16).

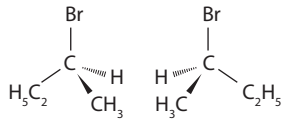


Figure 22.16: The enantiomers of 2-bromobutane.

If we take one of these enantiomers (the one on the right), Figure 22.17 shows what happens when it undergoes nucleophilic substitution by an S_N2 mechanism.

We started with just one enantiomer, and we get just one enantiomer as the product. The product of this reaction will be optically active – it will rotate the plane of plane-polarised light. Figure 22.18 shows two different views of the enantiomer we started with and the product. If we ignore the fact that one contains Br and the other OH, the product is the mirror image of the starting material.

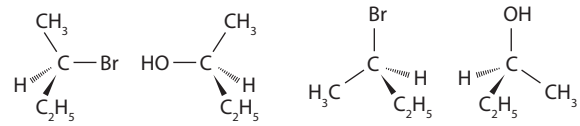
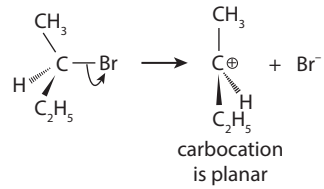


Figure 22.18: Two different views to show that an S_N2 reaction occurs with inversion of configuration.

This reaction is described as *stereospecific* because the stereochemistry (arrangement of groups around a chirality centre) of the reactant determines the stereochemistry of the product. For an S_N2 mechanism, the reaction occurs with inversion of configuration at the chirality centre – the mirror image form is obtained – a bit like an umbrella turning inside out.

If we look at the same enantiomer of 2-chlorobutane undergoing an S_N1 mechanism, the first step is



The carbocation formed is planar (three electron domains) and the nucleophile can attack from either

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side. If it attacks from one side, then one enantiomer is formed, and if it attacks from the other side, the other enantiomer of butan-2-ol is obtained (Figure 22.19). The nucleophile is equally likely to attack from either side, and so, equal amounts of the two enantiomers of butan-2-ol will be obtained – this is a racemic mixture and will have no effect on plane-polarised light (optically inactive) because the rotations cancel each other out.

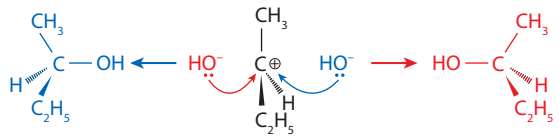


Figure 22.19: The OH^- in red attacks from the left and forms the enantiomer in red and the OH^- in blue attacks from the right and forms the enantiomer shown in blue.

That the products of this reaction are the two enantiomers (mirror images) can be seen in Figure 22.20.

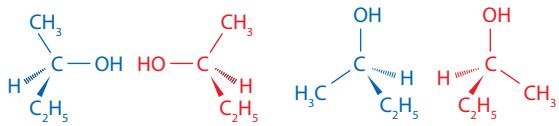


Figure 22.20: Two different views of the different forms of butan-2-ol that are formed when an S_N1 mechanism occurs.

The effect of the halogen on the rate of nucleophilic substitution

KEY POINT

The rate of nucleophilic substitution of halogenoalkanes by hydroxide ions is:

R—I > R—Br > R—Cl

because the C-halogen bond is weakest for I and strongest for Cl

Both S_N2 and S_N1 mechanisms involve the C—X bond breaking in the rate-determining step. The C—I bond is easiest to break (Table 22.2), so the reaction will be fastest using iodoalkanes. I^- can therefore be described as a better leaving group than Cl^-.

Bond	Bond energy / kJ mol^{-1}
C—Cl	338
C—Br	276
C—I	238

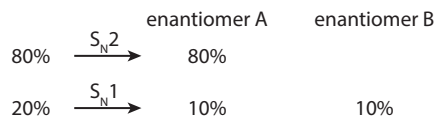
Table 22.2: Carbon–halogen bond enthalpies.

WORKED EXAMPLE 22.1

When one enantiomer of 2-chlorobutane is reacted with sodium hydroxide, 90% of one enantiomer and 10% of the other enantiomer of butan-2-ol are obtained. Deduce the proportion of molecules of 2-chlorobutane reacting via an S_N1 mechanism and the proportion reacting via an S_N2 mechanism.

Answer

We know that an S_N2 mechanism will produce just one enantiomer and an S_N1 mechanism will produce a racemic mixture. If the reaction were completely S_N2, then 100% of one enantiomer and none of the other isomer would be formed. The 10% of the other enantiomer must, therefore, have been produced by an S_N1 mechanism. But an S_N1 mechanism produces both isomers equally; therefore, it must also account for 10% of the other isomer. We can, therefore, conclude that 80% of the molecules must have reacted via an S_N2 mechanism and 20% via an S_N1 mechanism.



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Link

I^- being the best leaving group can also be related to HI being the strongest acid out of hydrogen halides, so it forms the most stable ion (weakest conjugate base), and also to I being the largest atom and therefore most polarisable and best able to form partial bonds, a requirement for formation of the transition state.

Reactions with other nucleophiles

We have concentrated so far on the reactions of halogenoalkanes with hydroxide ions, but, as mentioned in Section 22.1, halogenoalkanes can also react with other nucleophiles, such as CN^- or NH_3. The mechanism with negatively charged nucleophiles is the same as that described for the hydroxide ion, but there are a couple of changes when the nucleophile is neutral. The reaction of bromoethane with ammonia via an S_N2 mechanism (because bromoethane is a primary halogenoalkane) is shown in Figure 22.21.

The nitrogen of NH_3 is δ− and has a lone pair of electrons. It attacks the δ+ C of the halogenoalkane. The transition state is not charged, as it is formed when two neutral molecules react. The product has a positive charge on the nitrogen atom because the N forms a coordination bond to the C atom and essentially gives one electron to C to enable it to form a covalent bond.

The equation for the reaction could be written as

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-$$

ethylammonium bromide

The amine can be obtained from this salt by reacting it with sodium hydroxide. Sodium hydroxide is a stronger base than ethylamine and will remove the proton:

$$CH_3CH_2NH_3^+Br^- + NaOH \rightarrow CH_3CH_2NH_2 + H_2O + NaBr$$

This can be shown as an ionic equation:

$$CH_3CH_2NH_3^+Br^- + OH^- \rightarrow CH_3CH_2NH_2 + H_2O + Br^-$$

This is a Brønsted–Lowry acid–base reaction, involving the transfer of a proton from the acid to the base. The mechanism for this reaction is shown in Figure 22.22.

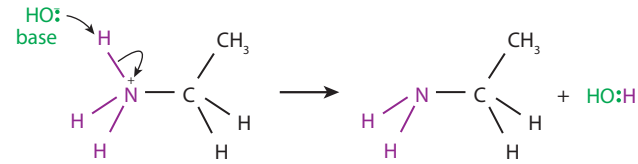
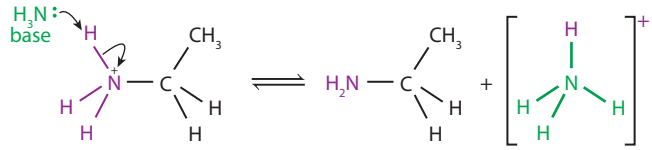


Figure 22.22: The hydroxide ion is acting as a base in this reaction.

Alternatively, if excess ammonia is present in the reaction mixture, H^+ can be removed from the ethylammonium ion by a molecule of ammonia:



The product of the reaction, $CH_3CH_2NH_2$, can also act as a nucleophile in the reaction, and so, further substitution is possible, for example:

$$CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow (CH_3CH_2)_2NH_2^+Br^-$$

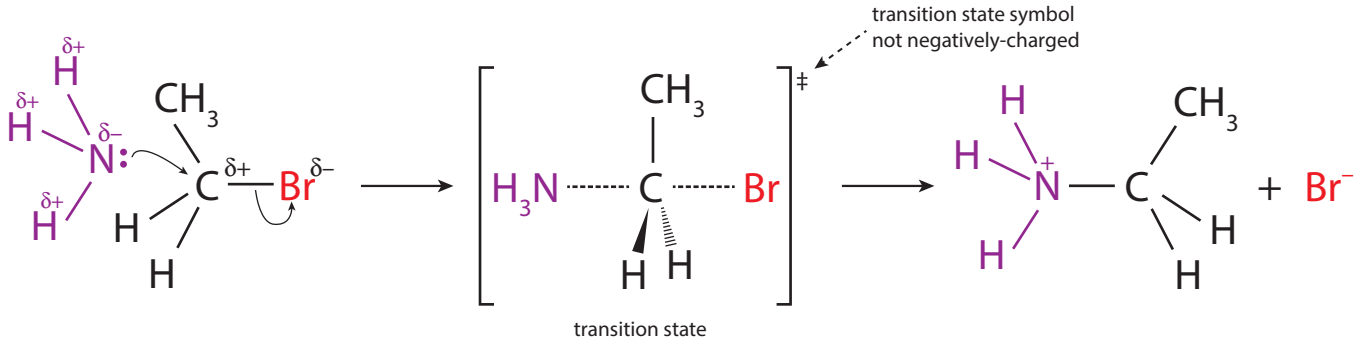


Figure 22.21: The reaction of bromoethane with ammonia via an S_N2 mechanism.

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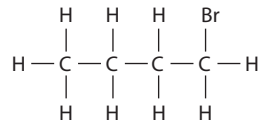
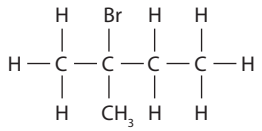
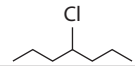
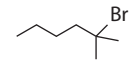
TEST YOUR UNDERSTANDING

13 **a** State whether each of the halogenoalkanes below reacts with NaOH(aq) via an S_N1 mechanism, an S_N2 mechanism or a mixture of both.

	
i	**ii**
$(CH_3)_3CCH_2Cl$	
iii	**iv**
$(CH_3)_2CHCHClCH_3$	
v	**vi**

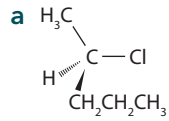
b Give the structural formula of the products formed when each of the substances in part **a** reacts with NaOH(aq).

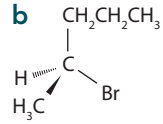
14 Which of the following will react most quickly with potassium cyanide solution?

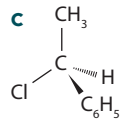
$(CH_3)_3CCl$, $(CH_3)_3CI$, $(CH_3)_3CBr$

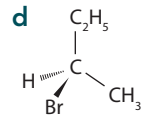
NOTE: $(CH_3)_3CI$ is 2-iodo-2-methylpropane

15 Draw a clear 3D diagram showing the structure of the product formed when each of the following reacts with NaOH via an S_N2 mechanism.

a 

b 

c 

d 

16 One enantiomer of a secondary halogenoalkane is reacted with sodium hydroxide. From the percentages of each enantiomer of the alcohol formed, determine the proportion of molecules of the halogenoalkane reacting via an S_N1 and the proportion reacting via an S_N2 mechanism.

a 100% of one enantiomer

b 50% of each enantiomer

c 75% of one enantiomer and 25% of the other enantiomer

d 80% of one enantiomer and 20% of the other enantiomer

e 60% of one enantiomer and 40% of the other enantiomer

22.5 Electrophilic addition reactions of alkenes

The addition reactions of alkenes were covered in Section 22.2. The mechanism for these reactions is electrophilic addition.

KEY POINT

An electrophile is an electron-deficient species (a positively charged ion or the positive end of a dipole) that is attracted to regions of relatively high electron density and accepts a pair of electrons to form a covalent bond. Electrophiles are Lewis acids.

The C=C bond has four electrons and is a region of relatively high electron density in a molecule; electrophiles will be attracted to this.

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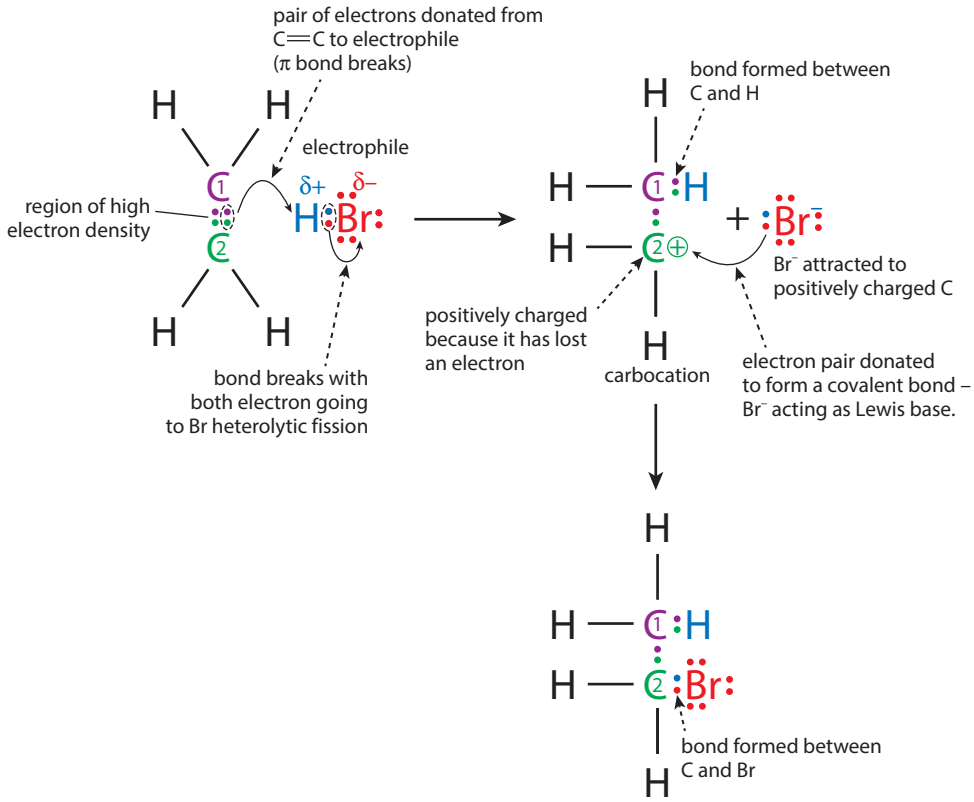
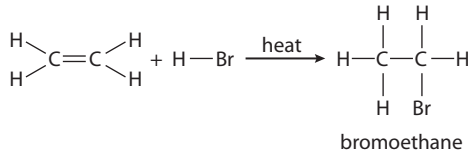


Figure 22.23: The mechanism of the reaction of ethene with hydrogen bromide, showing electrons.

The reaction of ethene with hydrogen bromide

The overall equation is:



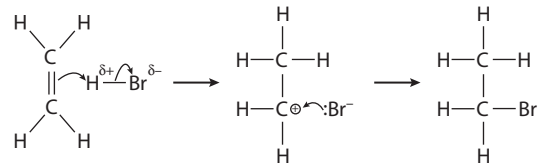
The mechanism is shown in terms of movement of electrons in Figure 22.23.

H—Br is the electrophile. It is polar because Br is more electronegative than H (therefore, $H^{\delta+}$ and $Br^{\delta-}$). The hydrogen atom is attracted to the high electron density in the C═C bond. The pair of electrons from the π component of the C═C bond is donated to $H^{\delta+}$ – the curly arrow represents the movement of the pair of electrons. This forms a bond between C and H. At the same time, the H—Br bond breaks and the pair of electrons from this bond goes to the bromine atom (heterolytic fission).

The alkene donates a pair of electrons and can be classified as a Lewis base; the hydrogen bromide accepts a pair of electrons and is, therefore, a Lewis acid.

C2 has lost an electron (this electron is now in the C—H bond), and so, C2 has a positive charge. The intermediate formed is a carbocation. The bromine atom gains an electron from the H—Br bond and, therefore, becomes a negatively charged bromide ion. In the second stage, the Br^- ion is attracted to the positively charged carbon (C2) and donates a pair of electrons to form a bond (Lewis acid–base reaction).

We usually show the mechanism as:



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THEORY OF KNOWLEDGE

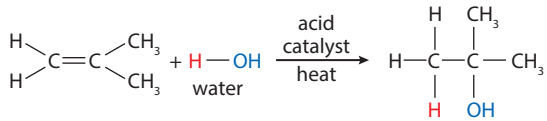
What is the electrophile in this reaction?

Some people refer to HBr as the electrophile in this reaction because it is the reactant/reagent that reacts with the alkene, whereas others will say it is the δ+ H of HBr that is the electrophile because this is the group which accepts the pair of electrons in the reaction. IUPAC defines an electrophile as: 'an electrophile (or electrophilic reagent) is a reagent that forms a bond to its reaction partner (the nucleophile) by accepting both bonding electrons from that reaction partner'.

Does this definition make the situation clearer? Does it matter whether we call HBr or $H^{\delta+}$ the electrophile, and does this affect our understanding of the reaction or our ability to convey that understanding to someone else?

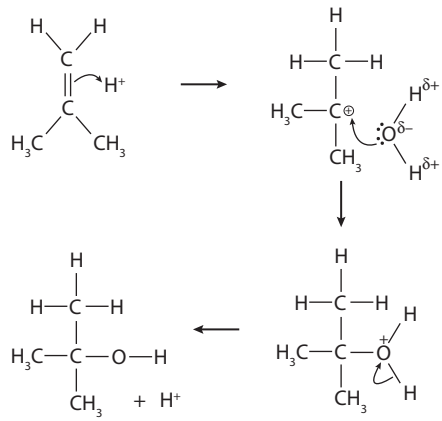
Reaction of alkenes with water

Alkenes react with water to form alcohols. For example, 2-methylpropene reacts with water to form 2-methylpropan-2-ol:



2-methylpropan-2-ol

The mechanism is similar to that described previously and can be shown as



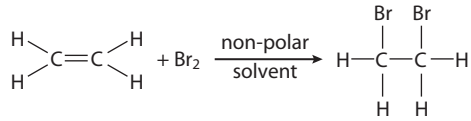
H^+ (from the acid) is the electrophile and, in the first stage, a pair of electrons is donated from the π bond of C═C to form a coordination bond to it. In this step, H^+ is the Lewis acid and the alkene is the Lewis base. H_2O (acting as a Lewis base) then donates a pair of electrons, to form a coordination bond to C⊕ of the carbocation (Lewis acid). Formation of a coordination bond results in a positive charge on O (it has essentially given an electron to C⊕ to allow it to form a bond). In the last stage, the O—H bond breaks and the pair of electrons goes to O so that it no longer has a positive charge.

H^+ is a catalyst in this reaction – it reacts but is then re-formed, and so, overall, it is not used up in the reaction.

Note that an alkene that would form a tertiary carbocation has been chosen to illustrate this mechanism because this type of carbocation is most stable (see below), and the reaction is therefore most likely to proceed via this mechanism. Water has also added according to **Markovnikov's rule** – see the next section.

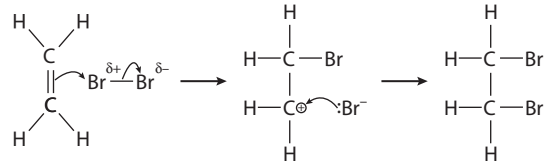
Reaction of ethene with bromine

The reaction is:



Although bromine molecules are not polar, as one approaches the high electron density in the C═C double bond, it becomes polarised (there is an induced dipole). Electrons are repelled in the Br_2 molecule so that the bromine atom closest to the C═C bond has a slight positive charge and the bromine atom further away has a slight negative charge.

The mechanism can be shown in two different ways. The first is exactly analogous to the reaction of HBr with ethene – via a carbocation intermediate:



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However, if we look at the intermediate here, the Br attached to C has lone pairs of electrons and, therefore, would stabilise the ion by forming a coordination bond to the C with the positive charge. The species formed is called a *bromonium ion* and is a better representation of the intermediate formed in this reaction (Figure 22.24).

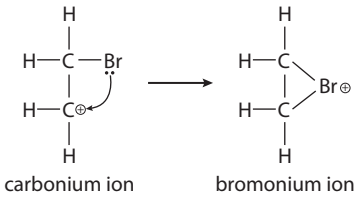
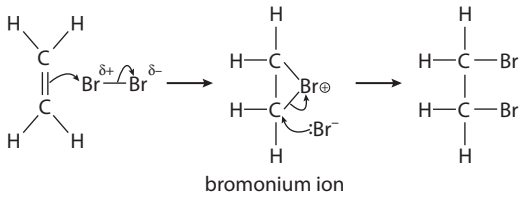


Figure 22.24: A bromonium ion is more stable than the carbonium ion.

The overall mechanism is:

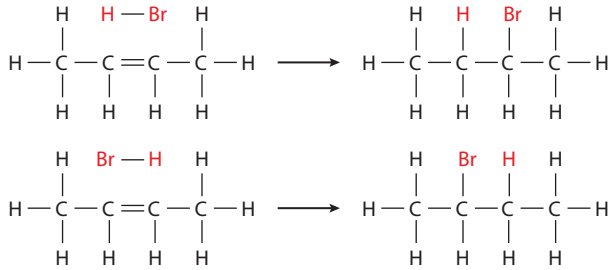


EXAM TIP

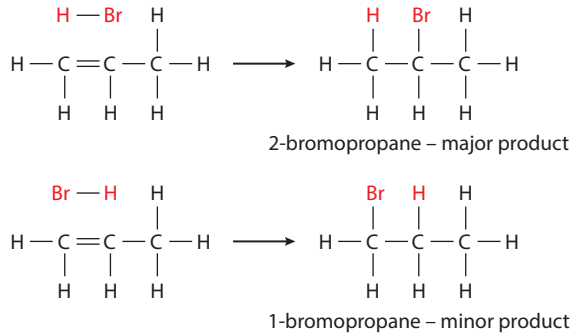
You need to learn only one version of this mechanism.

Reaction of unsymmetrical alkenes with hydrogen halides

When a symmetrical alkene reacts with a hydrogen halide, such as HBr or HCl, only one possible product can be formed. For example, when HBr reacts with but-2-ene, the same product, 2-bromobutane, is formed whichever way round HBr adds to C=C:



However, when HBr adds to an unsymmetrical alkene, such as propene, two products are possible:



We find that we get a significantly higher proportion of 2-bromopropane, and this is, therefore, called the *major product* of this reaction.

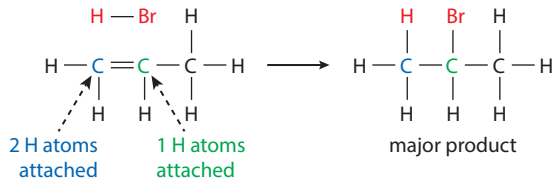
Markovnikov's rule

The reaction of any unsymmetrical alkene with a hydrogen halide (H—X) or water (H—OH) results in the formation of a major and a minor (usually made in only very small amounts) product. The major product can be predicted using Markovnikov's rule.

KEY POINT

Markovnikov's rule: when H—X (where X is a halogen atom or OH) adds across the double bond of an alkene, the H atom becomes attached to the C atom that has the larger number of H atoms already attached.

If we look again at the reaction between propene and HBr, we can see how the rule works:



We only look at the C atoms that make up the C=C bond because this is where the addition of HX occurs. The C highlighted in blue has two H atoms attached and, since this is more than the one H attached to the other C, the H from the H—Br joins to this C atom to form the major product.

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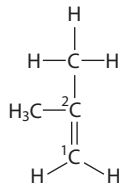
WORKED EXAMPLE 22.2

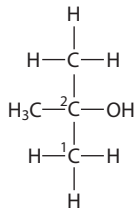
Deduce the identity of the major product when 2-methylpropene reacts with water.

Answer

The first stage is to draw out the structure of 2-methylpropene:



C1 has two hydrogen atoms already attached, but C2 has no hydrogen atoms attached. We can think of water, H_2O, as H—OH. The H from H—OH will become attached to C1 (more hydrogen atoms attached) and OH will become attached to C2 (fewer H atoms attached). The major product will, therefore, be 2-methylpropan-2-ol:



Explaining the formation of major and minor products

It is important to remember that Markovnikov's rule *predicts* the identity of the major product but does not *explain* why it should be the major product. Here, the formation of the major product will be explained in terms of the stability of the intermediate carbocation.

The two possible carbocations that can be formed when propene reacts with HBr are shown in Figure 22.25.

Alkyl groups have an electron-releasing effect (positive inductive effect).

The electron-releasing effect means that alkyl groups (—CH_3, —CH_2CH_3 etc.) donate electron density towards neighbouring atoms – this is called a positive inductive effect. This is the reverse of what a very electronegative atoms does (pulls electron density from neigbouring atoms) – a negative inductive effect. The electron-releasing effect depends very little on the size of an alkyl group – a methyl group donates approximately the same amount of electron density as an ethyl group.

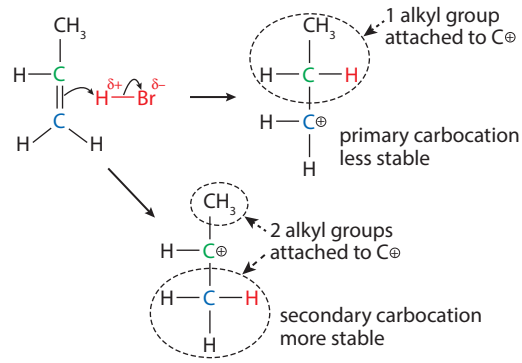


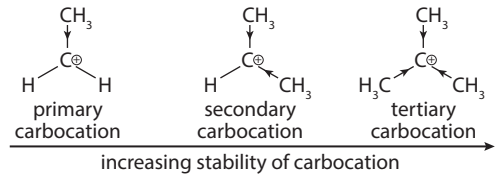
Figure 22.25: A secondary and a primary carbocation can be formed when propene reacts with HBr. Br^- is also formed, but this has been omitted for clarity.

There are two electron-releasing alkyl groups next to the positively charged carbon in the secondary carbocation in Figure 22.24 but only one in the primary carbocation. The electron-releasing effect of two alkyl groups reduces the positive charge on the carbon more (the positive charge is spread out more in this ion) than one alkyl group does and stabilises the ion more. Because the secondary carbocation is more stable, it is more likely to be formed – there will be more of it in the reaction mixture – so it is more likely to collide with a Br^- ion to form the final product.

KEY POINT

A secondary carbocation is more stable than a primary carbocation. This is because of the electron-releasing effect of more alkyl groups (larger positive inductive effect).

In general, the more alkyl groups there are attached to C⊕, the more stable the carbocation:



- A primary carbocation has one carbon atom attached to the C with the positive charge.
- A secondary carbocation has two carbon atoms attached to the C with the positive charge.
- A tertiary carbocation has three carbon atoms attached to the C with the positive charge.

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EXAM TIP

When asked to explain the formation of the major product when a hydrogen halide adds to an alkene, always explain it in terms of the stability of the intermediate carbocation – it is never enough to just say 'Markovnikov's rule'.

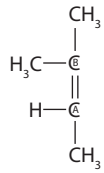
You must also make sure that you include a comparison – there are *more* electron-releasing alkyl groups around the positively charged carbon in a secondary carbocation than in a primary carbocation.

WORKED EXAMPLE 22.3

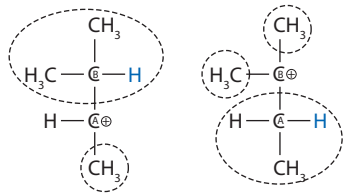
Explain the formation of the major product when 2-methylbut-2-ene reacts with HBr.

Answer

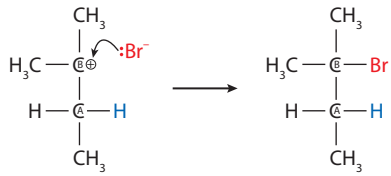
The first stage is to draw out the structure of 2-methylbut-2-ene:



The carbons of the C═C bond are labelled CA and CB to aid discussion. The two possible carbocations are obtained by breaking the C═C bond to form C—C, then putting H on one of the carbons that made up the C═C and a positive charge on the other:



The tertiary carbocation has more (three as opposed to two) electron-releasing alkyl groups joined to the positively charged C, and so, is more stable. This means that the tertiary carbocation will be more likely to be formed and, therefore, to react with Br^- to form the product:



The major product is, therefore, 2-bromo-2-methylbutane, where the H from HBr has become joined to CA, which was the C atom that originally had more H atoms attached.

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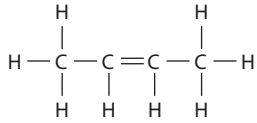
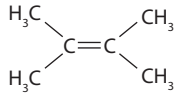
TEST YOUR UNDERSTANDING

17 Draw the structure of the carbocation formed when the following react with HX. In each case, identify the carbocation as primary, secondary or tertiary.

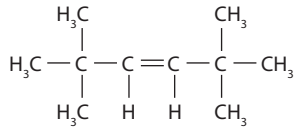
a



b

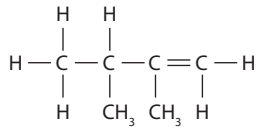


c

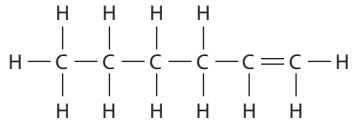


18 Draw the structure of the major product formed when the following react with HCl:

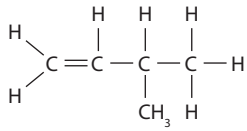
a



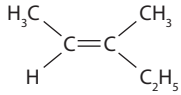
b



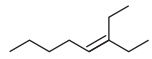
c



d



e



19 State the names of the major products formed when the following alkenes react with water:

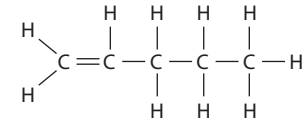
a but-1-ene

b 3-methylbut-1-ene

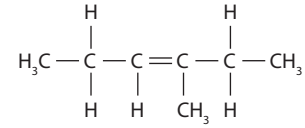
c 2,4-dimethylpent-2-ene.

20 Draw the structure of the more stable carbocation formed when each of the following reacts with HBr. Identify the carbocation as primary, secondary or tertiary.

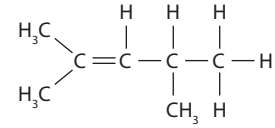
a



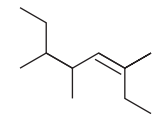
b



c

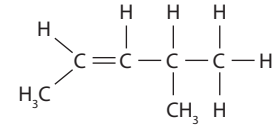


d

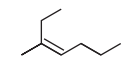


21 For which of the following could Markovnikov's rule **not** be used to predict the major product when it reacts with HBr? Explain your answer.

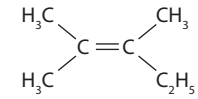
I



II



III



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NATURE OF SCIENCE

Knowing and understanding

Nobel Prize winning physicist Richard Feynman once said, 'I learned very early the difference between knowing the name of something and knowing something'. Science is about more than knowing the name of something – it is about understanding. There is a lot more to Markovnikov's rule than just knowing the name.

22.6 Electrophilic substitution reactions

The structure of benzene

We met benzene, C_6H_6, in Chapter 7. It consists of a hexagonal ring of sp^2 hybridised C atoms with an H atom joined to each C. All C—C bonds in benzene are equal and between the length of a C—C and C=C bond. The bonding and structure can either be described as a resonance hybrid with equal contributions from the two structures shown in Figure 22.26 or in terms of delocalisation (Figure 22.27).

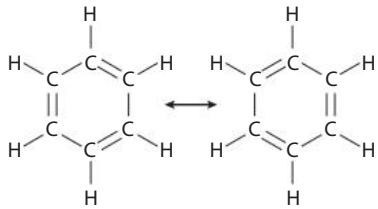
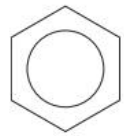
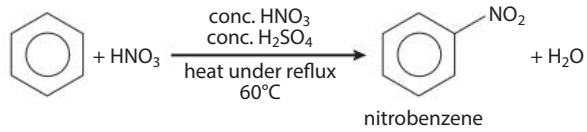


Figure 22.26: Benzene is a resonance hybrid of these two structures.

Benzene has a π ring system of six delocalised electrons that extends all around the ring of carbon atoms. The structure of benzene is usually drawn as a hexagon, with a circle in the middle indicating the π delocalised system:



The structure of benzene with three C=C double bonds would suggest that benzene would undergo addition reactions, like the alkenes we met above, however, benzene undergoes substitution reactions, for example:



Remember that there is an H atom joined to each C in the structure of benzene, and so, in this reaction one H atom has been substituted by an NO_2 group.

The π system of delocalised electrons imparts extra stability to benzene (resonance energy). Substitution reactions preserve the π system of delocalised electrons and the extra stability, but addition reactions would involve the loss of the delocalised system since single C—C bonds would be formed.

Electrophilic substitution

The π system, containing six delocalised electrons, represents a region of high electron density and, therefore, benzene is susceptible to attack by electrophiles.

KEY POINT

Benzene undergoes electrophilic substitution reactions.

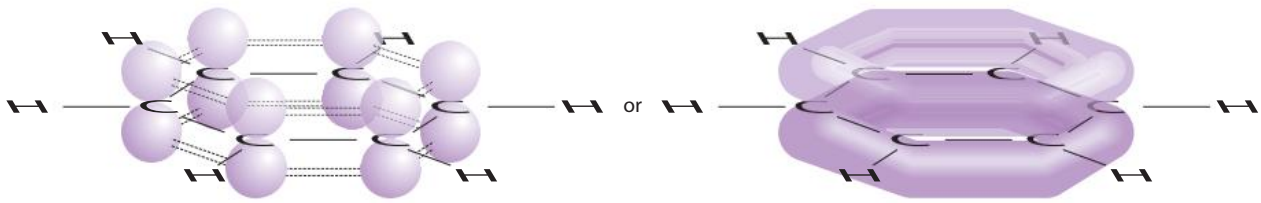


Figure 22.27: Delocalisation in benzene.

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The general mechanism for benzene undergoing **electrophilic substitution** with electrophile E^+ is shown in Figure 22.28.

Figure 22.28: The mechanism for electrophilic substitution.

EXAM TIP

The curly arrow in the first step in Figure 22.27 must come from the π ring system, and the partial ring in the second step must extend over five carbon atoms (not the one joined to the electrophile).

We can understand how this reaction works by looking more closely at what happens to the electrons (Figure 22.29). The first step involves attack by the electrophile, E^+. A pair of electrons from the π system of delocalised electrons is donated to the electrophile, so benzene is the Lewis base (electron-pair donor) and the electrophile is the Lewis acid (electron-pair acceptor).

Each C atom has four orbitals (one s and three p) that it can use for covalent bonding. The C atoms in benzene use three (sp^2) orbitals each for the formation of σ bonds (two to the adjacent C atoms and one to the H atom), leaving one p orbital, which is part of the π system. In the intermediate, however, the C in blue in Figure 22.28 uses all four of its orbitals to form σ bonds (two to adjacent C atoms, one to H and now one to the electrophile), so it does not have a p orbital that it can contribute to the π system. This means that the π system only extends over the remaining five C atoms (Figure 22.30).

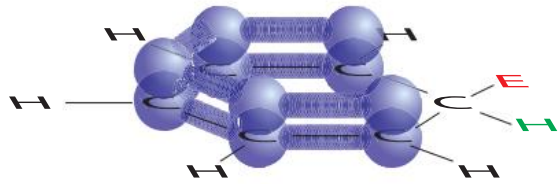

Figure 22.30: Partial delocalisation in the intermediate in electrophilic substitution.

The six C atoms in benzene contribute one electron each to the π system, but in the intermediate two of these electrons have been taken to form the bond to the electrophile, and so, the π system over the five C atoms is made up of only four delocalised electrons and there is, therefore, a positive charge. Another way of thinking about this is that the initial reaction involves a neutral species reacting with a positively charged species, therefore, the intermediate must also have a positive charge.

In the second step in Figure 22.28, the C—H bond breaks. This releases an orbital and a pair of electrons to restore the π ring system (Figure 22.31). The C atom in blue now only forms three σ bonds and, therefore, has a p orbital available to participate in the π system again.

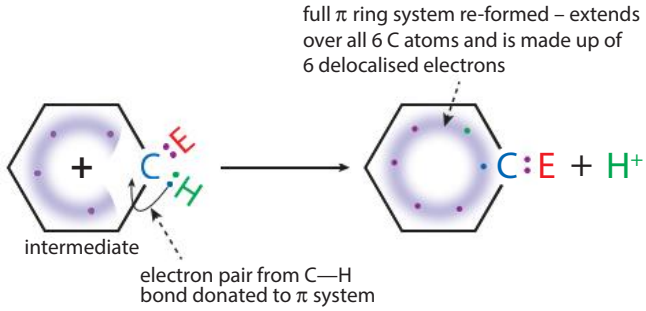

Figure 22.31: The second step in the electrophilic substitution reaction.

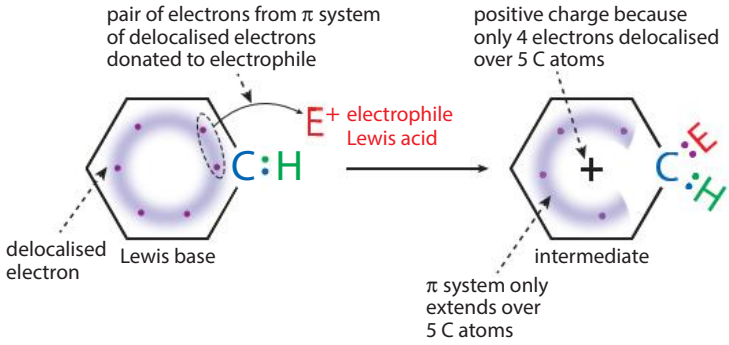

Figure 22.29: The first step in the electrophilic substitution reaction showing the electrons.

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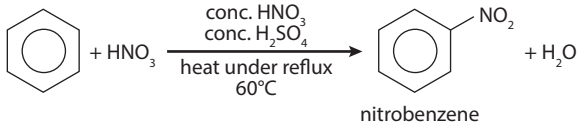
Link

The nitration of benzene

When benzene is heated with a mixture of concentrated nitric and sulfuric acids, nitrobenzene is formed:

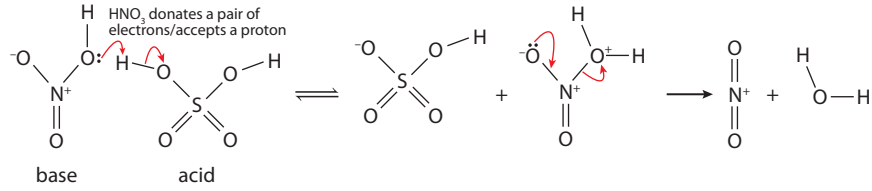
$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$



The first stage in the reaction is the formation of the electrophile – this is the nitronium ion, NO_2^+, which is formed when concentrated sulfuric acid reacts with concentrated nitric acid:

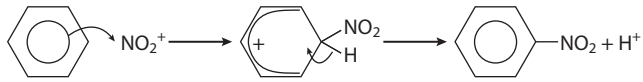
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

The mechanism for the formation of the electrophile is:



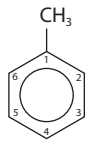
Sulfuric acid (the stronger acid) protonates the —OH group in nitric acid and the N—O bond breaks to form a water molecule, so, in this reaction, nitric acid donates a pair of electrons/accepts a proton; therefore, it can be described as a Lewis/Brønsted–Lowry base.

The rest of the mechanism is electrophilic substitution:



TEST YOUR UNDERSTANDING

22 The structure of methylbenzene is



When this reacts with an electrophile, E^+, substitution occurs on C2 or C4. Write the mechanism for the reaction that would result in substitution at position 4. Identify a Lewis acid and a Lewis base.

23 Methylbenzene reacts in the same way as benzene with a mixture of concentrated nitric acid and concentrated sulfuric acid.
Write a balanced equation, using condensed structural formulas, for the reaction.

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SELF-ASSESSMENT CHECKLIST

Think about the topics covered in this chapter. Which parts are you most confident with? Which topics require some extra practice?

I can...	Section	Needs more work	Nearly there	Confident to move on
explain the term nucleophile	22.1			
describe nucleophilic substitution reactions	22.1			
explain the term heterolytic fission	22.1			
explain the term electrophile	22.2			
explain why alkenes are more reactive than alkanes	22.2			
construct equations for the reaction of alkenes	22.2			
explain the Lewis definition of acids and bases	22.3			
describe the mechanism for nucleophilic substitution reactions	22.4			
explain how the nature of the leaving group affects the rate of nucleophilic substitution reactions	22.4			
explain the mechanism for electrophilic addition reactions	22.5			
explain the reactions of unsymmetrical alkenes with hydrogen halides	22.5			
explain the mechanism for electrophilic substitution reactions.	22.6			

REFLECTION

- To what extent do you think that looking back at other chapters would help you understand the material in this chapter?
- Has a lack of knowledge in the basics of organic chemistry hindered your progress? How could you rectify this?
- To what extent do you feel that you understand the reaction mechanisms or are going to rely on just learning them by rote?
- What opportunities have you identified in this topic for working with another student to improve your understanding?

EXAM-STYLE QUESTIONS

You can find questions in the style of IB exams in the digital coursebook.

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Glossary

absolute zero the temperature at which everything would be in its lowest energy state: 0 K or −273.15 °C. The absolute scale of temperature (Kelvin scale of temperature) starts at absolute zero.

accuracy how close a measurement is to the actual value of a particular quantity.

Acid deposition a more general term than acid rain that refers to any process in which acidic substances (particles, gases and precipitation) leave the atmosphere to be deposited on the surface of the Earth – it can be divided into wet deposition (acid rain, fog and snow) and dry deposition (acidic gases and particles).

acid dissociation constant (K_a) equilibrium constant for the dissociation of a weak acid. In general, for the dissociation of acid HA, $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, the expression for the acid dissociation constant is

$$K_a = \frac{[A^-(aq)][H^+(aq)]}{[HA(aq)]}$$

The higher the value of K_a, the stronger the acid.

acid rain rain with a pH of less than 5.6. It is caused by atmospheric pollution.

activation energy (E_a) the minimum energy that colliding particles must have before collision results in a chemical reaction.

addition polymerisation a large number of monomers are joined together into a polymer chain; no other groups are lost in the process. Alkenes (containing C=C) undergo addition polymerisation.

addition reaction in organic chemistry, a reaction in which a molecule is added to a compound containing a multiple bond without the loss of any other groups.

adsorption the tendency of atoms/molecules/ions to 'bond' to a surface either through a chemical or a physical interaction.

aliphatic organic compounds not containing a phenyl group.

alkali a base that is dissolved in water to form a solution containing hydroxide ions.

alkali metals the elements in Group 1 of the periodic table.

allotropes different forms of the same element, e.g. diamond, graphite and fullerene are allotropes of carbon.

alloy mixture of two or more metals or of a metal with a non-metal.

amphiprotic a substance that can donate a proton (acting as a Brønsted–Lowry acid) and accept a proton (acting as a Brønsted–Lowry base), e.g. HCO_3^-.

amphoteric a substance that can act as an acid and a base.

anion a negative ion. It can be formed when an atom gains (an) electron(s) so that the ion has more electrons (−) than protons (+).

anode the electrode at which oxidation occurs.

aromatic in organic chemistry, aromatic compounds are those that contain a phenyl group.

Arrhenius equation an equation that models the variation of the rate constant with temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

'A' is the pre-exponential factor or A-factor or Arrhenius A factor and contains information related to the frequency of collisions and the orientation of the collisions.

atom the smallest part of an element that can still be recognised as the element. In the simplest model of the atom, the electrons orbit around the central nucleus; the nucleus is made up of protons and neutrons (except for a hydrogen atom, which has no neutrons).

atom economy a measure of how efficient a particular reaction is in converting as much of the starting materials as possible into useful products.

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{total molar mass of all reactants}} \times 100\%$$

The higher the atom economy, the greener the process, because more of the starting materials end up in the desired product.

atomic number (Z) the number of protons in the nucleus of an atom.

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atomic radius half the internuclear distance between two atoms of the same element which are covalently bonded. Atomic radius is usually called 'covalent radius' in more advanced work. It is also possible for an element to have a 'van der Waals radius'.

Aufbau principle the process of putting electrons into atoms to generate the electron configuration.

average bond enthalpy the average quantity of energy required to break one mole of covalent bonds, in a gaseous molecule under standard conditions; 'average' refers to the fact that the bond enthalpy is different in different molecules and, therefore, the value quoted is the average quantity of energy to break a particular bond in a range of molecules.

Avogadro constant has the same numerical value as the Avogadro number but units of mol^{-1}, i.e. $6.02 \times 10^{23}\ mol^{-1}$. The symbol L or N_A is used for the Avogadro constant.

Avogadro number 6.02×10^{23}. This is the number of defined particles in 1 mol of substance.

Avogadro's law equal volumes of ideal gases measured at the same temperature and pressure contain the same number of molecules.

base ionisation constant (K_b) equilibrium constant for the ionisation of a weak base, B, which ionises according to the equation:

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

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

The higher the value of K_b, the stronger the base.

biodegradable can be broken down by microorganisms in the environment.

biofuel a fuel produced from organic matter obtained from plants, or waste material of plant/animal origin, e.g. ethanol (from the fermentation of sugar cane/corn starch), biogas (from decaying matter) and biodiesel (from vegetable oils).

biomass material of plant or animal origin that is used for fuel. The biomass can be burned directly (e.g. wood) or converted into biofuels.

boiling point the temperature at which a liquid boils under a specific set of conditions – usually we will be considering the boiling point at atmospheric pressure.

Bohr model of the atom atoms consist of a central nucleus with electrons moving around the nucleus in circular orbits. The energy of an electron in a particular orbit (energy level/shell) is constant. Only certain orbits (energy levels/shells) can exist so the electron within an atom can only have certain amounts of energy.

bond enthalpy the enthalpy change when one mole of covalent bonds, in a gaseous molecule, is broken under standard conditions. Bond breaking requires energy (endothermic), ΔH is positive; bond making releases energy (exothermic), ΔH is negative.

bond order the number of covalent bonds between two atoms. A single bond has a bond order of 1. A double bond a bond order of 2, and a triple bond a bond order of 3. When molecules/ions are best described as resonance hybrids, the bond orders will involve fractions.

Born–Haber cycle an enthalpy level diagram breaking down the formation of an ionic compound into a series of simpler steps.

Brønsted–Lowry definition of acids and bases an acid is a proton (H^+) donor; a base is a proton (H^+) acceptor.

buffer solution a solution that resists changes in pH when small amounts of acid or alkali are added.

calibration curve a graph relating a particular variable to concentration from which concentrations of unknown solutions can be determined. It is constructed by measuring a particular property (e.g. absorbance) of solutions of known concentrations.

calorimetry experimental determination of the heat given out/taken in during chemical reactions/physical processes.

carbocation an organic molecular species with a positive charge on a carbon atom.

carbon footprint a measure of the quantity of greenhouse gases (primarily carbon dioxide and methane) emitted as a result of human activities.

carbon neutral a process/fuel which results in no net release of carbon dioxide, or other greenhouse gases, into the atmosphere.

catalyst a substance that increases the rate of a chemical reaction without itself being used up in the reaction. A catalyst acts by allowing the reaction to proceed by an alternative pathway of lower activation energy.

cathode the electrode at which reduction occurs.

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cation a positive ion. It can be formed when an atom loses (an) electron(s) so that the ion has more protons (+) than electrons (−).

chain reaction a process in which one initial event causes a large number of subsequent reactions – the reactive species is regenerated in each cycle of reactions.

charge density the charge on an ion divided by its volume. The higher the charge or the smaller the ion, the greater the charge density.

chemical properties how a substance behaves in chemical reactions.

chemical shift (δ) The horizontal scale in an NMR spectrum that indicates the chemical environment of a proton (^{1}H) or group of protons. The value is a ratio and is expressed in ppm. Chemical shift values for protons in different environments are given in the IB data booklet.

chiral a molecule is chiral if mirror images are non-superimposable. To be chiral, the molecule must possess a chirality (chiral) centre and not have a centre of symmetry.

chirality centre (chiral centre) a carbon atom with four different atoms or groups attached to it (sometimes called an asymmetric carbon atom) that makes a molecule chiral.

***cis–trans* isomerism** where two compounds have the same structural formula, but the groups are arranged differently in space around a double bond or a ring.

closed system a system where there is no exchange of matter with the surroundings.

collision theory a model that is used to explain the variation of rate of reaction. A reaction can occur only when two particles collide in the correct orientation and with $E \geq E_a$.

complex ion an ion formed when a central transition metal atom/ion is bonded to ligands, e.g. $[Ni(H_2O)_6]^{2+}$. The ligands form coordination bonds to the transition metal atom/ion.

compound a pure substance formed when two or more elements combine chemically in a fixed ratio.

concentration quantity of solute dissolved in a unit volume of solution; the volume that is usually taken is 1 dm^3 (one litre); the quantity of solute may be expressed in g or mol, so the units of concentration are g dm^{-3} or mol dm^{-3}.

condensation polymerisation monomers, each containing two functional groups, join together to form a long chain, with the elimination of a small molecule, such as water or hydrogen chloride, each time two monomers join together.

condensed structural formula shows how the atoms are joined together in a molecule but does not show all of the bonds, e.g. $CH_3CH_2CH_2OH$.

conjugate acid–base pair two species that differ by one proton (H^+). When an acid donates a proton, it forms its conjugate base (CH_3COO^- is the conjugate base of CH_3COOH); when a base gains a proton, it forms its conjugate acid (H_3O^+ is the conjugate acid of H_2O).

continuous spectrum a spectrum consisting of all frequencies/wavelengths of light.

convergence limit the point in a line emission spectrum where the lines merge to form a continuum. In the emission spectrum of hydrogen, the frequency of the convergence limit in the series of lines where the electron falls down to $n = 1$, may be used to determine the ionisation energy of hydrogen.

coordination bond a type of covalent bond in which both electrons come from the same atom. Also called a dative bond or coordinate covalent bond.

coordination number in an ionic crystal, it is the number of nearest neighbours, of opposite charge, for an ion in a crystal. For a molecular entity/complex ion, it is the number of atoms that the central atom/ion is bonded to.

covalent bond the electrostatic attraction between a shared pair of electrons and the nuclei of the atoms making up the bond.

covalent network structure the structure of substances such as diamond and graphite that contain an extended network of covalently bonded atoms and not individual molecules. This is also called a giant covalent structure.

degenerate a set of orbitals with the same energy.

delocalisation the sharing of a pair of electrons between three or more atoms.

diamagnetism a magnetic property of atoms/ions/molecules caused by the presence of paired electrons – diamagnetic substances are repelled slightly by a magnetic field.

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diprotic acid H_2SO_4 is a diprotic acid, as it can dissociate to form two protons per molecule:

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

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

ductile can be drawn out into wires.

dynamic equilibrium in a reversible reaction (process), macroscopic properties (all concentrations of reactants and products) are constant and the rate of the forward reaction is equal to the rate of the reverse reaction.

effective nuclear charge the nuclear charge experienced by electrons when shielding is taken into account.
effective nuclear charge =
actual nuclear charge – shielding effect

electrochemical cells a device that interconverts chemical energy and electrical energy. These are of two main types:

- voltaic cell: chemical energy is converted into electrical energy – a chemical reaction produces electrical energy
- electrolytic cell: electrical energy is converted into chemical energy – electricity is used to bring about a chemical reaction.

electrochemical series metals can be arranged in an electrochemical series in order of how readily they are oxidised to an aqueous positive ion. The standard electrode potential (*standard reduction potential* in the IB data booklet) is a measure of this and metals can be arranged in order from the most negative standard electrode potential (most readily oxidised/strongest reducing agent/most reactive) to least negative/most positive standard electrode potential (least readily oxidised/weakest reducing agent/least reactive).

electrolysis the breaking down of a substance (in molten state or solution) by the passage of electricity through it.

electrolyte a solution, or a molten compound, that will conduct electricity due to the presence of ions that are free to move towards the electrodes.

electron domain a lone pair, the electron pair that makes up a single bond or the electron pairs that together make up a multiple bond. Each single, double or triple bond counts as one electron domain when working out shapes of molecules.

electronegativity a measure of the attraction of an atom in a molecule for the electron pair in the covalent bond of which it is a part. A more electronegative atom attracts electrons more strongly.

electrophile a reagent (a positively charged ion or the positive end of a dipole) that is attracted to regions of high electron density and accepts a pair of electrons to form a covalent bond. An electrophile is a Lewis acid.

electrophilic addition an addition reaction where the initial attack on the organic molecule is by an electrophile. Alkenes (and alkynes) undergo electrophilic addition reactions.

electrophilic substitution substitution reaction where the initial attack on the organic molecule is by an electrophile. Benzene undergoes electrophilic substitution.

electroplating the process of coating an object with a thin layer of a metal using electrolysis.

electrostatic attraction attraction between positive and negative charges.

element a chemical substance that cannot be broken down into a simpler substance by chemical means. Each atom has the same number of protons in the nucleus.

emission spectrum electromagnetic radiation given out when an electron in an atom falls from a higher energy level to a lower one. Only certain frequencies of electromagnetic radiation are emitted – a line spectrum. Each atom has a different emission spectrum. For hydrogen, the emission spectrum in the visible region consists of a series of coloured lines that get closer together at higher frequency.

empirical formula the simplest whole number ratio of the elements present in a compound.

enantiomers the non-superimposable mirror images of a chiral molecule.

endothermic reaction a chemical reaction in which heat is taken in from the surroundings – the reaction vessel gets colder; ΔH for an endothermic reaction is positive.

end point in a titration, the point at which an indicator changes colour.

enthalpy change (ΔH) the heat energy exchanged with the surroundings at constant pressure.

entropy (S) a measure of the disorder of a system (how the matter is dispersed/distributed) or how the available energy is distributed among the particles.

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Standard entropy ($S^{\ominus}$) is the entropy of a substance at 100 kPa and 298.15 K; units are J K^{-1} mol^{-1}. $\Delta S^{\ominus}$ is the entropy change under standard conditions – a positive value indicates an increase in entropy, i.e., the system becomes more disordered/the energy becomes more spread out (less concentrated).

equilibrium a reversible reaction will eventually reach a state of equilibrium. At this point, all concentrations are constant (macroscopic properties are constant). See also *dynamic equilibrium*.

equilibrium law / equilibrium constant the ratio of the concentrations (raised to the powers of the coefficients in the stoichiometric equation) of products to reactants at equilibrium is equal to the equilibrium constant, K.

So, for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

equivalence point in a titration, the point at which equivalent numbers of moles of acid and alkali have been added.

excited state an energy state for an atom (or molecule) that has higher energy than the ground state.

exothermic reaction a chemical reaction that results in the release of heat to the surroundings – the reaction vessel gets hotter; ΔH for an exothermic reaction is negative.

experimental (or actual) yield the amount/mass of desired product actually formed in a reaction.

first electron affinity enthalpy change when one electron is added to each atom in one mole of gaseous atoms under standard conditions: $X(g) + e^- \rightarrow X^-(g)$. The first electron affinity is exothermic for virtually all elements.

first ionisation energy the minimum amount of energy required to remove an electron from a gaseous atom/the energy required to remove one electron from each atom in one mole of gaseous atoms under standard conditions. The energy for the process: $M(g) \rightarrow M^+(g) + e^-$.

formal charge (FC) the charge that an atom in a molecule/ion would have if we assumed that the electrons in a covalent bond were equally shared between the atoms that are bonded – i.e., we assume that all atoms have the same electronegativity. Formal charge arises when there is a charge on an ion and/or when coordination bonds are formed. The two electrons in a coordination bond are shared equally between the donating atom (which, therefore, has a formal charge of +1) and the receiving atom (which then has a formal charge of −1).

fossil fuels fuels formed from things that were once alive and have been buried underground for millions of years, e.g. coal, oil and gas.

fragmentation pattern the series of peaks in a mass spectrum formed by ions that have been generated when the molecular ion breaks apart in the mass spectrometer.

fuel something that is burnt to produce energy.

fuel cell a type of electrochemical cell that uses the reaction between a fuel (such as hydrogen or methanol) and an oxidising agent (e.g. oxygen) to produce electrical energy directly. It uses a continuous supply of reactants from an external source.

full structural formula shows *all* atoms and *all* bonds in a molecule. This is also called a displayed or graphic formula.

functional group an atom or group of atoms that gives an organic molecule its characteristic chemical properties. A functional group also influences the physical properties of a compound.

giant structure one in which bonding extends fairly uniformly throughout the whole structure; there are no individual molecules, e.g. an ionic crystal or diamond.

Gibbs energy change (ΔG) (sometimes called the free energy change) ΔG is related to the entropy change of the universe and can be defined using the equation $\Delta G = \Delta H - T\Delta S$. For a reaction to be spontaneous, ΔG for the reaction must be negative. $\Delta G^{\ominus}$ is the standard Gibbs energy change.

ground state the lowest possible energy state for an atom (or molecule).

group vertical column in the periodic table. These are numbered from 1 to 18, including the transition element groups.

heat the energy that flows from something at a higher temperature to something at a lower temperature because of the temperature difference between them.

Hess's law the enthalpy change accompanying a chemical reaction is independent of the pathway between the initial and final states.

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heterogeneous mixture a mixture of two or more substances, that does not have uniform composition and consists of separate phases. A heterogeneous mixture can be separated by mechanical means. An example is a mixture of two solids.

heterolytic fission a covalent bond breaks so that both electrons go to the same atom.

homogeneous mixture a mixture of two or more substances with the same (uniform) composition throughout the mixture – it consists of only one phase. Examples are solutions or a mixture of gases.

homologous series a series of compounds with the same functional group, in which each member differs from the next by —CH_2—.

homolytic fission a covalent bond breaks such that one electron goes back to each atom making up the original covalent bond.

Hund's rule electrons fill orbitals of the same energy (degenerate orbitals) to give the maximum number of electrons with the same spin.

hybridisation the mixing of atomic orbitals when a compound forms to produce a new set of orbitals (the same number as originally), which are better arranged in space for covalent bonding.

hydrocarbon a compound containing carbon and hydrogen only.

hydrogenation addition of hydrogen (H_2) to a compound containing multiple bonds.

hydrogen bonding an intermolecular force resulting from the interaction of a lone pair on a very electronegative atom (N/O/F) in one molecule with an H atom attached to N/O/F in another molecule. These forces may also occur between atoms in different parts of the same molecule.

hydrolysis a reaction in which a covalent bond in a molecule is broken by reaction with water; most commonly, hydrolysis reactions occur when a molecule is reacted with aqueous acid or aqueous alkali.

ideal gas a theoretical model that approximates the behaviour of real gases. It can be defined in terms of macroscopic properties (a gas that obeys the equation $PV = nRT$) or in terms of microscopic properties (the main assumptions that define an ideal gas on a microscopic scale are that the molecules are point masses – their volume is negligible compared with the volume of the container – and that there are no intermolecular forces except during a collision).

indicator an acid–base indicator has different colours, according to the pH of the solution. Indicators are usually weak acids (HInd); they dissociate according to the following equation:

$$HInd(aq) \rightleftharpoons H^+(aq) + Ind^-(aq)$$

colour I colour II

the ionised (Ind^-) and un-ionised (HInd) forms must have different colours. Indicators may also be weak bases.

initiation step the step that starts off the chain reaction in a radical substitution reaction. It involves an increase in the number of radicals.

intermolecular forces forces between molecules. These include London forces, permanent dipole–permanent dipole interactions and hydrogen bonding.

intramolecular forces forces within a molecule – usually covalent bonding.

ion a charged particle that is formed when an atom (or molecular entity) loses or gains electron(s); a positive ion is formed when an atom loses (an) electron(s) and a negative ion is formed when an atom gains (an) electron(s).

ionic bonding the electrostatic attraction between oppositely charged ions.

ionisation energy see first ionisation energy.

ion product constant of water (K_w) an equilibrium constant for the dissociation of water:

$$K_w = [H^+(aq)][OH^-(aq)]$$

K_w has a value of 1.0×10^{-14} at 25 °C. The ion product constant is also known as the ionic product constant.

isoelectronic species with the same number of electrons.

isotopes different atoms of the same element with different mass numbers, i.e., different numbers of neutrons in the nucleus. Isotopes have the same chemical properties but different physical properties.

kinetic energy the energy a body has because of its motion; $E_k = \frac{1}{2}mv^2$.

lattice enthalpy see standard lattice enthalpy

lattice usually used when describing crystals – a structure with a regular, repeating (3D) arrangement.

leaving group an atom/ion/group of atoms that is lost from the substrate when a bond is broken in a reaction.

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Le Chatelier's principle if a system at equilibrium is subjected to some change, the position of equilibrium will shift in order to minimise the effect of the change.

Lewis definition of acids and bases an acid is an electron-pair acceptor; a base is an electron-pair donor.

Lewis (electron dot) formula a diagram showing all the valence (outer-shell) electrons in a molecule (or ion). Also called a Lewis structure.

ligand negative ion or neutral molecule that uses lone pairs of electrons to bond to a transition element ion to form a complex ion. Coordination bonds are formed between the ligand and the transition element ion.

limiting reactant the reactant that is used up first in a chemical reaction; when the amount in moles of each species is divided by their coefficient in the stoichiometric equation, the limiting reactant is the one with the lowest number; all other reactants are in excess.

line spectrum the emission spectrum of an atom consists of a series of lines; only certain frequencies/wavelengths of light are present.

lone pair of electrons a pair of electrons in the outer shell of an atom that is not involved in covalent bonding.

London (dispersion) forces intermolecular forces resulting from temporary (instantaneous) dipole–induced dipole interactions.

malleable can be hammered into different shapes.

Markovnikov's rule 'rule' that can be used to predict the major product when HX adds to an unsymmetrical alkene. When H—X adds across the double bond of an alkene, the H atom becomes attached to the C atom that has the larger number of H atoms already attached.

mass number (A) the total number of protons plus neutrons in the nucleus of an atom.

Maxwell–Boltzmann distribution a graph showing the distribution of molecular kinetic energies in a sample of gas at a particular temperature.

metallic bonding the electrostatic attraction between the positive ions in a metallic lattice and the delocalised electrons.

metalloid elements, such as Si, Ge and Sb, that have some of the properties of both metals and non-metals or properties that are intermediate between those of a metal and non-metal.

mixture two or more substances mixed together. The components of a mixture can be mixed together in any proportion (although there are limits for solutions). The components of a mixture are not chemically bonded together, and so, retain their individual properties. The components of a mixture can be separated from each other by physical processes.

mobile phase the phase that moves in chromatography, e.g. the solvent moving up the paper in paper chromatography.

molar mass (M) the mass that contains 1 mol of particles (atoms. molecules, ions) and is the A_r or M_r in grams of the substance. The units of molar mass are g mol^{-1}.

molar volume the volume occupied by one mole of a gas; the molar volume of an ideal gas at STP is 22.7 dm^3 mol^{-1}.

mole the unit of the amount of substance. The amount of substance that contains the Avogadro number (6.02×10^{23}) of particles (atoms, ions, molecules, etc.)

molecular formula the total number of atoms of each element present in a molecule of the compound. The molecular formula is a multiple of the empirical formula.

molecularity the number of reactant 'molecules' that take part in a particular elementary step in a reaction mechanism.

molecule an electrically neutral particle consisting of two or more atoms chemically bonded together.

monomer a molecule from which a polymer chain may be built up, e.g. ethene is the monomer for polyethene.

monoprotic acid HCl is a monoprotic acid as it dissociates to form one proton per molecule.

neutralisation reaction a chemical reaction in which an acid reacts with a base/alkali to form a salt plus water. Neutralisation reactions are exothermic.

noble gases the elements in Group 18 of the periodic table.

non-renewable energy sources sources of energy that are finite – they will eventually run out, e.g. coal.

nucleophile a molecule or a negatively charged ion, possessing a lone pair of electrons, which is attracted to a more positively charged region in a molecule (region with lower electron density) and donates a lone pair of electrons to form a covalent (coordination) bond. A nucleophile is a Lewis base.

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nucleophilic substitution a type of reaction in organic chemistry in which initial attack on the molecule is by a nucleophile and the nucleophile replaces an atom/group, e.g. when a halogenoalkane is attacked by an OH^- nucleophile, the OH replaces the halogen atom.

octet rule electrons will be shared so that the central atom has eight electrons in its outer (valence) shell. There are, however, many exceptions to the octet rule.

optical isomerism optical isomers (enantiomers) rotate the plane of plane-polarised light in opposite directions (by the same amount as long as concentrations are equal). Optical isomers have the same molecular and structural formula, but groups are arranged differently in space and the individual optical isomers are non-superimposable mirror images of each other.

optically active a substance is optically active/demonstrates optical activity if it rotates the plane of polarisation of plane-polarised light.

orbital a region of space in which there is a high probability of finding an electron; it represents a discrete energy level. There are s, p, d and f orbitals. One orbital can contain a maximum of two electrons.

orbital diagrams diagrams that show the electron configuration of atoms/ions using arrows (electrons) in boxes (orbitals).

order of a reaction the power of the concentration of a particular reactant in the experimentally determined rate equation. e.g. in the rate equation: rate = $k[A]^m[B]^n$, the order with respect to A is m and the order with respect to B is n.

overall order of reaction the sum of the powers of the concentration terms in the experimentally determined rate equation. e.g. in the rate equation: rate = $k[A]^m[B]^n$, the overall order is $m + n$.

oxidation a process which involves a loss of electrons or an increase in oxidation state. Oxidation can also be defined in terms of the gain of oxygen or the loss of hydrogen, but these are less general definitions.

oxidation state (oxidation number) the degree of oxidation of an atom in terms of counting electrons. It is a purely formal concept that regards all compounds as ionic and assigns charges to the components accordingly; it provides a guide to the distribution of electrons in covalent compounds.

oxidising agent (oxidant) oxidises other species and, in the process, is itself reduced; an oxidising agent takes electrons away from another species.

paramagnetism a magnetic property of atoms/ions/molecules caused by the presence of unpaired electrons – paramagnetic substances are attracted by a magnetic field.

partition the tendency of a solute to distribute itself between two immiscible solvents due to its solubility in each.

Pauli exclusion principle two electrons in the same orbital must have opposite spins.

percentage yield the percentage yield compares the actual, experimental, yield and the theoretical, maximum, yield:

$$\% \text{ yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

period horizontal row in the periodic table. Hydrogen and helium are in Period 1.

pH a measure of the concentration of H^+ ions in an aqueous solution; it can be defined as the negative logarithm to base ten of the hydrogen ion concentration in aqueous solution:

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

pH range of an indicator the pH range over which intermediate colours for an indicator can be seen because comparable amounts of the un-ionised and ionised forms are present.

photon particle of electromagnetic radiation. The energy of a photon is proportional to the frequency of the electromagnetic radiation and inversely proportional to its wavelength.

physical properties properties such as melting point, solubility and electrical conductivity, relating to the physical state of a substance and the physical changes it can undergo.

pi (π) bond bond formed by the sideways overlap/combination of parallel p orbitals; the electron density in the pi bond lies above and below the internuclear axis.

plane-polarised light light that vibrates in one plane only. Enantiomers rotate the plane of plane-polarised light in opposite directions.

polar molecule molecule in which one end is slightly positive relative to the other. Whether a molecule is polar or not depends on the differences in electronegativity of the atoms and the shape of the molecule.

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polyamide a polymer where the monomers are linked together by amide functional groups. They are formed in condensation polymerisation reactions.

polyester a polymer where the monomers are linked together by ester functional groups. They are formed in condensation polymerisation reactions.

polymerisation the process of joining together a large number of monomers to form a long chain molecule (polymer). There are two types of polymerisation: addition and condensation.

polymers long-chain molecules, usually based on carbon, which are formed when smaller molecules (monomers) join together.

position of equilibrium the relative amounts of reactants and products present in a system at equilibrium.

primary cell a cell (battery) that cannot usually be recharged by connecting to an electricity supply – the reaction in the cell is non-reversible. A voltaic cell is also referred to as a primary cell on the IB syllabus.

propagation step a step in a radical substitution reaction that involves production of products and no change in the number of radicals.

racemic mixture (racemate) an equimolar mixture of the two enantiomers of a chiral compound; it has no effect on plane-polarised light – it is optically inactive.

radical a molecular entity (atom or group of atoms) with an unpaired electron. Radicals are very reactive because of this unpaired electron.

random error uncertainty in a measurement due to the limitations of the measuring apparatus and other uncontrollable variables that are inevitable in any experiment. The effects of random uncertainties should mean that the measurements taken will be distributed either side of the mean, i.e. fluctuations will be in both directions. The effect of random uncertainties can be reduced by repeating the measurements more often, but random uncertainties can never be completely eliminated.

rate-determining step the slowest step in a reaction mechanism. It is the step with the highest activation energy.

rate constant (k) a constant of proportionality relating the concentrations in the experimentally determined rate expression to the rate of a chemical reaction. The rate constant is only a constant for a particular reaction at a particular temperature.

rate equation (rate expression/rate law) an experimentally determined equation that relates the rate of reaction to the concentrations of substances in the reaction mixture, e.g. rate = $k[A]^m[B]^n$.

rate of reaction the speed at which reactants are used up or products are formed or, more precisely, the change in concentration of reactants or products per unit time:

$$\text{average rate} = \frac{\text{change in concentration}}{\text{time}}$$

It could also be defined in terms of change in mass or volume etc. over time.

reaction quotient (Q) the ratio of the concentrations of the reactants and products (raised to the appropriate powers) at any point in time. An expression for Q is exactly the same as that for the equilibrium constant, except that the concentrations are not equilibrium concentrations.

So, for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$Q = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

redox reaction a reaction involving both oxidation and reduction; if one species is oxidised, another species must be reduced.

reducing agent (reductant) reduces other species and, in the process, is itself oxidised; a reducing agent gives electrons to another species.

reduction a process that involves gain of electrons or decrease in oxidation state. Reduction can also be defined in terms of the loss of oxygen or the gain of hydrogen, but these are less general definitions.

reflux a technique for heating volatile substances in a laboratory. The flask has a condenser attached vertically. The vapours cool in the condenser and condense so that they run back into the flask without escaping.

relative atomic mass (A_r) the average mass of the naturally occurring isotopes of an element relative to the mass of 1/12 of an atom of carbon-12.

relative formula mass if a compound contains ions, the relative formula mass is the average mass of the formula unit relative to the mass of 1/12 of an atom of carbon-12.

relative molecular mass (M_r) the average mass of a molecule of a compound relative to the average mass of 1/12 of an atom of carbon-12; M_r is the sum of the relative atomic masses of the individual atoms making up a molecule.

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renewable energy sources sources of energy that are naturally replenished – they will not run out, e.g. solar energy or wind power.

repeating unit (repeat unit) of a polymer the basic unit from which the whole polymer chain can be made up.

resonance energy the difference in energy between the actual (delocalised) structure of a molecule and the energy of a theoretical resonance structure. Used as a term to describe the 'extra' stability arising from delocalisation.

resonance hybrid the actual structure of a molecule/ion for which resonance structures can be drawn can be described as a resonance hybrid made up of contributions (not necessarily equal) from all possible resonance structures.

resonance structure one of several Lewis formulas that can be drawn for some molecules/ions.

R_F (retardation factor) value in chromatography:

$$R_F = \frac{\text{distance solute moves}}{\text{distance solvent front moves}}$$

reversible reaction a reaction that can go either way; the reactants become the products, but the products of the reaction can also react to re-form the reactants. The symbol $\rightleftharpoons$ shows that a reaction is reversible. A reversible reaction will eventually reach a state of equilibrium.

salt a compound formed when the hydrogen ion (H^+) in an acid is replaced by a metal ion (or ammonium ion).

salt bridge completes the circuit in a voltaic cell by providing an electrical connection between two half-cells, allowing ions to flow into or out of the half-cells to balance out the charges in the half-cells. A salt bridge contains a concentrated solution of an ionic salt, such as KCl.

saturated when referring to organic compounds, it is a compound containing only single bonds between carbon atoms.

saturated solution a solution that contains the maximum amount of dissolved solute at a particular temperature.

secondary cell a cell (battery) that can be recharged by connecting to an electricity supply, and is often called a rechargeable battery. The chemical reactions in a rechargeable battery are reversible and can be reversed by connecting them to an electricity supply.

serial dilutions successive dilutions of a solution.

shielding the ability of electrons (usually those in inner shells) to shield/screen/insulate other electrons from the attractive force of the nucleus.

sigma (σ) bond bond formed by the axial (head-on) overlap/combination of atomic orbitals. The electron density in a sigma bond lies mostly along the axis joining the two nuclei.

skeletal formula a representation of the structure of a molecule that shows only the bonds in the carbon skeleton and any groups joined to the carbon skeleton. The carbon atoms are not shown explicitly nor are hydrogen atoms joined to carbon.

S_N1 a unimolecular nucleophilic substitution reaction – only one species is involved in the rate-determining step. The main mechanism for nucleophilic substitution in tertiary halogenoalkanes.

S_N2 a bimolecular nucleophilic substitution reaction – two species are involved in the rate-determining step. The main mechanism for nucleophilic substitution in primary halogenoalkanes.

solute a substance that is dissolved in another (the solvent) to form a solution.

solution that which is formed when a solute dissolves in a solvent.

solvent a substance that dissolves another substance (the solute); the solvent should be present in excess of the solute.

specific energy the energy released from a fuel per unit mass of fuel consumed.

specific heat capacity the energy required to raise the temperature of 1 g of substance by 1 K (1 °C). It can also be defined as the energy to raise the temperature of 1 kg of substance by 1 K. Specific heat capacity has units of J g^{-1} K^{-1} or J g^{-1} $°C^{-1}$. Units that are also encountered are kJ kg^{-1} K^{-1} or J kg^{-1} K^{-1}.

spectrochemical series a series of ligands arranged in order of the extent to which they cause splitting of d orbitals in a transition metal complex ion.

spontaneous reaction a reaction that occurs without any outside influence, i.e., no input of energy. ΔG is negative for a spontaneous reaction.

stability usually refers to the relative energies of reactants and products – if the products are at lower enthalpy (energy) than the reactants, then they are more stable. It is also possible to define *kinetic* stability.

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standard cell potential the electromotive force (voltage) produced when two half-cells are connected under standard conditions (all concentrations 1 mol dm^{-3} and pressure 100 kPa). This drives the movement of electrons through the external circuit from the negative electrode to the positive electrode.

standard conditions a common set of conditions used to compare enthalpy changes; the pressure is 100 kPa and for reactions involving solutions, all solutions should have a concentration of 1 mol dm^{-3}. A temperature is not stated in the definition and should be specified – when it is not specified, we will assume in this course that it is 298.15 K (25 °C). All substances must be in their standard state.

standard electrode potential the electromotive force (voltage) of a half-cell connected to a standard hydrogen electrode, measured under standard conditions; all solutions must be of concentration 1 mol dm^{-3} and pressure must be 100 kPa. A standard electrode potential is always quoted for the reduction reaction.

standard enthalpy change of atomisation ($\Delta H_{at}^{\ominus}$) the enthalpy change when one mole of gaseous atoms is formed from an element in its standard state under standard conditions.

standard enthalpy change of combustion ($\Delta H_{c}^{\ominus}$) the enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

standard enthalpy change of formation ($\Delta H_{f}^{\ominus}$) the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions. $\Delta H_{f}^{\ominus}$ for any element in its standard state is zero.

standard enthalpy change of neutralisation ($\Delta H_{n}^{\ominus}$) the enthalpy change when one mole of H_2O molecules is formed when an acid (H^+) reacts with an alkali (OH^-) under standard conditions, i.e.

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

standard enthalpy change of reaction ($\Delta H_{r}^{\ominus}$) the enthalpy change (heat given out or taken in) when molar amounts of reactants, as shown in the stoichiometric equation, react together under standard conditions.

standard enthalpy change of solution ($\Delta H_{sol}^{\ominus}$) the enthalpy change when one mole of solute is dissolved in excess solvent to form a solution of 'infinite dilution' under standard conditions, e.g.

$$NH_4NO_3(s) \xrightarrow{\text{excess } H_2O} NH_4^+(aq) + NO_3^-(aq)$$

'infinite dilution' means that any further dilution of the solution produces no further enthalpy change, i.e., the solute particles are assumed not to interact with each other in the solution.

standard hydrogen electrode the standard half-cell relative to which standard electrode potentials are measured. Hydrogen gas at 100 kPa (1 bar) pressure is bubbled around a platinum electrode of very high surface area in a solution of H^+ ions of concentration 1 mol dm^{-3}.

The reaction occurring in this half-cell is

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

and this is assigned a standard electrode potential ($E^{\ominus}$) of 0.00 V.

standard lattice enthalpy ($\Delta H_{latt}^{\ominus}$) the enthalpy change when one mole of ionic compound is broken apart into its constituent gaseous ions under standard conditions, e.g., for NaCl:

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \quad \Delta H_{latt}^{\ominus} = +771 \text{ kJ mol}^{-1}$

Lattice enthalpy can be defined in either direction, i.e. as the making or breaking of the lattice, but in the IB syllabus it is usually defined in terms of breaking apart the lattice.

standard solution a solution of known concentration.

standard state the pure substance at 100 kPa and a specified temperature (assume 298.15 K if one is not given). It is often used to refer the state in which a substance exists under standard conditions, e.g. at 298.15 K for iodine it is $I_2(s)$ but for nitrogen it is $N_2(g)$.

standard temperature and pressure (STP) 273.15 K, 100 kPa pressure.

state symbols are used to indicate the physical state of an element or compound: (aq) = aqueous (dissolved in water); (g) = gas; (l) = liquid; (s) = solid.

stationary phase in chromatography, the phase that does not move; this may be the water coating the fibres in paper chromatography or the solid adsorbent in thin-layer chromatography.

stereochemical formula a diagram of a molecule that shows the spatial arrangement of the atoms/groups. Solid wedges show a bond coming out of the plane of the paper/screen and dashed wedges shows bonds going into the plane.

stereoisomers molecules with the same molecular formula and structural formula, but the atoms are arranged differently in space; *cis–trans* isomers and optical isomers are stereoisomers.

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strong acid an acid, such as HCl, H_2SO_4, HNO_3, that dissociates completely in aqueous solution:

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

strong base a base that ionises completely in aqueous solution; strong bases are the Group 1 hydroxides (LiOH, NaOH, etc.) and $Ba(OH)_2$.

structural isomers two or more compounds that have the same molecular formula but different structural formulas, i.e., the atoms are joined together in a different way.

sub-level/subshell an orbital (in the case of s) or a group of degenerate orbitals (for p, d ,f) in an atom, that make up part of a main energy level/shell. The p sub-level/subshell is made up of the p_x, p_y and p_z orbitals.

substitution reaction a reaction in which one atom or group is replaced by another atom or group.

substrate the main chemical species that undergoes a reaction and is transformed into something else.

systematic error an error introduced into an experiment due to the apparatus used or the procedure. Systematic errors result in a loss of accuracy, i.e., the measured value being further away from the true value. Systematic errors are always in the same direction. The effect of a systematic error cannot be reduced by repeating the readings.

temperature a measure of the average kinetic energy of particles.

termination step the step that ends a radical substitution chain reaction – it involves a decrease in the number of radicals.

theoretical yield the maximum possible amount/mass of the desired product formed in a reaction.

thermoplastic a type of polymer that softens when it is heated and hardens when it is cooled; it can be repeatedly heated and cooled and remoulded into different shapes.

thermoset polymer material with extensive cross-linking that cannot be remoulded.

titration a technique that involves adding measured volumes of a solution (from a burette) to another solution to determine the amounts that react exactly with each other.

transition metals/elements the elements in the central part (d block) of the periodic table. There are various ways of defining a transition element. IUPAC definition: 'an element whose atoms have an incomplete (partially filled) d sub-shell or forms positive ions with an incomplete (partially filled) d sub-shell'.

transition state (activated complex) a local maximum on an energy profile/the highest energy species on the reaction pathway between reactants/intermediates and intermediates/products.

unpaired electron an electron in an orbital by itself – it is not paired with another electron of the opposite spin.

unsaturated organic compounds containing multiple bonds between carbon atoms. This term is usually just applied to compounds containing C=C and C≡C and not to compounds containing multiple bonds to other atoms, e.g. C=O.

van der Waals forces the collective name given to the forces between molecules and includes London (dispersion) forces, dipole−dipole interactions and dipole−induced dipole interactions but not hydrogen bonding and ion–dipole interactions.

water of crystallisation water that is present in definite proportions in the crystals of hydrated salts, e.g.$CuSO_4 \cdot 5H_2O$. The water may or may not be directly bonded to the metal (in hydrated copper sulfate, four water molecules are bonded to the copper ion and one is not). When the crystals dissolve in water, the water of crystallisation just becomes part of the solvent.

weak acid an acid, such as a carboxylic acid (ethanoic acid, propanoic acid, etc.) or carbonic acid (H_2CO_3), that dissociates only partially in aqueous solution:

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

weak base a base that ionises only partially in aqueous solution, e.g., ammonia and amines:

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

yield the amount/mass of the desired product obtained from a chemical reaction. See also *experimental (or actual) yield, percentage yield* and *theoretical yield*.

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