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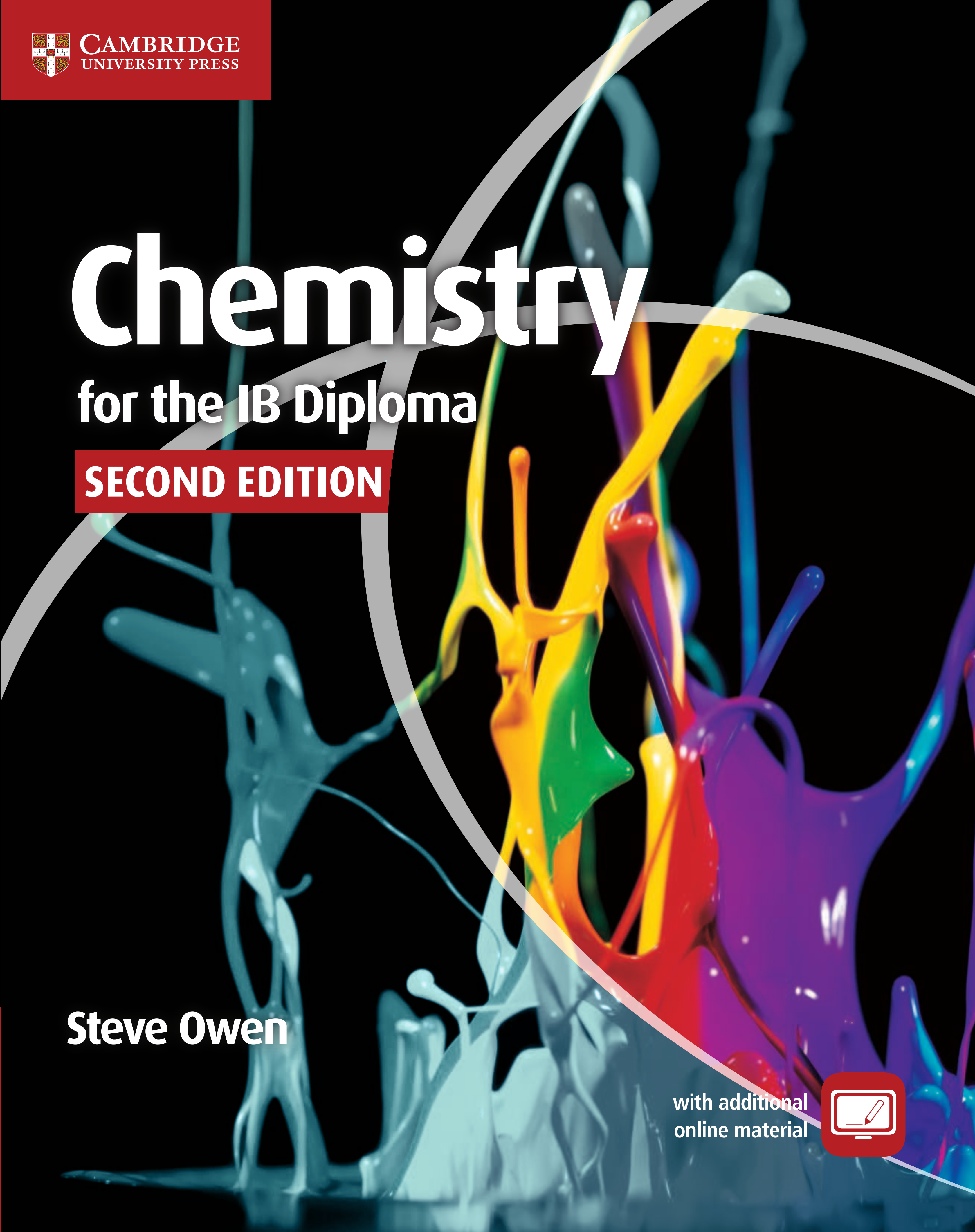

Chemistry

for the IB Diploma

SECOND EDITION

Steve Owen

with additional
online material

Chemistry

for the IB Diploma

Second edition

Steve Owen

with
Caroline Ahmed
Chris Martin
Roger Woodward

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Introduction

This second edition of *Chemistry for the IB Diploma* is fully updated to cover the content of the IB Chemistry Diploma syllabus that will be examined in the years 2016–2022.

Chemistry may be studied at Standard Level (SL) or Higher Level (HL). Both share a common core, and at HL the core is extended with additional HL material. In addition, at both levels, students then choose one Option to complete their studies. Each Option consists of common core and additional HL material. All common core and additional HL material is covered in this print book. The Options are included in the free online material that is accessible with the code available in this book.

The content is arranged in topics that match the syllabus topics, with core and additional HL material on each topic combined in the book topics. The HL content is identified by 'HL' included in relevant section titles, and by a yellow page border.

Each section in the book begins with learning objectives as starting and reference points. Test yourself questions appear throughout the text so students can check their progress and become familiar with the style and command terms used, and exam-style questions appear at the end of each topic. Many worked examples appear throughout the text to help students understand how to tackle different types of questions.

Theory of Knowledge (TOK) provides a cross-curricular link between different subjects. It stimulates thought about critical thinking and how we can say we know what we claim to know. Throughout this book, TOK features highlight concepts in Chemistry that can be considered from a TOK perspective. These are indicated by the 'TOK' logo, shown here.

Science is a truly international endeavour, being practised across all continents, frequently in international or even global partnerships. Many problems that science aims to solve are international, and will require globally implemented solutions. Throughout this book, International-Mindedness features highlight international concerns in Chemistry. These are indicated by the 'International-Mindedness' logo, shown here.

Nature of Science is an overarching theme of the Chemistry 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. A chapter giving a general introduction to the Nature of Science theme is available in the free online material.

Free online material

Additional material to support the IB Chemistry Diploma course is available online. Visit education.cambridge.org/ibsciences and register to access these resources.

Besides the Options and Nature of Science chapter, you will find a collection of resources to help with revision and exam preparation. This includes guidance on the assessments, interactive self-test questions and model exam papers. Additionally, answers to the exam-style questions in this book and to all the questions in the Options are available.

Stoichiometric relationships 1

1.1 Introduction to the particulate nature of matter and chemical change

Learning objectives

- Describe the three states of matter
- Understand the changes involved when there is a change in state

1.1.1 The particulate nature of matter

The three states of **matter** 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 **1.1** in which the individual particles are represented by spheres.

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 (gas → solid) is often called *deposition* (or sometimes *desublimation*, *reverse sublimation* or occasionally just sublimation).

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

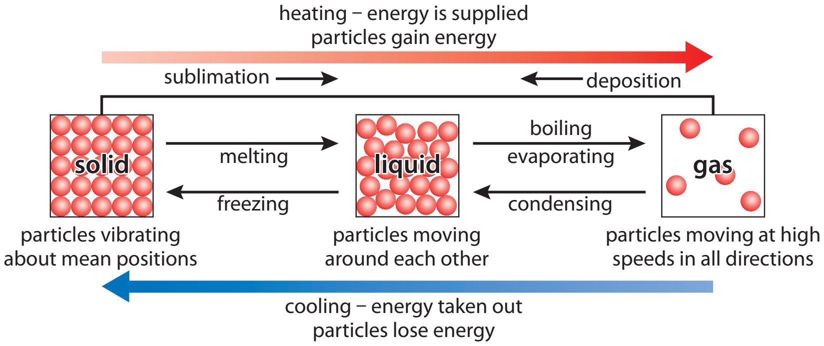


Figure 1.1 The arrangement of particles in solids, liquids and gases and the names of the changes of state. Note that evaporation can occur at any temperature – boiling occurs at a fixed temperature.

	Solids	**Liquids**	**Gases**
Distance between particles	close together	close but further apart than in solids	particles far apart
Arrangement	regular	random	random
Shape	fixed shape	no fixed shape – take up 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 The properties of the three states of matter.

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 **1.2**).

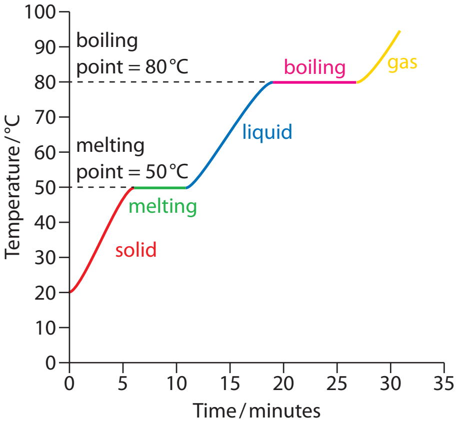


Figure 1.2 A heating curve showing changes of state.

As a solid is heated, its particles vibrate more violently – they gain **kinetic energy** and the temperature of the solid rises. At 50 °C, the solid in Figure **1.2** 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. 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. The 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 to gas. The continued supply of heat energy increases the kinetic energy of the particles of the gas so they move around faster and faster as the temperature of the gas increases.

Both refrigeration and air-conditioning involve changes of state of liquids and gases. In a refrigerator, heat energy is absorbed from the inside of the refrigerator and is used to convert a liquid coolant to a gas – the heat energy is given out to the surrounding as the gas is compressed back to a liquid. Refrigeration is essential in warm countries to preserve food and without it the food would go 'off' much more quickly and be wasted – but how essential is air-conditioning? CFCs (which cause destruction of the ozone layer) have been used as a refrigerant and in making the insulation for refrigerators. In many countries the disposal of old refrigerators is controlled carefully. More environmentally friendly refrigerators are being manufactured using alternatives to CFCs – they also use less electricity.

1.1.2 Chemical change

Elements and compounds

Chemistry is partly a study of how chemical elements combine to make the world and the Universe around us.

Gold is an **element** and all samples of pure gold contain only gold atoms.

An element is a pure substance that contains only one type of atom (but see *isotopes* in Topic 2).

An atom is the smallest part of an element that can still be recognised as that element.

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

Sodium and chlorine are elements – when they are mixed and heated they combine chemically to form a compound called sodium chloride. Sodium is a grey, reactive metal with a low melting point and chlorine is a yellow-green poisonous gas – but sodium chloride (common salt) is a non-toxic, colourless compound with a high melting point.

Similarly, when iron (a magnetic metal) is heated with sulfur (a non-magnetic yellow solid) a grey, non-metallic solid called iron sulfide is formed (Figure **1.3**).

Chemical properties dictate how something reacts in a chemical reaction.

Physical properties are basically all the other properties of a substance – such as melting point, density, hardness, electrical conductivity etc.

Learning objectives

- Understand that compounds have different properties to the elements they are made from
- Understand how to balance chemical equations
- Understand how to use state symbols in chemical equations
- Describe the differences between elements, compounds and mixtures
- Understand the differences between homogeneous and heterogeneous mixtures

A compound is a pure substance formed when two or more elements combine chemically.

Figure 1.3 Iron (left) combines with sulfur (centre) to form iron sulfide (right).

The meaning of chemical equations

When elements combine to form compounds, they always combine in **fixed ratios** depending on the numbers of atoms required. When sodium and chlorine combine, they do so in the mass ratio 22.99 : 35.45 so that 22.99 g of sodium reacts exactly with 35.45 g of chlorine. Similarly, when hydrogen (an explosive gas) combines with oxygen (a highly reactive gas) to form water (liquid at room temperature), 1 g of hydrogen combines with 8 g of oxygen, or 2 g of hydrogen reacts with 16 g of oxygen (using rounded relative atomic masses) – that is, they always combine in a mass ratio of 1 : 8.

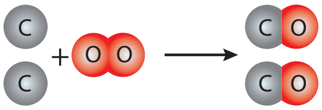


Figure 1.4 Two carbon atoms react with one oxygen molecule to form two molecules of carbon monoxide.

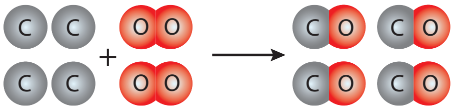


Figure 1.5 Four carbon atoms react with two oxygen molecules to form four molecules of carbon monoxide.

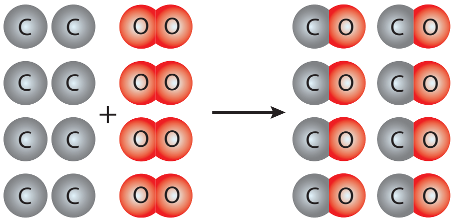


Figure 1.6 Eight carbon atoms react with four oxygen molecules to form eight molecules of carbon monoxide.

Mass is conserved in all chemical reactions.

Elements always combine in the same mass ratios because their atoms always combine in the same ratios, and each type of atom has a fixed mass.

Consider the reaction between carbon and oxygen to form carbon monoxide. This is shown diagrammatically in Figure **1.4**. In this reaction, two carbon atoms combine with one oxygen molecule to form two molecules of carbon monoxide. Now look at Figure **1.5**. If we started with four carbon atoms, they will react with two oxygen molecules to form four molecules of carbon monoxide.

The ratio in which the species combine is fixed in these equations. 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 (see Figures **1.4–1.6**). So, we can construct the equation:

$$2C + O_2 \rightarrow 2CO$$

which tells us that two carbon atoms react with one oxygen molecule to form two carbon monoxide molecules, and that this ratio is constant however many carbon atoms react.

Balancing equations

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 substance present. This 15.00 g may be made up of one or more 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.

A chemical reaction involves atoms joining together in different ways and electrons redistributing themselves between the atoms, but it is not possible for the reaction to involve atoms or electrons being created or destroyed.

When a chemical reaction is represented by a chemical equation, there must be exactly the same number and type of atoms on either side of the equation, representing the same number of atoms before and after this reaction:

	$C_3H_8 + 5O_2$		$\rightarrow$	$3CO_2 + 4H_2O$	
	reactants			**products**	
atoms	C	3		C	3
	H	8		H	8
	O	10		O	10

So this equation is balanced. 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.

State symbols are often used to indicate the physical state of substances involved in a reaction:
(s) = solid
(l) = liquid
(g) = gas
(aq) = aqueous (dissolved in water)

Worked examples

1.1 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.

In the unbalanced 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 in two stages, as follows:

$$\ldots\ N_2 + \ldots\ H_2 \rightarrow 2NH_3$$

atoms: 2 N 2 N
2 H 6 H

$$\ldots\ N_2 + 3H_2 \rightarrow 2NH_3$$

atoms: 2 N 2 N
6 H 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.

1.2 Balance the following equation:

$$\ldots\ C_4H_{10}(g) + \ldots\ O_2(g) \rightarrow \ldots\ CO_2(g) + \ldots\ H_2O(l)$$

Compounds are balanced first, then elements:

$$\ldots\ C_4H_{10}(g) + \ldots\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

There are two 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 $[(4 \times 2) + (5 \times 1)]$:

$$\ldots\ C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

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 2:

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

? Test yourself

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** $PH_3 + O_2 \rightarrow P_4O_{10} + H_2O$

Mixtures

Elements and compounds are pure substances but most things around us are not pure substances but 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.

> A mixture contains two or more substances mixed together.

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

The components of a mixture are not chemically bonded together and so retain their individual properties. In a mixture of iron and sulfur, the iron is shiny and magnetic; the sulfur is yellow and burns in air to form sulfur dioxide. When the mixture is heated and forms the compound iron sulfide, this is not shiny or magnetic or yellow – it is dull and grey and has completely different properties to its elements.

As you saw earlier, when atoms combine to form compounds they do so in fixed ratios, but the components of a mixture can be mixed together in any proportion. For example, ethanol and water can be mixed together in any ratio. 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 or 2 g of sodium chloride in 100 cm^3 water or 10 g of sodium chloride in 100 cm^3 of water or many other amounts.

The components of a mixture can be separated from each other by physical means – for example a mixture of sand and salt could be separated by dissolving the salt in water, filtering off the sand and then heating the salt solution to drive off the water.

Homogeneous and heterogeneous mixtures

> A homogeneous mixture has the same (uniform) composition throughout the mixture and consists of only one phase.

> A heterogeneous mixture does not have uniform composition and consists of separate phases. Heterogeneous mixtures can be separated by mechanical means.

One example of a **homogeneous mixture** is a solution. No individual particles can be seen in the solution and its 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 sodium chloride will be formed by each sample. Clean air (with no particulates) is also a homogeneous mixture.

One example of a **heterogeneous mixture** is sand in a beaker of water. The sand and water can be distinguished from each other and can also be separated by filtering.

Mixtures of different solids are also heterogeneous. For example, even though a mixture of iron and sulfur 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 and each particle of iron and sulfur represents a different phase. The components of the mixture could be separated from each other using a magnet – or even a pair of tweezers to pick out each individual piece of iron and sulfur.

Sea water is a mixture and the process of obtaining fresh water from sea water is called desalination. Desalination is very important in some parts of the world where sufficient fresh water is not available from other sources (for example, in the Middle East). Fresh water obtained by desalination can be used for human consumption, agriculture or in industry.

Nature of science

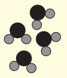
Data collection is essential in science. The discussion above has used both quantitative (regarding reacting masses) and qualitative data (about the properties of substances). Accurate quantitative data are essential for the advancement of science and scientists analyse such data to make hypotheses and to develop theories. The law of definite proportions governing how elements combine may seem obvious nowadays in the light of the atomic theory but in the seventeenth and eighteenth centuries it was the subject of much debate.

? Test yourself

2 Classify each of the following as an element, a compound or a mixture:
a water; **b** oxygen; **c** potassium iodide; **d** orange juice; **e** crude oil; **f** vanadium; **g** ammonia; **h** air; **i** hydrogen chloride; **j** magnesium oxide.

3 Classify each of the diagrams below using as many words as appropriate from the list:

element **compound** **mixture**
solid **liquid** **gas**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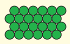
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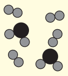
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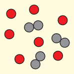
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1.2 The mole concept

Learning objectives

- Define relative atomic mass and relative molecular mass
- Understand what is meant by one mole of a substance
- Calculate the mass of one mole of a substance
- Calculate the number of moles present in a specified mass of a substance
- Work out the number of particles in a specified mass of a substance and also the mass of one molecule

1.2.1 Relative masses

Most chemical reactions involve two or more substances reacting with each other. Substances react with each other in certain ratios, and stoichiometry is the study of the ratios in which chemical substances combine. In order to know the exact quantity of each substance that is required to react we need to know the number of atoms, molecules or ions in a specific amount of that substance. However, the mass of an individual ion atom or molecule is so small, and the number of particles that make up even a very small mass so large, that a more convenient method of working out reacting quantities had to be developed.

Relative atomic mass (A_r)

The mass of a hydrogen atom is approximately 1.7×10^{-24} g. Such small numbers are not convenient to use in everyday life, so we use scales of relative mass. These compare the masses of atoms and molecules etc. to the mass of one atom of carbon-12, which is assigned a mass of exactly 12.00. As these quantities are relative, they have no units.

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 $\frac{1}{12}$ of a carbon-12 atom. No silver atoms actually exist with the mass of 107.87; this is just the average relative atomic mass of silver.

The relative atomic mass (A_r) of an element is the average of the masses of the isotopes in a naturally occurring sample of the element relative to the mass of $\frac{1}{12}$ of an atom of carbon-12.

The A_r of carbon is not 12.00, because carbon contains isotopes other than carbon-12 (see page **58**).

Relative molecular mass (M_r)

An **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:

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

The relative molecular mass of ethanoic acid (CH_3COOH) is:

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

If a compound is made up of ions, and therefore does not contain discrete molecules, we should really talk about **relative formula mass**. However, relative molecular mass is usually used to refer to the mass of the formula unit of an ionic compound as well.

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.

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.

Test yourself

4 Work out the relative molecular 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 $Mg_3(PO_4)_2$ $Na_2S_2O_3$ $CH_3CH_2CH_2COOCH_2CH_3$

Moles

One mole is the amount of substance that contains the same number of particles (atoms, ions, molecules, etc.) as there are carbon atoms in 12 g of carbon-12. This number is called **Avogadro's constant**, has symbol L (or N_A), and has the value $6.02 \times 10^{23}\,\text{mol}^{-1}$. So, 12.00 g of carbon-12 contains 6.02×10^{23} carbon atoms.

You can have a mole of absolutely anything. We usually consider a mole of atoms (6.02×10^{23} atoms) or a mole of molecules (6.02×10^{23} molecules), but we could also have, for instance, a mole of ping-pong balls (6.02×10^{23} ping-pong balls).

The molar mass (M) of a substance is its A_r or M_r in grams. The units of molar mass are g mol^{-1}. For example, the A_r of silicon is 28.09, and the molar mass of silicon is $28.09\,\text{g mol}^{-1}$. This means that 28.09 g of silicon contains 6.02×10^{23} silicon atoms.

The A_r of oxygen is 16.00, which means that, on average, each oxygen atom is $\frac{16}{12}$ times as heavy as a carbon-12 atom. Therefore 16 g of oxygen atoms must contain the same number of atoms as 12 g of carbon-12, i.e. one mole, or 6.02×10^{23} atoms. Similarly, one magnesium atom is on average $\frac{24.31}{12}$ times as heavy as a carbon-12 atom and, therefore, 24.31 g of magnesium atoms contains 6.02×10^{23} magnesium atoms.

When calculating the number of moles present in a certain mass of a substance, the mass must be in grams.

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

$$\text{number of moles } (n) = \frac{\text{mass of substance}}{\text{molar mass}}$$

The triangle in Figure **1.7** 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 of substance' is covered, we are left with number of moles multiplied by molar mass:

$$\text{mass of substance} = \text{number of moles} \times \text{molar mass}$$

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

$$\text{molar mass} = \frac{\text{mass of substance}}{\text{number of moles}}$$

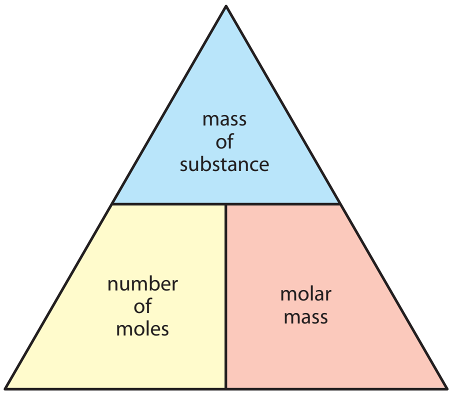


Figure 1.7 The relationship between the mass of a substance, the number of moles and molar mass.

One mole 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, one mole of ping-pong balls would cover the surface of the Earth to about 800 times the height of Mount Everest! We know what a ping-pong ball looks like and we may have a rough idea of the height of Mount Everest, so perhaps this description gives us a context in which we can understand 6.02×10^{23}. Another description sometimes used is in terms of a mole of computer paper: one mole of computer printer 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 things that are beyond our normal experience by reference to things with which we are more familiar.

Worked examples

1.3 Calculate the number of moles of magnesium atoms in 10.0 g of magnesium.

$$\text{number of moles } (n) = \frac{\text{mass of substance}}{\text{molar mass}}$$

Note: the unit for moles is mol.

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

10.0 g of magnesium is 0.411 mol.

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

1.4 Calculate the mass of 0.3800 mol CH_3COOH.

mass of substance = number of moles × molar mass

mass of substance = 0.3800 × 60.06 = 22.82 g

The mass of 0.3800 mol CH_3COOH is 22.82 g.

The answer is given to four significant figures, because the number of moles and the molar mass are given to four significant figures.

Test yourself

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

Compound	Molar mass / g mol^{-1}	Mass / g	Number of moles / 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}

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}):

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

$$\text{mass of one molecule} = \frac{\text{molar mass}}{\text{Avogadro's constant}}$$

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 1.

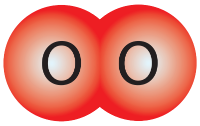
The number of particles

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; therefore, one mole of O_2 molecules contains $2 \times 6.02 \times 10^{23}$ $= 1.204 \times 10^{24}$ atoms. That is, one mole of O_2 **molecules** is made up of two moles of oxygen **atoms**.

When we talk about '0.1 mol H_2O', we mean 0.1 mol H_2O molecules; i.e. $0.1 \times 6.02 \times 10^{23}$ H_2O molecules; i.e. 6.02×10^{22} H_2O molecules. Each H_2O molecule contains two hydrogen atoms and one oxygen atom. The total number of hydrogen atoms in 0.1 mol H_2O is $2 \times 6.02 \times 10^{22}$; i.e. 1.204×10^{23} hydrogen atoms; i.e. 0.2 mol hydrogen atoms.

Each H_2O molecule contains three atoms. Therefore, the total number of atoms in 0.1 mol H_2O is $3 \times 6.02 \times 10^{22}$; i.e. 1.806×10^{23} atoms; or 0.3 mol atoms.

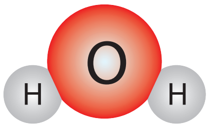
If you look at Table **1.2** you can see the connection between the number of moles of molecules and the number of moles of a particular atom in that molecule. Figure **1.8** illustrates the relationship between number of particles, number of moles and Avogadro's constant.



oxygen

Exam tip

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



water

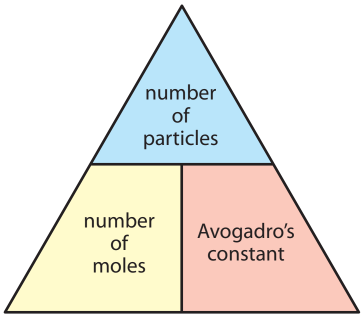


Figure 1.8 The relationship between the number of moles and the number of particles.

Compound	Moles of molecules	Moles of O atoms
H_2O	0.1	0.1
SO_2	0.1	0.2
SO_3	0.1	0.3
H_3PO_4	0.1	0.4
O_3	0.5	1.5
CH_3COOH	0.2	0.4

Table 1.2 The relationship between the number of moles of molecules and the number of moles of particular atoms.

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 H_2SO_4 there are 4×0.25 (i.e. 1.0) mol oxygen atoms.

? Test yourself

6 Work out the mass of one molecule of each of the following:
- **a** H_2O
- **b** NH_3
- **c** CO_2

7 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

8 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

9 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

Learning objectives

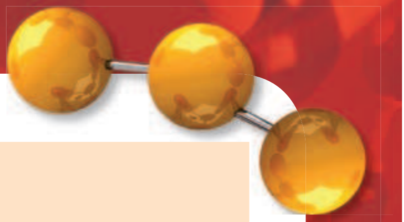
- Determine the percentage composition by mass of a substance
- Understand what is meant by empirical and molecular formulas
- Calculate empirical and molecular formulas

1.2.2 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 formula:

$$\text{\% by mass of an element} = \frac{\text{number of atoms of the element} \times \text{relative atomic mass}}{\text{relative molecular mass}}$$



Worked examples

1.5 Find the percentage by mass of each element present in $C_6H_5NO_2$.

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 the carbon atoms is 6 × 12.01, i.e. 72.06.

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

Percentage of the other elements present:

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

$$\%\text{ nitrogen} = \frac{14.01}{123.12} \times 100 = 11.38\%$$

$$\%\text{ oxygen} = \frac{2 \times 16.00}{123.12} \times 100 = 25.99\%$$

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

The relative molecular mass of CO_2 is 44.01. Of this, the amount contributed by the two oxygen atoms is 2 × 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 amount of oxygen is $\frac{32.00}{44.01} \times 2.20 = 1.60\text{ g}$

1.7 What mass of HNO_3 contains 2.00 g of oxygen?

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 oxygen and the HNO_3 are in the ratio 48.00 : 63.02.

Therefore the mass of HNO_3 containing 2.00 g of oxygen is:

$$\frac{63.02}{48.00} \times 2.00 = 2.63\text{ g}$$

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

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

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

? Test yourself

10 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

11 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}

12 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

Empirical and molecular formulas

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.

Empirical formula: the simplest whole number ratio of the elements present in a compound.

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.)

Worked examples

1.8 If the molecular formulas of two compounds are:

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

what are the empirical formulas?

a We need to find the simplest ratio of the elements present and therefore need to find the highest number that divides exactly into the subscript of each element. 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 $ReCl_3$.

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

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.

Chemical analysis of a substance can provide the composition by mass of the compound. The empirical formula can then be calculated from these data. In order to work out the molecular formula, the relative molecular mass of the compound is also required.

Worked examples

1.10 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.

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 number of moles	0.681 / 12.01	0.137 / 1.01	0.181 / 16.00
number of moles / mol	0.0567	0.136	0.0113
divide by smallest to get 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 of the compound is 88.17. This is the same as the relative molecular mass, and so the molecular formula is the same as the empirical formula ($C_5H_{12}O$).

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

A uranium fluoride contains only uranium and 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.

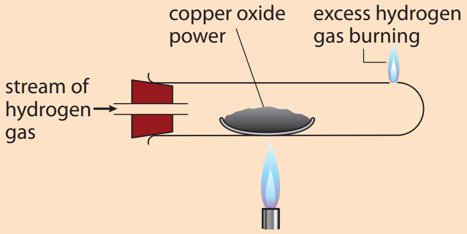
	U	**F**
percentage	67.62	32.38
mass in 100 g / g	67.62	32.38
divide by relative atomic mass to give number of moles	67.62 / 238.03	32.38 / 19.00
number of moles	0.2841	1.704
divide by smallest to get ratio	0.2841 / 0.2841	1.704 / 0.2841
ratio	1	6

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

1.12 The experimental set-up shown in the figure can be used to determine the empirical formula of copper oxide. The following experimental results were obtained.

Mass of empty dish / g	24.58
Mass of dish + copper oxide / g	30.12
Mass of dish + copper at end of experiment / g	29.00

Calculate the empirical formula of the copper oxide and write an equation for the reaction.



Hydrogen gas is passed over the heated copper oxide until all the copper oxide is reduced to copper.

mass of copper oxide at start = 30.12 − 24.58 = 5.54 g

mass of copper at end = 29.00 − 24.58 = 4.42 g

The difference in mass is due to the oxygen from the copper oxide combining with the hydrogen.

mass of oxygen in copper oxide = 5.54 − 4.42 = 1.12 g

From now on, the question is a straightforward empirical formula question:

$$\text{number of moles of copper} = \frac{4.42}{63.55} = 0.0696\,\text{mol}$$

$$\text{number of moles of oxygen} = \frac{1.12}{16.00} = 0.0700\,\text{mol}$$

If each number of moles is divided by the smaller number (0.0696):

Cu	**O**
$\frac{0.0696}{0.0696} = 1$	$\frac{0.0700}{0.0696} = 1.01$

the ratio of copper to oxygen is 1:1, and the empirical formula is CuO.

The equation for the reaction is: $CuO + H_2 \rightarrow Cu + H_2O$

Composition by mass from combustion data

Worked examples

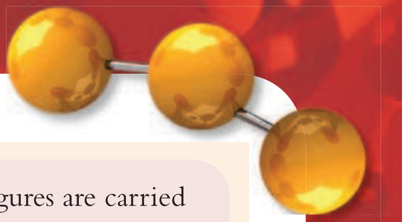
1.13 An organic compound, **A**, contains only carbon and hydrogen. When 2.50 g of **A** burns in excess oxygen, 8.08 g of carbon dioxide and 2.64 g of water are formed. Calculate the empirical formula.

The equation for the reaction is of the form: $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

All the C in the CO_2 comes from the hydrocarbon **A**.

$$\text{number of moles of } CO_2 = \frac{8.08}{44.01} = 0.184\,\text{mol}$$

Each CO_2 molecule contains one carbon atom. Therefore the number of moles of carbon in 2.50 g of the hydrocarbon is 0.184 mol.



More significant figures are carried through in subsequent calculations.

All the hydrogen in the water comes from the hydrocarbon **A**.

$$\text{number of moles of } H_2O = \frac{2.64}{18.02} = 0.147\,\text{mol}$$

Each H_2O molecule contains two hydrogen atoms, so the number of moles of hydrogen in 2.64 g of H_2O is $2 \times 0.147 = 0.293$ mol. Therefore, the number of moles of hydrogen in 2.50 g of the hydrocarbon is 0.293 mol. The empirical formula and molecular formula can now be calculated.

	C	H
number of moles	0.184	0.293
divide by smaller	0.184/0.184	0.293/0.184
ratio	1.00	1.60

The empirical formula must be a ratio of whole numbers, and this can be obtained by multiplying each number by five. Therefore the empirical formula is C_5H_8.

1.14 An organic compound, **B**, contains only carbon, hydrogen and oxygen. When 1.46 g of **B** burns in excess oxygen, 2.79 g of carbon dioxide and 1.71 g of water are formed.

a What is the empirical formula of **B**?

b If the relative molecular mass is 92.16, what is the molecular formula of **B**?

a The difficulty here is that the mass of oxygen in **B** cannot be worked out in the same way as the previous example, as only some of the oxygen in the CO_2 and H_2O comes from the oxygen in **B** (the rest comes from the oxygen in which it is burnt).

$$\text{mass of carbon in 2.79 g of } CO_2 = \frac{12.01}{44.01} \times 2.79 = 0.76\,\text{g}$$

$$\text{mass of hydrogen in 1.71 g of } H_2O = \frac{2.02}{18.02} \times 1.71 = 0.19\,\text{g}$$

Note: 2.02 as there are 2 H atoms in a water molecule

mass of oxygen in 1.46 g of **B** is $(1.46 - 0.76 - 0.19) = 0.51$ g

The empirical formula can now be calculated.

	C	H	O
mass/g	0.76	0.19	0.51
moles/mol	0.063	0.19	0.032
ratio	2	6	1

Therefore the empirical formula is C_2H_6O.

b The empirical formula mass is 46.08.

$$\frac{92.16}{46.08} = 2$$

Therefore, the molecular formula is $(C_2H_6O)_2$, i.e. $C_4H_{12}O_2$.

? Test yourself

13 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	$C_6H_5CH_3$

14 Copy the table below and complete it with the molecular formulas of the compounds, given the empirical formulas and relative molecular masses.

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

15 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.

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

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

18 When 4.76 g of an organic compound, **D**, which contains only carbon, hydrogen and oxygen, is burnt in excess oxygen, 10.46 g of carbon dioxide and 5.71 g of water are produced. What is the empirical formula of **D**?

19 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.

Learning objectives

- Solve problems involving masses of substances
- Calculate the theoretical and percentage yield in a reaction
- Understand the terms *limiting reactant* and *reactant in excess* and solve problems involving these

1.3 Reacting masses and volumes

1.3.1 Calculations involving moles and masses

Conservation of mass

The fact that mass is conserved in a chemical reaction can sometimes be used to work out the mass of product formed. For example, if 55.85 g of iron reacts *exactly* and *completely* with 32.06 g of sulfur, 87.91 g of iron sulfide is formed:

$$Fe(s) + S(s) \rightarrow FeS(s)$$

Worked example

1.15 Consider the combustion of butane:

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

10.00 g of butane reacts exactly with 35.78 g of oxygen to produce 30.28 g of carbon dioxide. What mass of water was produced?

The masses given represent an exact chemical reaction, so we assume that all the reactants are converted to products.

The total mass of the reactants = 10.00 + 35.78 = 45.78 g.

The total mass of the products must also be 45.78 g.

Therefore the mass of water = 45.78 − 30.28 = 15.50 g.

Using moles

We often want to work out the mass of one reactant that reacts exactly with a certain mass of another reactant – or how much product is formed when certain masses of reactants react. This can be done by calculating the numbers of each molecule or atom present in a particular mass or, much more simply, by using the mole concept.

As we have seen, one mole of any substance always contains the same number of particles, so if we know the number of moles present in a certain mass of reactant we also know the number of particles and can therefore work out what mass of another reactant it reacts with and how much product is formed.

There are three main steps in a moles calculation.

1. Work out the number of moles of anything you can.
2. Use the chemical (stoichiometric) equation to work out the number of moles of the quantity you require.
3. Convert moles to the required quantity – volume, mass etc.

Questions involving masses of substances

Worked examples

1.16 Consider the reaction of sodium with oxygen:

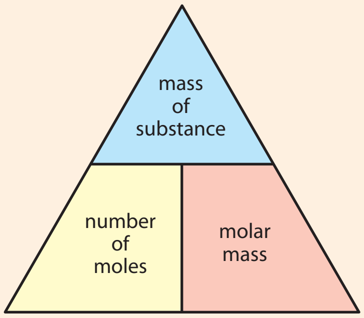
$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

a How much sodium reacts exactly with 3.20 g of oxygen?
b What mass of Na_2O is produced?

a Step 1 – the mass of oxygen is given, so the number of moles of oxygen can be worked out (you could use the triangle shown here).

$$\text{number of moles of oxygen} = \frac{3.20}{32.00} = 0.100\,\text{mol}$$

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 number of moles to the required quantity, mass in this case:

mass of sodium = 0.400 × 22.99 = 9.20 g

Note: the mass of sodium is worked out by multiplying the mass of one mole by the number of moles – the number of moles is *not* multiplied by the mass of four sodium atoms – the four was already taken into account when 0.100 mol was multiplied by 4 to give the number of moles of sodium.

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.

The molar mass of $Na_2O = 61.98\,\text{g mol}^{-1}$
So mass of $Na_2O = 0.200 \times 61.98 = 12.4\,\text{g}$

Alternatively, the mass of Na_2O can be worked out using the idea of conservation of mass, i.e.:
mass of Na_2O = mass of O_2 + mass of Na.

Exam tip

Masses may also be given in kilograms or tonnes.

1 kg = 1000 g

1 tonne = 1×10^6 g

Before working out the number of moles, you must convert the mass to grams. To convert kilograms to grams, multiply by 1000; to convert tonnes to grams, multiply the mass by 1×10^6.

1.17 Consider the following equation:

$$2NH_3 + 3CuO \rightarrow N_2 + 3H_2O + 3Cu$$

If 2.56 g of ammonia (NH_3) is reacted with excess CuO, calculate the mass of copper produced.

The CuO is in excess so there is more than enough to react with all the NH_3. This means that we do not need to worry about the number of moles of CuO.

Step 1 – the number of moles of NH_3 can be calculated:

$$\frac{2.56}{17.04} = 0.150\,\text{mol } NH_3$$

Step 2 – two moles of NH_3 produce three moles of copper, so 0.150 mol NH_3 produces $0.150 \times \frac{3}{2}$ mol copper, i.e. 0.225 mol copper.

The number of moles of copper is therefore 1.5 times the number of moles of NH_3.

Step 3 – the mass of 1 mol copper = 63.55 g, so the mass of copper produced = 0.225 × 63.55 = 14.3 g.

Formula for solving moles questions involving masses

An alternative way of doing these questions is to use a formula.

$$\frac{m_1}{n_1 M_1} = \frac{m_2}{n_2 M_2}$$

where

m_1 = mass of first substance

n_1 = coefficient of first substance (number in front in the chemical equation)

M_1 = molar mass of first substance

Worked example

1.18 The following equation represents the combustion of butane:

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

If 10.00 g of butane is used, calculate the mass of oxygen required for an exact reaction.

We will call butane substance 1 and oxygen substance 2 (it doesn't matter which you call what, but you have to be consistent).

$m_1 = 10.00\,\text{g}$	$m_2 = ?$
$n_1 = 2$	$n_2 = 13$
$M_1 = 58.14\,\text{g}\,\text{mol}^{-1}$	$M_2 = 32.00\,\text{g}\,\text{mol}^{-1}$

$$\frac{m_1}{n_1 M_1} = \frac{m_2}{n_2 M_2}$$

$$\frac{10.00}{2 \times 58.14} = \frac{m_2}{13 \times 32.00}$$

The equation can be rearranged:

$$m_2 = \frac{10.00 \times 13 \times 32.00}{2 \times 58.14} = 35.78$$

Therefore the mass of oxygen required for an exact reaction is 35.78 g.

? Test yourself

20 **a** How many moles of hydrogen gas are produced when 0.4 mol sodium react with excess water?

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

b How many moles of O_2 react with 0.01 mol C_3H_8?

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

c How many moles of H_2S are formed when 0.02 mol HCl react with excess Sb_2S_3?

$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$

d How many moles of oxygen are formed when 0.6 mol $KClO_3$ react?

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

e How many moles of iron are formed when 0.9 mol CO react with excess iron oxide?

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

f How many moles of hydrogen would be required to make 2.4×10^{-3} mol NH_3?

$N_2 + 3H_2 \rightarrow 2NH_3$

21 **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 below.

$2P + 3I_2 \rightarrow 2PI_3$

d Consider the reaction shown below. What mass of SCl_2 must be reacted with excess NaF to produce 2.25 g of NaCl?

$3SCl_2 + 4NaF \rightarrow S_2Cl_2 + SF_4 + 4NaCl$

The fact that a theory can explain experimental observations does not necessarily make it correct. The explanations presented in this book fit in with experimental observations, but this does not mean that they are 'true' – they just represent our interpretation of the data at this stage in time. Each generation of scientists believes that they are presenting a true description of reality, but is it possible for more than one explanation to fit the facts? You, or indeed I, may not be able to think of a better explanation to fit many of the experimental observations in modern science, but that does not mean that there isn't one. Consider the following trivial example.

Experimentally, when 100 kg of calcium carbonate ($CaCO_3$) is heated, 44 kg of carbon dioxide (CO_2) is obtained. The following calculation can be carried out to explain this.

The equation for the reaction is:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$\text{number of moles of } CaCO_3 = \frac{100}{(20 + 6 + (3 \times 8))} = 2 \text{ mol}$$

Two moles of $CaCO_3$ produces two moles of CO_2.

The mass of two moles of CO_2 is $2 \times (6 + (2 \times 8)) = 44$ kg.

Hopefully you can see some mistakes in this calculation, but the result is what we got experimentally. It is also interesting to note that if, in your IB examination, you had just written down the final answer, you would probably have got full marks!

Calculating the yield of a chemical reaction

In any commercial process it is very important to know the **yield** (the amount of desired product) of a chemical reaction. For instance, if a particular process for the preparation of a drug involves four separate steps and the yield of each step is 95%, it is probably quite a promising synthetic route to the drug. If, however, the yield of each step is only 60% then it is likely that the company would look for a more efficient synthetic process.

The yield of a chemical reaction is usually quoted as a percentage – this gives more information than just quoting the yield of the product as a mass. 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.

The **theoretical yield** for this reaction is 66.95 g – this is the maximum possible yield that can be obtained. The **actual yield** of $C_2H_4Br_2$ may be 50.00 g.

$$\%\ \text{yield} = \frac{50.00}{66.95} \times 100 = 74.68\%$$

$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Worked example

1.19 $C_2H_5OH(l) + CH_3COOH(l) \rightarrow CH_3COOC_2H_5(l) + H_2O(l)$

ethanol ethanoic acid ethyl ethanoate water

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.

The first step is to calculate the maximum possible yield, i.e. the theoretical yield:

molar mass of $C_2H_5OH = 46.08\ \text{g mol}^{-1}$

number of moles of $C_2H_5OH = \frac{20.00}{46.08} = 0.4340\ \text{mol}$

The 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 number of moles of CH_3COOH.

The chemical equation tells us that 1 mol C_2H_5OH produces 1 mol $CH_3COOC_2H_5$. Therefore, 0.4340 mol C_2H_5OH produces 0.4340 mol $CH_3COOC_2H_5$.

The molar mass of $CH_3COOC_2H_5 = 88.12\ \text{g mol}^{-1}$.

The mass of ethyl ethanoate $CH_3COOC_2H_5 = 0.4340 \times 88.12 = 38.24$ g.

So, the theoretical yield is 38.24 g. The actual yield is 30.27 g (given in the question).

$$\%\ \text{yield} = \frac{30.27}{38.24} \times 100 = 79.15\%$$

The percentage yield of $CH_3COOC_2H_5$ is 79.15%.

Test yourself

22 Calculate the percentage yield in each of the following reactions.

a When 2.50 g of SO_2 is heated with excess oxygen, 2.50 g of SO_3 is obtained.

$2SO_2 + O_2 \rightarrow 2SO_3$

b When 10.0 g of arsenic is heated in excess oxygen, 12.5 g of As_4O_6 is produced.

$4As + 3O_2 \rightarrow As_4O_6$

c When 1.20 g of C_2H_4 reacts with excess bromine, 5.23 g of CH_2BrCH_2Br is produced.

$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$

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 **1.9** illustrates the idea of a limiting reactant and shows how the products of the reaction depend on which reactant is limiting.

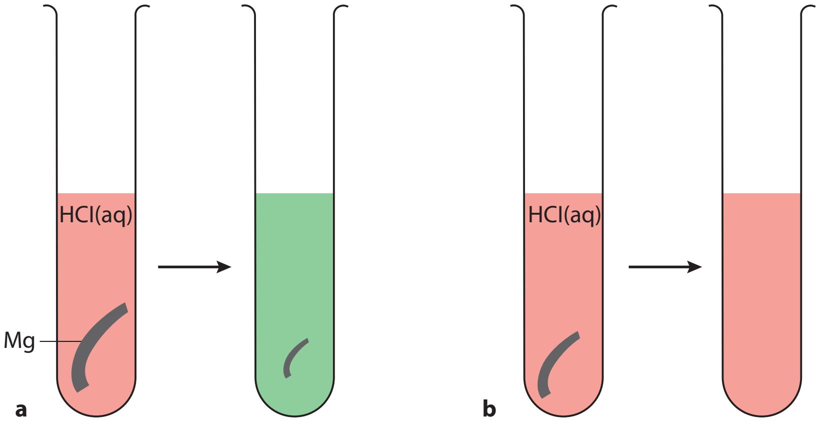


Figure 1.9 The reaction between magnesium and hydrochloric acid. In each test tube a small amount of universal indicator has been added. **a** In this test tube, the magnesium is in excess and the reaction finishes when the hydrochloric acid runs out. There is still magnesium left over at the end, and the solution is no longer acidic. **b** In this test tube, the hydrochloric acid is in excess. The magnesium is the limiting reactant, and the reaction stops when the magnesium has been used up. The solution is still acidic at the end.

Worked examples

1.20 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?

number of moles of magnesium $= \frac{10.00}{24.31} = 0.4114$ mol

number of moles of $N_2 = \frac{5.00}{28.02} = 0.178$ mol

The equation tells us that 3 mol magnesium reacts with 1 mol N_2. So 0.4114 mol magnesium reacts with $\frac{0.4114}{3}$ mol N_2, i.e. 0.1371 mol N_2.

Therefore, for an exact reaction, 0.1371 mol N_2 are required to react with 0.4114 mol magnesium. However, 0.178 mol N_2 are used, which is more than enough to react. This means that N_2 is in excess because there is more than enough to react with all the magnesium present. Magnesium is therefore the limiting reactant.

This can also be seen from working with the number of moles of N_2 – 0.178 mol N_2 was used in this reaction. This number of moles 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 are present; therefore, the magnesium will run out before all the N_2 has reacted.

Exam tip
If the number of moles of each reactant is divided by its coefficient in the stoichiometric equation, the smallest number indicates the limiting reactant.

1.21 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.

a Which is the limiting reactant?
b What mass of sulfur(VI) fluoride is formed?
c What mass of the reactant in excess is left at the end?

a number of moles of sulfur $= \frac{10.00}{32.07} = 0.3118$ mol number of moles of $F_2 = \frac{10.00}{38.00} = 0.2632$ mol

The coefficient of sulfur in the equation is 1 and that of F_2 is 3.
$0.3118 / 1 = 0.3118$ and $0.2632 / 3 = 0.08773$, therefore sulfur is in excess (larger number) and F_2 is the limiting reactant (smaller number).

Alternatively we can reason from the chemical equation that 0.2632 mol F_2 should react with 0.08773 mol sulfur (i.e. 0.2632 mol divided by three). There is more than 0.08773 mol sulfur present, so sulfur is present in excess and F_2 is the limiting reactant.

For the rest of the question we must work with the limiting reactant.

b When the limiting reactant is used up completely, the reaction stops. This means that the amount of product formed is determined by the amount of the limiting reactant we started with.

From the chemical equation, 0.2632 mol F_2 produces 0.08773 mol SF_6 (i.e. 0.2632 mol divided by three).

molar mass of $SF_6 = 146.07\,\text{g mol}^{-1}$

mass of SF_6 formed $= 0.08773 \times 146.07 = 12.81$ g

c From the chemical equation, 0.2632 mol F_2 reacts with 0.08773 mol sulfur (i.e. 0.2632 mol sulfur divided by three). Originally there were 0.3118 mol sulfur present; therefore the number of moles of sulfur left at the end of the reaction is $0.3118 - 0.08773 = 0.2241$.

The mass of sulfur left at the end of the reaction is $0.2241 \times 32.07 = 7.187$ g.

Exam tip
To do a moles question you need to know the mass of just one of the reactants. If you are given the masses of more than one reactant, you must consider that one of these reactants will be the limiting reactant and you must use this one for all calculations.

1.22 For the reaction:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

there are 100.0 g of each reactant available. Which is the limiting reactant?

This question could be done by working out the number of moles of each reactant and then comparing them, but there is a shortcut – to work out the masses of each substance if molar quantities reacted:

	$4FeCr_2O_4$	+	$8Na_2CO_3$	+	$7O_2$	→	$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
mass / g =	4 × 223.85		8 × 105.99		7 × 32.00		
mass / g =	895.40		847.92		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, the $FeCr_2O_4$ will run out first and must be the limiting reactant.

Nature of science

Science is a constantly changing body of knowledge. Scientists take existing knowledge and try to build on it to improve theories so that they are more widely applicable and have better explanatory power. The concept of the mole developed from the concept of equivalent weight.

? Test yourself

23 What is the limiting reactant in each of the following reactions?

a 0.1 mol Sb_4O_6 react 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 $AsCl_3$ react with 0.25 mol H_2O

$$4AsCl_3 + 6H_2O \rightarrow As_4O_6 + 12HCl$$

c 0.25 mol copper react with 0.50 mol dilute HNO_3 according to the equation:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

d 0.10 mol NaCl react with 0.15 mol MnO_2 and 0.20 mol H_2SO_4

$$2NaCl + MnO_2 + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

24 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 are reacted with 0.50 g magnesium?

25 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 tonnes of Fe_2O_3 are reacted with 1.00 tonne of carbon?

1.3.2 Calculations involving volumes of gases

Learning objectives

- Understand Avogadro's law and use it to calculate reacting volumes of gases
- Use the molar volume of a gas in calculations at standard temperature and pressure
- Understand the relationships between pressure, volume and temperature for an ideal gas
- Solve problems using the equation
  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- Solve problems using the ideal gas equation

Real gases and ideal gases

An 'ideal gas' is a concept invented by scientists to approximate (model) the behaviour of real gases. Under normal conditions (around 100 kPa [approximately 1 atmosphere] pressure and 0 °C) real gases such as hydrogen behave pretty much like ideal gases and the approximations work very well.

Two assumptions we make when defining the **ideal gas** are that the molecules themselves have no volume (they are point masses) and that no forces exist between them (except when they collide). If we imagine compressing a real gas to a very high pressure then the particles will be much closer together and, under these conditions, the forces between molecules and the volumes occupied by the molecules will be significant. This means that we can no longer ignore these factors and the behaviour of the gas will deviate significantly from our ideal gas model. This will also be the case at very low temperatures when the molecules are moving more slowly. Under conditions of very low temperature and very high pressure a gas is approaching the liquid state and will be least like our predictions for an ideal gas.

> Gases deviate most from ideal behaviour at high pressure and low temperature.

The idea that the volumes of the individual gas molecules are zero (so it makes no difference if the gas is H_2 or NH_3) and that there are no forces between the molecules (again no difference between NH_3 and H_2) means that all ideal gases must behave in the same way. This means that the volume occupied by a gas at a certain temperature and pressure depends only on the number of molecules present and not on the nature of the gas. In other words, at a certain temperature and pressure, the volume of a gas is proportional to the number of moles of the gas.

> Volume of gas $\propto$ number of moles of the gas

Using volumes of gases

> Avogadro's law: equal volumes of ideal gases measured at the same temperature and pressure contain the same number of molecules.

1 cm^3 is the same as 1 ml.

In other words 100 cm^3 of H_2 contains the same number of molecules at 25 °C and 100 kPa 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.

This means that volumes can be used directly (instead of moles) in equations involving gases:

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

The above equation tells us that one mole of H_2 reacts with one mole of Cl_2 to give two moles of HCl. Or one volume of H_2 reacts with one volume of Cl_2 to give two volumes of HCl; i.e. 50 cm^3 of H_2 reacts with 50 cm^3 of Cl_2 to give 100 cm^3 of HCl.

The ideal gas concept is an approximation which is used to model the behaviour of real gases. Why do we learn about ideal gases when they do not exist? What implications does the ideal gas concept have on the limits of knowledge gained from this course?

Worked examples

In both of these worked examples, assume that all gases behave as ideal gases and that all measurements are made under the same conditions of temperature and pressure.

1.23 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?

a From the equation we know that 1 mol CO reacts with 2 mol H_2. Therefore, one volume of CO reacts with two volumes of H_2 – 2.50 dm^3 of CO reacts 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.

1.24 If 100 cm^3 of oxygen reacts with 30 cm^3 of methane in the following reaction, how much oxygen will be left at the end of the reaction?

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

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 reacts 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.

STP = standard temperature and pressure = 273 K, 100 kPa (1 bar)

100 kPa = 1.00×10^5 Pa

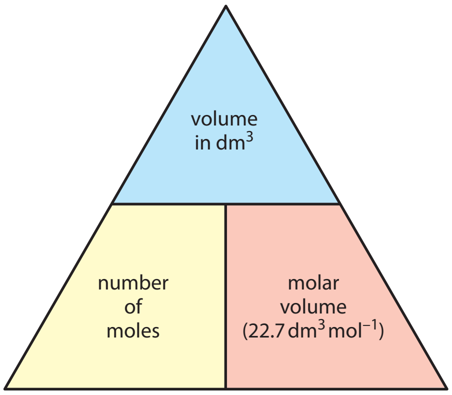


Figure 1.10 The relationship between the number of moles of a gas and its volume.

Converting volumes of gases to number of moles

Because the volume occupied by an ideal gas depends only on the number of particles present (assuming that pressure and temperature are constant) and not on the nature of the particles, the volume occupied by one mole of any ideal gas under a certain set of conditions will always be the same. The volume occupied by one mole of a gas under certain conditions is called the **molar volume**.

molar volume of an ideal gas at STP = 22.7 $dm^3\ mol^{-1}$ or 2.27×10^{-2} **$m^3\ mol^{-1}$**

This means that 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.

The relationship between the number of moles of a gas and its volume is:

$$\text{number of moles} = \frac{\text{volume}}{\text{molar volume}}$$

This is summarised in Figure **1.10**.

The absolute, or Kelvin, scale of temperature starts at absolute zero, which is the lowest temperature possible. It is the temperature at which everything would be in its lowest energy state. **Absolute zero** corresponds to 0 K or −273.15 °C (usually taken as −273 °C) and is also the temperature at which the volume of an ideal gas would be zero. It is not possible to actually reach absolute zero, but scientists have managed to get very close – about 1 nanokelvin!

A change of 1 °C is the same as a change of 1 K, and 0 °C is equivalent to 273 K

To convert °C to K add 273:
e.g. 25 °C is equivalent to 25 + 273, i.e. 298 K

To convert K to °C subtract 273:
e.g. 350 K is equivalent to 350 − 273, i.e. 77 °C

Volumes of gases are often given in cm^3 and so it is important to know how to convert between cm^3 and dm^3.

Because 1 dm^3 (1 litre) is equivalent to 1000 cm^3 to convert cm^3 to dm^3 we divide by 1000 (to go from 1000 (cm^3) to 1 (dm^3)). The conversion is shown in Figure **1.11**.

In different countries around the world's different scales of temperature are used – e.g. the Celsius and Fahrenheit scales. The Celsius and Fahrenheit scales are both artificial scales, but the Kelvin scale is an absolute scale. What is the advantage to scientists of using an absolute scale? Why has the **absolute scale of temperature** not been adopted in everyday life?

The Kelvin scale of temperature is named in honour of William Thompson, Lord Kelvin (1824–1907), a Scottish mathematican and physicist, who first suggested the idea of an absolute scale of temperature. Despite making many important contributions to the advancement of science, Kelvin had doubts about the existence of atoms, believed that the Earth could not be older than 100 million years and is often quoted as saying that 'heavier-than-air flying machines are impossible'.

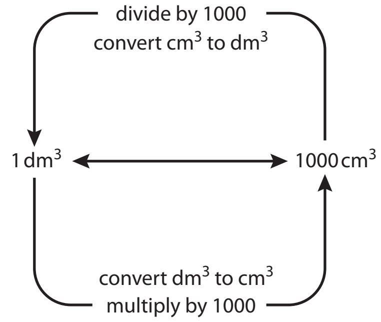


Figure 1.11 Converting between cm^3 and dm^3.

Worked examples

1.25 **a** Calculate the number of moles in 250 cm^3 of O_2 at STP.
b Calculate the volume of 0.135 mol CO_2 at STP.

a $$\text{number of moles} = \frac{\text{volume in dm}^3}{22.7}$$

$$250\ \text{cm}^3 = \frac{250}{1000}\ \text{dm}^3 = 0.250\ \text{dm}^3$$

$$\text{number of moles} = \frac{0.250}{22.7} = 0.0110\ \text{mol}$$

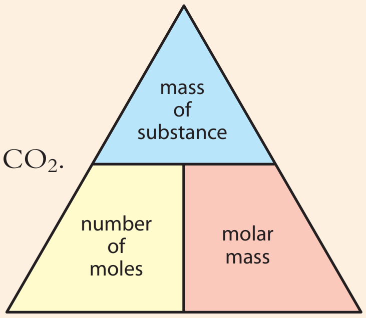
b $$\text{volume} = \text{number of moles} \times 22.7 = 0.135 \times 22.7 = 3.06\ \text{dm}^3$$

1.26 Calculate the volume of carbon dioxide (collected at STP) produced when 10.01 g of calcium carbonate decomposes according to the equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Step 1 – work out the number of moles of $CaCO_3$:

$$\text{number of moles of } CaCO_3 = \frac{10.01}{100.09} = 0.1000\,\text{mol}$$



Step 2 – the chemical equation tells us that 1 mol $CaCO_3$ decomposes to give 1 mol CO_2.

Therefore 0.1000 mol $CaCO_3$ decomposes to give 0.1000 mol CO_2.

Step 3 – convert the number of moles to volume:

1 mol CO_2 occupies 22.7 dm^3 at STP

$$\text{volume of } CO_2 = \text{number of moles} \times \text{volume of 1 mole } (22.7\,dm^3)$$

$$\text{volume of } CO_2 = 0.1000 \times 22.7 = 2.27\,dm^3$$

The volume of CO_2 produced is 2.27 dm^3.

1.27 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?

Step 1 – work out the number of moles of O_2. The volume of O_2 must first be converted to dm^3:

$$\text{volume of } O_2 \text{ in } dm^3 = \frac{100.0}{1000} = 0.1000\,dm^3$$

$$\text{number of moles of } O_2 = \frac{0.1000}{22.7} = 4.405 \times 10^{-3}\,\text{mol}$$

Step 2 – the chemical equation tells us that 3 mol O_2 are produced from 2 mol $KClO_3$. Therefore the number of moles of $KClO_3$ is two-thirds of the number of moles of O_2:

$$\tfrac{2}{3} \times 4.405 \times 10^{-3} = 2.937 \times 10^{-3}\,\text{mol}$$

Step 3 – convert the number of moles of $KClO_3$ to mass:

$$\text{molar mass of } KClO_3 = 122.55\,\text{g mol}^{-1}$$

$$\text{mass of } KClO_3 = 122.55 \times 2.937 \times 10^{-3} = 0.3599\,\text{g}$$

The mass of $KClO_3$ required is 0.3599 g.

Formula for solving moles questions involving volumes of gases

An alternative way of doing these questions is to use a formula.

$$\frac{m_1}{n_1 M_1} = \frac{V_2}{n_2 M_v}$$

Note: this is very similar to the formula that was used earlier with masses.

where:

m_1 = mass of first substance (in g)
n_1 = coefficient of first substance
M_1 = molar mass of first substance
V_2 = volume (in dm^3) of second substance if it is a gas
n_2 = coefficient of second substance
M_v = molar volume of a gas = 22.7 dm^3 at STP

This formula can be used if the mass of one substance is given and the volume of another substance is required, or vice versa.

If a volume is given and a volume is required, then an alternative form of this equation is:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

There is no need to convert units of volume to dm^3 with this equation – but V_2 must have the same units as V_1.

where:

V_1 = volume of first substance if it is a gas
V_2 = volume of second substance

However, with questions involving just gases it is usually easier to work them out using Avogadro's law, as described earlier.

Test yourself

Assume that all gases behave as ideal gases and that all measurements are made under the same conditions of temperature and pressure.

26 **a** Calculate the volume of carbon dioxide produced when 100 cm^3 of ethene burns in excess oxygen according to the equation:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

b Calculate the volume of nitric oxide (NO) produced when 2.0 dm^3 of oxygen is reacted with excess ammonia according to the equation:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

27 Determine the number of moles present in each of the following at standard temperature and pressure:

a 0.240 dm^3 of O_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

28 Work out the volume of each of the following at standard temperature and pressure:

a 0.100 mol C_3H_8
b 100.0 mol SO_3
c 0.270 mol N_2
d 0.8500 mol NH_3
e 0.600 mol O_2

29 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) decompose.

30 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 are reacted with excess nitric acid what volume of nitrogen dioxide (in cm^3) is produced at STP?

31 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.

$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

32 **a** Oxygen can be converted to ozone (O_3) by passing it through a silent electric discharge:

$3O_2(g) \rightarrow 2O_3(g)$

If 300 cm^3 of oxygen are used and 10% of the oxygen is converted to ozone, calculate the total volume of gas present at the end of the experiment.

b Hydrogen reacts with chlorine according to the equation:

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

What is the total volume of gas present in the container at the end of the experiment if 100 cm^3 of hydrogen are reacted with 200 cm^3 of chlorine?

'Macroscopic' means 'on a large scale'. The opposite is 'microscopic'. The microscopic properties of a gas are the properties of the particles that make up the gas.

Macroscopic properties of ideal gases

So far, all the questions we have dealt with have involved working out volumes of gases at STP. In order to work out volumes of gases under other conditions we must understand a little more about the properties of gases.

The relationship between pressure and volume (Boyle's law)

At a constant temperature, the volume of a fixed mass of an ideal gas is inversely proportional to its pressure.

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 **1.12**.

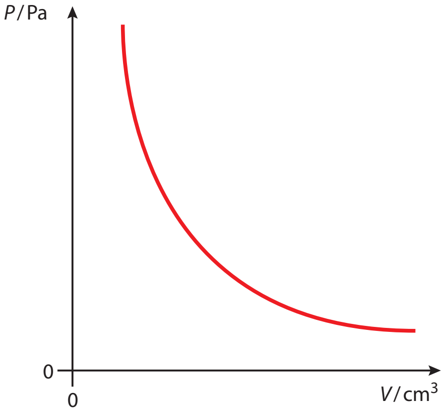


Figure 1.12 The relationship between pressure and volume of a fixed mass of an ideal gas at constant temperature.

$$P \propto \frac{1}{V}$$

The relationship can also be written as:

$$P = \frac{k}{V}$$

where k is a constant.

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.

Other graphs can also be drawn to illustrate this relationship (see Figures **1.13** and **1.14**).

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 is shown in Figure **1.13**.

Because $PV = k$, where k is a constant, a graph of PV against pressure (or volume) will be a straight, horizontal line. This is shown in Figure **1.14**.

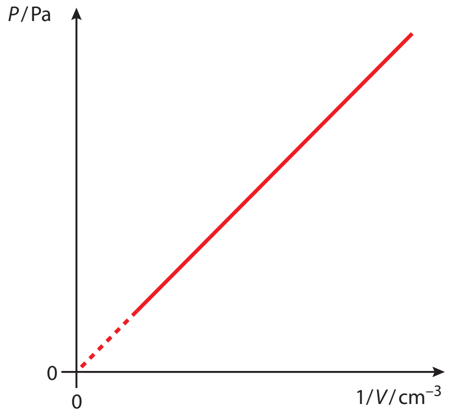


Figure 1.13 The relationship between the pressure and $\frac{1}{\text{volume}}$ of a fixed mass of an ideal gas at constant temperature.

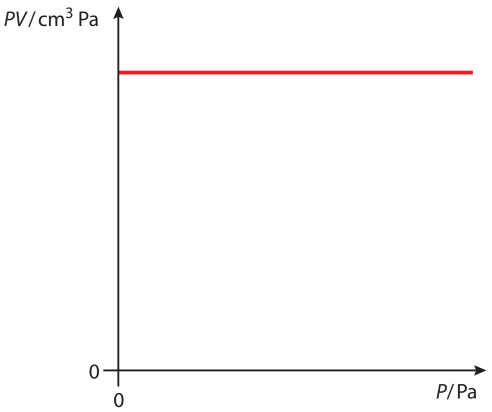


Figure 1.14 The relationship between PV and P for a fixed mass of an ideal gas at constant temperature.

The relationship between volume and temperature (Charles' law)

If the temperature is in kelvin, the following relationship exists between the volume and the temperature:

> **The volume of a fixed mass of an ideal gas at constant pressure is directly proportional to its kelvin temperature.**
> $V \propto T$

Therefore, if the kelvin temperature 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 **1.15**.

This relationship does not work for temperatures in °C (Figure **1.16**). 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.

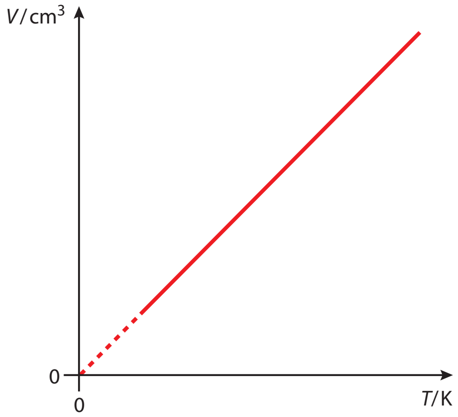


Figure 1.15 The relationship between the volume and temperature (in kelvin) of a fixed mass of an ideal gas at constant pressure.

An ideal gas can never liquefy because there are no forces between the molecules.

This is a linear relationship but not a proportional one because the graph does not pass through the origin.

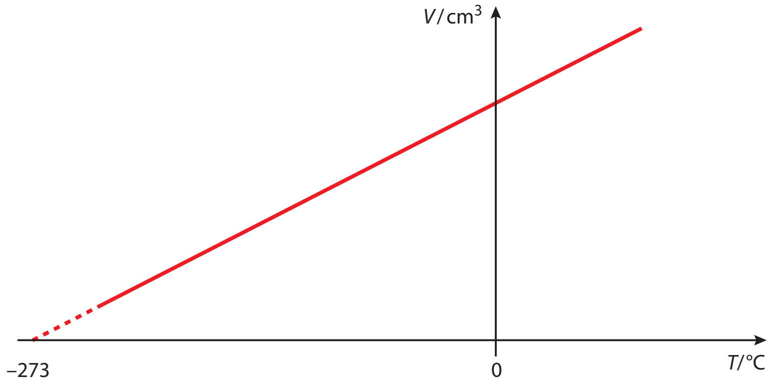


Figure 1.16 The relationship between the volume and temperature (in °C) of a fixed mass of an ideal gas at constant pressure. As can be seen, the temperature at which the volume of an ideal gas is zero will be −273 °C. This temperature is **absolute zero**.

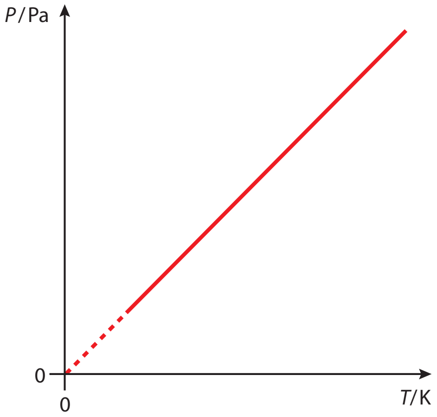


Figure 1.17 The relationship between the pressure and temperature (kelvin) of a fixed mass of an ideal gas at constant volume.

The relationship between pressure and temperature

For a fixed mass of an ideal gas at constant volume, the pressure is directly proportional to its absolute 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 **1.17**).

The overall gas law equation

An ideal gas is one that obeys all of the above laws exactly.

The three relationships above can be combined to produce the following equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Note: any units may be used for P and V, so long as they are consistent on both sides of the equation.

The temperature must be kelvin.

Worked examples

1.28 If the volume of an ideal gas collected at 0 °C and 100 kPa, i.e. at STP, is 50.0 cm^3, what would be the volume at 60 °C and 108 kPa?

$P_1 = 100$ kPa $\quad P_2 = 108$ kPa

$V_1 = 50.0\,cm^3$ $\quad V_2 = ?$

The units of P_1 and P_2 are consistent with each other.

$T_1 = 0\,°C = 273\,K$ $\quad T_2 = 60\,°C = 60 + 273\,K = 333\,K$

Temperature must be in K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{100 \times 50.0}{273} = \frac{108 \times V_2}{333}$$

Rearranging the equation:

$$V_2 = \frac{100 \times 50.0 \times 333}{273 \times 108} = 56.5\,cm^3$$

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.

1.29 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 STP?

$P_1 = 200$ kPa $\quad P_2 = 100$ kPa

$V_1 = 1.34\,dm^3$ $\quad V_2 = 756\,cm^3$, i.e. $\frac{756}{1000}\,dm^3$ or $0.756\,dm^3$

$T_1 = ?$ $\quad T_2 = 273\,K$

The units of P_1 are the same as those of P_2.

$$\frac{200 \times 1.34}{T_1} = \frac{100 \times 0.756}{273}$$

The units of V_1 and V_2 were made consistent with each other. We could have also changed V_1 to cm^3.

Rearranging the equation:

$$200 \times 1.34 \times 273 = 100 \times 0.756 \times T_1$$

$$T_1 = \frac{200 \times 1.34 \times 273}{100 \times 0.756} = 968\,K$$

This must now be converted to °C by subtracting 273.

Temperature = 968 − 273 = 695 °C

The temperature must be 695 °C for the gas to occupy a volume of 1.34 dm^3.

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** and n is the number of moles. 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 $\text{J K}^{-1}\,\text{mol}^{-1}$, and this requires the following set of units:

$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Pressure: N m^{-2} or Pa
Volume: m^3
Temperature: K

A consistent set of units must be used.

Exam tip
A set of units that is equivalent to this uses volume in dm^3 and pressure in kPa – if you use these units you can avoid the problem of converting volumes into m^3.

SI stands for Système International d'Unités and refers to the internationally accepted system of units used in science.

$1\,000\,000\,\text{cm}^3 \Leftrightarrow 1\,\text{m}^3$
$1000\,\text{dm}^3 \Leftrightarrow 1\,\text{m}^3$
To convert m^3 to cm^3 multiply by 1 000 000.
To convert cm^3 to m^3 divide by 1 000 000.
To convert m^3 to dm^3 multiply by 1000.
To convert dm^3 to m^3 divide by 1000.

Worked examples

1.30 An ideal gas occupies $590\,\text{cm}^3$ at 120 °C and 202 kPa. What amount of gas (in moles) is present?

If we use the value of $8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$ for the gas constant, all values must be converted to the appropriate set of units:

$P = 202\text{ kPa} = 2.02 \times 10^5\text{ Pa}$

$V = 590\,\text{cm}^3 = \dfrac{590}{1\,000\,000}\,\text{m}^3 = 5.90 \times 10^{-4}\,\text{m}^3$
$n = ?$
$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
$T = 120\,°\text{C} = 120 + 273\,\text{K} = 393\,\text{K}$

$$PV = nRT$$

$$2.02 \times 10^5 \times 5.90 \times 10^{-4} = n \times 8.31 \times 393$$

Rearranging the equation:

$$n = \frac{2.02 \times 10^5 \times 5.90 \times 10^{-4}}{8.31 \times 393} = 0.0365\,\text{mol}$$

The number of moles is 0.0365 mol.

1.31 A gas has a density of $1.24\,\text{g}\,\text{dm}^{-3}$ at $0\,°\text{C}$ and $1.00 \times 10^5\,\text{Pa}$. Calculate its molar mass.

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

We know the density, so we know the mass of $1\,\text{dm}^3$ of the gas. If we can find the number of moles in $1\,\text{dm}^3$, we can work out the molar mass.

$P = 1.00 \times 10^5\,\text{Pa}$

$V = 1.00\,\text{dm}^3 = \frac{1.00}{1000}\,\text{m}^3 = 1.00 \times 10^{-3}\,\text{m}^3$

$n = ?$

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

$T = 0\,°\text{C} = 273\,\text{K}$

Using $PV = nRT$

$$n = \frac{1.00 \times 10^5 \times 1.00 \times 10^{-3}}{8.31 \times 273} = 0.0441\,\text{mol}$$

This number of moles has a mass of 1.24 g.

$$\text{molar mass} = \frac{\text{mass}}{\text{number of moles}}$$

$$\text{molar mass} = \frac{1.24}{0.0441} = 28.1\,\text{g}\,\text{mol}^{-1}$$

1.32 What is the molar volume of an ideal gas at $18\,°\text{C}$ and $1.10 \times 10^5\,\text{Pa}$? (Give your answer in $\text{m}^3\,\text{mol}^{-1}$ and $\text{dm}^3\,\text{mol}^{-1}$.)

The molar volume of a gas is the volume occupied by one mole of the gas. We are familiar with the value for the molar volume of a gas at STP, which is $22.7\,\text{dm}^3\,\text{mol}^{-1}$.

$P = 1.10 \times 10^5\,\text{Pa}$

$n = 1.00\,\text{mol}$

$T = 18\,°\text{C} = 18 + 273\,\text{K} = 291\,\text{K}$

$V = ?$

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

Using $PV = nRT$:

$$V = \frac{1.00 \times 8.31 \times 291}{1.10 \times 10^5} = 0.0220\,\text{m}^3$$

The molar volume is $0.0220\,\text{m}^3\,\text{mol}^{-1}$ at $18\,°\text{C}$ and $1.10 \times 10^5\,\text{Pa}$. This must be multiplied by 1000 to convert to dm^3 i.e., $22.0\,\text{dm}^3\,\text{mol}^{-1}$.

1.33 When sodium nitrate(V) (often just called sodium nitrate) is heated, it decomposes to give sodium nitrate(III) (also called sodium nitrite) and oxygen gas. When a certain mass of sodium nitrate(V) is heated, 241 cm^3 of oxygen is obtained, measured at 97.0 kPa and 22 °C. Calculate the mass of sodium nitrate(III) formed.

$$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$$

We can use $PV = nRT$ to work out the number of moles of O_2:

$P = 97.0\text{ kPa} = 9.70 \times 10^4\text{ Pa}$

$V = 241\text{ cm}^3 = \frac{241}{1\,000\,000}\text{ m}^3 = 2.41 \times 10^{-4}\text{ m}^3$

$n = ?$

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

$T = 22\,°C = 295\text{ K}$

Using $PV = nRT$: $n = \frac{9.70 \times 10^4 \times 2.41 \times 10^{-4}}{8.31 \times 295} = 9.54 \times 10^{-3}\text{ mol}$

This gives the number of moles of O_2.

From the chemical equation, the number of moles of O_2 is half the number of moles of $NaNO_2$. Therefore, the number of moles of $NaNO_2$ is $9.54 \times 10^{-3} \times 2 = 1.91 \times 10^{-2}$ mol.

The molar mass of $NaNO_2$ is 69.00 g mol^{-1}, so the mass of $NaNO_2$ is $69.00 \times 1.91 \times 10^{-2} = 1.32$ g.

You would probably say that the room you are sitting in at the moment is full of air. If, however, you do a quick calculation (making a couple of approximations) you should be able to work out that the volume of the molecules of gas in the room is only about 0.01% of the volume of the room – scientific reality is very different from our everyday reality. (There is actually a very small probability that all these molecules could at any one time all end up in the same corner of the room – our survival depends on the fact that this probability is very small!)

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.

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 theory can be used to explain Boyle's law.

There is no progression from a theory to a law – they are different things.

Avogadro's original hypothesis was that equal volumes of different gases contain the same number of molecules. This was based on deductions from careful measurements and observations made by other scientists such as Gay-Lussac.

? Test yourself

In all questions, take the value of the ideal gas constant as 8.31 J K⁻¹ mol⁻¹.

33 If a certain mass of an ideal gas occupies $20.0\,cm^3$ at 0 °C and 1.01×10^5 Pa, what volume would it occupy at 38 °C and 1.06×10^5 Pa?

34 A certain mass of an ideal gas occupies $250.0\,cm^3$ at 20 °C and 9.89×10^4 Pa. At what temperature (in °C) will it occupy $400.0\,cm^3$ if the pressure remains the same?

35 How many moles of an ideal gas are present in a container if it occupies a volume of $1.50\,dm^3$ at a pressure of 1.10×10^5 Pa and a temperature of 30 °C?

36 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 °C.

37 What is the molar volume of an ideal gas at 1.10×10^5 Pa and 100 °C?

38 Copper nitrate decomposes when heated according to the equation:

$$2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$$

If 1.80 g of copper nitrate is heated and the gases collected at a temperature of 22 °C and 105 kPa:

a what volume (in dm^3) of oxygen is collected?

b what is the total volume of gas collected in cm^3?

39 When a certain mass of manganese heptoxide (Mn_2O_7) decomposed, it produced $127.8\,cm^3$ of oxygen measured at 18 °C and 1.00×10^5 Pa. What mass of manganese heptoxide decomposed?

$$2Mn_2O_7(aq) \rightarrow 4MnO_2(s) + 3O_2(g)$$

1.3.3 Calculations involving solutions

Learning objective

- Solve problems involving solutions

Solutions

Solute: a substance that is dissolved in another substance.
Solvent: a substance that dissolves another substance (the solute). The solvent should be present in excess of the solute.
Solution: the substance that is formed when a solute dissolves in a solvent.

When a sodium chloride (NaCl) **solution** is prepared, NaCl solid (the **solute**) is dissolved in water (the **solvent**).

Solutions in water are given the symbol (aq) in chemical equations. *aq* stands for *aqueous*.

Note: 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 volume of 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. This is why concentration is defined in terms of the volume of the solution rather than the volume of the solvent.

Reported values for the concentration of gold in seawater vary greatly. A value of about 2×10^{-11} g dm^{-3} or 1×10^{-13} mol dm^{-3} is probably a reasonable estimate. The volume of water in the oceans is estimated to be about 1.3×10^{21} dm^3, so there is an awful lot of gold in the oceans. Many people (including Nobel Prize-winning scientist Fritz Haber) have tried to come up with ways to extract the gold. The problem is that the concentrations are so low.

The **concentration** of a solution is the amount of solute dissolved in a unit volume of **solution**. The volume that is usually taken is 1 dm^3. The amount of solute may be expressed in g or mol therefore the units of concentration are g dm^{-3} or mol dm^{-3}.

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 of concentration 2 mol dm^{-3}.

The relationship between concentration, number of moles and volume of solution is:

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

This is summarised in Figure **1.18**.

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

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

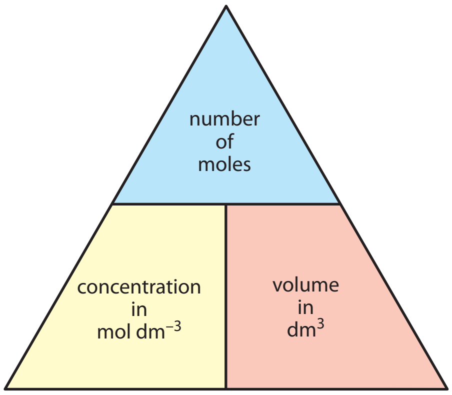


Figure 1.18 The relationship between concentration, number of moles and volume of solution.

Worked examples

1.34 If 10.00 g of sodium hydroxide (NaOH) is dissolved in water and the volume is made up to 200.0 cm^3, calculate the concentration in mol dm^{-3} and g dm^{-3}.

Concentration (g dm^{-3})

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

$$\text{volume in dm}^3 = \frac{200.0}{1000} = 0.2000 \text{ dm}^3$$

$$\text{concentration} = \frac{10.00}{0.2000} = 50.00 \text{ g dm}^{-3}$$

Concentration (mol dm^{-3})

molar mass of NaOH = $40.00\ \text{g mol}^{-1}$

number of moles = $\frac{10.00}{40.00} = 0.2500\ \text{mol}$

concentration = $\frac{\text{number of moles}}{\text{volume in dm}^3}$

concentration = $\frac{0.2500}{0.2000} = 1.250\ \text{mol dm}^{-3}$

Alternatively, once we have the concentration in g dm^{-3} we can simply divide by the molar mass to get the concentration in mol dm^{-3}:

concentration = $\frac{50.00}{40.00} = 1.250\ \text{mol dm}^{-3}$

1.35 Calculate the number of moles of hydrochloric acid (HCl) present in $50.0\ \text{cm}^3$ of $2.00\ \text{mol dm}^{-3}$ hydrochloric acid.

number of moles = concentration × volume in dm^3

number of moles = $2.00 \times \frac{50}{1000} = 0.100\ \text{mol}$

Therefore the number of moles is 0.100 mol.

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 $[\text{HCl}] = 2.00\ \text{mol dm}^{-3}$ in this worked example.

Concentrations of very dilute solutions

When dealing with very small concentrations, you will occasionally come across the unit *parts per million*, *ppm*. For instance, if 1 g of a solute is present in 1 million grams of a solution then the concentration is 1 ppm. So, in general, the concentration in ppm is given by:

$$\text{concentration in ppm} = \frac{\text{mass of solute} \times 10^6}{\text{mass of solution}}$$

The ppm notation is most often used when writing about pollution – e.g. *the concentration of arsenic in drinking water in the US should not exceed 0.010 ppm*.

The units of mass of solute and mass of solution must be the same so that they cancel.

Worked examples

1.36 If a sample of 252.10 g of water is found to contain 2.03 mg of cyanide, what is the cyanide concentration in ppm?

The mass in mg must first be converted to a mass in g by dividing by 1000:

mass of cyanide = $2.03 \times 10^{-3}\ \text{g}$

concentration of cyanide in ppm = $\frac{2.03 \times 10^{-3} \times 10^6}{252.10} = 8.05\ \text{ppm}$

Although the concentration in ppm is properly defined as above, it is often used in newspaper articles etc. in a slightly more convenient (but not completely correct) way as the mass of solute, in mg, per dm^3 (litre) of solution. This is a reasonable approximation because the mass of $1\ \text{dm}^3$ of water (which will make up most of the solution) is 1000 g – i.e. 1 000 000 mg. So if the copper concentration in a sample of tap water is 1.2 ppm, this is roughly equivalent to 1.2 mg of copper per dm^3 of water.

The companion units of parts per billion (ppb) and parts per trillion (ppt) are often used when discussing extremely low concentrations – these units can cause some confusion because the definitions of billion and trillion are different in different countries. It used to be that a billion in British English referred to 1×10^{12} but now the US definition of 1×10^{9} is the commonly accepted value.

The ppm notation is also used when discussing the concentrations of various pollutant gases in air. In this case it is defined as:

$$\text{concentration in ppm} = \frac{\text{volume of gas} \times 10^{6}}{\text{volume of air}}$$

For instance, the carbon monoxide concentration in a sample of air might be 10 ppm. This indicates that there would be 10 dm^3 of CO per 1 000 000 dm^3 of air. At STP this would roughly convert to 12 g CO per million dm^3 of air. So, in a classroom with dimensions of about 5 m × 4 m × 2 m, there would be approximately 0.5 g of carbon monoxide.

Working out the concentration of ions

When ionic substances (see page **119**) 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:

$$CuCl_2(aq) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$

Therefore when 0.100 mol $CuCl_2$ dissolves in water, 2×0.100 mol (i.e. 0.200 mol) Cl^- ions are produced. The concentration of the chloride ions is therefore twice the concentration of the $CuCl_2$.

Worked example

1.37 Calculate the number of moles 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.

$$\text{number of moles} = \text{concentration} \times \text{volume in dm}^3$$

$$\text{number of moles of } FeCl_3 = \frac{50.0}{1000} \times 0.0500 = 2.50 \times 10^{-3} \text{ mol } FeCl_3$$

$$FeCl_3(aq) \rightarrow Fe^{3+}(aq) + 3Cl^-(aq)$$

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 number of moles 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 the ions present is four times the concentration of the $FeCl_3$, i.e. 4×0.0500 mol dm^{-3}.

The total concentration of ions present is 0.200 mol dm^{-3}.

Titrations

Titration is a technique for finding the volumes of solutions that react exactly with each other. One solution is added from a burette to the other solution in a conical flask (Figure **1.19**). An indicator is often required to determine the end point of the titration.

In order for the technique to be used to determine the concentration of a particular solution, the concentration of one of the solutions it reacts with must be known accurately – this is a standard solution.

Worked example

1.38 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.

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

Step 1 – work out the number of moles of NaOH:

$$\text{number of moles} = \text{concentration} \times \text{volume in dm}^3$$

$$\text{number of moles} = 0.2000 \times \frac{25.00}{1000} = 5.000 \times 10^{-3}\,\text{mol}$$

Step 2 – the balanced equation tells us that 2 mol NaOH react with 1 mol H_2SO_4. Therefore 5.000×10^{-3} mol NaOH react with $\frac{5.000 \times 10^{-3}}{2}$ mol H_2SO_4, i.e. 2.500×10^{-3} mol H_2SO_4. This is the number of moles of H_2SO_4 in 23.20 cm^3 of H_2SO_4.

Step 3 – convert number of moles to concentration:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume in dm}^3}$$

$$23.20\,\text{cm}^3 = \frac{23.20}{1000}\,\text{dm}^3 = 0.02320\,\text{dm}^3$$

$$[H_2SO_4] = \frac{2.500 \times 10^{-3}}{0.02320} = 0.1078\,\text{mol dm}^{-3}$$

The concentration of the H_2SO_4 is 0.1078 mol dm^{-3}.

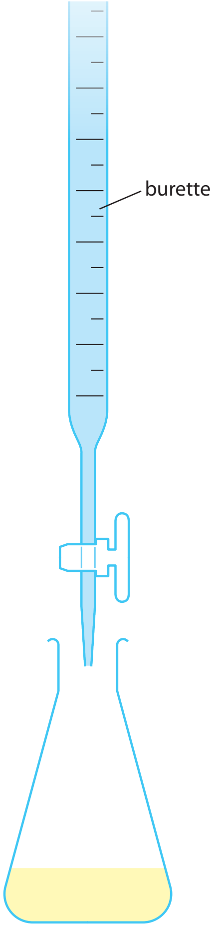


Figure 1.19 Titration set-up.

A standard solution can be made up from a solid (primary standard). A certain mass of the solute is weighed out accurately and then dissolved in a small amount of distilled water in a beaker. 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, water is added to make the solution up to the mark so that the total volume of the solution is known.

Alternatively, the concentration of a standard solution may be known because it has been titrated against another standard solution.

Exam tip
This equation is useful for solving titration problems in the multiple-choice paper.

Equation for solving moles questions involving solutions

The following equation may be used as an alternative method for solving problems:

$$\frac{c_1 v_1}{n_1} = \frac{c_2 v_2}{n_2}$$

where:

c_1 = concentration of first substance
v_1 = volume of first substance
n_1 = coefficient of first substance
c_2 = concentration of second substance
v_2 = volume of second substance
n_2 = coefficient of second substance

Worked example

1.39 For neutralisation, 25.00 cm^3 of phosphoric(V) acid (H_3PO_4) requires 28.70 cm^3 of sodium hydroxide (NaOH) of concentration 0.1500 mol dm^{-3}. What is the concentration of the phosphoric(V) acid?

$$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$$

Let H_3PO_4 be substance 1 and NaOH be substance 2.

$c_1 = ?$
$v_1 = 25.00\ \text{cm}^3$
$n_1 = 1$

$c_2 = 0.1500\ \text{mol dm}^{-3}$
$v_2 = 28.70\ \text{cm}^3$
$n_2 = 3$

$$\frac{c_1 v_1}{n_1} = \frac{c_2 v_2}{n_2}$$

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.

$$\frac{c_1 \times 25.00}{1} = \frac{0.1500 \times 28.70}{3}$$

Rearranging the equation: $c_1 = \dfrac{1 \times 0.1500 \times 28.70}{3 \times 25.00} = 0.057\,40\ \text{mol dm}^{-3}$

The concentration of H_3PO_4 is 0.057 40 mol dm^{-3}.

? Test yourself

40 **a** What mass of sodium sulfate (Na_2SO_4) must be used to make up 250 cm^3 of a 0.100 $mol\,dm^{-3}$ solution?

b What is the concentration of sodium ions in the solution in **a**?

41 Work out the numbers of moles of solute present in the following solutions:

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)

42 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.

$$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

43 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?

44 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?

$$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$$

45 If 0.100 g of magnesium is reacted with 25.00 cm^3 of 0.200 $mol\,dm^{-3}$ hydrochloric acid, calculate the volume of hydrogen gas produced at STP.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Water of crystallisation

Some substances crystallise with water as an integral part of the crystal lattice. Examples are hydrated copper sulfate ($CuSO_4{\cdot}5H_2O$) and hydrated magnesium chloride ($MgCl_2{\cdot}6H_2O$). The water is necessary for the formation of the crystals and is called **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 sulfate' ($CuSO_4{\cdot}5H_2O$) and 'anhydrous copper sulfate' ($CuSO_4$). Hydrated copper sulfate can be obtained as large blue crystals, but anhydrous copper sulfate is white and powdery.

In the case of $CuSO_4{\cdot}5H_2O$, the 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. 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 examples

1.40 When 2.56 g of hydrated magnesium sulfate ($MgSO_4{\cdot}xH_2O$) is heated, 1.25 g of anhydrous magnesium sulfate ($MgSO_4$) is formed. Determine the value of x in the formula.

mass of water given off = 2.56 − 1.25, i.e. 1.31 g

mass of $MgSO_4$ = 1.25 g

This is now basically just an empirical formula question, and we need to find the ratio between the numbers of moles of $MgSO_4$ and H_2O.

molar mass of $H_2O = 18.02\,\text{g mol}^{-1}$

number of moles of $H_2O = \frac{1.31}{18.02} = 0.0727\,\text{mol}$

molar mass of $MgSO_4 = 120.38\,\text{g mol}^{-1}$

number of moles of $MgSO_4 = \frac{1.25}{120.38} = 0.0104\,\text{mol}$

Divide by the smaller number to get the ratio:

$$\frac{0.0727}{0.0104} = 7$$

The value of x is 7, and the formula of hydrated magnesium sulfate is $MgSO_4{\cdot}7H_2O$.

1.41 **a** If 10.00 g of hydrated copper sulfate ($CuSO_4{\cdot}5H_2O$) are dissolved in water and made up to a volume of $250.0\,\text{cm}^3$, what is the concentration of the solution?

b What mass of anhydrous copper sulfate would be required to make $250.0\,\text{cm}^3$ of solution with the same concentration as in **a**?

a molar mass of $CuSO_4{\cdot}5H_2O = 249.72\,\text{g mol}^{-1}$

number of moles $CuSO_4{\cdot}5H_2O = \frac{10.00}{249.72} = 0.04004\,\text{mol}$

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume in dm}^3} = \frac{0.04004}{0.2500} = 0.1602\,\text{mol dm}^{-3}$$

When a hydrated salt is dissolved in water, the water of crystallisation just becomes part of the solvent, and the solution is the same as if the anhydrous salt were dissolved in water.

So dissolving 10.00 g of $CuSO_4{\cdot}5H_2O$ in water and making up the solution to $250.0\,\text{cm}^3$ produces a $CuSO_4$ solution of concentration $0.1602\,\text{mol dm}^{-3}$.

b The number of moles of $CuSO_4$ present in $250.0\,\text{cm}^3$ solution will be exactly the same as above, i.e. 0.04004 mol because the concentration is the same.

0.04004 mol $CuSO_4{\cdot}5H_2O$ contains 0.04004 mol $CuSO_4$

molar mass of $CuSO_4 = 159.62\,\text{g mol}^{-1}$

mass of $CuSO_4$ = molar mass × number of moles = 159.62 × 0.04004 = 6.391 g

The mass of $CuSO_4$ required to make $250\,\text{cm}^3$ of a solution of concentration $0.1602\,\text{mol dm}^{-3}$ is 6.391 g, as opposed to 10.00 g of $CuSO_4{\cdot}5H_2O$. The two solutions will be identical.

1.42 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 $Na_2CO_3 \cdot xH_2O$.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Step 1 – work out the number of moles of HCl:

$$\text{number of moles} = \text{concentration} \times \text{volume in } dm^3$$

$$\text{number of moles} = 0.100 \times \frac{27.40}{1000} = 2.74 \times 10^{-3}\,\text{mol}$$

Step 2 – the balanced equation tells us that 2 mol HCl react with 1 mol Na_2CO_3. Therefore 2.74×10^{-3} mol HCl react with $\frac{2.74 \times 10^{-3}}{2} = 1.37 \times 10^{-3}$ 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 number of moles to mass:

$$\text{molar mass of } Na_2CO_3 = 105.99\,g\,mol^{-1}$$

$$\text{mass of } 1.37 \times 10^{-2}\,\text{mol } Na_2CO_3 = \text{number of moles} \times \text{molar mass}$$

$$\text{mass of } Na_2CO_3 = 1.37 \times 10^{-2} \times 105.99 = 1.45\,g$$

The total mass of $Na_2CO_3 \cdot xH_2O = 3.92$ g.
The mass of this that is due to the water of crystallisation $= 3.92 - 1.45 = 2.47$ g.

$$\text{number of moles of water of crystallisation} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.74}{18.02} = 0.137\,\text{mol}$$

The ratio moles of water of crystallisation : moles of sodium carbonate can be worked out by dividing the number of moles of water by the number of moles 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 $Na_2CO_3 \cdot 10H_2O$.

Back titration

This is a technique by which a known excess of a particular reagent, A, is added to another substance, X, so that they react. Then the excess A is titrated against another reagent to work out how much A reacted with the substance – and therefore how many moles of X were present. This is useful when X is an impure substance.

Worked example

1.43 Limestone is impure calcium carbonate ($CaCO_3$). 2.00 g of limestone is put into a beaker and 60.00 cm^3 of 3.000 mol dm^{-3} hydrochloric acid (HCl) is added. They are left to react and then the impurities are filtered off and the solution is made up to a total volume of 100.0 cm^3. Of this solution, 25.00 cm^3 require 35.50 cm^3 of 1.000 mol dm^{-3} sodium hydroxide (NaOH) for neutralisation. Work out the percentage calcium carbonate in the limestone (assume that none of the impurities reacts with hydrochloric acid).

Let us consider the first part of the question: '2.00 g of limestone is put into a beaker and 60.00 cm^3 of 3.000 mol dm^{-3} hydrochloric acid is added':

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

The limestone is impure, so we cannot work out the number of moles of $CaCO_3$ present, but we do have enough information to work out the number of moles of HCl:

If the limestone were pure $CaCO_3$, the number of moles present in 2.00 g would be 0.0200 mol, which would react with 0.0400 mol HCl.

$$\text{number of moles of HCl} = \text{concentration} \times \text{volume in dm}^3$$

$$\text{number of moles of HCl} = 3.000 \times \frac{60.00}{1000} = 0.1800\ \text{mol}$$

This is excess HCl, and when the limestone is reacted with it there will be some HCl left over.

The second part of the question is: 'They are left to react and then . . . the solution is made up to a total volume of 100.0 cm^3'.

This 100.0 cm^3 of solution now contains the HCl left over after the reaction with the $CaCO_3$.

In order to work out the number of moles of HCl that did not react, we must consider the third part of the question: 'Of this solution, 25.00 cm^3 require 35.50 cm^3 of 1.000 mol dm^{-3} sodium hydroxide for neutralisation':

$$\text{number of moles of NaOH} = \text{concentration} \times \text{volume in dm}^3$$

$$\text{number of moles of NaOH} = 1.000 \times \frac{35.50}{1000} = 0.03550\ \text{mol}$$

This reacts with HCl according to the equation:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Therefore 0.03550 mol NaOH react with 0.03550 mol HCl. This means that 25.00 cm^3 of the HCl solution contained 0.03550 mol HCl. Therefore in 100.0 cm^3 of this solution there were 4 × 0.03550, i.e. 0.1420 mol HCl. This is the number of moles of HCl left over after it has reacted with the $CaCO_3$.

Because 0.1800 mol HCl was originally added to the limestone, the amount that reacted with the $CaCO_3$ was 0.1800 − 0.1420, i.e. 0.0380 mol.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

$$0.0380\ \text{mol HCl reacts with } \frac{0.0380}{2}\text{, i.e. 0.0190, mol } CaCO_3$$

$$\text{molar mass of } CaCO_3 = 100.09\ \text{g mol}^{-1}$$

$$\text{mass of } CaCO_3 = \text{number of moles} \times \text{molar mass} = 100.09 \times 0.0190 = 1.90\ \text{g}$$

$$\%\ CaCO_3 \text{ in the limestone} = \frac{1.90}{2.00} \times 100 = 95.1\%$$

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.

Worked example

1.44 A 25.0 cm^3 sample of a solution of copper(II) nitrate is added to 10.0 cm^3 of 1 mol dm^{-3} potassium iodide. 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.

The initial reaction of copper(II) ions with iodide ions is:

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq) \qquad \textbf{(reaction 1)}$$

This is a redox titration and these will be considered again in Topic **9**.

A large excess of iodide ions is added to make sure that all the copper ions react. A precipitate of CuI is formed as well as the iodine. If we can determine the number of moles of iodine produced in the solution, we can also find the number of moles of copper ions.

The amount of iodine is determined by titration with sodium thiosulfate solution:

$$\underset{\text{thiosulfate ion}}{2S_2O_3^{2-}(aq)} + I_2(aq) \rightarrow 2I^{-}(aq) + \underset{\text{tetrathionate ion}}{S_4O_6^{2-}(aq)} \qquad \textbf{(reaction 2)}$$

The number of moles of thiosulfate in 22.50 cm^3 of 0.0200 mol dm^{-3} solution:

$$\text{number of moles} = \text{volume in dm}^3 \times \text{concentration} = \frac{22.50}{1000} \times 0.0200 = 4.50 \times 10^{-4}\,\text{mol } S_2O_3^{2-}$$

From reaction **2** we can see that 2 mol $S_2O_3^{2-}$ react with 1 mol I_2. Therefore 4.50×10^{-4} mol $S_2O_3^{2-}$ react with $\frac{4.50 \times 10^{-4}}{2}$ mol I_2, i.e. 2.25×10^{-4} mol I_2. This is the amount of iodine produced in reaction **1**.

From reaction **1**, 2 mol Cu^{2+} produce 1 mol I_2, so the number of moles of Cu^{2+} is twice the number of moles of I_2. Therefore the number of moles of Cu^{2+} is $2 \times 2.25 \times 10^{-4}$, i.e. 4.50×10^{-4} mol.

From reaction **1**, 2 mol Cu^{2+} react to form 1 mol I_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 $S_2O_3^{2-}$.

The volume of the solution containing Cu^{2+} ions was 25.0 cm^3, and this allows us to work out the concentration:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume in dm}^3} = \frac{4.50 \times 10^{-4}}{0.0250} = 0.0180\,\text{mol dm}^{-3}$$

Therefore the concentration of the copper(II) nitrate solution was 0.0180 mol dm^{-3}.

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 number of moles of whatever you can and see where you can go from there.

Worked examples

1.45 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 number of moles of silver nitrate.

b Calculate the number of moles of the chloride.

c Calculate the formula of the chloride.

a number of moles = concentration × volume in dm^3

$$\text{number of moles of } AgNO_3 = \frac{25.0}{1000} \times 0.0110 = 2.75 \times 10^{-4}\,\text{mol}$$

b $\text{number of moles of } MCl_x = \dfrac{5.40}{1000} \times 0.0170 = 9.18 \times 10^{-5}\,\text{mol}$

c The general equation for the reaction is:

$$MCl_x(aq) + xAgNO_3(aq) \rightarrow xAgCl(s) + M(NO_3)_x(aq)$$

The silver ions in the solution react with the chloride ions to precipitate silver chloride. The ratio of the number of moles of $AgNO_3$ to the number of moles of MCl_x will give us the value of x.

$$\frac{\text{number of moles of } AgNO_3}{\text{number of moles of } MCl_x} = \frac{2.75 \times 10^{-4}}{9.18 \times 10^{-5}} = 3$$

Therefore the value of x is 3, and the formula of the chloride is MCl_3.

1.46 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 15 °C and 101 kPa pressure to produce 0.335 g of M_2O_3. Determine the identity of the element M.

We can use $PV = nRT$ to work out the number of moles of oxygen. Substituting the values gives:

$$n = \frac{101000 \times 1.80 \times 10^{-4}}{8.31 \times 288} = 7.60 \times 10^{-3}\text{ mol}$$

We can now use the balanced chemical equation to work out the number of moles of M_2O_3.

From the chemical equation, 9 mol O_2 react to form 2 mol M_2O_3. Therefore, the number of moles of M_2O_3 is two-ninths of the number of moles of O_2:

$$\text{number of moles of } M_2O_3 = \tfrac{2}{9} \times 7.60 \times 10^{-3} = 1.69 \times 10^{-3}\,\text{mol}$$

Now that we have the number of moles and the mass of M_2O_3, we can work out the molar mass:

$$\text{molar mass} = \frac{\text{mass}}{\text{number of moles}} = \frac{0.335}{1.69 \times 10^{-3}} = 198\,\text{g}\,\text{mol}^{-1}$$

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 two:

$$\text{mass of } M_2 = 198 - (3 \times 16) = 150$$

$$\text{relative atomic mass of M} = \frac{150}{2} = 75$$

This value is closest to the relative atomic mass of arsenic (74.92) therefore the element M is arsenic.

Exam-style questions

1 What is the total number of atoms in 1.80 g of water?

A 6.02×10^{22} **B** 6.02×10^{23} **C** 1.80×10^{23} **D** 1.80×10^{24}

2 88 kg of carbon dioxide contains:

A 2.0 mol **B** 2000 mol **C** 0.50 mol **D** 3872 mol

3 What is the sum of the coefficients when the following equation is balanced with the smallest possible whole numbers?

$$CuFeS_2 + O_2 \rightarrow Cu_2S + SO_2 + FeO$$

A 7 **B** 8 **C** 11 **D** 12

4 Iron(III) oxide reacts with carbon monoxide according to the equation:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

How many moles of iron are produced when 180 mol carbon monoxide react with excess iron(III) oxide?

A 120 mol **B** 180 mol **C** 270 mol **D** 360 mol

5 Propene undergoes complete combustion to produce carbon dioxide and water.

$$2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

What volume of carbon dioxide is produced when $360\,cm^3$ of propene react with $360\,cm^3$ of oxygen at 273 K and 100 kPa pressure?

A $120\,cm^3$ **B** $240\,cm^3$ **C** $540\,cm^3$ **D** $1080\,cm^3$

6 What mass of $Na_2S_2O_3{\cdot}5H_2O$ must be used to make up $200\,cm^3$ of a $0.100\,mol\,dm^{-3}$ solution?

A 3.16 g **B** 4.96 g **C** 24.8 g **D** 31.6 g

7 20.00 cm^3 of potassium hydroxide (KOH) is exactly neutralised by 26.80 cm^3 of 0.100 $mol\,dm^{-3}$ sulfuric acid (H_2SO_4). The concentration of the potassium hydroxide is:

A 0.0670 $mol\,dm^{-3}$
B 0.134 $mol\,dm^{-3}$
C 0.268 $mol\,dm^{-3}$
D 1.34 $mol\,dm^{-3}$

8 Barium chloride solution reacts with sodium sulfate solution according to the equation:

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

When excess barium chloride solution is reacted with 25.00 cm^3 of sodium sulfate solution, 0.2334 g of barium sulfate (molar mass 233.40 $g\,mol^{-1}$) is precipitated.

The concentration of sodium ions in the sodium sulfate solution was:

A 0.08000 $mol\,dm^{-3}$
B 0.04000 $mol\,dm^{-3}$
C 0.001000 $mol\,dm^{-3}$
D 0.002000 $mol\,dm^{-3}$

9 When potassium chlorate(V) (molar mass 122.6 $g\,mol^{-1}$) is heated, oxygen gas (molar mass 32.0 $g\,mol^{-1}$) is produced:

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

When 1.226 g of potassium chlorate(V) are heated, 0.320 g of oxygen gas are obtained. The percentage yield of oxygen is:

A 100%
B 66.7%
C 26.1%
D 17.4%

10 Elemental analysis of a nitrogen oxide shows that it contains 2.8 g of nitrogen and 8.0 g of oxygen. The empirical formula of this oxide is:

A NO
B NO_2
C N_2O_3
D N_2O_5

11 Nitrogen can be prepared in the laboratory by the following reaction:

$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3H_2O(l) + 3Cu(s)$

If 227 cm^3 of ammonia, when reacted with excess copper oxide, produce 85 cm^3 of nitrogen, calculate the percentage yield of nitrogen. All gas volumes are measured at STP. **[3]**

12 Manganese can be extracted from its ore, hausmannite, by heating with aluminium.

$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$

a 100.0 kg of Mn_3O_4 are heated with 100.0 kg of aluminium. Work out the maximum mass of manganese that can be obtained from this reaction. **[4]**

b 1.23 tonnes of ore are processed and 200.0 kg of manganese obtained. Calculate the percentage by mass of Mn_3O_4 in the ore. **[3]**

13 A hydrocarbon contains 88.8% C. 0.201 g of the hydrocarbon occupied a volume of 98.9 cm^3 at 320 K and 1.00×10^5 Pa.

a Determine the empirical formula of the hydrocarbon. **[3]**

b Determine the molecular formula of the hydrocarbon. **[3]**

14 Limestone is impure calcium carbonate. A 1.20 g sample of limestone is added to excess dilute hydrochloric acid and the gas collected; 258 cm^3 of carbon dioxide were collected at a temperature of 27 °C and a pressure of 1.10×10^5 Pa.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

a Calculate the number of moles of gas collected. **[3]**

b Calculate the percentage purity of the limestone (assume that none of the impurities in the limestone react with hydrochloric acid to produce gaseous products). **[3]**

15 25.0 cm^3 of 0.100 mol dm^{-3} copper(II) nitrate solution is added to 15.0 cm^3 of 0.500 mol dm^{-3} potassium iodide. The ionic equation for the reaction that occurs is:

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$$

a Determine which reactant is present in excess. **[3]**

b Determine the mass of iodine produced. **[3]**

16 0.0810 g of a group 2 metal iodide, MI_2, was dissolved in water and the solution made up to a total volume of 25.00 cm^3. Excess lead(II) nitrate solution ($Pb(NO_3)_2(aq)$) was added to the MI_2 solution to form a precipitate of lead(II) iodide (PbI_2). The precipitate was dried and weighed and it was found that 0.1270 g of precipitate was obtained.

a Determine the number of moles of lead iodide formed. **[2]**

b Write an equation for the reaction that occurs. **[1]**

c Determine the number of moles of MI_2 that reacted. **[1]**

d Determine the identity of the metal, M. **[3]**

17 0.4000 g of hydrated copper sulfate ($CuSO_4{\cdot}xH_2O$) are dissolved in the solution water and made up to a total volume of 100.0 cm^3 with distilled water. 10.00 cm^3 of this solution are reacted with excess barium chloride ($BaCl_2$) solution. The mass of barium sulfate that forms is 3.739×10^{-2} g.

a Calculate the number of moles of barium sulfate formed. **[2]**

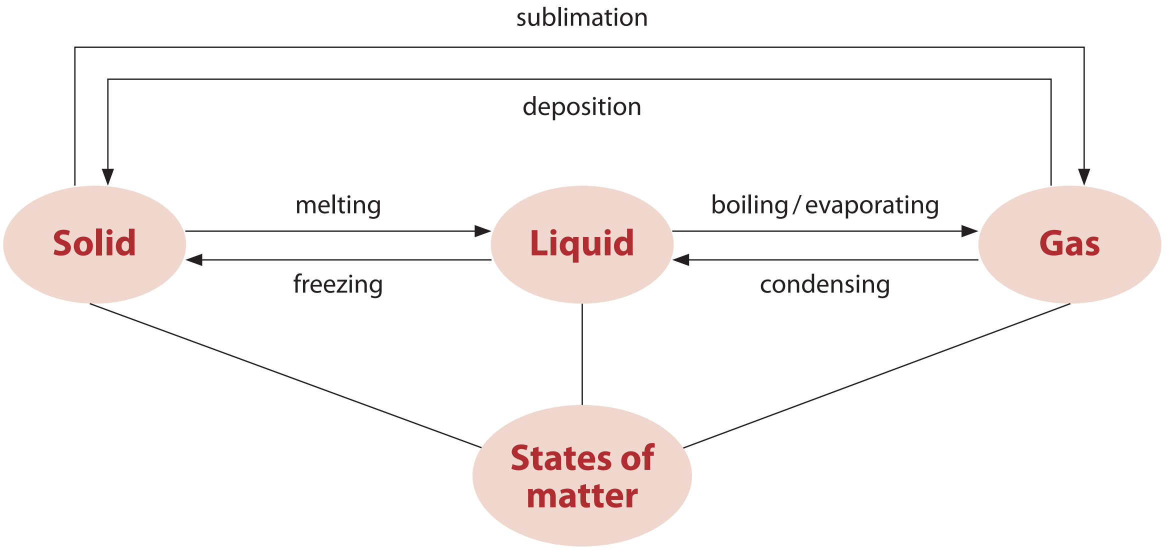
b Write an equation for the reaction between copper sulfate solution and barium chloride solution. **[1]**

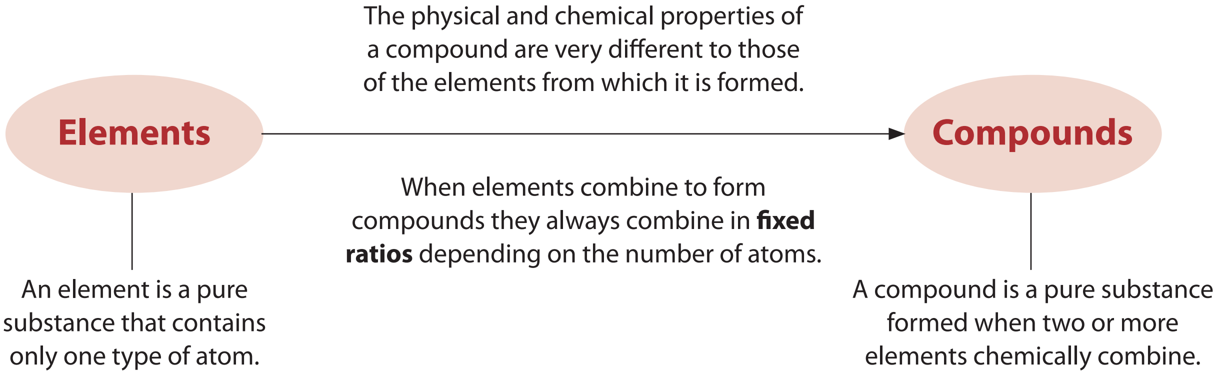
c Calculate the number of moles of copper sulfate that reacted with the barium chloride. **[1]**

d Calculate the number of moles of $CuSO_4$ in 0.4000 g of hydrated copper sulfate. **[1]**

e Determine the value of x. **[3]**

Summary



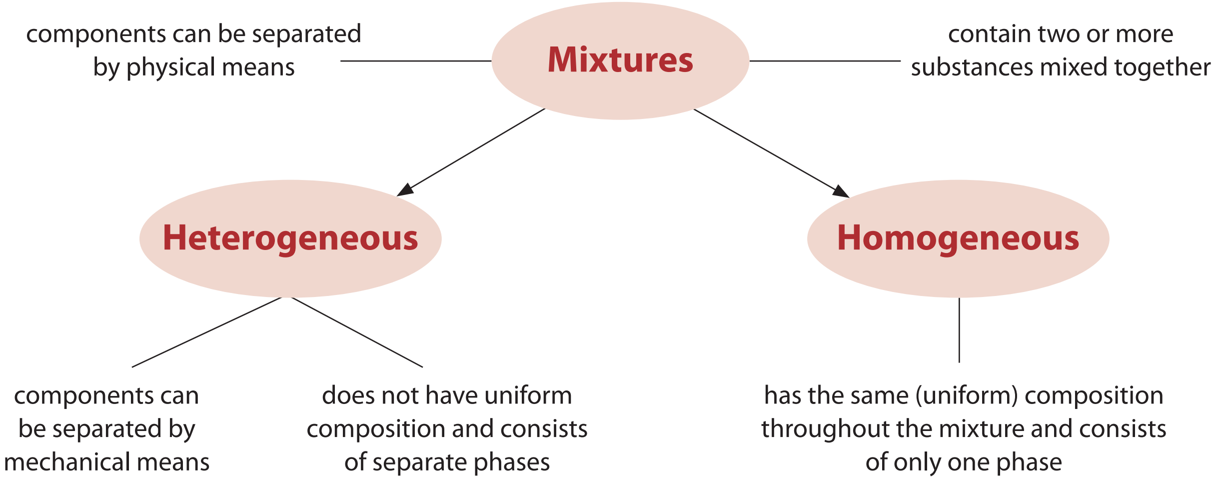


The physical and chemical properties of a compound are very different to those of the elements from which it is formed.

When elements combine to form compounds they always combine in **fixed ratios** depending on the number of atoms.

An element is a pure substance that contains only one type of atom.

A compound is a pure substance formed when two or more elements chemically combine.



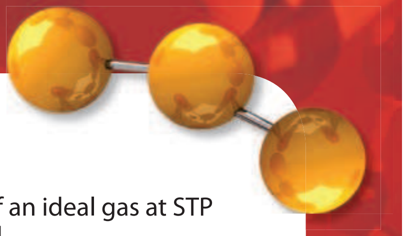
components can be separated by physical means

contain two or more substances mixed together

components can be separated by mechanical means

does not have uniform composition and consists of separate phases

has the same (uniform) composition throughout the mixture and consists of only one phase



MOLES

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

for ideal gases: $pV = nRT$ (T in kelvin)

Real gases deviate most from ideal behaviour at low temperature and high pressure.

molar volume of an ideal gas at STP $= 22.7\ \text{dm}^3\ \text{mol}^{-1}$

$$\text{number of moles} = \frac{\text{volume}}{\text{molar volume}}$$

Avogadro's law: equal volumes of ideal gases at the same temperature and pressure contain the same number of molecules.

$$\frac{c_1V_1}{n_1} = \frac{c_2V_2}{n_2}$$

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

$$\text{concentration (ppm)} = \frac{\text{mass of solute x } 10^6}{\text{mass of solution}}$$

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Moles calculations

1 Work out the number of moles of anything you can.
2 Use the chemical equation to work out the number of moles of the quantity you require.
3 Convert moles to the required quantity – volume, mass etc.

Use the limiting reactant to determine the amount of products in a reaction.

To find the limiting reactant in a reaction, divide the number of moles of each reactant by its coefficient. The lowest number indicates the limiting reactant.

1 mol is the amount of substance which contains the same number of particles as there are carbon atoms in 12 g of ^{12}C.

Avogadro's constant $(L) = 6.02 \times 10^{23}\ \text{mol}^{-1}$

$$\text{mass of 1 molecule} = \frac{\text{molar mass}}{\text{Avogadro's constant}}$$

$$\text{number of moles} = \frac{\text{mass of substance}}{\text{molar mass}}$$

molar mass $= M_r$ in g mol^{-1}

Relative molecular mass (M_r): sum of all A_r values in a molecule.

Relative atomic mass (A_r): average of the masses of the isotopes in a naturally occurring sample of the element relative to $\frac{1}{12}$ mass of a ^{12}C atom.

Empirical formula: simplest whole number ratio of the elements present in a compound.

Molecular formula: total number of atoms of each element present in a molecule of the compound.

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

2 Atomic structure

Learning objectives

- Understand that an atom is made up of protons, neutrons and electrons
- Define mass number, atomic number and isotope
- Work out the numbers of protons, neutrons and electrons in atoms and ions
- Discuss the properties of isotopes
- Calculate relative atomic masses and abundances of isotopes
- Understand that a mass spectrometer can be used to determine the isotopic composition of a sample

2.1 The nuclear atom

There are approximately 92 naturally occurring elements, plus several more that have been made artificially in nuclear reactions, and probably a few more that have yet to be discovered. As far as we know, there are no more naturally occurring elements – these are the only elements that make up our universe.

Chemistry is the study of how **atoms** of the various elements are joined together to make everything we see around us. It is amazing when one imagines that the entire Universe can be constructed through combinations of these different elements. With just 92 different building blocks (and in most cases many fewer than this), objects as different as a table, a fish and a piece of rock can be made. It is even more amazing when one realises that these atoms are made up of three subatomic ('smaller than an atom') particles, and so the whole Universe is made up of combinations of just three things – protons, neutrons and electrons.

2.1.1 Atoms

> In the simplest picture of the atom the negatively charged electrons orbit around the central, positively charged nucleus (Figure **2.1**). The nucleus is made up of protons and neutrons (except for a hydrogen atom, which has no neutrons).

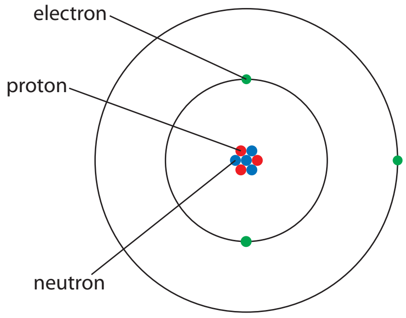


Figure 2.1 A simple representation of a lithium atom (not to scale).

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

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. Relative masses and charges, shown in Table **2.1**, are used to compare the masses of particles more easily. 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. The mass of an electron is often regarded as negligible.

From these values it can be seen that virtually all the mass of the atom is concentrated in the nucleus. However, 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} 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.

Protons and neutrons are made up of other particles called quarks.

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 will 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 them?

The **atomic number** (*Z*) defines an element – it is unique to that particular element. For example, the element with atomic number 12 is carbon and that with atomic number 79 is gold. 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.

The overall charge on an atom is zero and therefore:

number of protons in an atom = number of electrons

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

Mass number (*A*) is the number of protons plus neutrons in the nucleus of an atom.

Therefore:

number of neutrons in an atom = mass number − atomic number

The full symbol of an element includes the atomic number and the mass number (see Figure **2.2**). For example, sodium has an atomic number of 11 and a mass number of 23. The nucleus of a sodium atom contains 11 protons and 12 neutrons (23 − 11). Surrounding the nucleus are 11 electrons. The symbol for sodium is ${}^{23}_{11}\text{Na}$.

Ions

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

A **positive** ion (cation) is formed when an atom **loses** (an) **electron**(s) so that the ion has more protons(+) than electrons(−) (Figure **2.3**). A **negative** ion (anion) is formed when an atom **gains** (an) **electron**(s) so that the ion has more electrons(−) than protons(+).

Democritus and his teacher Leucippus, fifth-century BC Greek philosophers, are often credited with first suggesting the idea of the atom as the smallest indivisible particle of which all matter is made.

John Dalton (1766–1844) is generally regarded as the founder of modern atomic theory.

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

The electron was discovered in 1897 by J. J. Thompson at the University of Cambridge, UK.

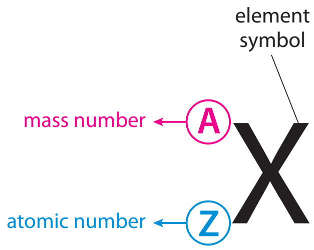


Figure 2.2 Where to place the mass number (*A*) and atomic number (*Z*) in the full symbol of an element.

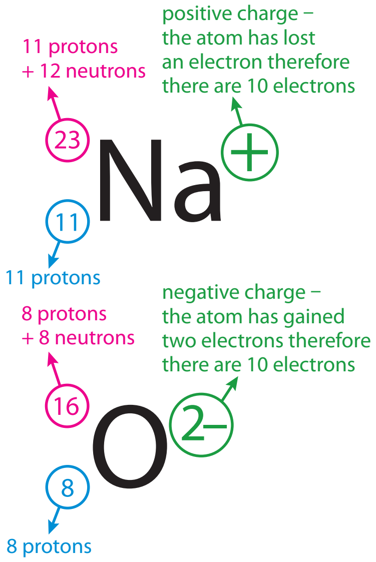


Figure 2.3 The number of subatomic particles in the Na^+ and O^{2-} ions.

2.1.2 Isotopes

The mass number of chlorine is given in many periodic tables as 35.5. It is not possible to have half a neutron – the mass number that is given is an average, taking into account the presence of isotopes.

> **Isotopes are different atoms of the same element with different mass numbers: i.e. different numbers of neutrons in the nucleus.**

The two isotopes of chlorine are ^{35}Cl (chlorine-35) and ^{37}Cl (chlorine-37). Most naturally occurring samples of elements are composed of a mixture of isotopes, but 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 common isotopes.

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).

> **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).**

Isotopes react in the same way because they have the same numbers of electrons, and chemical reactions depend only on the number and arrangement of electrons and not on the composition of the nucleus. For example, both protium and deuterium would react in the same way with nitrogen:

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

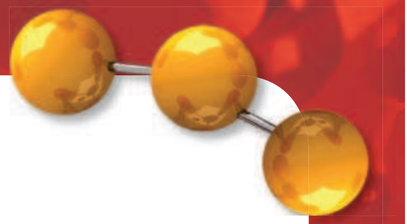
Isotopes have different physical properties because, for example, the different masses mean that their atoms move at different speeds. The boiling point of $^{1}H_2$ is −253 °C, whereas that of $^{2}H_2$ is −250 °C. Heavy water (D_2O) has a melting point of 3.8 °C and a boiling point of 101.4 °C.

Nature of science

In science, things change! Science is an ever changing and increasing body of knowledge. This is what Richard Feynman meant when he talked about science as '… *the belief in the ignorance of experts*'.

An important example of how knowledge and understanding have changed is the development of atomic theory. Since the days of John Dalton (1766–1844) our view of the world around us has changed dramatically. These developments have happened through careful observation and experiment and have gone hand-in-hand with improvements in equipment and the development of new technology.

Radioactivity was discovered towards the end of the 19th century and this gave scientists a new tool to probe the atom. In a famous experiment Geiger and Marsden subjected a thin film of metal foil to a beam of alpha particles (helium nuclei, $^{4}He^{2+}$) and found that some of the particles were reflected back at large angles. Their experimental data allowed Rutherford to develop the theory of the nuclear atom.



The discovery of subatomic particles (protons, neutrons and electrons) in the late nineteenth and early twentieth centuries necessitated a paradigm shift in science and the development of much more sophisticated theories of the structure of matter.

Test yourself

1 Give the number of protons, neutrons and electrons in the following atoms:

${}^{238}_{92}\mathrm{U}$ ${}^{75}_{33}\mathrm{As}$ ${}^{81}_{35}\mathrm{Br}$

2 Give the number of protons, neutrons and electrons in the following ions:

${}^{40}_{20}\mathrm{Ca}^{2+}$ ${}^{127}_{53}\mathrm{I}^{-}$ ${}^{140}_{58}\mathrm{Ce}^{3+}$

3 If you consider the most common isotopes of elements as given in a basic periodic table, how many elements have more protons than neutrons in an atom?

4 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?

Relative atomic masses

Because of the different isotopes present, it is most convenient to quote an average mass for an atom – this is the **relative atomic mass (A_r)**.

> The relative atomic mass (A_r) of an element is the average of the masses of the isotopes in a naturally occurring sample of the element relative to the mass of $\frac{1}{12}$ of an atom of carbon-12.

How to calculate relative atomic mass

Worked examples

2.1 Lithium has two naturally occurring isotopes:

${}^{6}\mathrm{Li}$: natural abundance 7% ${}^{7}\mathrm{Li}$: 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.

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

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 that have 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: $\dfrac{191x+193(100-x)}{100}$

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

$$191x+193(100-x)=19\,222$$

$$191x+19\,300-193x=19\,222$$

$$-2x=19\,222-19\,300$$

$$-2x=-78$$

Therefore $x=39$.

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

Alternatively:

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

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

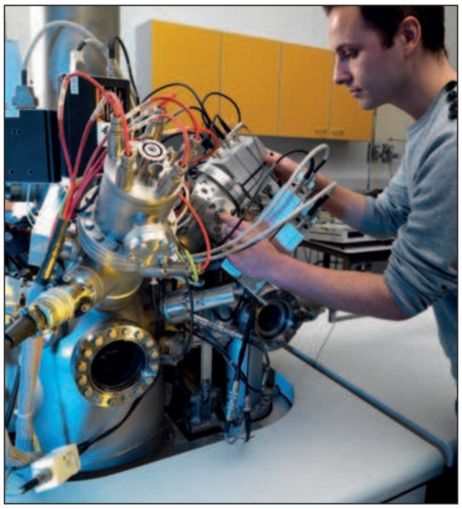


Figure 2.4 Setting up a mass spectrometer.

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 **2.4**).

The readout from a mass spectrometer is called a mass spectrum. In a 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 **2.5**.

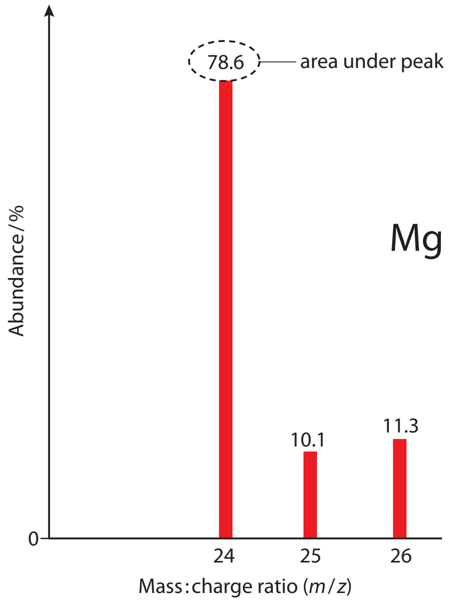


Figure 2.5 The mass spectrum of magnesium showing the amounts of the different isotopes present.

The scale on the x-axis in a mass spectrum is the mass : charge ratio (m/z or m/e). In order to pass through a mass spectrometer, atoms are bombarded with high-energy electrons to produce positive ions. Sometimes more than one electron is knocked out of the atom, which means that the ions behave differently, as if they have smaller masses – 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 (the mass of the electron removed is negligible).

The relative atomic mass can be calculated using:

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

? Test yourself

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

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.

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

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.

7 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.

Learning objectives

- Describe the electromagnetic spectrum
- Describe the emission spectrum of hydrogen
- Explain how emission spectra arise

2.2 Electron configuration

2.2.1 The arrangement of electrons in atoms

At the simplest level of explanation, the electrons in an atom are arranged in **energy levels** (**shells**) around the nucleus. For example, the electron arrangement of potassium can be represented as shown in Figure **2.6** and is written as 2,8,8,1 (or 2.8.8.1).

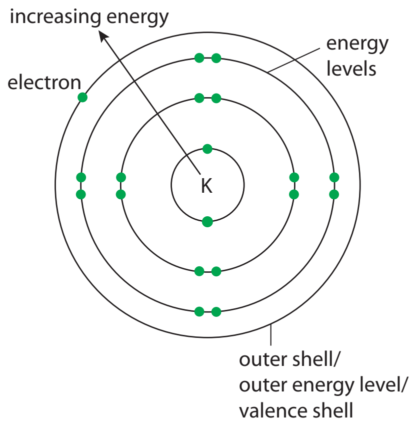


Figure 2.6 The electron arrangement of potassium.

The lowest energy level, called the first energy level or first shell (sometimes also called the K shell), is the one closest to the nucleus. The shells increase in energy as they get further from the nucleus. The maximum number of electrons in each main energy level is shown in Table **2.3**.

The main energy level number is sometimes called the **principal quantum number** and is given the symbol n. The maximum number of electrons in each shell is given by $2n^2$.

main energy level number	1	2	3	4	5
maximum number of electrons	**2**	**8**	**18**	**32**	**50**

Table 2.3 Distribution of electrons in energy levels.

> The general rule for filling these energy levels is that the electrons fill them from the lowest energy to the highest (from the nucleus out). The first two energy levels must be completely filled before an electron goes into the next energy level. The third main energy level is, however, only filled to 8 before electrons are put into the fourth main energy level. This scheme works for elements with atomic number up to 20.

The electromagnetic spectrum

Light is a form of energy. Visible light is just one part of the electromagnetic spectrum (Figure **2.7**).

> $\text{frequency} \propto \dfrac{1}{\text{wavelength}}$

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

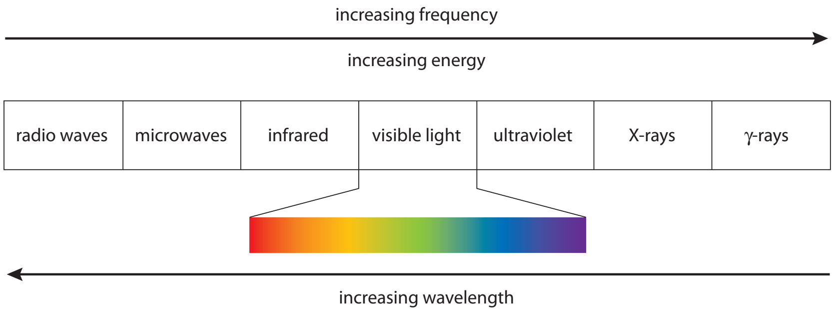


Figure 2.7 The electromagnetic spectrum.

The various forms of electromagnetic radiation are usually regarded as waves that travel at the speed of light in a vacuum ($3.0 \times 10^8\ \mathrm{m\,s^{-1}}$) but vary in their frequency/energy/wavelength.

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 radiation called **photons**.

White light is visible light made up of all the colours of the spectrum. In order of increasing energy, the colours of the spectrum are:
red < orange < yellow < green < blue < indigo < violet.

Would our interpretation of the world around us be different if our eyes could detect light in other regions of the electromagnetic spectrum?

Are there really seven colours in the visible spectrum?

Evidence for energy levels in atoms

The hydrogen atom spectrum

When hydrogen gas at low pressure is subjected to a very high voltage, the gas glows pink (Figure **2.8**). The glowing gas can be looked at through a **spectroscope**, which contains a diffraction grating and separates the various wavelengths of light emitted from the gas. Because light is emitted by the gas, this is called an **emission spectrum**.

In the visible region, the spectrum consists of a series of sharp, bright lines on a dark background (Figure **2.9**). This is a **line spectrum**, as opposed to a **continuous spectrum**, which consists of all the colours merging into each other (Figure **2.10**).

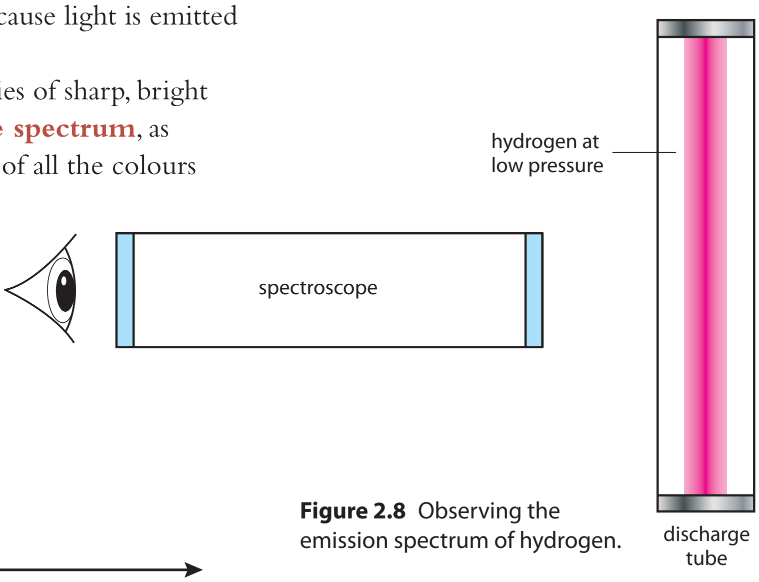


Figure 2.8 Observing the emission spectrum of hydrogen.

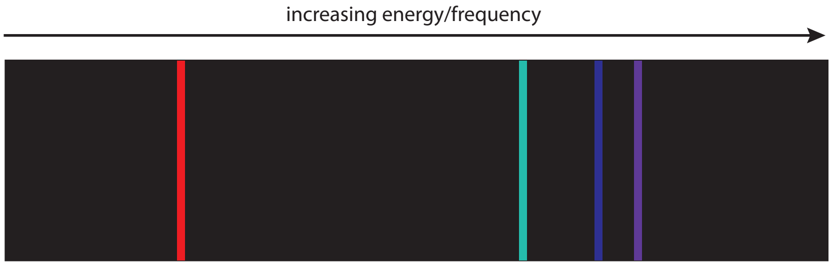


Figure 2.9 A representation of the atomic emission spectrum of hydrogen.

The lines get closer together at higher frequency/energy.

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

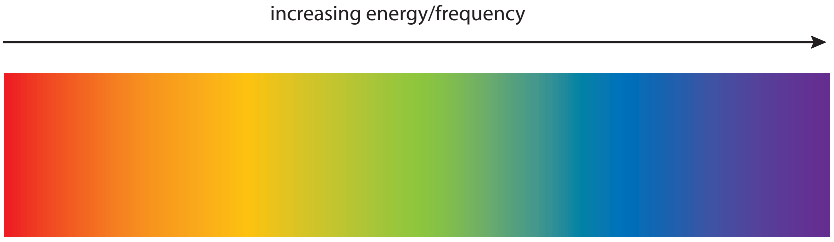


Figure 2.10 A continuous spectrum.

Line spectrum – only certain frequencies/wavelengths of light present.
Continuous spectrum – **all** frequencies/wavelengths of light present.

How an emission spectrum is formed

Passing an electric discharge through a gas causes an electron to be **promoted to a higher energy level** (shell) (Figure **2.11**).

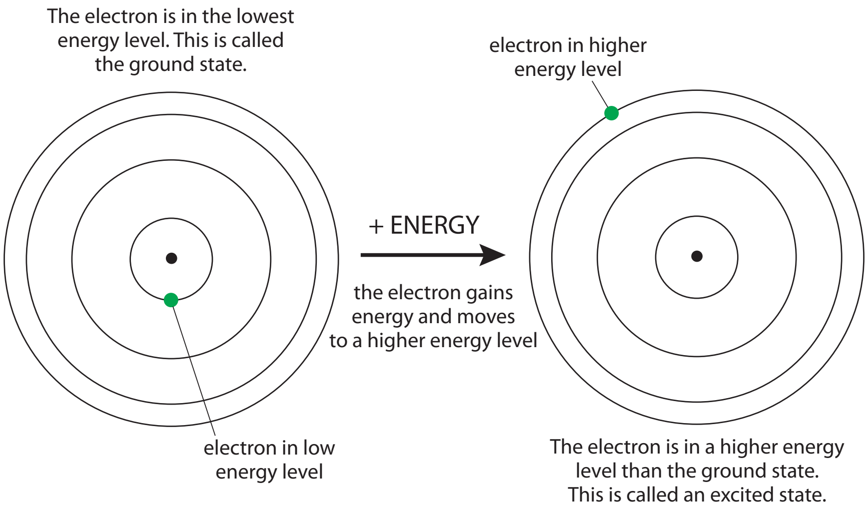


Figure 2.11 An electron can be promoted to a higher energy level in a discharge tube.

The electron is unstable in this higher level and will **fall to a lower energy level** (Figure **2.12**). As it returns from a level at energy E_2 to E_1, the extra energy $(E_2 - E_1)$ is given out in the form of a photon of light. This contributes to a line in the spectrum.

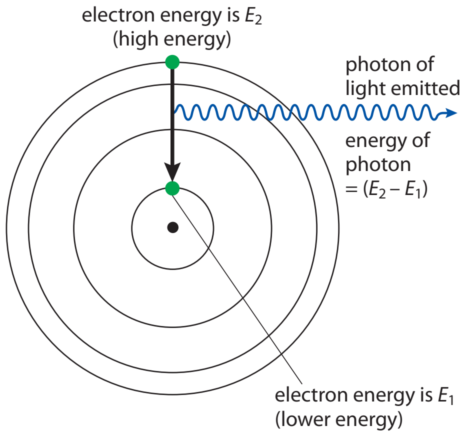


Figure 2.12 When an electron falls from a higher to a lower energy level in an atom, a photon of light is emitted.

The energy levels can also be shown as in Figure **2.13**.

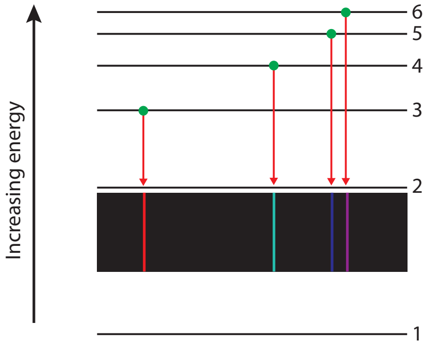


Figure 2.13 How the lines arise in the emission spectrum of hydrogen.

The fact that a line spectrum is produced provides evidence for electrons being in energy levels (shells): i.e. electrons in an atom are allowed to have only certain amounts of energy (Figure **2.14**).

Because light is given out, this type of spectrum is an emission spectrum.

Each line in the spectrum comes from the transition of an electron **from a high energy level to a lower one.**

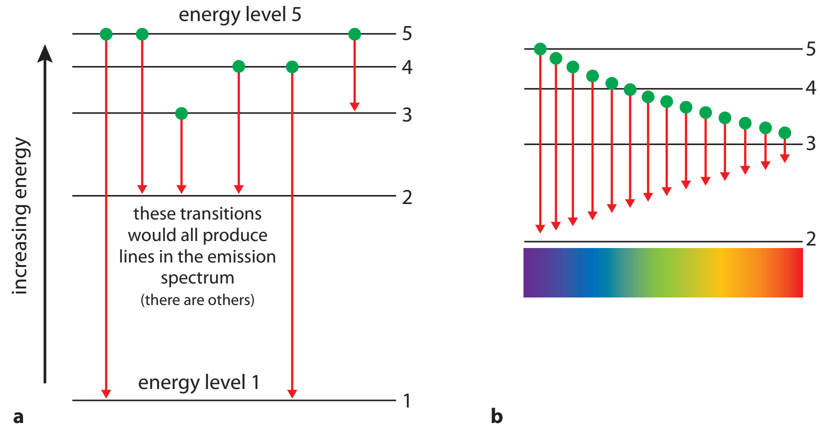


Figure 2.14 **a** Electrons in energy levels: only transitions between two discrete energy levels are possible, and a line spectrum is produced. **b** If the electrons in an atom could have any energy, all transitions would be possible. This would result in a continuous spectrum.

Different series of lines

Figure **2.15** 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.

> The different series of lines occur when electrons fall back down to different energy levels.

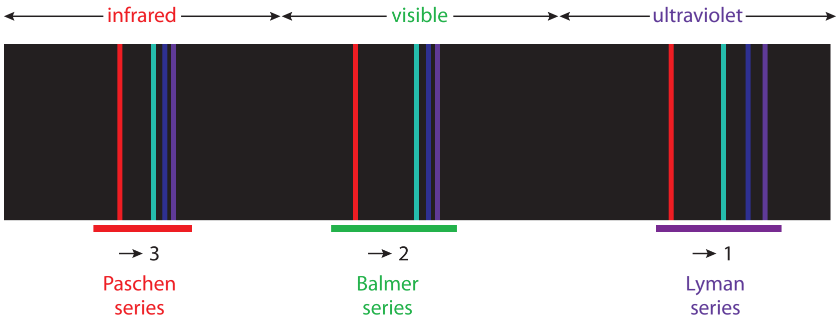


Figure 2.15 A representation of the emission spectrum of hydrogen. The colours and lines in the spectrum in the infrared and ultraviolet regions are just for illustrative purposes.

All the transitions that occur in the visible region of the spectrum (those we can see) involve electrons falling down to level 2 (creating the Balmer series). All transitions down to level 1 occur in the ultraviolet region. Therefore we can deduce that the energy difference between level 1 and any other level is bigger than that between level 2 and any other higher 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 also influences the electron energy levels.

Infrared and ultraviolet radiation can be detected only with the aid of technology – we cannot interact with them directly. Does this have implications as to how we view the knowledge gained from atomic spectra in these regions?

Exam tip
The names of the series do not have to be learnt for the examination.

Convergence

The lines in the emission spectrum get closer together at higher frequency/energy (Figure **2.16**).

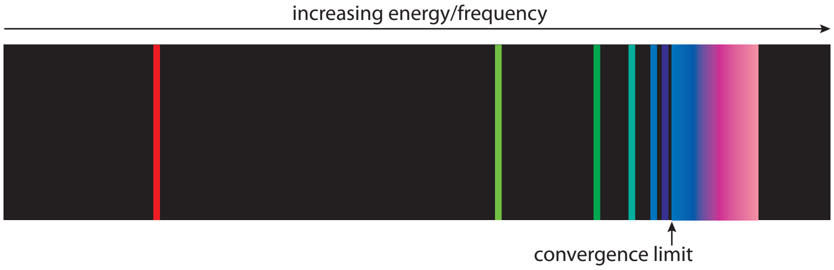


Figure 2.16 A representation of the Lyman series of hydrogen in the ultraviolet region of the electromagnetic spectrum.

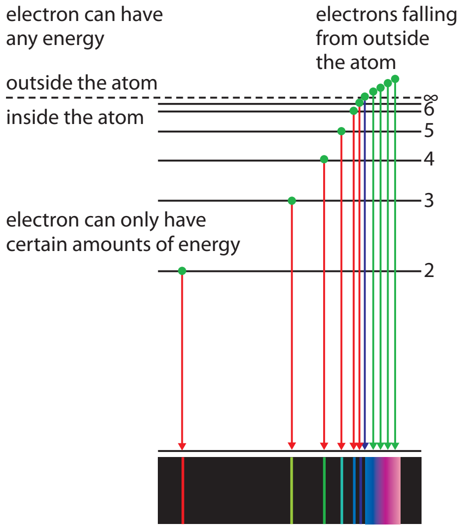


Figure 2.17 The purple arrow represents the transition giving rise to the convergence limit in the Lyman series for hydrogen.

Eventually, at the **convergence limit**, the lines merge to form a **continuum**. 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 **2.17**).

Extension

The convergence limit is not usually observed, but the frequency can be worked out by plotting a graph of the difference in frequency of successive lines against their frequency and extrapolating the graph to give the frequency when the difference in frequency between successive lines is zero.

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 a model for the atom in which electrons orbit the nucleus and only exist in certain allowed energy levels. He then used this model to explain the line spectra of hydrogen and other elements.

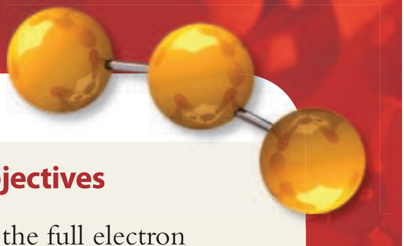
? Test yourself

8 Arrange the following in order of:
- **a** increasing energy
- **b** decreasing wavelength

ultraviolet radiation **infrared radiation**
microwaves **orange light** **green light**

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

10 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:
- **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.



2.2.2 Full electron configurations

Learning objectives

- Determine the full electron configuration of atoms with up to 36 electrons
- Understand what is meant by an orbital and a subshell (sub-energy level)

The emission spectra of atoms with more than one electron, along with other evidence such as ionisation energy data (see later), suggest that the simple treatment of considering that electrons in atoms occupy only main energy levels is a useful first approximation but it can be expanded.

Sub-energy levels and orbitals

Each main energy level in an atom is made up of **sub-energy 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 **2.4**.

Main energy level	Sub-levels				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 2.4 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, but there are sometimes reversals of orders between sub-levels in different energy levels. The relative energies of the subshells are shown in Figure **2.18**.

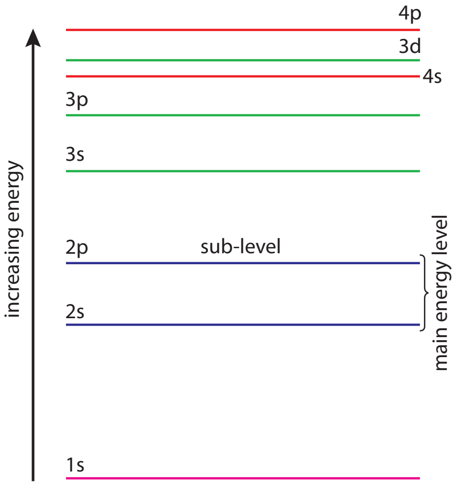


Figure 2.18 The ordering of the energy levels and sub-levels within an atom. The sub-levels within a main energy level are shown in the same colour.

The Aufbau (building-up) principle (part 1)

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

> Electrons fill sub-levels from the lowest energy level upwards – this gives the lowest possible (potential) energy.

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 **2.19**). This can also be abbreviated to $[Ne]3s^1$, where the electron configuration of the previous noble gas is assumed and everything after that is given in full.

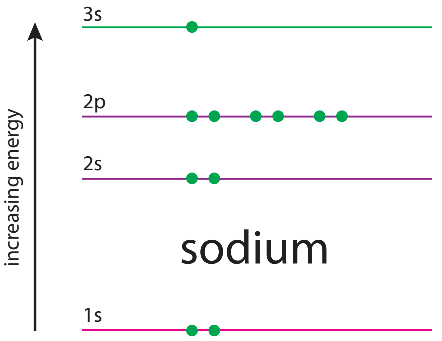


Figure 2.19 The arrangement of electrons in energy levels for a sodium atom.

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

from neon

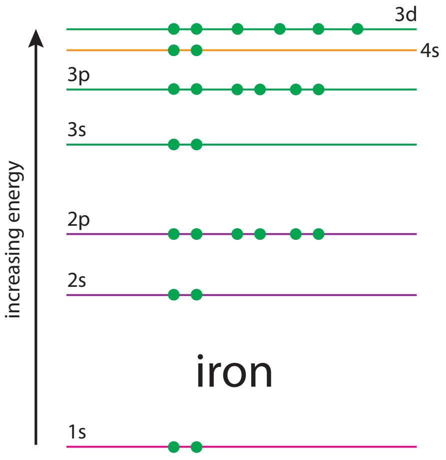


Figure 2.20 The arrangements of electrons in energy levels for an iron atom.

The full electron configuration of iron (26 electrons) is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ (Figure **2.20**). Note that because the 4s sub-level is lower in energy than the 3d sub-level, it is filled first. In other words, two electrons go into the fourth main energy level before the third main energy level is filled. This can be written as $[Ar]4s^2 3d^6$.

This is sometimes written as $[Ar]3d^6 4s^2$ to keep the sub-levels in order of the main energy levels.

The full electronic configuration of germanium (32 electrons) is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$. Or, in abbreviated form: $[Ar]4s^2 3d^{10} 4p^2$.

The order in which the sub-levels are filled can be remembered most easily from the periodic table. For example, Selenium (Se) is in period 4 and 4 along in the p block – therefore the last part of the electron configuration is $4p^4$. The full electron configuration can be worked out by following the arrows in Figure **2.21**:

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 in the d block)

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

Figure **2.22** shows an alternative way of remembering the order in which sub-levels are filled.

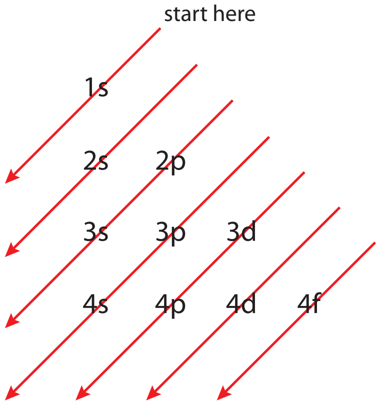


Figure 2.22 Draw out the sub-levels in each main energy level. Starting at 1s, follow the arrows to give the ordering of the sub-levels.

Note: all the atoms in the same group (vertical column) of the periodic table have the same outer shell electron configuration. For example, all the elements in group 16 (like Se) have the outer shell electron configuration $ns^2 np^4$, where n is the period number.

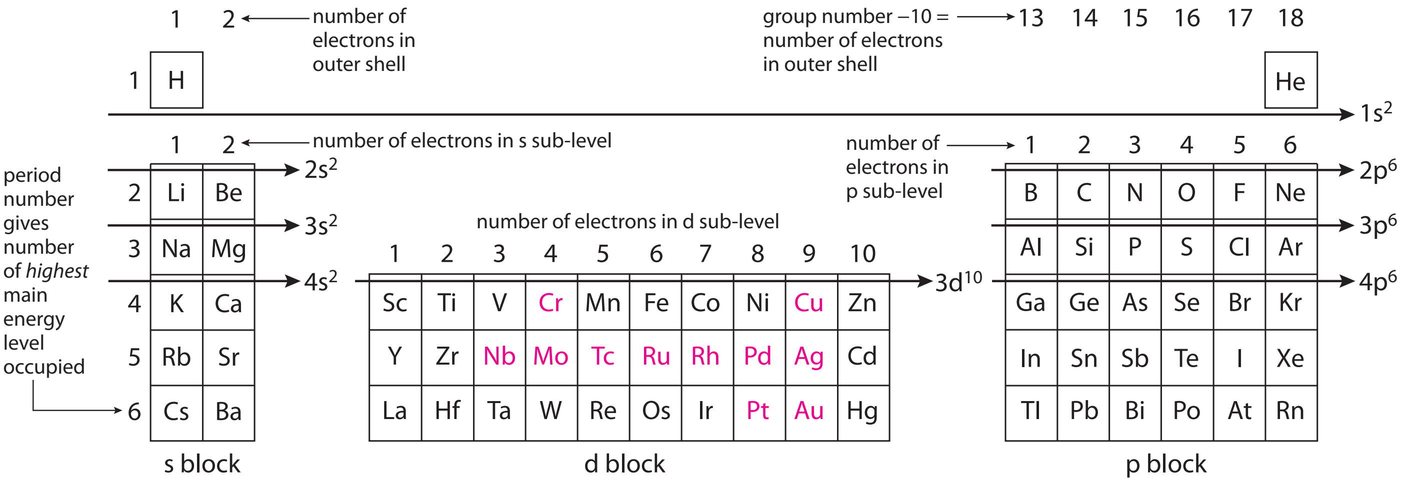


Figure 2.21 Electron configurations can be worked out from the periodic table. The 'p block' is so named because the highest occupied sub-level is a p sub-level. The period number indicates the highest occupied main energy level. Some exceptions to the general rules for filling sub-levels are highlighted in pink. Helium has the configuration $1s^2$ and has no p electrons, despite the fact that it is usually put in the p block.

Test yourself

11 Give the full electron configurations of the following atoms:

a N
b Si
c Ar
d As
e V

Orbitals

Electrons occupy atomic orbitals in atoms.

> An **orbital** is a region of space in which there is a high probability of finding an electron. It represents a discrete energy level.

> An orbital can contain a maximum of two electrons.

There are four different types of atomic orbital: **s** **p** **d** **f**

The first shell (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 **2.23a**).

The 1s orbital is centred on the nucleus (Figure **2.23b**). 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 (like all other s orbitals) is spherical in shape and bigger than the 1s orbital (Figure **2.24**).

p orbitals have a 'dumb-bell' shape (Figure **2.25**). Three p orbitals make up the 2p sub-level. These lie at 90° to each other and are named appropriately as p_x, p_y, p_z (Figure **2.26**). The p_x orbital points along the x-axis. The three 2p orbitals all have the same energy – they are described as **degenerate**.

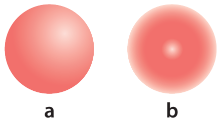


Figure 2.23 **a** The shape of a 1s orbital; **b** the electron density in a 1s orbital.

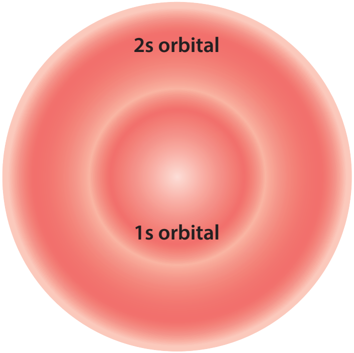


Figure 2.24 A cross section of the electron density of the 1s and 2s orbitals together.

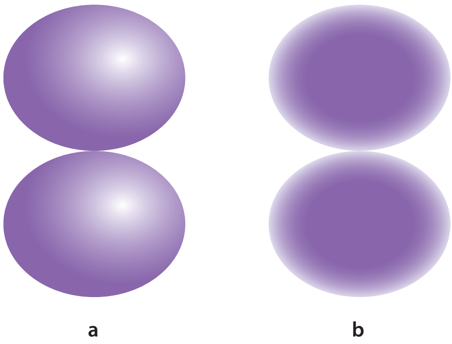


Figure 2.25 **a** The shape of a 2p orbital; **b** the electron density in a 2p orbital.

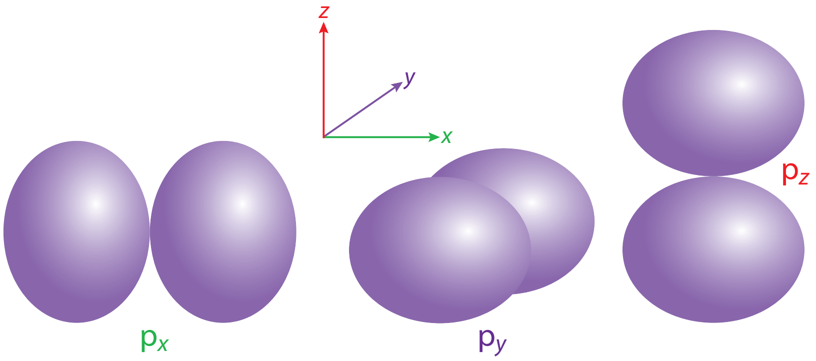


Figure 2.26 The three p orbitals that make up a p sub-level point at 90° to each other.

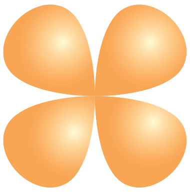


Figure 2.28 One of the five d orbitals in the 3d sub-level.

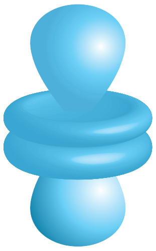


Figure 2.29 One of the f orbitals in the 4f sub-level.

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

Table 2.5 The number of orbitals in each energy level.

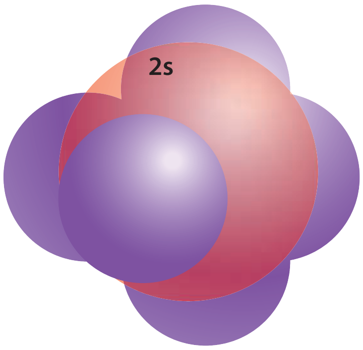


Figure 2.27 The 2s and 2p sub-levels in the second main energy level.

Figure **2.27** shows the orbitals that make up the 2s and 2p sub-levels in the second main energy level.

The third shell (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 **2.28**.

The fourth shell (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 **2.29**.

> Within any subshell, all the orbitals have the same energy (they are **degenerate**) – e.g. the three 2p orbitals are degenerate and the five 3d orbitals are degenerate.

The number of orbitals in each energy level is shown in Table **2.5**.

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.

Electrons can be regarded as either spinning in one direction (clockwise);

↑

or in the opposite direction (anticlockwise).

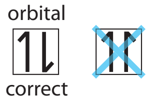
↓

Putting electrons into orbitals – the Aufbau principle (part 2)

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

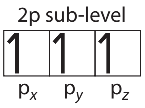
There are two rules that must be considered before electrons are put into orbitals.

1 **The Pauli exclusion principle:** the maximum number of electrons in an orbital is two. If there are two electrons in an orbital, they must have opposite spin.



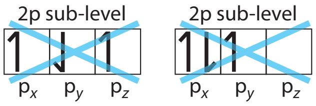
2 **Hund's rule:** electrons fill orbitals of the same energy (degenerate orbitals) so as to give the maximum number of electrons with the same spin.

Here we can see how three electrons occupy the orbitals of the 2p sub-level:



Exam tip
These diagrams are sometimes described as 'orbital diagrams', 'arrows in boxes' or 'electrons in boxes'.

By contrast, these higher energy situations do not occur:



Figures **2.30a** and **b** show the full electron configuration of oxygen and silicon atoms, respectively.

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 $[Ar]3d^n4s^2$ have only one electron in the 4s sub-level:

$_{24}Cr: [Ar]3d^5 4s^1$ $_{29}Cu: [Ar]3d^{10}4s^1$

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 orbitals gives a lower energy (more stable) situation.

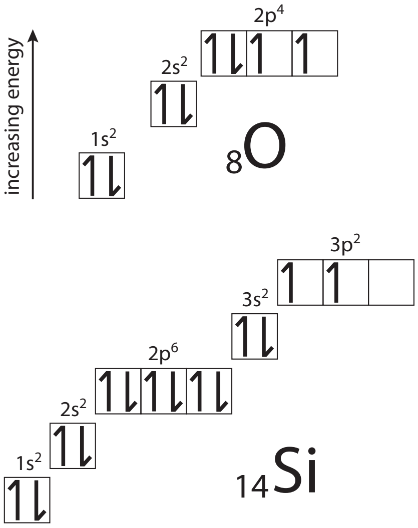


Figure 2.30 Electron configuration: **a** oxygen; **b** silicon.

Nature of science

Scientific theories are constantly being modified, improved or replaced as more data become available and the understanding of natural phenomena improves. The most up-to-date theory of the structure of the atom involves quantum mechanics and this has replaced previous theories.

Developments in apparatus and techniques have been essential in the advancement of science. For instance, J.J. Thomson used electric and magnetic fields to investigate the properties of cathode rays, which led to the discovery of the electron.

? Test yourself

12 Draw out the full electron configurations of the following atoms, showing electrons in boxes:
a C **b** P **c** Cr

Learning objectives

- Solve problems using $E = h\nu$
- Explain successive ionisation data for elements
- Explain the variation in first ionisation energy across a period and down a group

2.3 Electrons in atoms (HL)

2.3.1 Ionisation energy and the convergence limit

As discussed on page **66**, the lines in the emission spectrum of an atom get closer together at higher frequency/energy.

Eventually, at the convergence limit, the lines merge to form a continuum. 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 **2.17** on page **66**). Knowing the frequency of the light emitted at the convergence limit enables us us to work out the **ionisation energy** of an atom – the energy for the process:

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

> **The ionisation energy is the minimum amount of energy required to remove an electron from a gaseous atom.**

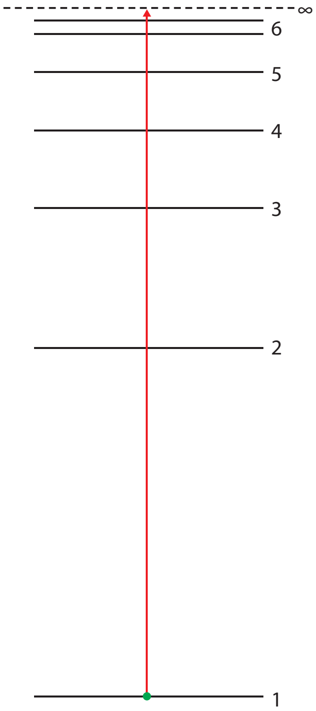


Figure 2.31 The ionisation process in a hydrogen atom.

The ionisation energy for hydrogen represents the minimum energy for the removal of an electron (from level 1 to ∞) (Figure **2.31**), and the frequency of the convergence limit in the Lyman series represents the amount of energy given out when an electron falls from outside the atom to level 1 (∞ to 1). These are therefore the same amount of energy.

The relationship between the energy of a photon and the frequency 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:

$$E = h\nu$$

where

ν is the frequency of the light (Hz or s^{-1})
h is Planck's constant (6.63×10^{-34} J s)

This equation can be used to work out the differences in energy between various levels in the hydrogen atom.

Worked example

2.3 The frequency of a line in the visible emission spectrum of hydrogen is 4.57×10^{14} Hz. Calculate the energy of the photon emitted.

$E = h\nu$

Therefore $E = 6.63 \times 10^{-34} \times 4.57 \times 10^{14}$

$= 3.03 \times 10^{-19}$ J

This line in the spectrum represents an electron falling from level 3 to level 2 and so the energy difference between these two levels is 3.03×10^{-19} J.

The wavelength of the light can be worked out from the frequency using the equation:

$$c = \nu\lambda$$

where
λ is the wavelength of the light (m)
c is the speed of light ($3.0 \times 10^8\,\mathrm{m\,s^{-1}}$)

The two equations $E = h\nu$ and $c = \nu\lambda$ can be combined:

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

This relates the energy of a photon to its wavelength.

Worked example

2.4 If the frequency of the convergence limit in the Lyman series for hydrogen is 3.28×10^{15} Hz, calculate the ionisation energy of hydrogen in $\mathrm{kJ\,mol^{-1}}$.

$$E = h\nu$$

$$\text{Therefore E} = 6.63 \times 10^{-34} \times 3.28 \times 10^{15}$$

$$= 2.17 \times 10^{-18}\,\mathrm{J}$$

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 Avogadro's constant.

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

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

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.

Ionisation energy and evidence for energy levels and sub-levels

The **first** ionisation energy for an element is the energy for the process:

$$\mathrm{M(g)} \rightarrow \mathrm{M^+(g)} + \mathrm{e^-}$$

The full definition is **the energy required to remove one electron from each atom in one mole of gaseous atoms under standard conditions**, but see later.

The **second** ionisation energy is:

$$M^{+}(g) \rightarrow M^{2+}(g) + e^{-}$$

The ***n*th** ionisation energy is:

$$M^{(n-1)+}(g) \rightarrow M^{n+}(g) + e^{-}$$

The highest energy electrons are removed first. Figure **2.32** shows this for potassium, in which the highest energy electron is the $4s^1$, and this is the first to be removed:

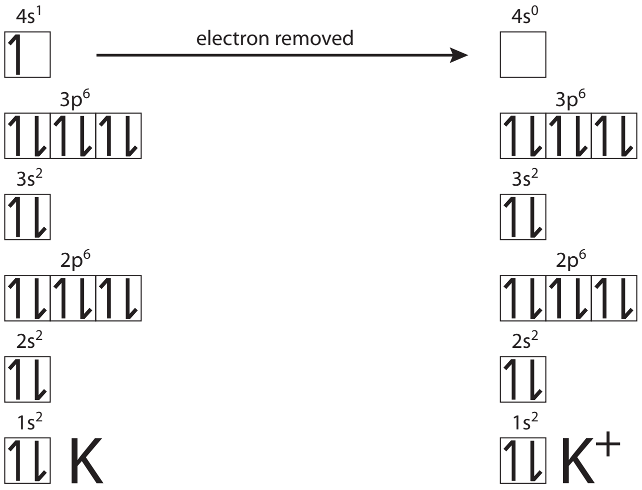


Figure 2.32 The first ionisation of potassium.

The second ionisation energy 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 **2.33**). If they are closer to the nucleus, they are more strongly attracted and more difficult to remove.

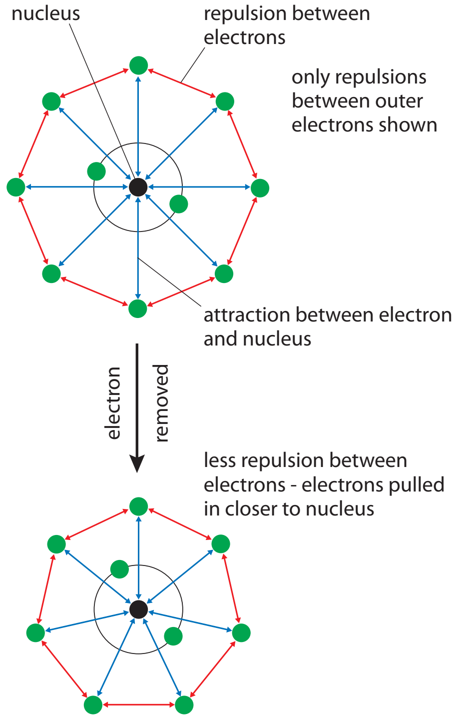


Figure 2.33 When an electron is removed from an atom, the remaining electrons are drawn closer to the nucleus due to reduced repulsion.

Successive ionisation energies of potassium

The graph in Figure **2.34** shows the energy required to remove each electron in turn from a gaseous potassium atom.

The simple electron arrangement of potassium is 2,8,8,1 and this can be deduced directly from Figure **2.34**. The large jumps in the graph occur between the main energy levels (shells).

The outermost electron in potassium is furthest from the nucleus and therefore least strongly attracted by the nucleus – so this electron is easiest to remove. It is also **shielded** (screened) from the full attractive force of the nucleus by the other 18 electrons in the atom (Figure **2.35**).

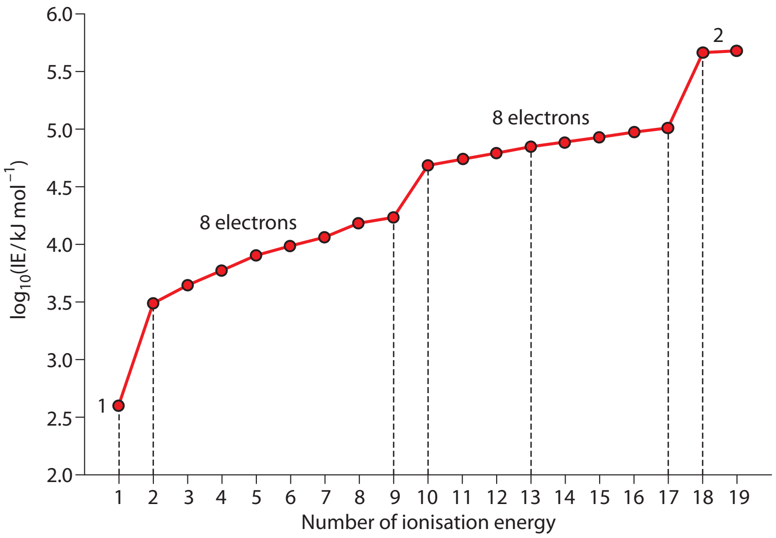


Figure 2.34 Successive ionisation energies (IE) for potassium.

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.

A log scale is used here 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 support the explanations that have been given, it has also distorted the data. The difference between the first and second 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}! How can the way data are presented be used by scientists to support their theories? Can you find examples where the scale on a graph has been chosen to exaggerate a particular trend – 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.

Complete shells of electrons between the nucleus and a particular electron reduce the attractive force of the nucleus for that electron. There are three full shells of electrons between the outermost electron and the nucleus, and if this shielding were perfect the **effective nuclear charge** felt by the outer electron would be 1+ (19+ in nucleus − 18 shielding electrons). 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.

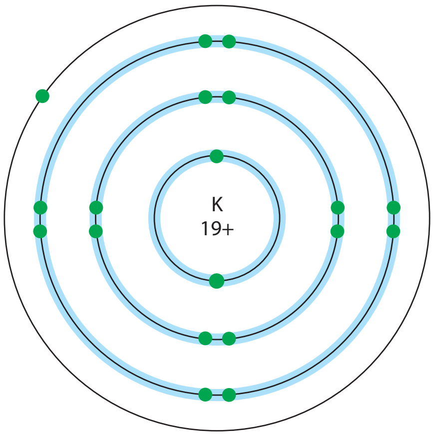


Figure 2.35 The outer electron in a potassium atom is shielded from the full attractive force of the nucleus by the inner shells of electrons (shaded in blue).

Extension

In electrostatics, a sphere of charge behaves like a point charge at its centre; therefore relative to the outer electron, spheres of charge inside (the electron shells) behave as if their charge is at the nucleus. The charge felt by the outer electron is (**19+**) + (**18−**) = **1+** acting at the nucleus.

The electrons do not form perfect spheres of charge, and the movement of the outer electron is not simply in an orbit around the nucleus as shown, and this is why the effective nuclear charge felt by the outer electron in potassium is greater than 1. There are various ways of estimating or calculating the effective nuclear charge for a particular electron in an atom (e.g. Slater's rules). Calculations suggest that the effective nuclear charge felt by the outer electron in potassium is about 3.5+.

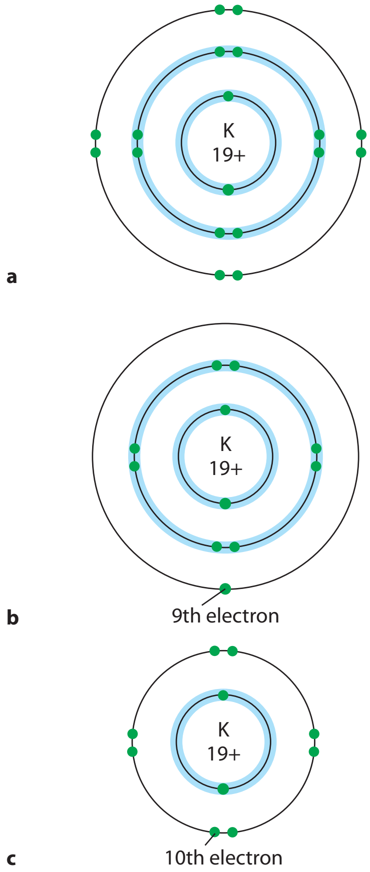


Figure 2.36 The ionisation energy depends on which main energy level the electron is removed from.

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 **2.36a**). It is also shielded by fewer electrons (the ten electrons in the inner main energy levels), because electrons in the same shell do not shield each other very well (they do not get between the electron and 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 the tenth (Figure **2.36b** and **c**) 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 to be removed.

Graphs of successive ionisation energy give us information about how many electrons are in a particular energy level. Consider the graph

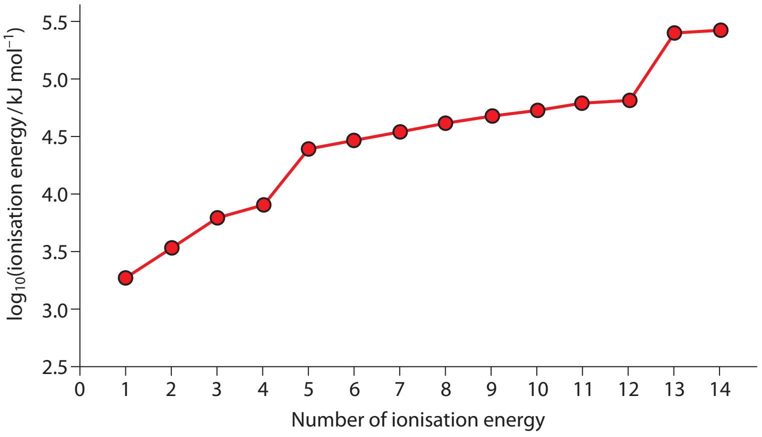


Figure 2.37 The successive ionisation energies of silicon.

for silicon shown in Figure **2.37**. There is a large jump in the ionisation energy between the fourth and the fifth ionisation energies, which suggests that these electrons are removed from different main energy levels. It can therefore be deduced that silicon has four electrons in its outer main energy level (shell) and is in group 14 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 **2.38**). 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 (Figure **2.39**). The 3p sub-level is higher in energy than the 3s sub-level, and therefore less energy is required to remove the electron. This provides evidence for the existence of sub energy levels (subshells) in an atom.

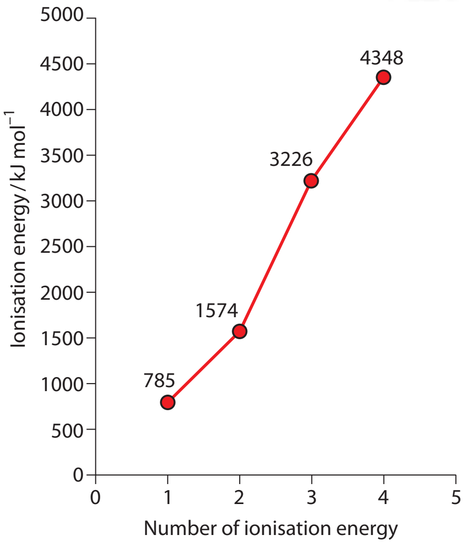


Figure 2.38 The first four ionisation energies of silicon.

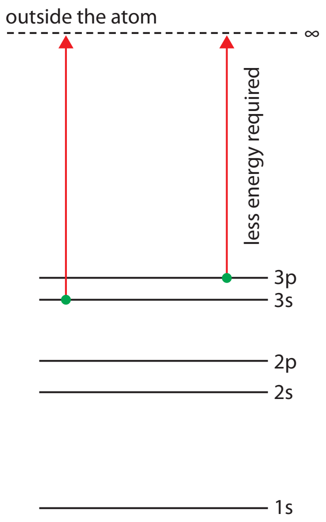


Figure 2.39 More energy is required to remove an electron from the 3s sub-level of silicon than from the 3p sub-level.

Test yourself

13 a The frequency of a line in the emission spectrum of hydrogen is 7.31×10^{14} Hz. Calculate the energy of the photon emitted.

b The energy of a photon is 1.53×10^{-18} J. Calculate the frequency of the electromagnetic radiation.

14 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	1 085	736	1 400
2	2 349	1 448	2 851
3	4 612	7 719	4 570
4	6 212	10 522	7 462
5	37 765	13 606	9 429
6	47 195	17 964	53 174

We are using reasoning to deduce the existence of energy levels in an atom. Do we **know** that energy levels exist?

Variation in ionisation energy across a period

The general trend is that ionisation energy increases from left to right across a period.

The first ionisation energies for the elements in period 2, from lithium to neon, are plotted in Figure **2.40**.

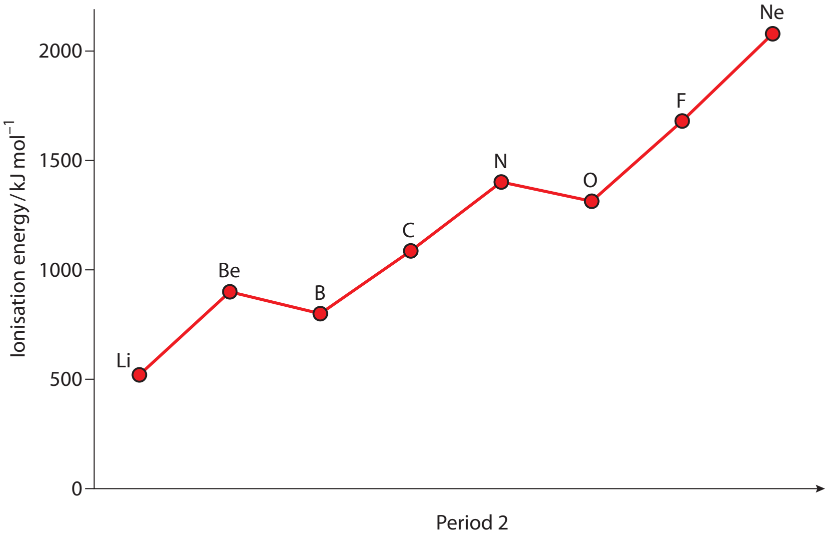


Figure 2.40 The first ionisation energies for the period 2 elements.

The nuclear charge increases from lithium (3+) to neon (10+) as protons are added to the nucleus (Figure **2.41**). The electrons are all removed from the same main energy level and, because electrons in the same energy level do not shield each other very well, there is no big change in shielding. Therefore the attractive force on the outer electrons increases from left to right across the period, and the outer electron is more difficult to remove for neon. The neon atom is also smaller than the lithium atom, and so the outer electron is closer to the nucleus and more strongly held.

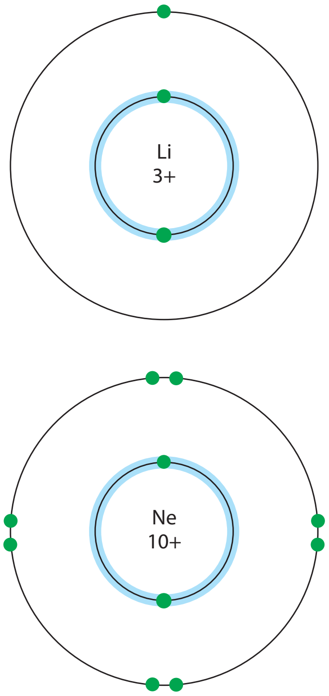


Figure 2.41 Ne has more protons in the nucleus, but the amount of shielding from inner electrons is roughly the same as in lithium.

This can also be explained in terms of the effective nuclear charge felt by the outer electron in neon being higher.

There are two exceptions to the general increase in ionisation energy across a period.

Despite the fact that boron has a higher nuclear charge (more protons in the nucleus) than beryllium the ionisation energy is lower. The electron configurations of beryllium and boron are:

Be $1s^22s^2$ B $1s^22s^22p^1$

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 B is higher in energy than the 2s sub-level in beryllium (Figure **2.42**), and therefore less energy is required to remove an electron from boron.

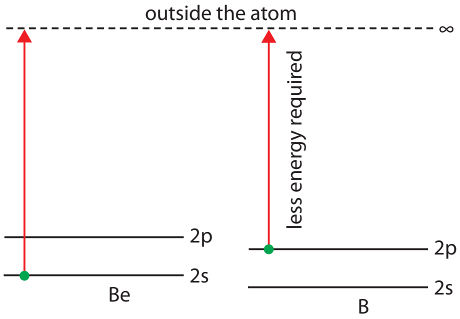


Figure 2.42 The 2p subshell in boron is higher in energy than the 2s subshell in beryllium.

Extension

An alternative, more in-depth, 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 offsets the effect of the increase in nuclear charge. 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 $1s^2 2s^2 2p^3$ 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 **2.43**). 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.

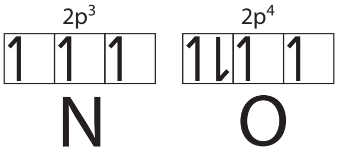


Figure 2.43 Electrons in the 2p sub-level of nitrogen and oxygen.

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.

Down a group in the periodic table the ionisation energy **decreases**.

The variation in first ionisation energy down a group is discussed on page **92**.

The transition metals

The transition metals will be considered in more detail in a later topic, but they are mentioned here for completeness. These elements represent a slight departure from the 'last in, first out' rule for ionisation energy. Although the sub-levels are filled in the order 4s and then 3d, the 4s electrons are always removed before the 3d electrons.

The full electron configuration for an iron atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. The electron configuration for Fe^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$. The electron configuration for Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

Extension

When removing electrons, we should not really think about the order they were put into the atom but consider the stability of the final ion. The electron configuration of the final ion will be that which generates the ion of lowest energy. s electrons are generally better at shielding other electrons than are d electrons; by removing the 4s electrons, the shielding of the remaining 3d electrons is reduced, and these are lowered in energy. If the 3d electrons are removed, there is no real energy advantage in terms of reduced shielding – therefore it is less favourable to remove the 3d electrons. Overall, what this all amounts to is that, in the ion, the 3d sub-level is lower in energy than the 4s orbital.

Nature of science

Theories in science must be supported by evidence. Experimental evidence from emission spectra and ionisation energy is used to support theories about the electron arrangements of atoms.

Test yourself

15 Work out the full electron configurations of the following ions:

a Ca^{2+} **b** Cr^{3+} **c** Co^{2+} **d** Rb^+

Exam-style questions

1 Which of the following contains 50 neutrons?

A $^{50}_{23}\text{V}$
B $^{89}_{39}\text{Y}^{+}$
C $^{91}_{40}\text{Zr}^{+}$
D $^{86}_{37}\text{Rb}^{+}$

2 Which of the following has more electrons than neutrons?

A $^{9}_{4}\text{Be}^{2+}$
B $^{31}_{15}\text{P}^{3-}$
C $^{79}_{35}\text{Br}^{-}$
D $^{40}_{20}\text{Ca}^{2+}$

3 Rhenium has two naturally occurring isotopes, ^{185}Re and ^{187}Re. The relative atomic mass of rhenium is 186.2. What are the natural abundances of these isotopes?

A 40% ^{185}Re and 60% ^{187}Re
B 60% ^{185}Re and 40% ^{187}Re
C 12% ^{185}Re and 88% ^{187}Re
D 88% ^{185}Re and 12% ^{187}Re

4 Which of the following electron transitions in the hydrogen atom will be of highest energy?

A $n=8 \rightarrow n=4$
B $n=7 \rightarrow n=2$
C $n=9 \rightarrow n=3$
D $n=6 \rightarrow n=2$

HL **5** Within any main energy level the correct sequence, when the sub-energy levels (subshells) are arranged in order of increasing energy, is:

A s p f d
B d s f p
C s p d f
D s d p f

HL **6** Which of the following electron configurations is **not** correct?

A Mg: $1s^22s^22p^63s^2$
B Cu: $1s^22s^22p^63s^23p^64s^23d^9$
C Ge: $1s^22s^22p^63s^23p^63d^{10}4s^24p^2$
D Br: $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$

HL **7** Planck's constant is 6.63×10^{-34} J s. The energy of a photon of light with frequency 5.00×10^{14} Hz is:

A 7.54×10^{47} J
B 1.33×10^{-48} J
C 3.32×10^{-19} J
D 1.33×10^{-20} J

HL **8** Which of the following does **not** have three unpaired electrons?

A P
B V
C Mn^{3+}
D Ni^{3+}

HL **9** In which of the following does the second element have a lower first ionisation energy than the first?

A Si C
B Na Mg
C Be B
D Ar Ne

HL **10** The first four ionisation energies of a certain element are shown in the table below.

Number of ionisation energy	Ionisation energy / kJ mol^{-1}
1	418
2	3046
3	4403
4	5866

In which group in the periodic table is this element?

A group 1 **B** group 2 **C** group 13 **D** group 14

11 **a** Define the terms **atomic number** and **isotopes**. **[3]**

b State the number of protons, neutrons and electrons in an atom of $^{57}_{26}$Fe. **[2]**

c A sample of iron from a meteorite is analysed and the following results are obtained.

Isotope	Abundance / %
^{54}Fe	5.80
^{56}Fe	91.16
^{57}Fe	3.04

i Name an instrument that could be used to obtain this data. **[1]**

ii Calculate the relative atomic mass of this sample, giving your answer to two decimal places. **[2]**

12 **a** Describe the difference between a **continuous spectrum** and a **line spectrum**. **[2]**

b Sketch a diagram of the emission spectrum of hydrogen in the visible region, showing clearly the relative energies of any lines. **[2]**

c Explain how a line in the visible emission spectrum of hydrogen arises. **[3]**

HL **d** The frequencies of two lines in the emission spectrum of hydrogen are given in the table. Calculate the energy difference between levels 5 and 6 in a hydrogen atom. **[2]**

Higher level	Lower level	Frequency / Hz
5	3	2.34×10^{14}
6	3	2.74×10^{14}

13 **a** Write the full electron configuration of an atom of potassium. **[1]**

HL **b** Write an equation showing the second ionisation energy of potassium. **[2]**

HL **c** Explain why the second ionisation energy of potassium is substantially higher than its first ionisation energy. **[3]**

HL **d** State and explain how the first ionisation energy of calcium compares with that of potassium. **[3]**

14 **a** Write the full electron configuration of the O^{2-} ion. **[1]**

b Give the formula of an atom and an ion that have the same number of electrons as an O^{2-} ion. **[2]**

HL **c** Explain why the first ionisation energy of oxygen is lower than that of nitrogen. **[2]**

HL **d** Sketch a graph showing the variation of the **second** ionisation energy for the elements in period 2 of the periodic table from lithium to neon. **[3]**

Summary

ATOMS *contain* nucleus *contains* protons — number of protons = atomic number

neutrons — number of neutrons + protons = mass number

electrons

Isotopes are atoms of the same element that have different mass numbers.

can be separated by mass spectrometry

electrons — arranged in energy levels (shells) — filled from lowest to highest energy

To SUBSHELLS on next page

Atomic emission spectra are caused by electrons falling from a higher energy level to a lower one.

line spectra – only certain frequencies are present

spectrum becomes continuous at the **convergence limit**

HL

$E = h\nu$ can be used to work out the ionisation energy of hydrogen from the convergence limit of the Lyman series

HL

To IONISATION ENERGY on next page

series of lines

Lyman series – electron falls to energy level 1

emitted radiation is ultraviolet

Balmer series – electron falls to energy level 2

emitted radiation is visible light

Paschen series – electron falls to energy level 3

emitted radiation is infrared

all part of the electromagnetic spectrum

Summary – continued

SUBSHELLS — *contain* — orbitals — *types* — s (spherical)

p (dumb-bell shaped)

p_x p_y p_z

s (max $2e^-$)
p (max $6e^-$)
d (max $10e^-$)
f (max $14e^-$)

increasing energy in a shell

example — The full electron configuration of an atom shows the distribution of its electrons over its subshells.

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

The **Pauli exclusion principle**: The maximum number of electrons in an orbital is 2. If there are 2 electrons in an orbital, they must have opposite spins.

Hund's rule: Electrons fill degenerate orbitals to give the maximum number of electrons with the same spin.

remember

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

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

HL

IONISATION ENERGY — The electron with the highest energy is removed first. — The 4s electrons are removed first from transition metals.

first ionisation energy (energy required to remove the first electron)

*n*th ionisation energy (energy required to remove the *n*th electron) — *n*th ionisation energy > (*n* – 1)th ionisation energy because the electron is removed from a more positive ion

(in general) increases across a period as the nuclear charge increases

large jump when an electron is removed from a new main energy level (shell) — The electron in the new energy level is closer to the nucleus and so more strongly attracted.

BUT!

B has a lower 1st ionisation energy than Be because the electrons are removed from different subshells.

O has a lower 1st ionisation energy than N because O has $2e^-$ paired in the same p orbital.

The periodic table 3

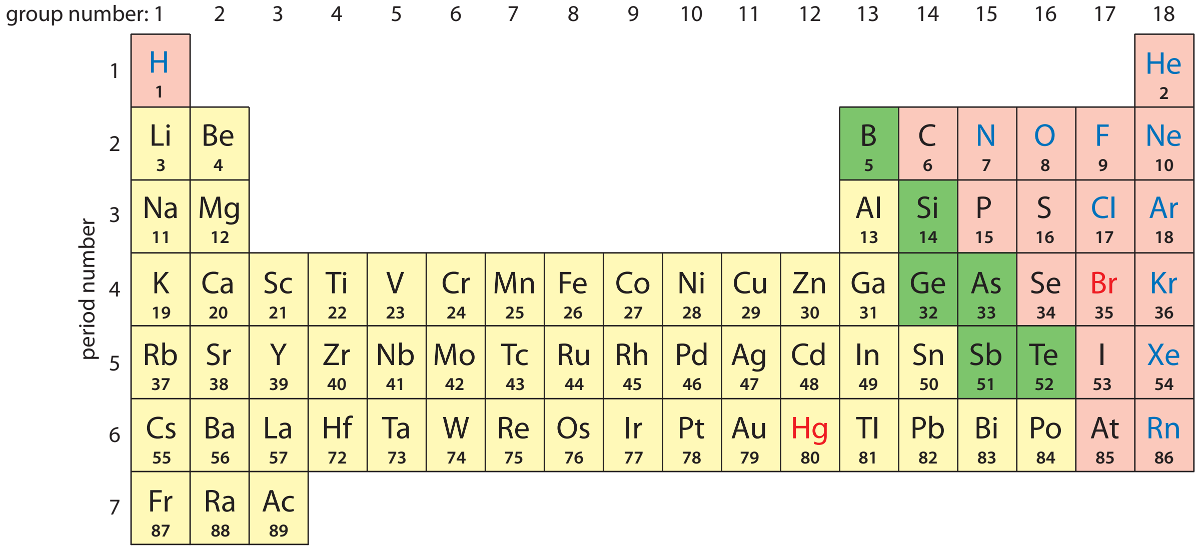
3.1 The periodic table

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 **3.1**).

Most of the elements in the periodic table are metals – these are shown in yellow in Figure **3.1**. The elements shown in pink are non-metals.

Learning objectives

- Understand how the elements in the periodic table are arranged
- Understand the terms **group** and **period**
- Understand how the electron configuration of an element relates to its position in the periodic table



group number: period number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89															

Figure 3.1 The periodic table showing the distribution of metals, metalloids and non-metals.

There are some elements, such as Si, Ge and Sb, that have some of the properties of both metals and non-metals – 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 **3.1**, whereas those that are gases are in blue and liquids are in red.

Some of the groups in the periodic table are given names. Commonly used names are shown in Figure **3.2**. The noble gases are sometimes also called the 'inert gases'.

In the periodic table shown in Figure **3.1** it can be seen that the atomic numbers jump from 57 at La (lanthanum) to 72 at Hf (hafnium). This is because some elements have been omitted – these are the lanthanoid elements. The actinoid elements, which begin with Ac (actinium), have also been omitted from Figure **3.1**. Figure **3.2** shows a long form of the periodic table, showing these elements as an integral part.

There is some disagreement among chemists about just which elements should be classified as metalloids – polonium and astatine are sometimes included in the list.

Hydrogen is the most abundant element in the Universe: about 90% of the atoms in the Universe are hydrogen. Major uses of hydrogen include making ammonia and the hydrogenation of unsaturated vegetable oils.

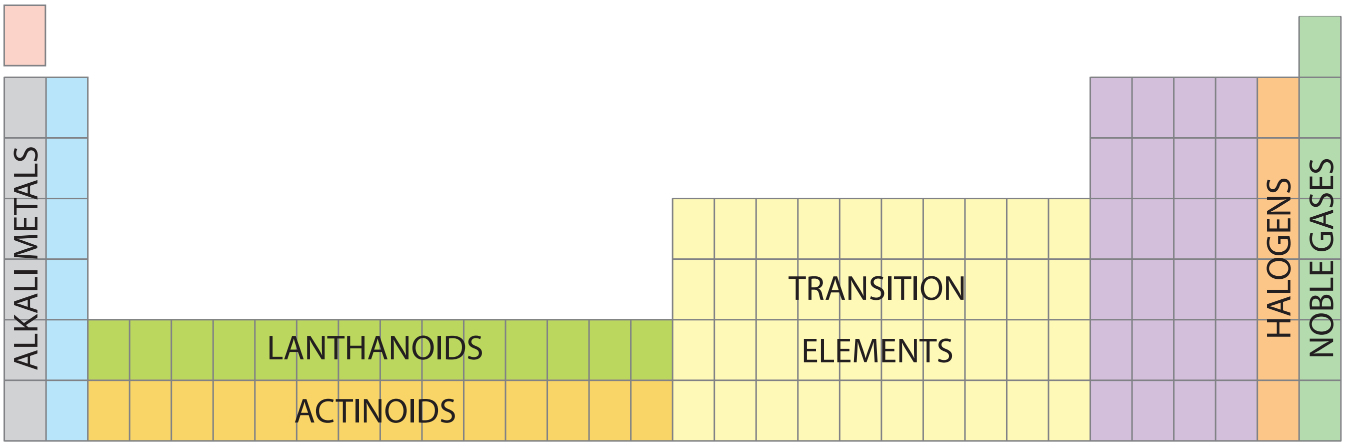


Figure 3.2 The long form of the periodic table, with the names of some of the groups. Hydrogen, though sometimes placed in group 1, does not count as an alkali metal. The lanthanoids and actinoids are also often called 'lanthanides' and 'actinides'.

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?

Tin has a non-metallic allotrope (grey tin) and prolonged exposure of tin to low temperatures can bring about the transformation to the brittle non-metallic form. The transformation is sometimes called 'tin pest' and there are tales (not necessarily true!) that Napoleon lost the Russian campaign in 1812 because his soldiers had buttons made of tin – in the cold Russian winter the buttons became brittle and their trousers fell down!

Metallic properties

The metallic and non-metallic properties of elements can be related to ionisation energies (see later in this topic).

A metallic structure consists of a regular lattice of positive ions in a sea of delocalised electrons (page **160**). 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.

> In general, metallic elements tend to have large atomic radii, low ionisation energies, less exothermic electron affinity values and low electronegativity.

3.1.1 The periodic table and electron configurations

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 three valence electrons and so on. The period number indicates the number of shells (main energy levels) in the atom – or which is the outer shell (main energy level).

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) and in the p block it is the p subshell that is being filled (Figure **3.3**).

Four elements are named after the small village of Ytterby in Sweden – yttrium, terbium, erbium and ytterbium.

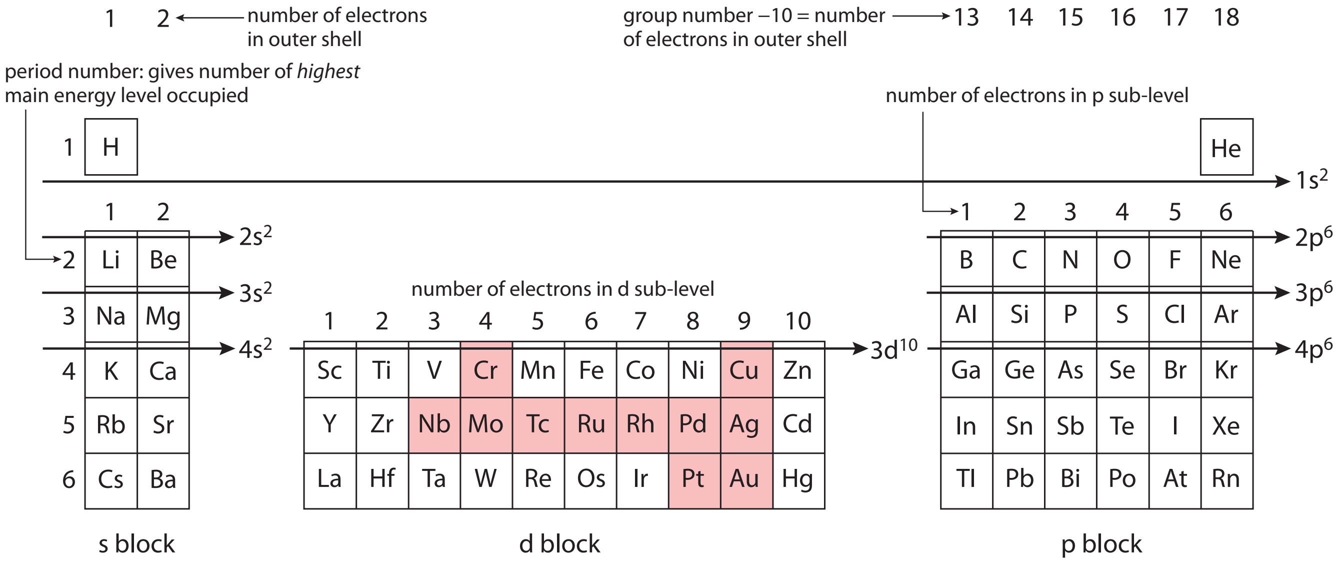


Figure 3.3 Division of the periodic table into blocks.

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. It is in the p block – therefore its highest energy occupied subshell is a p subshell and the outer shell electron configuration is $3s^2 3p^4$ (six valence electrons).

The noble gases (group 18) have either two (He) or eight electrons (Ne–Rn) 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.

Nature of science

Scientists look for patterns in data. They gather evidence, not necessarily just from their own work but also from the published work of other scientists, and analyse the data to discover connections and to try to come up with general laws.

The modern periodic table has developed from one originally conceived by Russian chemist Dmitri Mendeleev in 1869. Mendeleev suggested that the elements were arranged in order of atomic weight (what we would now call relative atomic mass) and produced a table in which elements with similar chemical properties were arranged in vertical groups. Mendeleev took several risks when presenting his data – he suggested that some elements had not been discovered and left spaces for them in his table. Not only did he leave spaces but he also predicted the properties of these unknown elements – he made his hypotheses falsifiable, which added great weight to his theory. The predictions he made were later found to be extremely accurate – the mark of a good theory is that it should be able to be used to predict results that can be experimentally confirmed or refuted. He also suggested that the atomic weights of some elements were incorrect – he realised that tellurium (Te) belonged in the same group as O, S and Se but its atomic weight was higher than iodine and so it should be placed after iodine. Instead of abandoning his theory, he questioned the accuracy of the atomic weight of tellurium and placed it before iodine. This is, of course, the correct place, but Mendeleev's assumption that the atomic weight was lower than that of iodine was not correct.

Henry Moseley, working at the beginning of the 20th century established the connection between atomic number and the periodic table. Like Mendeleev he realised that there were still some elements to be discovered and proposed that three elements between Al and Au were yet to be discovered.

The development of science is not without controversy with regard to who has discovered what. Scientists publish work to make their material available to other scientists and also to establish prior claim on discoveries. For example, the German chemist Julius Lothar Meyer was working on the arrangements of elements at the same time as Mendeleev and came to very similar conclusions – so why is Mendeleev remembered as the father of the modern periodic table rather than Meyer?

3.2 Physical properties

Learning objectives

- Understand trends in atomic radius, ionic radius, first ionisation energy, electron affinity and electronegativity across a period
- Understand trends in atomic radius, ionic radius, first ionisation energy, electron affinity and electronegativity down a group

3.2.1 Variation of properties down a group and across a period

In the next few sections, we will consider how various physical properties vary down a group and across a period in the periodic table.

Atomic radius

The **atomic radius** is basically used to describe the size of an atom. The larger the atomic radius, the larger the atom.

The atomic radius is usually taken to be half the internuclear distance in a molecule of the element. 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 **3.4**.

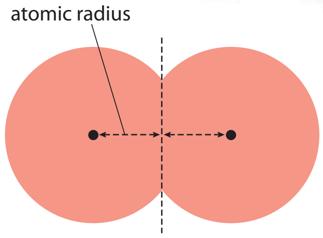


Figure 3.4 The atomic radius of chlorine atoms in a molecule.

Atomic radius increases down a group.

This is because, as we go 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 **3.5**).

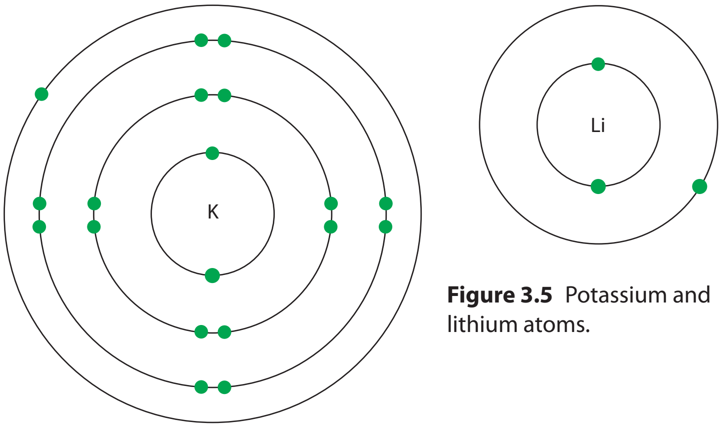


Figure 3.5 Potassium and lithium atoms.

Although the nuclear charge is higher for K, the number of electrons and hence the repulsion between electrons is also greater, and this counteracts any effects due to a greater number of protons in the nucleus.

Atomic radius decreases across a period.

Figure **3.6** shows the variation in atomic radius across period 3 in the periodic table. The reason that atomic radius decreases across a period is that nuclear charge increases across the period with no significant change in shielding. The shielding remains approximately constant because atoms in the same period have the same number of inner shells.

Sodium and chlorine (Figure **3.7**) have the same number of inner shells of electrons (and hence the amount of shielding is similar). However, chlorine has a nuclear charge of 17+ whereas sodium has a nuclear charge of only 11+. This means that the outer electrons are pulled in more strongly in chlorine than in sodium and the atomic radius is smaller.

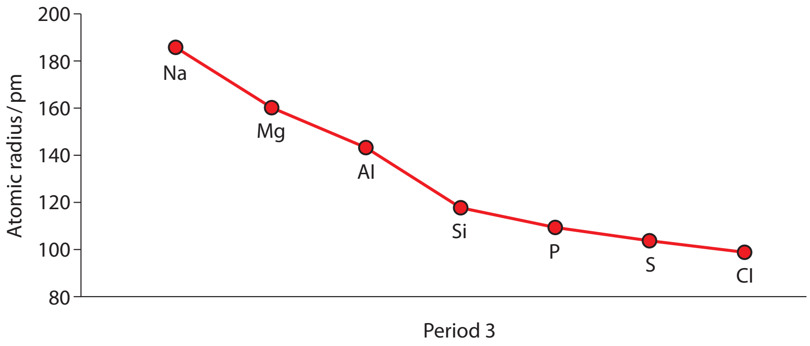


Figure 3.6 The variation in atomic radius across period 3. No atomic radius is shown for argon because it does not form covalent bonds and the internuclear distance between atoms bonded together therefore cannot be measured.

Extension

It is possible to define two different atomic radii: the covalent radius and the van der Waals' radius.

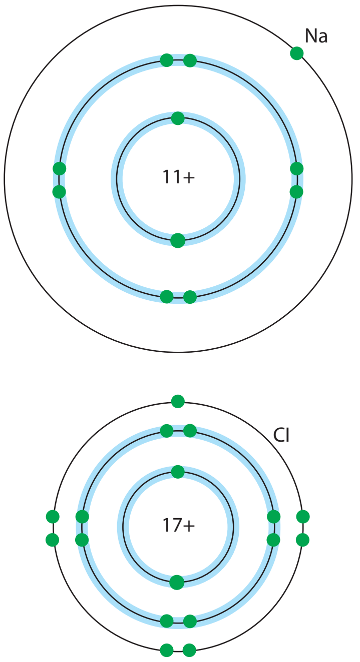


Figure 3.7 Sodium and chlorine atoms. Inner shells, which shield the outer electrons, are highlighted in blue.

Extension

Although it is not possible to measure an atomic radius for Ar, it is possible to measure a value for the van der Waals' radius of this element.

Ionic radius

The ionic radius is a measure of the size of an ion.

> In general, the ionic radii of positive ions are smaller than their atomic radii, and the ionic radii of negative ions are greater than their atomic radii.

Figure **3.8** shows a comparison of the atomic and ionic radii (1+ ion) for the alkali metals. Each ion is smaller than the atom from which it is formed (by loss of an electron).

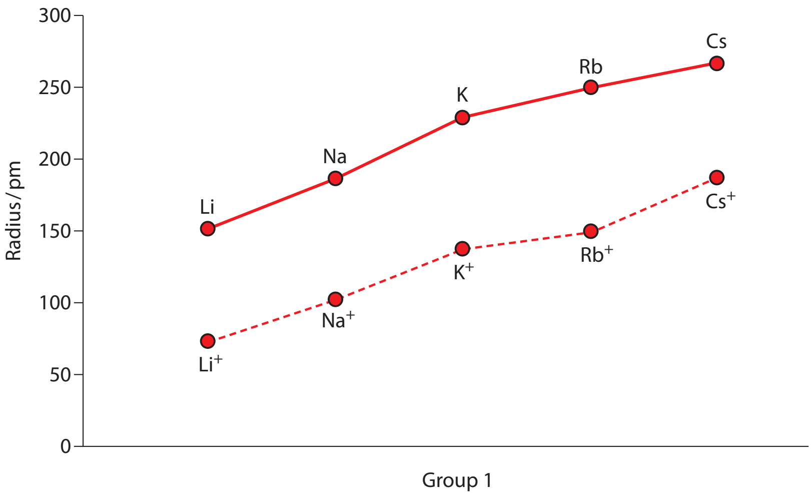


Figure 3.8 Atomic and ionic radii for the alkali metals.

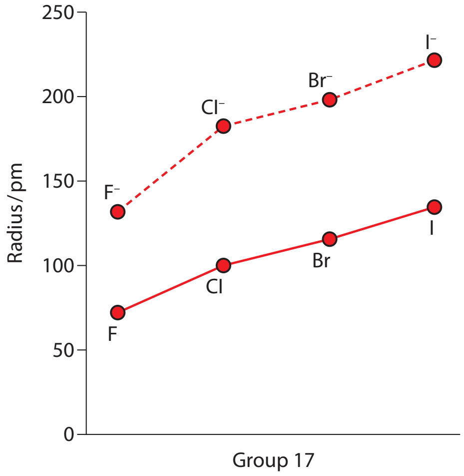


Figure 3.9 A comparison of size between halogen atoms and their ions.

Na is larger than Na$^+$ because the former has one extra shell of electrons – the electron configuration of Na is 2,8,1, whereas that of Na$^+$ is 2,8. Also, they both have the same nuclear charge pulling in the electrons (11+), but there is a greater amount of electron–electron repulsion in Na because there are 11 electrons compared with only 10 in Na$^+$. The electron cloud is therefore larger in Na than in Na$^+$ because there are more electrons repelling for the same nuclear charge pulling the electrons in.

The fact that negative ions are larger than their parent atoms can be seen by comparing the sizes of halogen atoms with their ions (1−) in Figure **3.9**. 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 electron cloud expands as an extra electron is added to a Cl atom to make Cl$^-$.

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.

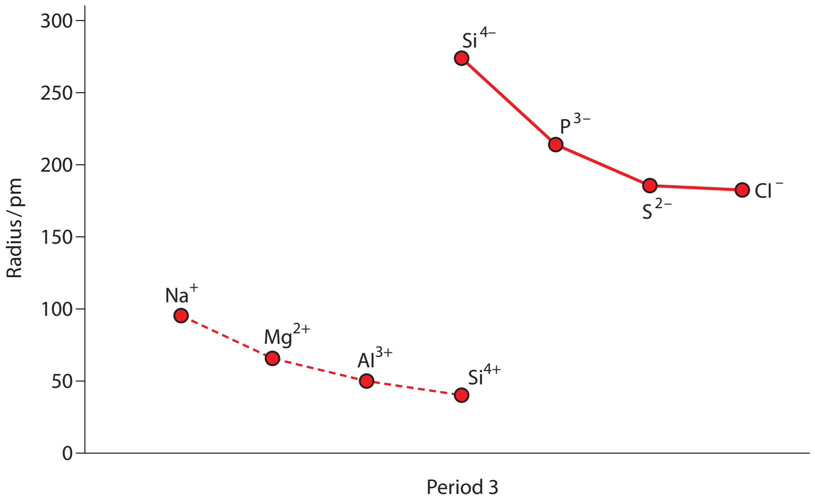


Figure 3.10 Variation of ionic radius of positive and negative ions across period 3.

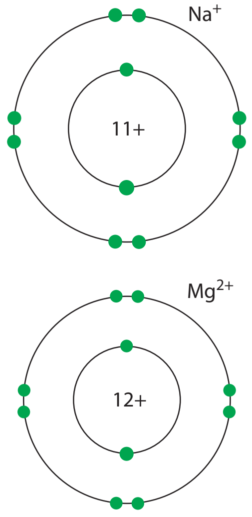


Figure 3.11 Mg^{2+} is smaller than Na^+.

For positive ions there is a decrease in ionic radius as the charge on the ion increases, but for negative ions the size increases as the charge increases (Figure **3.10**).

Let us consider Na^+ and Mg^{2+} – both ions have the same electron configuration, but Mg^{2+} has one more proton in the nucleus (Figure **3.11**). Because there is the same number of electrons in both ions, the amount of electron–electron repulsion is the same; however, the higher nuclear charge in Mg^{2+} means that the electrons are pulled in more strongly and so the ionic radius is smaller.

Now let us consider P^{3-} and S^{2-}. Both ions have the same number of electrons. S^{2-} has the higher nuclear charge and, therefore, because the amount of electron–electron repulsion is the same in both ions, the electrons are pulled in more strongly in S^{2-} (Figure **3.12**).

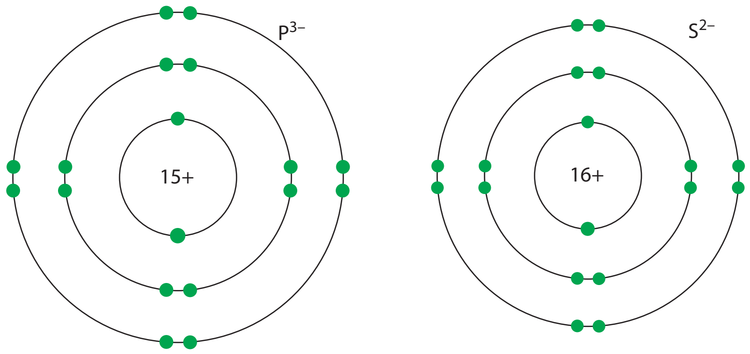


Figure 3.12 S^{2-} is smaller than P^{3-}.

The full definition of first ionisation energy is: the energy required to remove one electron from each atom in one mole of gaseous atoms under standard conditions.

First ionisation energy

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:

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

Variation in first ionisation energy down a group

> Down any group in the periodic table, the first ionisation energy decreases.

The decrease in first ionisation energy down a group is shown in Figure **3.13**. The size of the atom increases down the group so that the outer electron is further from the nucleus and therefore less strongly attracted by the nucleus (Figure **3.14**).

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 electron energy levels (shells). It is the increase in size that governs the change in first ionisation energy.

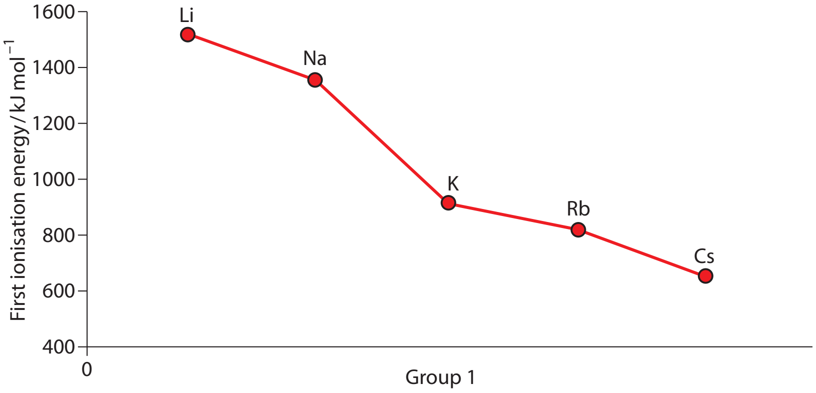


Figure 3.13 First ionisation energy for group 1.

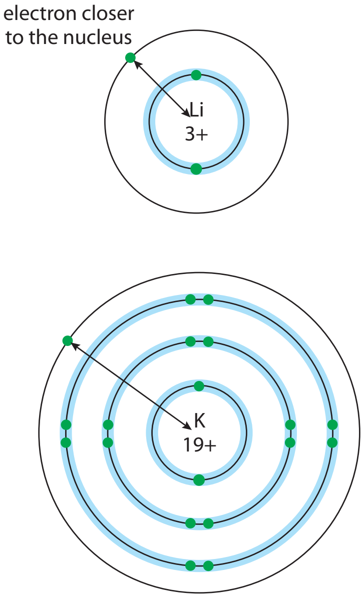


Figure 3.14 Potassium has a lower first ionisation energy than lithium. Electrons that shield the outer electron are highlighted in blue.

Variation in first ionisation energy across a period

> The general trend is that first ionisation energy increases from left to right across a period. This is because of an increase in nuclear charge across the period.

The nuclear charge increases from Na (11+) to Ar (18+) as protons are added to the nucleus. The electrons are all removed from the same main energy level (third shell) and electrons in the same energy level do not shield each other very well. Therefore the attractive force on the outer electrons due to the nucleus increases from left to right across the period

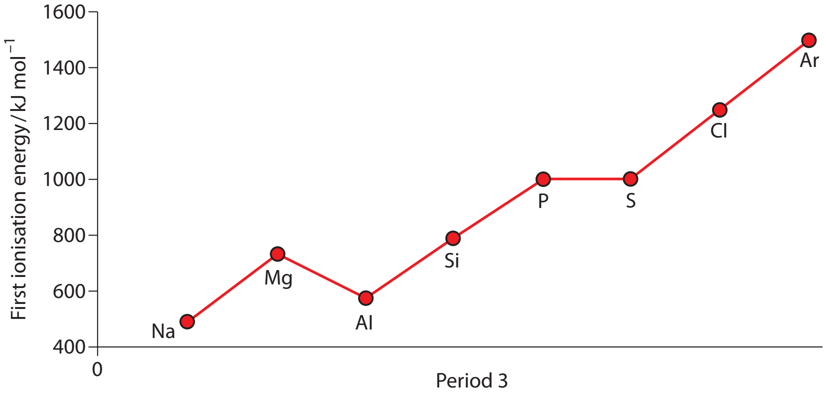


Figure 3.15 The variation in first ionisation energy across period 3 in the periodic table.

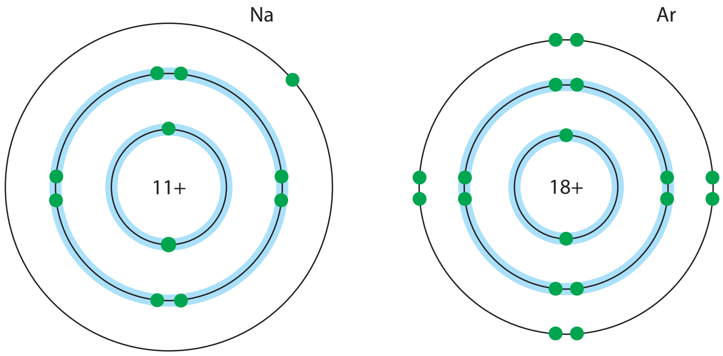


Figure 3.16 Sodium and argon atoms.

The increase in first ionisation energy (Figure **3.15**) can also be explained in terms of the effective nuclear charge felt by the outer electron in argon being higher. The effective nuclear charge felt by the outer electron in a sodium atom would be 11 (nuclear charge) − 10 (number of inner shell electrons), i.e. 1+ if shielding were perfect. The effective nuclear charge felt by the outer electrons in an argon atom would be 18 (nuclear charge) − 10 (number of inner shell electrons), i.e. 8+ if shielding were perfect.

and the outer electron is more difficult to remove from an argon atom (Figure **3.16**). The argon atom is also smaller than the sodium atom and, therefore, 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, and these are discussed on page **78**.

Exam tip
The exceptions to the trend are required knowledge for all students – refer to page **78**.

Electron affinity

The **first electron affinity** involves the energy 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. 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 to bring an electron from far away (infinity) to the outer shell of an atom, where it feels the attractive force of the nucleus.

Variation of electron affinity down group 17

A graph of electron affinity down group 17 is shown in Figure **3.17**. The general trend is that electron affinity decreases down a group, but it can be seen that chlorine has the most exothermic value for electron affinity. A similar trend in electron affinity values is seen going down group 16 and group 14.

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 which is further from the nucleus.

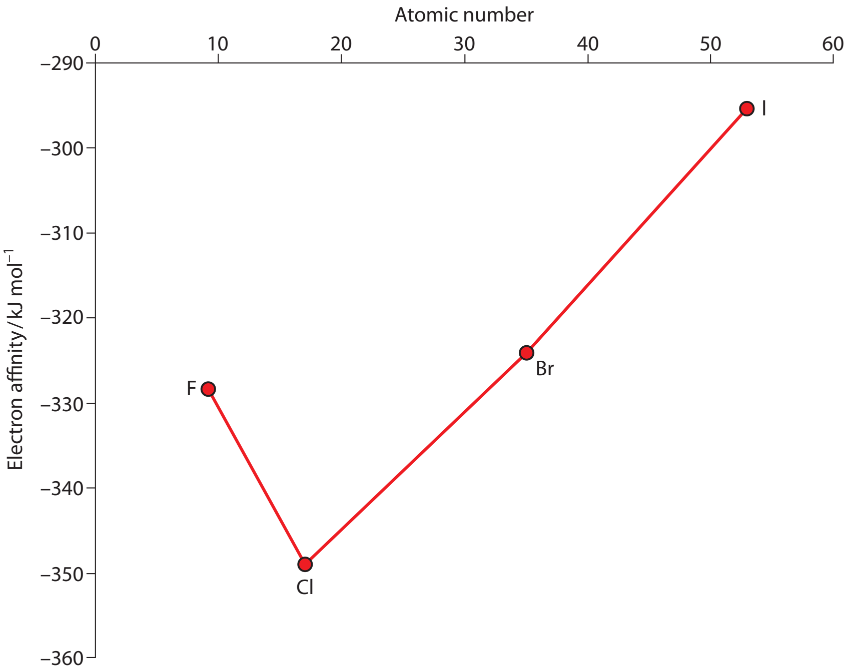


Figure 3.17 Electron affinity values of group 17 elements.

Extension

Electron–electron repulsion also affects the electron affinity and as the atom gets smaller the electrons are, on average, closer together and there is more electron–electron repulsion. This means that the electron affinity should be less exothermic when an electron is added to a smaller atom. 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.

Variation in electron affinity across a period

The general trend in electron affinity from group 13 to group 17 is shown in Figure **3.18**.

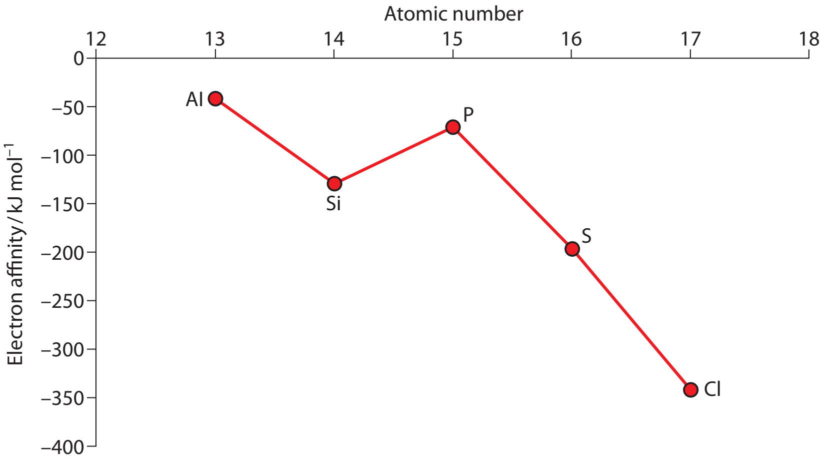


Figure 3.18 Electron affinity values across period 3.

The general trend is that the electron affinity becomes more exothermic. This is because of an increase in nuclear charge and a decrease in atomic radius from left to right across the period. For instance, F has a higher nuclear charge and a smaller radius than O and so the electron will be more strongly attracted when it is brought into the outer shell of the F atom.

Extension

Phosphorus has a less exothermic electron affinity than silicon because of its electron configuration. P has three unpaired electrons in three separate p orbitals and 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 Topic **2**.

Electronegativity

> **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.

Electronegativity decreases down a group – this is because the size of the atoms increases down a group. Consider hydrogen bonded to either F or Cl (Figure **3.19**). 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.

Electronegativity is discussed in more detail on page **128**.

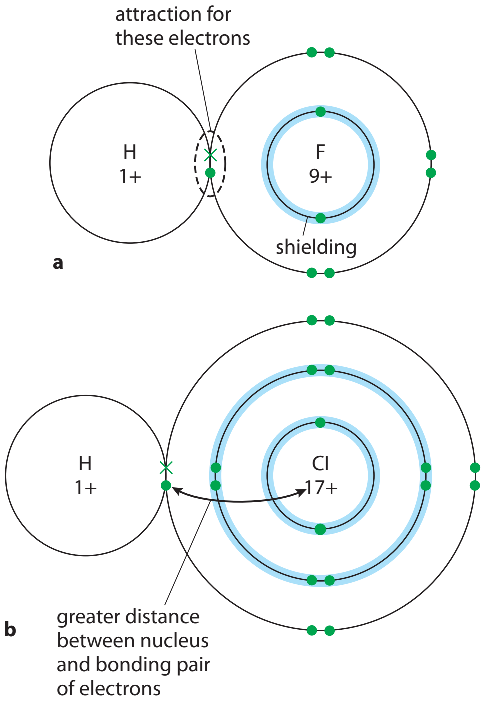


Figure 3.19 Hydrogen bonded to **a** fluorine and **b** chlorine.

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 **3.19**) increases from F to Cl such that the effective nuclear charge felt by the bonding electrons is approximately the same in each case (+7 if shielding were perfect).

Electronegativity increases across a period – the reason for this is the increase in nuclear charge across the period with no significant change in shielding. The 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 **3.20**), 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 the shielding is approximately the same (because of two inner shell electrons).

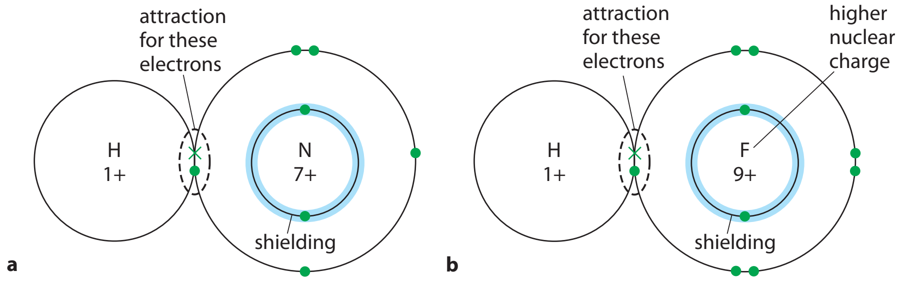


Figure 3.20 Hydrogen bonded to **a** nitrogen and **b** fluorine.

? Test yourself

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

2 State whether the following properties increase or decrease across a period:

a electronegativity

b atomic radius

3 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 S Cl I^- Cl^- S^{2-}

4 Are the following **true** or **false**?

a A germanium atom is smaller than a silicon atom, but silicon has a higher first ionisation energy.

b Selenium has a higher first ionisation energy and electronegativity than sulfur.

c Antimony has a higher first ionisation energy and electronegativity than tin.

d Cl^- is bigger than Cl, but Se^{2-} is smaller than Se.

e Iodine has a higher electronegativity than tellurium but a lower electronegativity than bromine.

5 Based on the following data, which element (**X** or **Y**) is more likely to be a metal?

	First ionisation energy / kJ mol^{-1}	Atomic radius / nm	Electronegativity
X	736	0.136	1.3
Y	1000	0.104	2.6

3.2.2 Properties of elements in group 1 and group 17

Learning objectives

- Understand that elements in the same group have similar chemical properties and show a gradual variation in physical properties
- Describe some reactions of elements in 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 **3.1**). They are placed together in group 1 for two reasons – they all have one electron in their outer shell and they react in very similar ways (similar chemical properties).

> 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.

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 page **160**).

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 **3.22**). This means that less energy is required to break apart the lattice going down group 1.

> Melting point decreases down group 1 (Figure **3.21**).

Liquid sodium is used as a coolant in some nuclear reactors.

Element	Symbol	Atomic number	Electron configuration	Density / g cm^{-3}	Melting point / °C	Boiling point / °C
lithium	Li	3	[He]2s^1	0.53	180	1330
sodium	Na	11	[Ne]3s^1	0.97	98	890
potassium	K	19	[Ar]4s^1	0.86	64	774
rubidium	Rb	37	[Kr]5s^1	1.53	39	688
caesium	Cs	55	[Xe]6s^1	1.87	29	679

Table 3.1 Similarities in alkali metal properties.

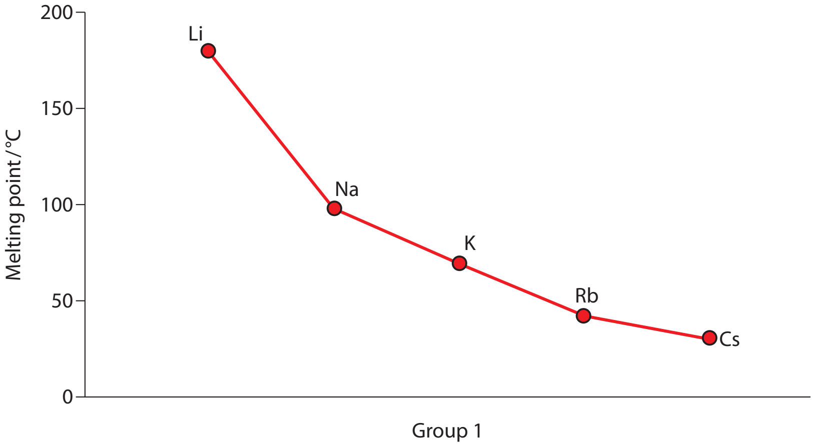


Figure 3.21 Variation in melting point in group 1.

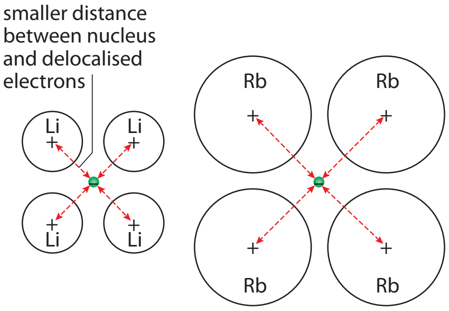


Figure 3.22 The delocalised electrons are attracted more strongly in lithium than in rubidium.

Reactions of the elements in 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:

$$4M(s) + O_2(g) \rightarrow 2M_2O(s)$$

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:

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

Lithium, sodium and potassium are all less dense than water.

An alkaline solution is formed. The alkali metal hydroxides are strong bases and ionise completely in aqueous solution (page **321**).

The reaction with water becomes more vigorous going down the group – sodium melts into a ball, fizzes rapidly and moves around on the surface of the water; potassium bursts into flames (lilac); and caesium explodes as soon as it comes into contact with water.

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 **3.2**.

Element	Symbol	Atomic number	Electron configuration	Colour	Melting point / °C	Boiling point / °C	Physical state at room temperature and pressure
fluorine	F	9	$[He]2s^22p^5$	pale yellow	−220	−188	gas
chlorine	Cl	17	$[Ne]3s^23p^5$	yellow–green	−101	−35	gas
bromine	Br	35	$[Ar]3d^{10}4s^24p^5$	deep red liquid, orange vapour	−7	59	liquid
iodine	I	53	$[Kr]4d^{10}5s^25p^5$	grey shiny solid, purple vapour	114	184	solid

Table 3.2 Properties of halogens.

Variation of melting point in group 17

The melting points of the halogens increase going down the group (Figure **3.23**).

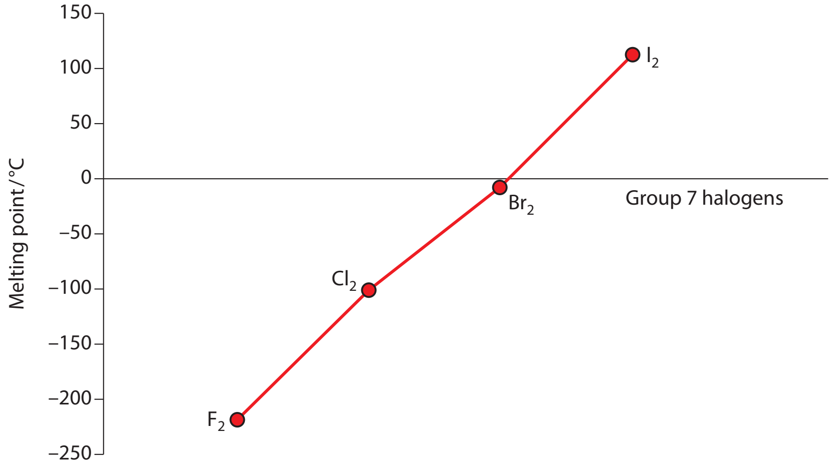


Figure 3.23 Variation in melting point in group 17.

As the relative molecular masses of the X_2 halogen molecules increase, the London forces (page **148**) between molecules get stronger. This means that more energy must be supplied to separate the molecules from each other.

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^- ions or by forming covalent compounds. Reactivity decreases down the group, and fluorine is the most reactive element known, reacting directly with virtually every other element in the periodic table. 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 electron affinity (energy released when an electron is added to a neutral atom) going down the group 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.

The halogens all react with the alkali metals to form salts. The general equation is:

$$2M(s) + X_2(g) \rightarrow 2MX(s)$$

The salts formed are all white/colourless, fairly typical ionic compounds. They contain M^+ and X^- ions. All alkali metal chlorides, bromides and iodides are soluble in water and form colourless, neutral solutions.

Chlorine is produced by the electrolysis of brine. Worldwide annual production is about 60 million tonnes. Chlorine and its compounds are involved in the production of about 90% of the most important pharmaceuticals. Its biggest single use is in the production of PVC.

How vigorous the reaction is depends on the particular halogen and alkali metal used – the most vigorous reaction occurs between fluorine and caesium, and the least vigorous between lithium and iodine.

Displacement reactions of halogens

These are reactions between a solution of a halogen and a solution containing halide ions – they are discussed in more detail on page **404**. A small amount of a solution of a halogen is added to a small amount of a solution containing a halide ion, and any colour changes are observed (see Table **3.3**). Potassium chloride, bromide and iodide solutions are all colourless. The colours of chlorine, bromine and iodine solutions are shown in Figure **3.24**.

Orange colour, due to the production of bromine.

Red-brown colour, due to the production of iodine.

	KCl(aq)	**KBr(aq)**	**KI(aq)**
Cl_2(aq)	no reaction	orange solution	dark red–brown solution
Br_2(aq)	no reaction	no reaction	dark red–brown solution
I_2(aq)	no reaction	no reaction	no reaction

Table 3.3 Results of reactions between halogen solutions and solutions containing halide ions.

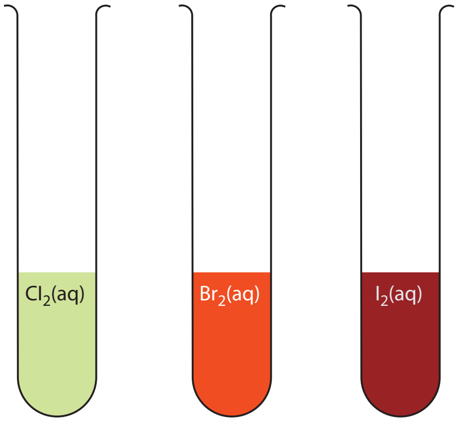


Figure 3.24 Chlorine solution is pale yellow–green (almost colourless if it is dilute), bromine solution is orange, and iodine solution is red–brown.

The reactions that occur are:

$$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq)$$

Ionic equation: $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$

Ionic equation: $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

$$Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$$

Ionic equation: $Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

The more reactive halogen displaces the halide ion of the less reactive halogen from solution – chlorine displaces bromide ions and iodide ions from solution, and bromine displaces iodide ions from solution.

These reactions are all **redox reactions** (Topic **9**), in which a more reactive halogen oxidises a less reactive halide ion. Chlorine is a stronger oxidising agent than bromine and iodine; it 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.

3.2.3 Oxides of period 2 and period 3 elements

Learning objectives

- Describe the changes from basic to acidic oxides across a period
- Write equations for the reactions of oxides with water and predict the acidity of the resulting solutions

Oxides of elements may be classified as basic, acidic or amphoteric. The nature of the oxides changes across a period and Table **3.4** 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**.

A basic oxide is one that will react with an acid to form a salt and, if soluble in water, will produce an alkaline solution. Sodium oxide reacts with water to form sodium hydroxide:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

Sodium oxide reacts with acids such as sulfuric acid to form salts:

$$Na_2O(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

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 alkaline:

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$$

Exam tip
Reactions highlighted like this must be learnt for examinations.

Aluminium is on the dividing line between metals and non-metals and forms an amphoteric oxide – these have some of the properties of a basic oxide and some of an acidic oxide. Aluminium is exhibiting properties between those of a metal (basic) oxide and those of a non-metal (acidic) oxide.

Aluminium oxide does not react with water but it does display amphoteric behaviour in that it reacts with both acids and bases to form salts:

reaction with acids: $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$

reaction with alkalis/bases: $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$

Amphoteric oxides react both with acids and with bases.

	Sodium	**Magnesium**	**Aluminium**	**Silicon**	**Phosphorus**	**Sulfur**
Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2 SO_3
Nature of element	metal			non-metal		
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 3.4 The acid–base nature of some period 3 oxides.

The remaining oxides in Table **3.4** are all acidic oxides. An acidic oxide is one that reacts with bases/alkalis to form a salt and, if soluble in water, will produce an acidic solution.

P_4O_6 (phosphorus(III) oxide) and P_4O_{10} (phosphorus(V) oxide) form phosphoric(III) and phosphoric(V) acid, respectively, when they react with water:

Phosphoric(V) acid is an ingredient of Coca-Cola®.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

SO_2 (sulfur(IV) oxide) and SO_3 (sulfur(VI) oxide) form sulfuric(IV) and sulfuric(VI) acid, respectively, when they react with water:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Nitrogen oxides

There are many oxides of nitrogen, ranging in formula from N_2O to N_2O_5. Two of the most environmentally important are nitrogen(II) oxide (NO) and nitrogen(IV) oxide (NO_2).

Nitrogen reacts with oxygen at very high temperatures to form NO (nitrogen monoxide, nitric oxide or nitrogen(II) oxide):

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

This reaction occurs in the internal combustion engine. NO is virtually insoluble in water and is classified as a neutral oxide.

NO can be oxidised in the atmosphere to NO_2, which can react with water to produce nitric(V) acid (HNO_3), which is one of the acids responsible for acid deposition (see Subtopic **8.5**). NO_2 can be classified as an acidic oxide:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

N_2O (nitrogen(I) oxide, nitrous oxide) is another neutral oxide. N_2O is also known as laughing gas and major uses include as an anaesthetic and as the propellant in 'squirty cream'.

Non-metal oxides such as SO_2 are produced in various industrial processes and when coal is burnt. This can be responsible for **acid rain**, which can, among other things, kill fish in lakes and trees in forests.

Nitrogen oxides (NO_x) may be formed in internal combustion engines, and these are involved in the formation of photochemical smog in cities (Figure **3.25**).

Figure 3.25 A photochemical smog over Hong Kong.

Nature of science

Science and the technology that develops from it have been used to solve many problems – but it can also *cause* them. The development of industrial processes that produce acidic gases led to acid rain being a major environmental problem. Acid rain, and its associated problems, is important to people across the world and it is vital that scientists work to improve the public understanding of the issues involved. Scientists also work as advisors to politicians in developing policies to solve these problems.

Advancements in science have often arisen from finding patterns in data. An understanding of the patterns in physical and chemical properties of elements in the periodic table has allowed chemists to make new substances. For instance, the knowledge that sulfur formed a range of compounds with nitrogen probably led scientists to attempt to make selium-nitrogen and tellurium-nitrogen compounds.

Test yourself

6 Write balanced equations for the following reactions:
  a rubidium with water
  b potassium with bromine
  c chlorine solution with potassium bromide solution
  d sodium oxide with water
  e sulfur(VI) oxide with water

7 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

8 State whether an acidic or alkaline solution will be formed when each of the following is dissolved in/reacted with water:
  a SO_3
  b MgO
  c Na

3.3 First-row d-block elements (HL)

Learning objectives

- Describe the characteristic properties of transition metals
- Explain why transition metals have variable oxidation numbers
- Explain the formation and describe the shape of complex ions
- Explain why transition metal complex ions are coloured
- Explain the factors that affect the colour of a transition metal complex
- Understand the magnetic properties of transition metal atoms and ions
- Describe some uses of transition metals and their compounds as catalysts

Exam tip
Remember that chromium and copper have slightly different electron configurations.

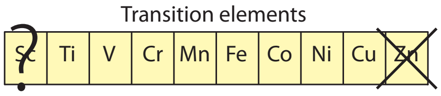


Figure 3.26 Zinc is not a transition element but the classification of scandium is more controversial.

Exam tip
Scandium is regarded as a transition element on the syllabus.

The 'transition elements' are often called the 'transition metals'.

3.3.1 The transition elements (d block)

The first-row d-block elements are:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30

There are also two other rows of d-block elements.

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	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar]$4s^2 3d^1$	[Ar]$4s^2 3d^2$	[Ar]$4s^2 3d^3$	[Ar]$4s^1 3d^5$	[Ar]$4s^2 3d^5$	[Ar]$4s^2 3d^6$	[Ar]$4s^2 3d^7$	[Ar]$4s^2 3d^8$	[Ar]$4s^1 3d^{10}$	[Ar]$4s^2 3d^{10}$

The **transition elements** can be defined as different from 'the d-block elements', and the definition we will use here is:

> a transition element is an element that forms at least one stable ion with a partially filled d subshell

According to this definition, zinc is not counted as a transition element because the only ion it forms is the 2+ ion, with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (full d subshell). Zinc (Figure **3.26**) does not exhibit some of the typical characteristic properties of transition metals detailed below (e.g. it does not form coloured compounds). The inclusion/exclusion of scandium as a transition element according to this definition is much more controversial. In virtually every compound scandium has oxidation number +3 (no d electrons) however, it also forms a couple of compounds (ScH_2 and $CsScCl_3$) with formal oxidation number +2, but the bonding in these compounds is more complicated and they do not necessarily contain the 2+ ion.

Properties of the transition elements

We have already studied the variation in properties of a set of eight elements across the periodic table when we looked at the properties of period 3 elements. The transition elements also form a set of eight elements across the periodic table, but these are much more similar to each other than the elements across period 3. 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 **3.27** and **3.28**. It can be seen that the variation of ionisation energy and atomic radius across the series of the transition elements is much smaller than across period 3.

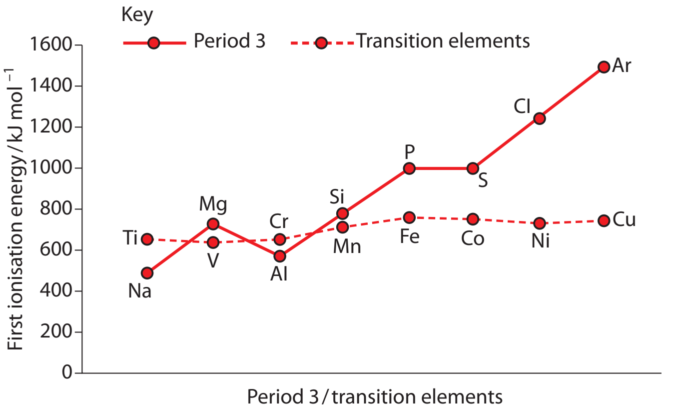


Figure 3.27 A comparison of the variation of first ionisation energy across period 3 with that across the transition metal series.

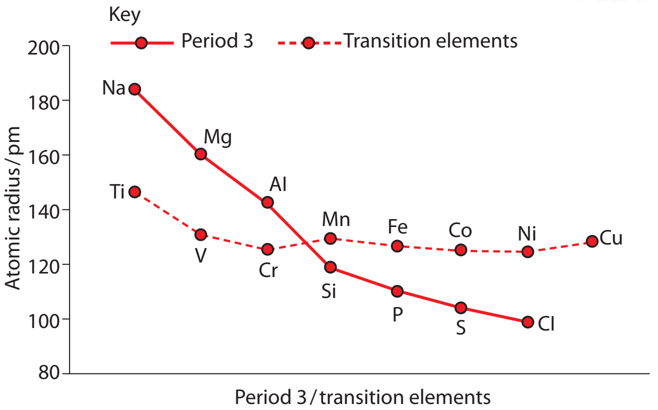


Figure 3.28 A comparison of the variation of atomic radius across period 3 with that across the transition metal series.

Because of their similarity it is possible to draw up a list of characteristic properties of transition elements:

- Transition elements are all typical metals – they have high melting points and densities.
- Transition elements can exhibit more than one oxidation number 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.

Exam tip
The last five properties are the most important for examinations.

Ionisation of transition elements

Transition elements form positive ions. The electron configurations of some transition metal ions are shown in Table **3.5**.

The 4s electrons are always removed before the 3d electrons when an ion is formed.

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 3.5 Electron configurations of transition metals and their ions.

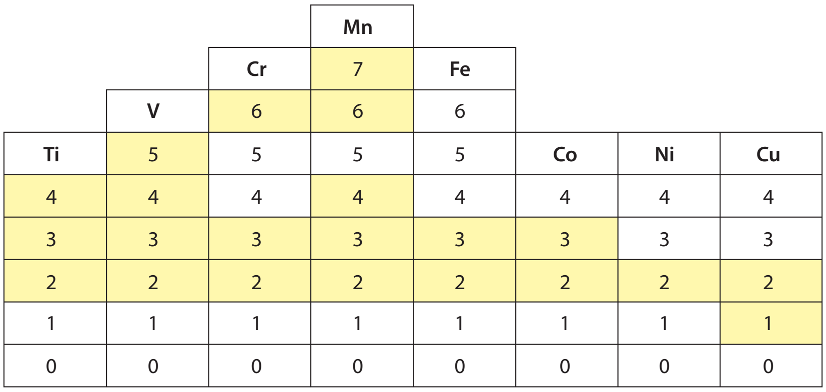
Oxidation numbers are discussed further on page **369**.

Oxidation number and oxidation state are often used interchangeably.

3.3.2 Variable oxidation numbers

The positive oxidation numbers (oxidation states) exhibited by the transition elements are shown in Figure **3.29**. The greatest number of different oxidation numbers and the highest oxidation numbers are found in the middle of the series. From titanium to maganese there is an increase in the total number of electrons in the 4s and 3d subshells, so the maximum oxidation number increases. Maganese has the electron configuration [Ar]$4s^2 3d^5$ and therefore a maximum oxidation number of +7. Iron has eight electrons in the 4s and 3d subshells and would be expected to have a maximum oxidation number of +8, but the ionisation energy increases from left to right across the transition elements series and it becomes more difficult to reach the highest oxidation numbers towards the right-hand side of the series. The chemistry of copper and nickel is, for the same reason, dominated by the lower oxidation numbers.

> **All transition metals show oxidation number +2.** In most cases this is because they have two electrons in the 4s subshell, and removal of these generates an oxidation number of +2.



Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			7				
		6	6	6			
	5	5	5	5			
4	4	4	4	4	4	4	4
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

Figure 3.29 Oxidation numbers of transition metals in compounds. Not all oxidation numbers are common.

Exam tip
The oxidation numbers highlighted in Figure **3.29** are mentioned specifically in the data booklet.

Why more than one oxidation number?

The 4s and 3d subshells 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 in order to generate the nearest noble gas electron configuration. The graph in Figure **3.30** 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, but that there are no such jumps for manganese.

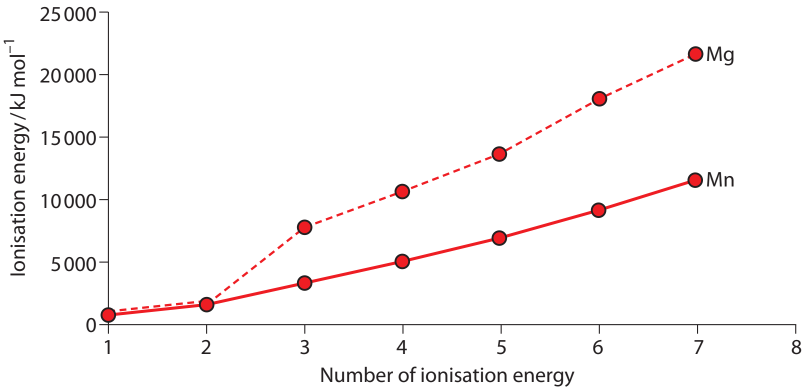


Figure 3.30 Comparison of successive ionisation energies of magnesium and manganese.

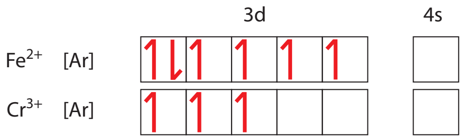
Magnetic properties of transition metal compounds

There are two forms of magnetism we need to be concerned with – **paramagnetism** and **diamagnetism**.

> 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.

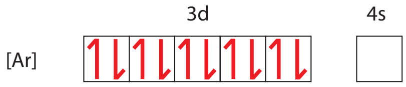
All substances have some paired electrons and so all substances exhibit diamagnetism. However, the diamagnetic effect is much smaller than the paramagnetic effect and so, if there are any unpaired electrons present, the paramagnetic effect will dominate and the substance will be paramagnetic overall and attracted by a magnetic field. The more unpaired electrons, the greater the paramagnetism (magnetic moment).

Consider the electron configurations of two transition metal ions:



Both contain unpaired electrons and their compounds are paramagnetic – so both $FeCl_2$ and $CrCl_3$ are paramagnetic. Because an Fe^{2+} ion has four unpaired electrons and a Cr^{3+} ion has only three, the iron(II) compound is more paramagnetic (higher magnetic moment).

The Cu^+ ion has the following electron configuration:



All the electrons are paired so compounds of copper(I), such as CuCl, are diamagnetic only.

Extension

The situation is more complicated with complex ions. Depending on the energy difference between the higher and lower set of d orbitals and the amount of energy required to pair up two electrons in the same d orbital (overcoming the repulsions), complexes can be high spin (maximum number of unpaired electrons) or low spin (maximum number of electrons in the lower set of d orbitals). How paramagnetic a substance is then depends on the ligands because they influence the splitting of the d orbitals.

A ligand must possess a lone pair of electrons.

A ligand is a Lewis base.

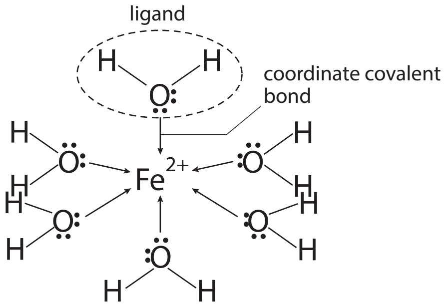


Figure 3.31 A complex ion is formed when ligands bond to a transition metal ion. The ligands donate lone pairs into vacant orbitals (3d, 4s or 4p) on the transition metal ion.

Extension

There is a strong case for considering the bonding in a transition metal complex ion as having a significant ionic component. Crystal field theory and ligand field theory consider the bonding from a more ionic point of view.

Complex ions

A complex ion consists of a central metal ion surrounded by **ligands** – transition metal ions form many complexes.

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. **Coordinate covalent bonds** (dative bonds) are formed between the ligand and the transition metal ion.

The structure of $[Fe(H_2O)_6]^{2+}$ is shown in Figure **3.31**. H_2O is the ligand in this complex ion. The shape of this complex ion is octahedral and it is called the hexaaquairon(II) ion. Other ways of drawing this are shown in Figure **3.32**.

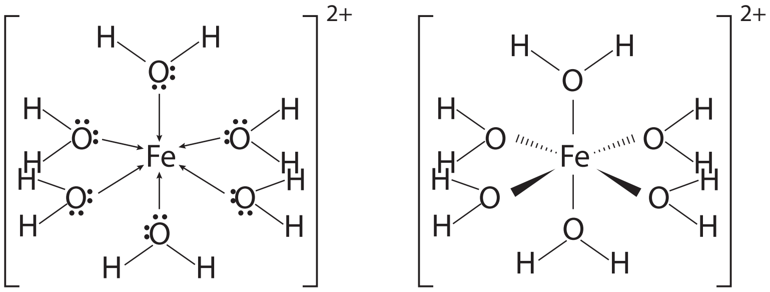
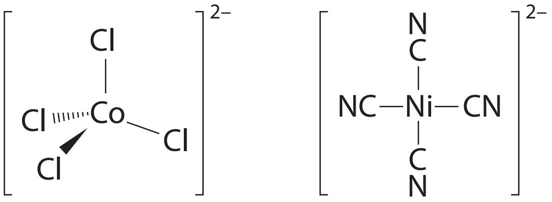


Figure 3.32 Alternative representations of the $[Fe(H_2O)_6]^{2+}$ complex ion.

All transition elements, with the exception of titanium, 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 page **137**) because more subtle factors also govern the overall shape. If a complex ion contains 6 ligands it will almost certainly be octahedral, but complexes containing 4 ligands may be tetrahedral or square planar (Figure **3.33**).



$[CoCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$

Figure 3.33 $[CoCl_4]^{2-}$ is tetrahedral but $[Ni(CN)_4]^{2-}$ is square planar.

Complex ions can undergo substitution reactions in which, for example, H_2O ligands are replaced by other ligands. For example, in the addition of concentrated hydrochloric acid to blue copper(II) sulfate solution:

$$\underset{\text{blue}}{[Cu(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{yellow}}{[CuCl_4]^{2-}(aq)} + 6H_2O(l)$$

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 Topic **7**) the position of equilibrium shifts to the right as Cl^- is added.

The oxidation number of a transition metal in a complex ion

The oxidation number of a transition metal in a complex ion can be worked out from the charges on the ligands. Ligands may be either neutral or negatively charged (see Table **3.6**).

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 number 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 number of nickel must be +2 to cancel out 2− from the 4− charge.

Neutral ligands	1– ligands
H_2O	Cl^-
NH_3	CN^-
CO	Br^-

Table 3.6 Charges on ligands.

Exam tip
Oxidation numbers are discussed in more detail in Topic **9**.

Working out the overall charge on a complex ion

If the oxidation number (charge) of the central transition metal ion and the charges on the ligands are known, the overall charge on the complex ion can be worked out.

Worked example

3.1 Platinum(II) can form a complex ion with 1 ammonia and 3 chloride ligands. What is the overall charge and formula of the complex ion?

Platinum(II) has a charge of 2+
Ammonia is a neutral ligand (NH_3)
Chloride has a 1– charge (Cl^-)

The overall charge is (2+) + (0) + 3(1–) = 1–

The formula of the complex ion is: $[Pt(NH_3)Cl_3]^-$

Catalytic ability

Transition elements and their compounds/complexes can act as catalysts. 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 the above reaction is a heterogeneous catalyst (one that is in a different physical state to 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 metal atom or ion having varying oxidation numbers and also being able to coordinate to other molecules/ions to form complex ions.

Some scientists believe that the bonding between a transition metal and a ligand is purely ionic. All scientists have the same experimental data available to them – to what extent is scientific knowledge objective and to what extent is it a matter of interpretation and belief?

Nature of science

Science is about finding patterns and these patterns allow us to make predictions. However, it is not always the patterns that are most interesting and careful observation is essential to spot anomalies and exceptions to patterns that could lead to new discoveries and theories. Zinc can be regarded as anomalous in the first row of the d block, for instance, it does not generally form coloured compounds; this has resulted in it not being included as a transition element.

3.4 Coloured complexes (HL)

The colours of some complex ions are shown in Table **3.7**.

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 3.7 The colours of some complex ions.

In a gaseous transition metal ion, all the 3d orbitals have the same energy – that is, they are degenerate. However, when the ion is surrounded by ligands in a complex ion, these d orbitals are split into two groups. In an octahedral complex ion there are two orbitals in the upper group and three orbitals in the lower groups (Figure **3.34**).

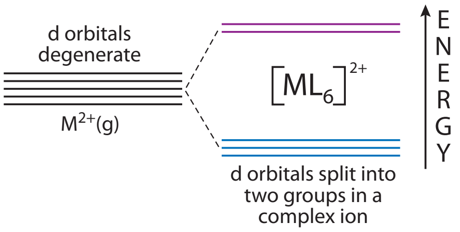


Figure 3.34 The splitting of d orbitals in a complex ion.

The splitting may be regarded as being caused by the repulsion between the electrons in the metal ion d orbitals and the lone pairs on the ligands. Two of the metal ion d orbitals point directly at the ligands and so are raised in energy, whereas the other three d orbitals point between the ligands and are lowered in energy relative to the other two d orbitals.

Energy in the form of a certain frequency of visible light can be absorbed to promote an electron from the lower set of orbitals to the higher set (Figure **3.35**).

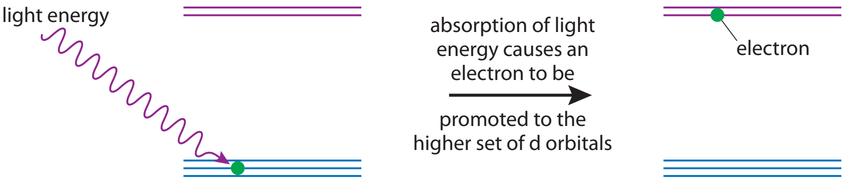


Figure 3.35 Absorption of light by a complex ion.

Extension

All the d orbitals in a complex ion are higher in energy than the d orbitals in an isolated gaseous ion.

Extension

The electrons in d_{z^2} and $d_{x^2-y^2}$ orbitals are repelled more by the ligand electrons because they point directly at the ligands – greater repulsion leads to higher energy.

Extension

The d orbitals are split in different ways in different-shaped complex ions.

When white light passes through copper sulfate solution (Figure **3.36**), orange light is absorbed, promoting an electron from the lower set of d orbitals to the higher set. This means that the light coming out contains all the colours of the spectrum except orange and so appears blue, the complementary colour to orange.

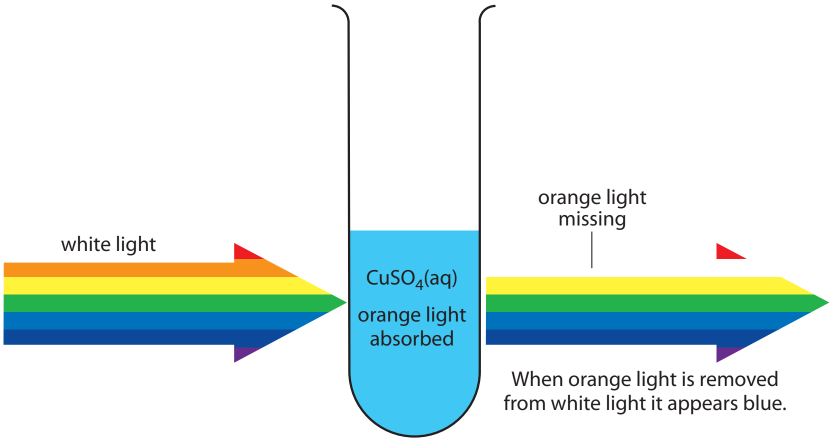


Figure 3.36 Colour and absorption.

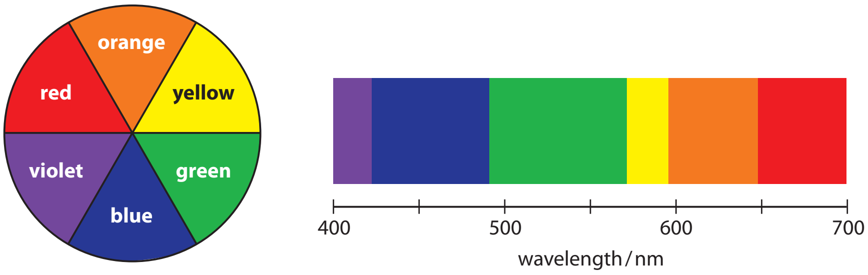


Figure 3.37 A colour wheel – along with the approximate wavelengths of visible light. Complementary colours are opposite each other in the colour wheel, therefore blue is complementary to orange and green is complementary to red.

White light is a mixture of all colours (frequencies) of visible light.

For a substance to appear coloured, certain frequencies of light in the visible region of the spectrum must be absorbed.

The colour of a substance will appear to an observer as the **complementary colour** to the light that is absorbed. A colour wheel (Figure **3.37**) shows which pairs of colours are complementary (opposite each other in the colour wheel). If we know the colour of the complex ion, the colour of light that is absorbed can be worked out, and vice versa. For example, because a solution of nickel(II) chloride is green, it must absorb red light – the complementary colour to green.

The formation of coloured substances requires the presence of a partially filled d subshell.

Let us consider the Sc^{3+} ion or the Ti^{4+} ion. These both have no electrons in the 3d subshell and so are colourless, as it is not possible to absorb energy to promote a 3d electron.

Extension

$Cr_2O_7^{2-}$ (orange), CrO_4^{2-} (yellow) and MnO_4^- (purple) are all very highly coloured, but they have no d electrons. They are coloured because of a different mechanism from the one described here.

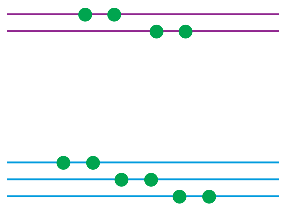


Figure 3.38 A Cu^+ or Zn^{2+} ion has ten 3d electrons.

Extension

The actual theory behind the spectra of transition metal complexes is significantly more complex than described here, and the simple idea of an electron being promoted from the lower set of d orbitals to the upper set is only really applicable to transition metal ions with one d electron (d^9 ions also produce relatively simple spectra). This is evident by the fact that transition metal ions will usually absorb more than one frequency of electromagnetic radiation – not just one as predicted by the simple model. For transition metals with more than one d electron, the repulsion between d electrons is important in determining the energies of the various energy states. The absorption of electromagnetic radiation by a transition metal ion could be better described as 'causing a rearrangement of electrons within the d orbitals'.

Most aqueous solutions of Fe^{3+} are actually yellow, but they do not contain $[Fe(H_2O)_6]^{3+}$(aq).

In general, for complex ions containing the same metal and the same ligands, the greater the oxidation number of the transition metal, the greater the splitting of the d orbitals.

The Cu^+ ion and the Zn^{2+} ion both have ten 3d electrons (Figure **3.38**), and as there is no space in the upper set of orbitals it is not possible to promote an electron to the upper set of orbitals. No light in the visible region of the spectrum is absorbed and these ions are colourless.

What do we mean when we say that a solution of copper sulfate is blue? Is blueness a property of copper sulfate solution, or is the blueness in our minds? What colour would copper sulfate solution be in orange light? Or in the dark?

Factors that affect the colour of transition metal complexes

At the simplest level, the colours of transition metal 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 have a part to play.

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 due to different amounts of repulsion between electrons.

If **isoelectronic** (same number of electrons) transition metal ions 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 d orbitals in $[Fe(H_2O)_6]^{3+}$. A higher nuclear charge on the metal ion (26+ for Fe and 25+ for Mn) for the same number of electrons 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 number

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 repulsion between the ligand electrons and the d electrons of the transition metal ion – and therefore greater splitting of the d orbitals.

Nature of the ligand

The same metal ion can exhibit different colours with different ligands. This is mainly because of the different 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.

Ligands that cause greater splitting of d orbitals are called stronger field ligands.

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a larger energy gap between the two sets of d orbitals than $[Cu(H_2O)_6]^{2+}$ and absorbs a shorter wavelength (higher frequency) of light (Figure **3.39**). $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is dark blue/violet and absorbs more in the yellow–green (higher frequency) region of the visible spectrum.

A full explanation of the spectrochemical series is difficult at this level. The fact that fluoride ions cause greater splitting of d orbitals than iodide ions can be explained in terms of **charge density** (charge per unit volume) of the ligand – both F^- and I^- have the same charge but the F^- ion is much smaller and therefore causes greater repulsion of the metal ion d electrons and greater splitting of the d orbitals. This explanation cannot, however, be extended to the rest of the spectrochemical series – as can be seen by the fact that CO, a neutral ligand, causes greater splitting of d orbitals than negatively charged ligands that would be expected to have a higher charge density. However, the spectrochemical series can

A water molecule is more polar than an ammonia molecule and there would be expected to be a higher charge density on the O in H_2O than the N in NH_3.

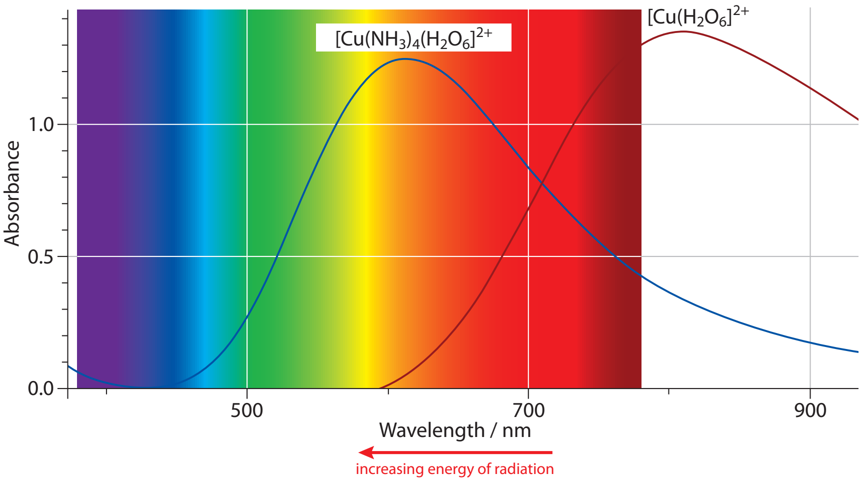


Figure 3.39 $[Cu(H_2O)_6]^{2+}(aq)$ is blue and absorbs mostly at the red–orange end of the spectrum. $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is dark blue/violet and absorbs more in the yellow–green (shorter wavelength) region of the visible spectrum.