



01

# Stoichiometric relationships

## Essential ideas

- 1.1** Physical and chemical properties depend on the ways in which different atoms combine.
- 1.2** The mole makes it possible to correlate the number of particles with the mass that can be measured.
- 1.3** Mole ratios in chemical equations can be used to calculate reacting ratios by mass and gas volume.

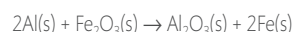
The birth of chemistry as a physical science can be traced back to the first successful attempts to quantify chemical change. Carefully devised experiments led to data that revealed one simple truth. *Chemical change involves interactions between particles that have fixed mass.* Even before knowledge was gained of the atomic nature of these particles and of the factors that determine their interactions, this discovery became the guiding principle for modern chemistry. We begin our study with a brief introduction to this particulate nature of matter, and go on to investigate some of the ways in which it can be quantified.

The term **stoichiometry** is derived from two Greek words – *stoicheion* for element and *metron* for measure. Stoichiometry describes the relationships between the amounts of reactants and products during chemical reactions. As it is known that matter is conserved during chemical change, stoichiometry is a form of book-keeping at the atomic level. It enables chemists to determine what amounts of substances they should react together and enables them to predict how much product will be obtained. The application of stoichiometry closes the gap between what is happening on the atomic scale and what can be measured.

In many ways this chapter can be considered as a toolkit for the mathematical content in much of the course. It covers the universal language of chemistry, **chemical equations**, and introduces the **mole** as the unit of amount. Applications include measurements of mass, volume, and concentration.

You may choose not to work through all of this at the start of the course, but to come back to these concepts after you have gained knowledge of some of the fundamental properties of chemical matter in Chapters 2, 3, and 4.

The reaction between ignited powdered aluminium and iron oxide, known as the thermite reaction:



Significant heat is released by the reaction, and it is used in welding processes including underwater welding. The stoichiometry of the reaction, as shown in the balanced equation, enables chemists to determine the reacting masses of reactants and products for optimum use.

## 1.1

### Introduction to the particulate nature of matter and chemical change

#### Understandings:

- Atoms of different elements combine in fixed ratios to form compounds, which have different properties from their component elements.

#### Guidance

*Names and symbols of the elements are in the IB data booklet in section 5.*

- Mixtures contain more than one element and/or compound that are not chemically bonded together and so retain their individual properties.
- Mixtures are either homogeneous or heterogeneous.



- Deduction of chemical equations when reactants and products are specified.

Balancing of equations should include a variety of types of reactions.

- Application of the state symbols (s), (l), (g), and (aq) in equations.
- Explanation of observable changes in physical properties and temperature during changes of state.

- Names of the changes of state – melting, freezing, vaporization (evaporation and boiling), condensation, sublimation and deposition – should be covered.

- The term 'latent heat' is not required.



Antoine-Laurent Lavoisier (1743–1794) is often called the ‘father of chemistry’. His many accomplishments include the naming of oxygen and hydrogen, the early development of the metric system, and a standardization of chemical nomenclature. Most importantly, he established an understanding of combustion as a process involving combination with oxygen from the air, and recognized that matter retains its mass through chemical change, leading to the law of conservation of mass. In addition, he compiled the first extensive list of elements in his book *Elements of Chemistry* (1789). In short, he changed chemistry from a qualitative to a quantitative science. But, as an unpopular tax collector in France during the French Revolution and Terror, he was tried for treason and guillotined in 1794. One and a half years after his death he was exonerated, and his early demise was recognized as a major loss to France.

The English language is based on an alphabet of just 26 letters. But as we know, combining these in different ways leads to an almost infinite number of words, and then sentences, paragraphs, books, and so on. It is similar to the situation in chemistry, where the 'letters' are the single substances known as **chemical elements**. There are

Antoine-Laurent Lavoisier,  
French chemist (1743–1794).

**A chemical element is a single pure substance, made of only one type of atom.**

Pictographic symbols used at the beginning of the 18th century to represent chemical elements and compounds. They are similar to those of the ancient alchemists.

As more elements were discovered during the 18th century, attempts to devise a chemical nomenclature led to the modern alphabetic notational system. This system was devised by the Swedish chemist Berzelius and introduced in 1814.

[illegible]

only about 100 of these, but because of the ways in which they combine with each other, they make up the almost countless number of different chemical substances in our world.

In Chapter 2 we will learn about atomic structure, and how each element is made up of a particular type of atom. The atoms of an element are all the same as each other (with the exception of isotopes, which we will also discuss in Chapter 2), and are different from those of other elements. It is this distinct nature of its atoms that gives each element its individual properties. A useful definition of an atom is that it is the smallest particle of an element to show the characteristic properties of that element.

To help communication in chemistry, each element is denoted by a **chemical symbol** of either one upper case letter, or one upper case letter followed by a lower case letter. A few examples are given below.

Name of element	Symbol
carbon	C
fluorine	F
potassium	K
calcium	Ca
mercury	Hg
tungsten	W

You will notice that often the letter or letters used are derived from the English name of the element, but in some cases they derive from other languages. For example, Hg for mercury comes from Latin, whereas W for tungsten has its origin in European dialects. Happily, these symbols are all accepted and used internationally, so they do not need to be translated. A complete list of the names of the elements and their symbols is given in section 5 of the IB data booklet.

## Chemical compounds are formed from more than one element

Some elements, such as nitrogen and gold, are found in **native** form, that is uncombined with other elements in nature. But more commonly, elements exist in chemical combinations with other elements, in substances known as **chemical compounds**. Compounds contain a fixed proportion of elements, and are held together by chemical bonds (discussed in Chapter 4). The bonding between atoms in compounds changes their



Assorted minerals, including elements such as sulfur and silver, and compounds such as  $\text{Al}_2\text{O}_3$  (sapphire) and  $\text{CaF}_2$  (fluorite). Most minerals are impure and exist as mixtures of different elements and compounds.



The International Union of Pure and Applied Chemistry (IUPAC) was formed in 1919 by chemists from industry and academia. Since then it has developed into the world authority on chemical nomenclature and terminology. It has succeeded in fostering worldwide communications in the chemical sciences and in uniting academic, industrial, and public sector chemistry in a common language.



Chemistry is a very exact subject, and it is important to be careful in distinguishing between upper and lower case letters. For example, Co (cobalt, a metallic element) means something completely different from CO (carbon monoxide, a poisonous gas).



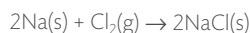
The number of elements that exist is open to change as new ones are discovered, although there is often a time-lag between a discovery and its confirmation by IUPAC. During this time a provisional systematic three-letter symbol is used, using Latin abbreviations to represent the atomic number. The letters u (un) = 1, b (bi) = 2, t (tri) = 3 and so on are used. So the provisional element of atomic number 118 will continue to be known as ununoctium or uuo until it is confirmed and a name formally agreed according to the process established by IUPAC.



**A compound is a chemical combination of different elements, containing a fixed ratio of atoms. The physical and chemical properties of a compound are different from those of its component elements.**



A combustion spoon holding sodium, Na, is lowered into a gas jar containing chlorine, Cl<sub>2</sub>. The vigorous reaction produces white crystals of sodium chloride, NaCl.



The properties of the compound are completely different from those of its component elements.

A chemical equation shows:

direction of  
change

reactants  $\longrightarrow$  products

Chemical equations are the universal language of chemistry. What other languages are universal, and to what extent do they help or hinder the pursuit of knowledge?

**TOK**

**Figure 1.1** When hydrogen and oxygen react to form water, the atoms are rearranged, but the number of atoms of each element remains the same.

properties, so compounds have completely different properties from those of their component elements.

A classic example of this is that sodium, Na, is a dangerously reactive metal that reacts violently with water, while chlorine, Cl<sub>2</sub>, is a toxic gas used as a chemical weapon. Yet when these two elements combine, they form the compound sodium chloride, NaCl, a white crystalline solid that we sprinkle all over our food.

Compounds are described using the chemical symbols for elements. A subscript is used to show the number of atoms of each element in a unit of the compound. Some examples are given below. (The reasons for the different ratios of elements in compounds will become clearer after we have studied atomic structure and bonding in Chapters 2 and 4.)

Name of compound	Symbol	Name of compound	Symbol
sodium chloride	NaCl	water	H <sub>2</sub> O
potassium oxide	K <sub>2</sub> O	glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>
copper bromide	CuBr <sub>2</sub>	ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>

Chemical equations summarize chemical change


The formation of compounds from elements is an example of **chemical change** and can be represented by a **chemical equation**. A chemical equation is a representation using chemical symbols of the simplest ratio of atoms, as elements or in compounds, undergoing chemical change. The left-hand side shows the **reactants** and the right-hand side the **products**.

For example:      calcium + chlorine → calcium chloride  
                          Ca      +      Cl<sub>2</sub>      →      CaCl<sub>2</sub>

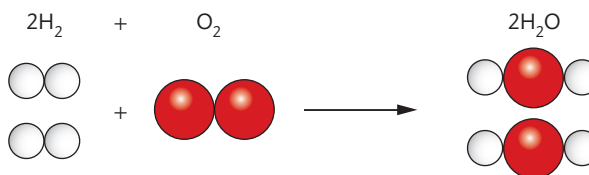
As atoms are neither created nor destroyed during a chemical reaction, *the total number of atoms of each element must be the same on both sides of the equation*. This is known as **balancing the equation**, and uses numbers called **stoichiometric coefficients** to denote the number of units of each term in the equation.

For example:

hydrogen	+	oxygen	→	water
2H <sub>2</sub>	+	O <sub>2</sub>	→	2H <sub>2</sub> O



	total on left side	total on right side
hydrogen atoms	4	4
oxygen atoms	2	2



Note that when the coefficient is 1, this does not need to be explicitly stated.



## NATURE OF SCIENCE



Early ideas to explain chemical change in combustion and rusting included the 'phlogiston' theory. This proposed the existence of a fire-like element that was released during these processes. The theory seemed to explain some of the observations of its time, although these were purely qualitative. It could not explain later quantitative data showing that substances actually gain rather than lose mass during burning. In 1783, Lavoisier's work on oxygen confirmed that combustion and rusting involve combination with oxygen from the air, so overturning the phlogiston theory. This is a good example of how the evolution of scientific ideas, such as how chemical change occurs, is based on the need for theories that can be tested by experiment. Where results are not compatible with the theory, a new theory must be put forward, which must then be subject to the same rigour of experimental test.

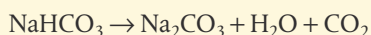
Chemical equations are used to show all types of reactions in chemistry, including reactions of decomposition, combustion, neutralization, and so on. Examples of these are given below and you will come across very many more during this course. Learning to write equations is an important skill in chemistry, which develops quickly with practice.

### Worked example

Write an equation for the reaction of thermal decomposition of sodium hydrogencarbonate ( $\text{NaHCO}_3$ ) into sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), water ( $\text{H}_2\text{O}$ ), and carbon dioxide ( $\text{CO}_2$ ).

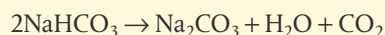
### Solution

First write the information from the question in the form of an equation, and then check the number of atoms of each element on both sides of the equation.



	total on left side	total on right side
sodium atoms	1	2
hydrogen atoms	1	2
carbon atoms	1	2
oxygen atoms	3	6

In order to balance this we introduce coefficient 2 on the left.



Finally check that it is balanced for each element.



An equation by definition has to be *balanced*, so do not expect this to be specified in a question. After you have written an equation, *always* check the numbers of atoms of each element on both sides of the equation to ensure it is correctly balanced.



When a question refers to 'heating' a reactant or to 'thermal decomposition', this does not mean the addition of oxygen, only that heat is the source of energy for the reaction. If the question refers to 'burning' or 'combustion', this indicates that oxygen is a reactant.

### Exercises

- Write balanced chemical equations for the following reactions:
  - The decomposition of copper carbonate ( $\text{CuCO}_3$ ) into copper(II) oxide ( $\text{CuO}$ ) and carbon dioxide ( $\text{CO}_2$ ).
  - The combustion of magnesium ( $\text{Mg}$ ) in oxygen ( $\text{O}_2$ ) to form magnesium oxide ( $\text{MgO}$ ).
  - The neutralization of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with sodium hydroxide ( $\text{NaOH}$ ) to form sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and water ( $\text{H}_2\text{O}$ ).
  - The synthesis of ammonia ( $\text{NH}_3$ ) from nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ).
  - The combustion of methane ( $\text{CH}_4$ ) to produce carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ).
- Write balanced chemical equations for the following reactions:
  - $\text{K} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2$
  - $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
  - $\text{Cl}_2 + \text{KI} \rightarrow \text{KCl} + \text{I}_2$
  - $\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + \text{O}_2$
  - $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow \text{CO} + \text{Fe}$



Remember when you are balancing an equation, change the stoichiometric coefficient but never change the subscript in a chemical formula.

When balancing equations, start with the most complex species, and leave terms that involve a single element to last.



3 Use the same processes to balance the following examples:

- (a)  $\text{C}_4\text{H}_{10} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- (b)  $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$
- (c)  $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
- (d)  $\text{H}_2\text{O}_2 + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{O}_2$
- (e)  $\text{C}_2\text{H}_7\text{N} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$



A chemical equation can be used to assess the efficiency of a reaction in making a particular product. The **atom economy** is a concept used for this purpose and is defined as:

$$\% \text{ atom economy} = \frac{\text{mass of desired product}}{\text{total mass of products}} \times 100$$

Note that this is different from % yield discussed later in this chapter, which is calculated using only one product and one reactant. Atom economy is an indication of how much of the reactants ends up in the required products, rather than in waste products. A higher atom economy indicates a more efficient and less wasteful process. The concept is increasingly used in developments in green and sustainable chemistry. This is discussed further in Chapters 12 and 13.

A mixture is composed of two or more substances in which no chemical combination has occurred.



## Mixtures form when substances combine without chemical interaction

Air is described as a **mixture** of gases because the separate components – different elements and compounds – are interspersed with each other, but are not chemically combined. This means, for example, that the gases nitrogen and oxygen when mixed

in air retain the same characteristic properties as when they are in the pure form. Substances burn in air because the oxygen present supports combustion, as does pure oxygen.

Another characteristic of mixtures is that their composition is not fixed. For example, air that we breathe in typically contains about 20% by volume oxygen, whereas the air that we breathe out usually contains only about 16% by volume oxygen. It is still correct to call both of these mixtures of air, because there is no fixed proportion in the definition.



Tide of oily water heading towards Pensacola Beach, Florida, USA, after the explosion of the offshore drilling unit in the Gulf of Mexico in 2010. The oil forms a separate layer as it does not mix with the water.

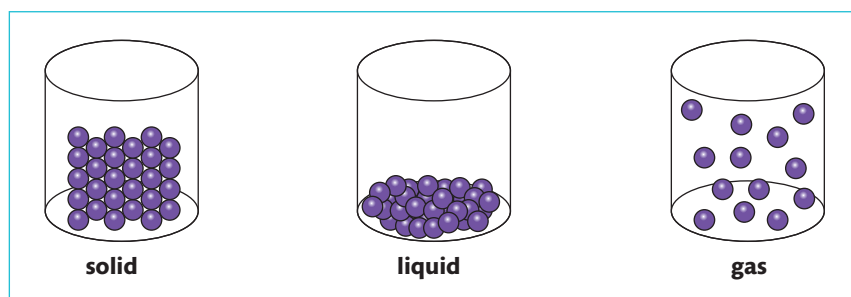
Air is an example of a **homogeneous mixture**, meaning that it has uniform composition and properties throughout. A solution of salt in water and a metal alloy such as bronze are also homogeneous. By contrast, a **heterogeneous mixture** such as water and oil has non-uniform composition, so its properties are not the same throughout. It is usually possible to see the separate components in a heterogeneous mixture but not in a homogeneous mixture.

Because the components retain their individual properties in a mixture, we can often separate them relatively easily. The technique we choose to achieve this will take advantage of a suitable difference in the physical properties of the components, as shown in the table below. Many of these are important processes in research and industry and are discussed in more detail in the following chapters.

Mixture	Difference in property of components	Technique used
sand and salt	solubility in water	solution and filtration
hydrocarbons in crude oil	boiling point	fractional distillation
iron and sulfur	magnetism	response to a magnet
pigments in food colouring	adsorption to solid phase	paper chromatography
different amino acids	net charge at a fixed pH	gel electrophoresis

## Matter exists in different states determined by the temperature and pressure

From our everyday experience, we know that all matter (elements, compounds, and mixtures) can exist in different forms depending on the temperature and pressure. Liquid water changes into a solid form such as ice, hail, or snow, as the temperature drops and it becomes a gas, steam, at high temperatures. These different forms are known as the **states of matter** and are characterized by the different energies of the particles.



increasing temperature

increasing kinetic energy of particles

- |  |  |  |
|--|--|--|
| <ul style="list-style-type: none"> <li>• particles close packed</li> <li>• inter-particle forces strong, particles vibrate in position</li> <li>• fixed shape</li> <li>• fixed volume</li> </ul> | <ul style="list-style-type: none"> <li>• particles more spaced</li> <li>• inter-particle forces weaker, particles can slide over each other</li> <li>• no fixed shape</li> <li>• fixed volume</li> </ul> | <ul style="list-style-type: none"> <li>• particles spread out</li> <li>• inter-particle forces negligible, particles move freely</li> <li>• no fixed shape</li> <li>• no fixed volume</li> </ul> |
|--|--|--|



Ocean oil spills are usually the result of accidents in the industries of oil extraction or transport. The release of significant volumes of oil causes widespread damage to the environment, especially wildlife, and can have a major impact on local industries such as fishing and tourism. Efforts to reduce the impact of the spill include the use of dispersants, which act somewhat like soap in helping to break up the oil into smaller droplets so it can mix better with water. Concern is expressed, however, that these chemicals may increase the toxicity of the oil and they might persist in the environment. The effects of an oil spill often reach countries far from the source and are the subject of complex issues in international law. With the growth in demand for offshore drilling for oil and projected increases in oil pipelines, these issues are likely to become all the more pressing.

**Figure 1.2** Representation of the arrangement of the particles of the same substance in the solid, liquid, and gas states.



Depending on the chemical nature of the substance, matter may exist as atoms such as  $\text{Ar(g)}$ , or as molecules such as  $\text{H}_2\text{O(l)}$ , or as ions such as  $\text{Na}^+$  and  $\text{Cl}^-$  in  $\text{NaCl(aq)}$ . The term **particle** is therefore used as an inclusive term that is applied in this text to any or all of these entities of matter.



Temperature is a measure of the average kinetic energy of the particles of a substance.



▲ Bromine liquid,  $\text{Br}_2(\text{l})$ , had been placed in the lower gas jar, and its vapour has diffused to fill both jars. Bromine vaporizes readily at room temperature and the gas colour allows the diffusion to be observed. Because gas molecules can move independently of each other and do so randomly, a gas spreads out from its source in this way.

This is known as the **kinetic theory** of matter. It recognizes that the average kinetic energy of the particles is directly related to the temperature of the system. The state of matter at a given temperature and pressure is determined by the strength of forces that may exist between the particles, known as **inter-particle forces**. The average kinetic energy is proportional to the temperature in kelvin, introduced on page 37.

### Worked example

Which of the following has the highest average kinetic energy?

A He at  $100^\circ\text{C}$

B  $\text{H}_2$  at  $200^\circ\text{C}$

C  $\text{O}_2$  at  $300^\circ\text{C}$

D  $\text{H}_2\text{O}$  at  $400^\circ\text{C}$

### Solution

Answer = D. The substance at the highest temperature has the highest average kinetic energy.

Liquids and gases are referred to as **fluids**, which refers to their ability to flow. In the case of liquids it means that they take the shape of their container. Fluid properties are why **diffusion** occurs predominantly in these two states. Diffusion is the process by which the particles of a substance become evenly distributed, as a result of their random movements.

Kinetic energy (KE) refers to the energy associated with movement or motion. It is determined by the mass ( $m$ ) and velocity ( $v$ ) of a substance according to the relationship:

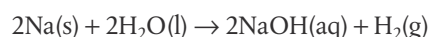
$$\text{KE} = \frac{1}{2}mv^2$$

As the kinetic energy of the particles of substances at the same temperature is equal, this means there is an inverse relationship between mass and velocity or speed. This is why substances with lower mass diffuse more quickly than those with greater mass, when measured at the same temperature. This is discussed in more detail in Chapter 14, Option C: Energy.

**State symbols** are used to show the states of the reactants and products taking part in a reaction. These are abbreviations, which are given in brackets after each term in an equation, as shown below.

State	Symbol	Example
solid	(s)	$\text{Mg}(\text{s})$
liquid	(l)	$\text{Br}_2(\text{l})$
gas	(g)	$\text{N}_2(\text{g})$
aqueous (dissolved in water)	(aq)	$\text{HCl}(\text{aq})$

For example:



### Exercises

4 Classify the following mixtures as homogeneous or heterogeneous:

(a) sand and water

(b) smoke

(c) sugar and water

(d) salt and iron filings

(e) ethanol and water in wine

(f) steel

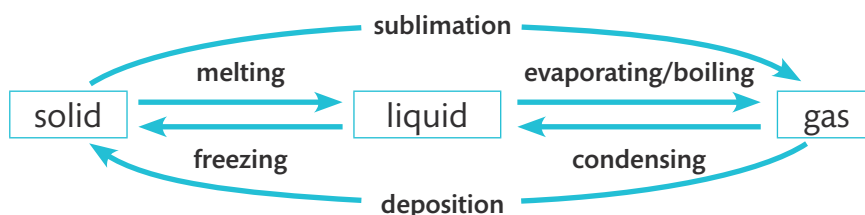
- 5 Write balanced equations for the following reactions and apply state symbols to all reactants and products, assuming room temperature and pressure unless stated otherwise. If you are not familiar with the aqueous solubilities of some of these substances, you may have to look them up.
- (a)  $\text{KNO}_3 \rightarrow \text{KNO}_2 + \text{O}_2$  (when heated (500 °C))
  - (b)  $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$
  - (c)  $\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$
  - (d)  $\text{Pb}(\text{NO}_3)_2 + \text{NaCl} \rightarrow \text{PbCl}_2 + \text{NaNO}_3$  (all reactants are in aqueous solution)
  - (e)  $\text{C}_3\text{H}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  (combustion reaction)
- 6 A mixture of two gases, X and Y, which both have strong but distinct smells, is released. From across the room the smell of X is detected more quickly than the smell of Y. What can you deduce about X and Y?
- 7 Ice floats on water. Comment on why this is not what you would expect from the kinetic theory of matter.



It is good practice to show state symbols in all equations, even when they are not specifically requested.

## Matter changes state reversibly

As the movement or kinetic energy of the particles increases with temperature, they will overcome the inter-particle forces and change state. These state changes occur at a fixed temperature and pressure for each substance, and are given specific names shown below.



Sublimation, the direct inter-conversion of solid to gas without going through the liquid state, is characteristic at atmospheric pressure of some substances such as iodine, carbon dioxide, and ammonium chloride. Deposition, the reverse of sublimation that changes a gas directly to solid, is responsible for the formation of snow, frost, and hoar frost.

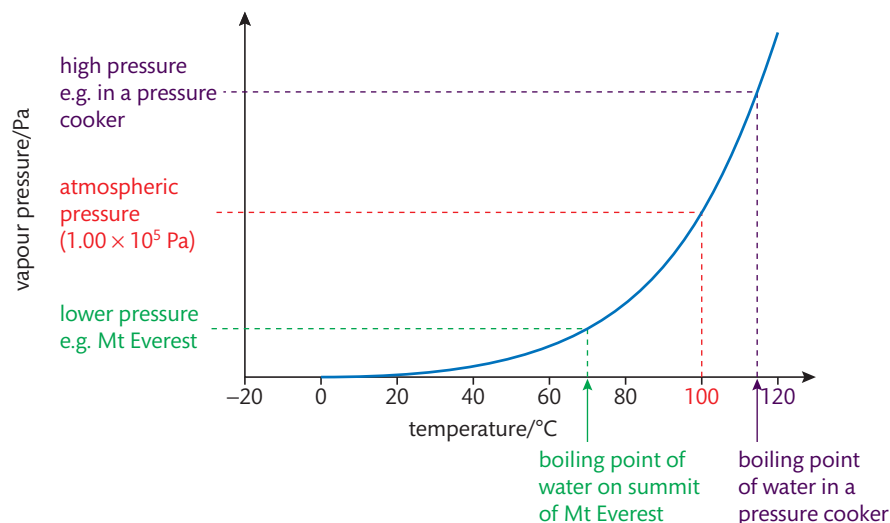
Note that evaporation involves the change of liquid to gas, but, unlike boiling, evaporation occurs only at the surface and takes place at temperatures below the boiling point.



▲ Drying clothes. The heat of the Sun enables all the water to evaporate from the clothes.

Ice crystals, known as Hair Ice, formed by deposition on dead wood in a forest on Vancouver Island, Canada.

Boiling, on the other hand, is a volume phenomenon, characterized by particles leaving throughout the body of the liquid – which is why bubbles occur. Boiling occurs at a specific temperature, determined by when the vapour pressure reaches the external pressure. The influence of pressure on the temperature at which this occurs is demonstrated in Figure 1.3.



**Figure 1.3** Graph showing the increase in vapour pressure with temperature. This explains why boiling point changes with pressure. The boiling point of water at three different pressures is shown.

A pressure cooker is a sealed container in which a higher pressure can be generated. This raises the boiling point of water and so cooking time decreases. Conversely, at altitude, where the atmospheric pressure is lower, the boiling point of water is reduced so it takes much longer to cook food.



A butane gas camping stove.

Butane,  $C_4H_{10}$ , is stored as a liquid because the high pressure in the canister raises its boiling point. When the valve is opened the release of pressure causes it to boil, releasing a gas that can be burned.



## CHALLENGE YOURSELF

- Propane ( $C_3H_8$ ) and butane ( $C_4H_{10}$ ) are both commonly used in portable heating devices. Their boiling points are butane  $-1^\circ\text{C}$  and propane  $-42^\circ\text{C}$ . Suggest why butane is less suitable for use in very cold climates.



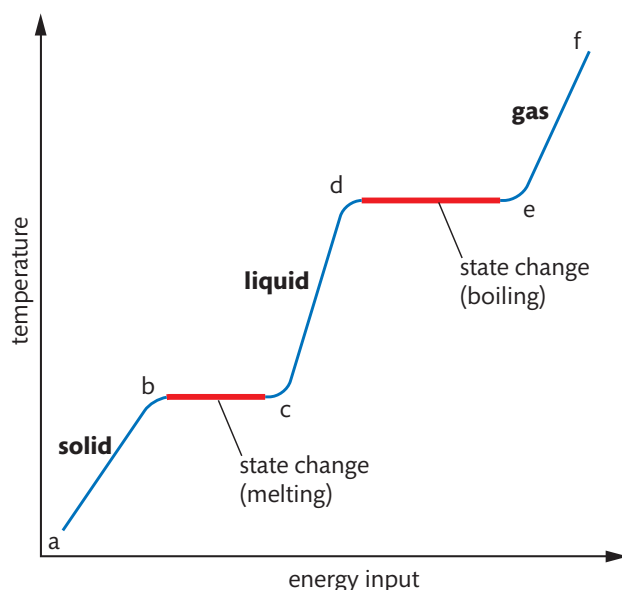
Macro photograph of freeze-dried instant coffee granules.



Freeze-drying is an effective process for the preservation of food and some pharmaceuticals. It differs from standard methods of dehydration in that it does not use heat to evaporate water, but instead depends on the sublimation of ice. The substance to be preserved is first frozen, and then warmed gently at very low pressure which causes the ice to change directly to water vapour. The process is slow but has the significant advantage that the composition of the material, and so its flavour, are largely conserved. The freeze-dried product is stored in a moisture-free package that excludes oxygen, and can be reconstituted by the addition of water.



At night as the temperature is lowered, the rate of condensation increases. As the air temperature drops below its saturation point, known as the **dew point**, the familiar condensed water called **dew** forms. The temperature of the dew point depends on the atmospheric pressure and the water content of the air – that is, the relative humidity. A relative humidity of 100% indicates that the air is maximally saturated with water and the dew point is equal to the current temperature. Most people find this uncomfortable, as the condensation inhibits the evaporation of sweat, one of the body's main cooling mechanisms.



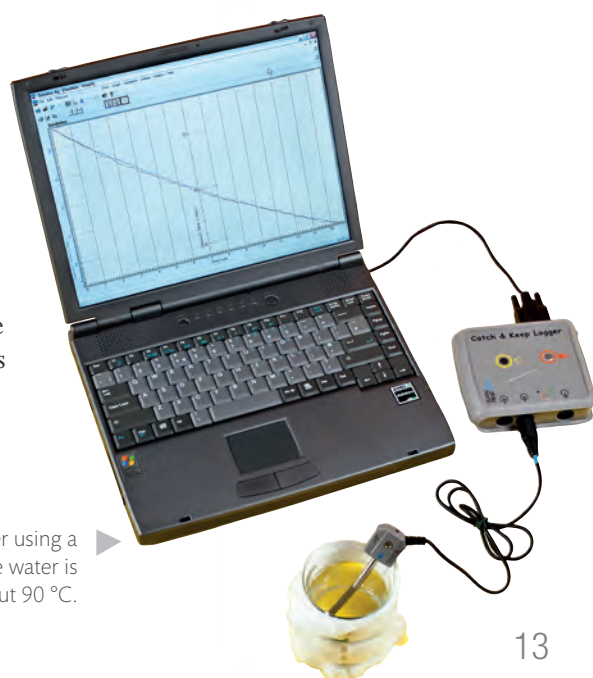
**Figure 1.4** Temperature change versus energy input at fixed pressure as a solid substance is heated. The flat regions shown in red are where the state change is occurring, as heat energy is used to overcome the inter-particle forces.

Simple experiments can be done to monitor the temperature change while a substance is heated and changes state. Figure 1.4 shows a typical result. The graph can be interpreted as follows:

- a–b As the solid is heated, the vibrational energy of its particles increases and so the temperature increases.
- b–c This is the melting point. The vibrations are sufficiently energetic for the molecules to move away from their fixed positions and form liquid. Energy added during this stage is used to break the inter-particle forces, not to raise the kinetic energy, so the temperature remains constant.
- c–d As the liquid is heated, the particles gain kinetic energy and so the temperature increases.
- d–e This is the boiling point. There is now sufficient energy to break all of the inter-particle forces and form gas. Note that this state change needs more energy than melting, as all the inter-particle forces must be broken. The temperature remains constant as the kinetic energy does not increase during this stage. Bubbles of gas are visible throughout the volume of the liquid.
- e–f As the gas is heated under pressure, the kinetic energy of its particles continues to rise, and so does the temperature.

A fourth state of matter, plasma, exists only at conditions of very high temperatures and pressures, such as are commonly found in space. It is characterized by atoms that have been stripped of their electrons, and so exist as positively charged ions in loose association with their electrons. Plasma is a fluid, like liquid and gas, but also generates electromagnetic forces due to the charged particles present. All matter in the stars, including our Sun, exists in the plasma state.

Experiment to measure the change in temperature of water using a temperature probe. In this example, the temperature of the water is decreasing as it cools from about 90 °C.



The global demand for refrigeration and air-conditioning systems is increasing sharply with increases in population and industrialization. It is estimated that world consumption of energy for cooling could increase tenfold by 2050, and that China will surpass the USA as the world's biggest user of energy for cooling by 2020. The increased energy demand has significant consequences for the environment, as both the energy use and the release of refrigerants such as HFCs contribute to greenhouse gas emissions, linked to climate change.



The process of refrigeration is usually based on energy changes during the evaporation and condensation cycle under changing pressure of a volatile liquid known as the **refrigerant**. At low pressure the liquid vaporizes and absorbs heat, causing cooling of the surroundings. Chlorofluorocarbons (CFCs) were commonly widely used as refrigerants, but these are now mostly phased out owing to their harmful role in causing ozone depletion. This is discussed further in Chapter 4. CFCs are largely replaced by hydrofluorocarbons (HFCs).

### Exercises

- 8 A closed flask contains a pure substance, a brown liquid that is at its boiling point. Explain what you are likely to observe in the flask, and distinguish between the inter-particle distances and the average speeds of the particles in the two states present.
- 9 During very cold weather, snow often gradually disappears without melting. Explain how this is possible.
- 10 Explain why a burn to the skin caused by steam is more serious than a burn caused by the same amount of boiling water at the same temperature.
- 11 Which of the following occurs at the melting point when solid sulfur is converted to its liquid form?
  - I movement of the particles increases
  - II distance between the particles increases

**A** I only      **B** II only      **C** Both I and II      **D** Neither I nor II
- 12 You are given a liquid substance at 80 °C and told that it has a melting point of 35 °C. You are asked to take its temperature at regular time intervals while it cools to room temperature (25 °C). Sketch the cooling curve that you would expect to obtain.

The SI (Système International d'Unités) refers to the metric system of measurement based on seven base units. These are metre (m) for length, kilogram (kg) for mass, second (s) for time, ampere (A) for electric current, kelvin (K) for temperature, candela (cd) for luminous intensity and mole (mol) for amount. All other units are derived from these. The SI system is the world's most widely used system of measurement.



## 1.2 The mole concept

### Understandings:

- The mole is a fixed number of particles and refers to the amount,  $n$ , of substance.

#### Guidance

The value of the Avogadro's constant ( $L$  or  $N_A$ ) is given in the IB data booklet in section 2 and will be given for Paper 1 questions.

- Masses of atoms are compared on a scale relative to  $^{12}\text{C}$  and are expressed as relative atomic mass ( $A_r$ ) and relative formula/molecular mass ( $M_r$ ).
- Molar mass ( $M$ ) has the units  $\text{g mol}^{-1}$ .

#### Guidance

The generally used unit of molar mass ( $\text{g mol}^{-1}$ ) is a derived SI unit.

- The empirical and molecular formula of a compound give the simplest ratio and the actual number of atoms present in a molecule respectively.

### Applications and skills:

- Calculation of the molar masses of atoms, ions, molecules, formula units.
- Solution of problems involving the relationship between the number of particles, the amount of substance in moles, and the mass in grams.
- Interconversion of the percentage composition by mass and the empirical formula.
- Determination of the molecular formula of a compound from its empirical formula and molar mass.
- Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

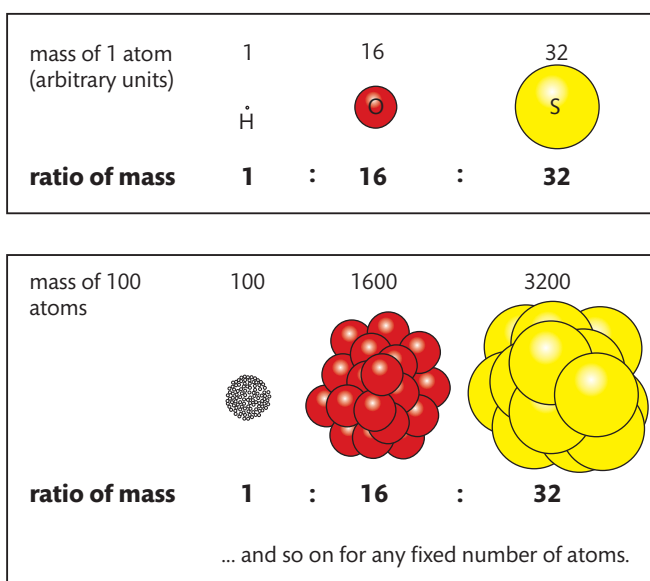
The International Bureau of Weights and Measures (BIPM according to its French initials) is an international standards organization, which aims to ensure uniformity in the application of SI units around the world.



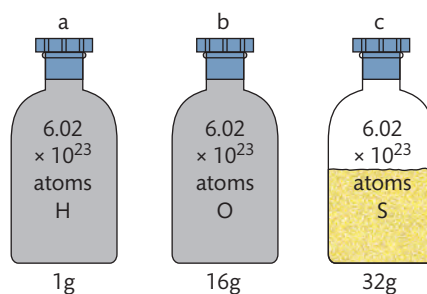
## The Avogadro constant defines the mole as the unit of amount in chemistry

A problem in studying chemical change is that atoms are too small to measure individually. For example, even a relatively large atom like gold (Au) has a mass of  $3.27 \times 10^{-25}$  kg – not a very useful figure when it comes to weighing it in a laboratory. But it's not really a problem, because all we need to do is to weigh an appropriately large number of atoms to give a mass that will be a useful quantity in grams. And in any case, atoms do not react individually but in very large numbers, so this approach makes sense. So how many atoms shall we lump together in our base unit of amount?

To answer this, let's first consider that atoms of different elements have different masses because they contain different numbers of particles, mostly **nucleons** in their nucleus, as we will discuss in Chapter 2. This means we can compare their masses with each other in relative terms. For example, an atom of oxygen has a mass approximately 16 times greater than an atom of hydrogen, and an atom of sulfur has a mass about twice that of an atom of oxygen. Now the good news is that these ratios will stay the same when we increase the number of atoms, *so long as we ensure we have the same number of each type*.



Now if we could take  $6 \times 10^{23}$  atoms of hydrogen, it happens that this would have a mass of 1 g. It follows from the ratios above, that *the same number of atoms* of oxygen would have a mass of 16 g while *the same number of atoms* of sulfur has a mass of 32 g. So we now have a quantity of atoms that we can measure in grams.



Amedeo Avogadro (1776–1856) was an Italian scientist who made several experimental discoveries. He clarified the distinction between atoms and molecules, and used this to propose the relationship between gas volume and number of molecules. His ideas were not, however, accepted in his time, largely due to a lack of consistent experimental evidence. After his death, when his theory was confirmed by fellow Italian Cannizzaro, his name was given in tribute to the famous constant that he helped to establish.

**Figure 1.5** One hundred atoms of H, O, and S have the same mass ratio as one atom of each element, 1 : 16 : 32.

**Figure 1.6**  $6.02 \times 10^{23}$  atoms of H, O, and S have the same mass ratio by mass as one atom of each element. This number of atoms gives an amount that we can see and measure in grams. (Note that this is illustrative only; in reality hydrogen and oxygen do not occur stably as single atoms, but as diatomic molecules – as explained in Chapter 4.)



The Avogadro constant,  $6.02 \times 10^{23}$ , is the number of particles in one mole of a substance and has the units  $\text{mol}^{-1}$ .



This number, accurately stated as  $6.02214129 \times 10^{23}$ , is known as the **Avogadro number**, and it is the basis of the unit of **amount** used in chemistry known as the **mole**. In other words, a mole of a substance contains the Avogadro number of particles. Mole, the unit of amount, is one of the base units in the SI system and has the unit symbol **mol**.

So 'mole' is simply a word that represents a number, just as 'couple' is a word for 2, 'dozen' is a word for 12, and 'score' is a word that was commonly used for 20. A mole is a very large number, bigger than we can easily imagine or ever count, but it is nonetheless a fixed number. So a mole of any substance contains that Avogadro number,  $6.02 \times 10^{23}$ , of particles. You can refer to a mole of atoms, molecules, ions, electrons, and so on – it can be applied to any entity as it is just a number. And from this, we can easily calculate the number of particles in any portion or multiple of a mole of a substance.

Each beaker contains one mole,  $6.02 \times 10^{23}$  particles, of a specific element. Each has a characteristic mass, known as its molar mass. From left to right the elements are tin (Sn), magnesium (Mg), iodine (I), and copper (Cu).



Avogadro's constant is so large that we cannot comprehend its scale. For example:

- $6.02 \times 10^{23}$  pennies distributed to everyone alive would make everyone on Earth a dollar trillionaire;
- $6.02 \times 10^{23}$  pencil erasers would cover the Earth to a depth of about 500 m;
- $6.02 \times 10^{23}$  drops of water would fill all the oceans of the Earth many times over.

What ways of knowing can we use to grasp the magnitude of Avogadro's constant even though it is beyond the scale of our everyday experience?

**TOK**

In Paper 1 of the IB examinations you are not allowed to use a calculator, so you may well be asked questions that you can solve by simple arithmetic and by manipulating expressions using scientific notation.



### Worked example

A tablespoon holds 0.500 moles of water. How many molecules of water are present?

#### Solution

1.00 mole of water has  $6.02 \times 10^{23}$  molecules of water

$$\therefore 0.500 \text{ moles of water has } \frac{0.500}{1.00} \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 3.01 \times 10^{23} \text{ molecules of water}$$



When doing multiplication or division, the answer is given to the same number of significant figures as the data value with the least number of significant figures. When doing addition or subtraction, the answer is given to the same number of decimal places as the data value with the least number of decimal places.

### Worked example

A solution of water and ammonia contains  $2.10 \times 10^{23}$  molecules of  $\text{H}_2\text{O}$  and  $8.00 \times 10^{21}$  molecules of  $\text{NH}_3$ . How many moles of hydrogen atoms are present?

### Solution

First total the number of hydrogen atoms:

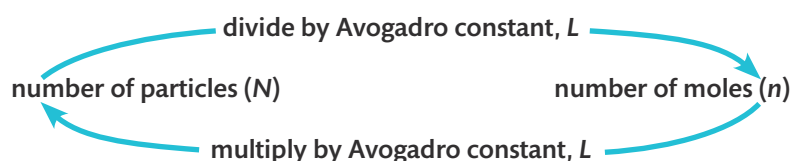
$$\begin{aligned} \text{from water } \text{H}_2\text{O}: \quad \text{number of H atoms} &= 2 \times (2.10 \times 10^{23}) \\ &= 4.20 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{from ammonia } \text{NH}_3: \quad \text{number of H atoms} &= 3 \times (8.00 \times 10^{21}) \\ &= 0.240 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \therefore \text{total H atoms} &= (4.20 \times 10^{23}) + (0.240 \times 10^{23}) \\ &= 4.44 \times 10^{23} \end{aligned}$$

To convert atoms to moles, divide by the Avogadro constant:

$$\frac{4.44 \times 10^{23}}{6.02 \times 10^{23}} = 0.738 \text{ mol H atoms}$$



### Exercises

**13** Calculate how many hydrogen atoms are present in:

(a) 0.020 moles of  $\text{C}_2\text{H}_5\text{OH}$

(b) 2.50 moles of  $\text{H}_2\text{O}$

(c) 0.10 moles of  $\text{Ca}(\text{HCO}_3)_2$

**14** Propane has the formula  $\text{C}_3\text{H}_8$ . If a sample of propane contains 0.20 moles of C, how many moles of H are present?

**15** Calculate the amount of sulfuric acid,  $\text{H}_2\text{SO}_4$ , which contains  $6.02 \times 10^{23}$  atoms of oxygen.

Dealing with Avogadro's constant to calculate the number of particles in a sample has its uses, but it still leaves us with numbers that are beyond our comprehension. What is much more useful, as you have probably realized, is the link between the Avogadro number and the mass of one mole of a substance, which is based on the relative atomic mass.

## Relative atomic mass is used to compare the masses of atoms

On page 15 the numbers used to compare the masses of the elements H, O, and S are only approximate. A slight complexity is that most elements exist naturally with atoms that differ in their mass. These different atoms are known as **isotopes**, and we will look at them in Chapter 2. So a sample of an element containing billions of atoms will include a mix of these isotopes according to their relative abundance. The mass of an individual atom in the sample is therefore taken as a **weighted average** of these different masses.



### NATURE OF SCIENCE

Accurate determinations of Avogadro's number require the measurement of a single quantity using the same unit on both the atomic and macroscopic scales. This was first done following Millikan's work measuring the charge on a single electron. The charge on a mole of electrons, known as the Faraday constant (see Chapters 12 and 14), was already known through electrolysis experiments. Dividing the charge on a mole of electrons ( $96\,485.3383 \text{ C}$ ) by the charge on a single electron ( $1.60217653 \times 10^{-19} \text{ C e}^{-1}$ ) gives a value for Avogadro's number of  $6.02214154 \times 10^{23}$ . Later work used X-ray crystallography (see Chapter 12) of very pure crystals to measure the spacing between particles and so the volume of one mole. The validity of data in science is often enhanced when different experimental approaches lead to consistent results.



**Number of particles ( $N$ )**  
**= number of moles ( $n$ )  $\times$**   
**Avogadro constant ( $L$ ).**

**Relative atomic mass,  $A_r$ , is the weighted average of one atom of an element relative to  $\frac{1}{12}$  of an atom of carbon-12.**

The nomenclature and the reference point used for describing atomic mass have been a subject for debate since John Dalton's work on atomic structure in the early 1800s. The original term 'atomic weight' is now considered largely obsolete. Chemists and physicists previously used two different reference points for mass based on isotopes of oxygen, but since the 1960s the unified scale based on carbon-12 ( $^{12}\text{C}$ ) has gained wide acceptance. The current IUPAC definition of the *unified atomic mass unit* is one-twelfth of the mass of a carbon-12 atom in its ground state with a mass of  $1.66 \times 10^{-27}$  kg.

$A_r$  values are often rounded to whole numbers for quick calculations, but when using values from the IB data booklet for calculations it is usually best to use the exact value given in section 6.

## CHALLENGE YOURSELF

- 2 Three of the compounds in the photograph are hydrated, containing water of crystallization, as described on page 23. Use the formulas given in the caption and the masses marked on the photograph to deduce which compounds are hydrated, and the full formula of each.

The relative scale for comparing the mass of atoms needs a reference point. The international convention for this is to take the specific form of carbon known as the **isotope carbon-12** (see Chapter 2) as the standard, and assign this a value of 12 units. In other words, one-twelfth of an atom of carbon-12 has a value of exactly 1.

Putting this together, we can define the **relative atomic mass** as follows:

$$\text{relative atomic mass } A_r = \frac{\text{weighted average of one atom of the element}}{\frac{1}{12} \text{ mass of one atom of carbon-12}}$$

Values for  $A_r$  do not have units as it is a relative term, which simply compares the mass of atoms against the same standard. As they are average values, they are not whole numbers; the IB data booklet in section 6 gives  $A_r$  values to two decimal places. Some examples are given below.

Element	Relative atomic mass ( $A_r$ )
hydrogen, H	1.01
carbon, C	12.01
oxygen, O	16.00
sodium, Na	22.99
sulfur, S	32.07
chlorine, Cl	35.45

You will notice that the  $A_r$  of carbon is slightly greater than the mass of the isotope carbon-12 used as the standard, suggesting that carbon has isotopes with masses slightly greater than 12. In Chapter 2 we discuss how relative atomic mass is calculated from isotope abundances, using data from mass spectrometry.

## Relative formula mass is used to compare masses of compounds

We can extend the concept of relative atomic mass to compounds (and to elements occurring as molecules), to obtain the **relative formula mass**,  $M_r$ . This simply involves adding the relative atomic masses of all the atoms or ions present in its formula. Note that  $M_r$ , like  $A_r$ , is a relative term and so has no units.



One mole of different compounds, each showing the molar mass. The chemical formulas of these ionic compounds are, clockwise from lower left:  $\text{NaCl}$ ,  $\text{FeCl}_3$ ,  $\text{CuSO}_4$ ,  $\text{KI}$ ,  $\text{Co}(\text{NO}_3)_2$  and  $\text{KMnO}_4$ .



### Worked example

Use the values for  $A_r$  in section 6 of the IB data booklet to calculate the  $M_r$  of the following:

(a) chlorine,  $\text{Cl}_2$

$$M_r = 35.45 \times 2 = 70.90$$

(b) ammonium nitrate,  $\text{NH}_4\text{NO}_3$

$$M_r = 14.01 + (1.01 \times 4) + 14.01 + (16.00 \times 3) = 80.06$$

(c) aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3$

$$M_r = (26.98 \times 2) + [32.07 + (16.00 \times 4)] \times 3 = 342.17$$



Note that the term *relative molecular mass* was previously used for  $M_r$ , but can accurately be applied only to substances that exist as molecules. This excludes all ionic compounds, so the term *relative formula mass* is preferred as it is a more inclusive term, not dependent on the bonding present.

## Molar mass is the mass of one mole of a substance

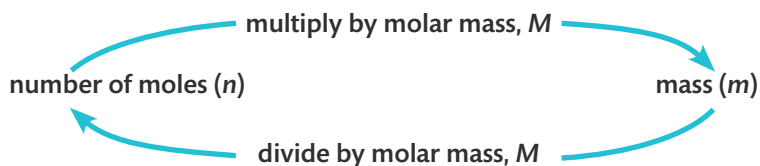
The Avogadro number is defined so that the mass of one mole of a substance is exactly equal to the substance's relative atomic mass expressed in grams. This is known as the **molar mass** and is given the symbol  $M$  with the unit  $\text{g mol}^{-1}$ , which is a derived SI unit. Using the examples discussed already in this chapter, we can now deduce the following:

Element or compound	Molar mass ( $M$ )
hydrogen, H	1.01 $\text{g mol}^{-1}$
oxygen, O	16.00 $\text{g mol}^{-1}$
sulfur, S	32.07 $\text{g mol}^{-1}$
chlorine, $\text{Cl}_2$	70.90 $\text{g mol}^{-1}$
ammonium nitrate, $\text{NH}_4\text{NO}_3$	80.06 $\text{g mol}^{-1}$
aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3$	342.17 $\text{g mol}^{-1}$

From our knowledge of molar mass we can state the definition of the mole as the mass of substance that contains as many particles as there are atoms in 12 g of carbon-12.

Now we are truly able to use the concept of the mole to make that all-important link between the number of particles and their mass in grams. The key to this is conversions of grams to moles and moles to grams. In the calculations that follow, we use the following notation:

- $n$  = number of moles (mol);
- $m$  = mass in grams (g);
- $M$  = molar mass ( $\text{g mol}^{-1}$ ).



Relative formula mass,  $M_r$ , is the sum of the weighted average of the masses of the atoms in a formula unit relative to one-twelfth of an atom of carbon-12.



The molar mass of a substance,  $M$ , is its relative atomic mass,  $A_r$ , or its relative formula mass,  $M_r$ , expressed in grams. It has the unit  $\text{g mol}^{-1}$ .



One mole is the mass of substance that contains as many particles as there are atoms in 12 g of carbon-12.

**Dimensional analysis**, or the factor-label method, is a widely used technique to determine conversion factors on the basis of cancelling the units. This method is not specifically used in the examples here, but the units are shown through the calculations. This method can be helpful to check that the units on both sides of the equation are balanced, and are appropriate for the answer, which is often a useful check on the steps taken. As in all cases, there is no one correct way to set out calculations, so long as the steps are clear.

Note the units cancel to give the correct units for mass. This is often a useful check that we are using the terms correctly in a calculation.



### Worked example

What is the mass of the following?

- (a) 6.50 moles of NaCl  
(b) 0.10 moles of OH<sup>-</sup> ions

### Solution

In all these questions, we must first calculate the molar mass,  $M$ , to know the mass of one mole in  $\text{g mol}^{-1}$ . Multiplying  $M$  by the specified number of moles,  $n$ , will then give the mass,  $m$ , in grams.

$$(a) \quad M(\text{NaCl}) = 22.99 + 35.45 = 58.44 \text{ g mol}^{-1}$$

$$n(\text{NaCl}) = 6.50 \text{ mol}$$

$$\therefore m(\text{NaCl}) = 58.44 \text{ g mol}^{-1} \times 6.50 \text{ mol} = 380 \text{ g}$$

- (b) OH<sup>-</sup> ions carry a charge because electrons have been transferred, but the change to the mass is negligible and so can be ignored in calculating  $M$ .

$$M(\text{OH}^-) = 16.00 + 1.01 = 17.01 \text{ g mol}^{-1}$$

$$n(\text{OH}^-) = 0.10 \text{ mol}$$

$$\therefore m(\text{OH}^-) = 17.01 \text{ g mol}^{-1} \times 0.10 \text{ mol} = 1.7 \text{ g}$$



### Worked example

What is the amount in moles of the following?

- (a) 32.50 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>  
(b) 273.45 g N<sub>2</sub>O<sub>5</sub>

### Solution

Again we calculate the molar mass,  $M$ , to know the mass of one mole. Dividing the given mass,  $m$ , by the mass of one mole will then give the number of moles,  $n$ .

$$(a) \quad M((\text{NH}_4)_2\text{SO}_4) = [14.01 + (1.01 \times 4)] \times 2 + 32.07 + (16.00 \times 4) = 132.17 \text{ g mol}^{-1}$$

$$m((\text{NH}_4)_2\text{SO}_4) = 32.50 \text{ g}$$

$$\therefore n((\text{NH}_4)_2\text{SO}_4) = \frac{32.50 \text{ g}}{132.17 \text{ g mol}^{-1}} = 0.2459 \text{ mol}$$

$$(b) \quad M(\text{N}_2\text{O}_5) = (14.01 \times 2) + (16.00 \times 5) = 108.02 \text{ g mol}^{-1}$$

$$m(\text{N}_2\text{O}_5) = 273.45 \text{ g}$$

$$\therefore n(\text{N}_2\text{O}_5) = \frac{273.45 \text{ g}}{108.02 \text{ g mol}^{-1}} = 2.532 \text{ mol}$$

These simple conversions show that:

$$\text{number of moles (amount)} = \frac{\text{mass}}{\text{molar mass}} \quad n(\text{mol}) = \frac{m(\text{g})}{M(\text{g mol}^{-1})}$$

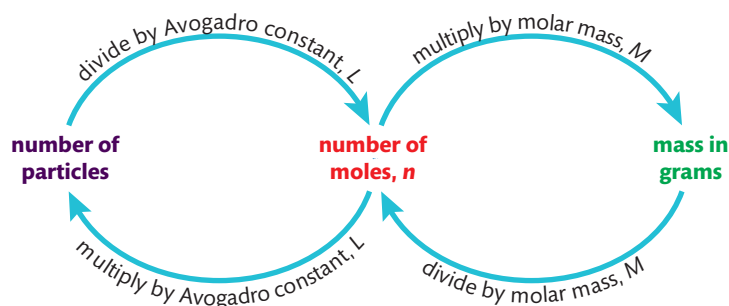
This is a very useful relationship, but it is hoped that you understand how it is derived, rather than rote learn it.

We can now put together the conversions shown on pages 17 and 19, to see the central role of the mole in converting from number of particles to mass in grams.

$$\text{amount} = \frac{\text{mass}}{\text{molar mass}}$$

$$n(\text{mol}) = \frac{m(\text{g})}{M(\text{g mol}^{-1})}$$





**Figure 1.7** Summary of the central role of the number of moles,  $n$ , in converting between the number of particles and the mass in grams.



Calculations involving mass in chemistry always involve converting grams to moles and moles to grams. Think of these conversions as fundamental tools for chemists, and so make sure you are fully comfortable with carrying them out effectively.

## Exercises

\* indicates you should be able to do this question without a calculator.

Note that you should refer to section 6 of the IB data booklet for the values of  $A_r$ .

**16** Calculate the molar mass of the following compounds:

- (a) magnesium phosphate,  $\text{Mg}_3(\text{PO}_4)_2$       (b) ascorbic acid (vitamin C),  $\text{C}_6\text{H}_8\text{O}_6$   
 (c) calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$       (d) hydrated sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

**17** Calcium arsenate,  $\text{Ca}_3(\text{AsO}_4)_2$ , is a poison which was widely used as an insecticide. What is the mass of 0.475 mol of calcium arsenate?

**18\*** How many moles of carbon dioxide are there in 66 g of carbon dioxide,  $\text{CO}_2$ ?

**19** How many moles of chloride ions ( $\text{Cl}^-$ ) are there in 0.50 g of copper(II) chloride,  $\text{CuCl}_2$ ?

**20** How many carbon atoms are there in 36.55 g of diamond (which is pure carbon)?

**21\*** What is the mass in grams of a 0.500 mol sample of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ?

**22\*** Which contains the greater number of particles, 10.0 g of water ( $\text{H}_2\text{O}$ ) or 10.0 g of mercury ( $\text{Hg}$ )?

**23\*** Put the following in descending order of mass.

1.0 mol  $\text{N}_2\text{H}_4$

2.0 mol  $\text{N}_2$

3.0 mol  $\text{NH}_3$

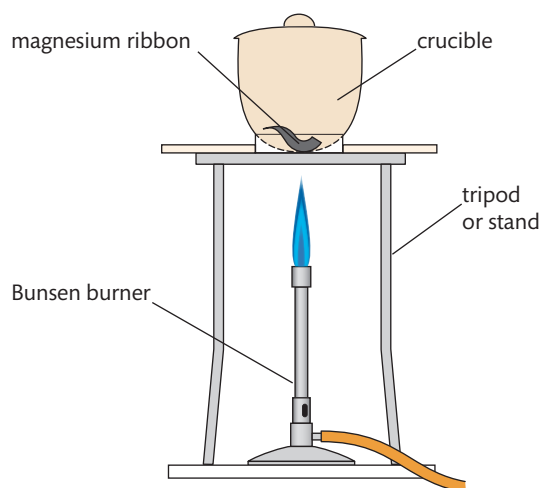
25.0 mol  $\text{H}_2$

## The empirical formula of a compound gives the simplest ratio of its atoms

Magnesium burns brightly in air to form a white solid product, and we might ask how many atoms of magnesium combine with how many atoms of oxygen in this reaction? Thanks to the mole, and its central role in relating the number of particles to a mass that can be measured, we can find the answer to this quite easily.

All we have to do is:

- burn a known mass of Mg, and from this calculate the moles of Mg;
- calculate the mass of oxygen that reacted from the increase in mass, and from this calculate the moles of O;
- express the ratio of moles Mg to moles O in its simplest form;
- the ratio of moles is the ratio of atoms, so we can deduce the simplest formula of magnesium oxide.



▲ Magnesium burns with a bright white flame, combining with oxygen from the air to form the white solid magnesium oxide.

**Figure 1.8** Apparatus used to investigate mass changes on burning magnesium.



## NATURE OF SCIENCE

Scientific investigations based on quantitative measurements are subject to errors, both random and systematic. Analysis of the impact of these errors is inherent in the practice of science. It is good practice in all experimental work to record the sources of errors, consider their effect on the results, and suggest modifications that aim to reduce their impact. This is discussed in detail in Chapter 11. Scientists have the responsibility to communicate their results as realistically and honestly as possible, and this must include uncertainties and errors.

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



## Experiment to determine the empirical formula of MgO

Full details of how to carry out this experiment with a worksheet are available on your eBook. A sample of magnesium is heated and the change in mass recorded. From this, the ratio of moles of magnesium to oxygen can be determined.

## Sample results

	Mass / g $\pm$ 0.001	Observations
mass of crucible + lid	19.777	
mass of crucible + lid + Mg	19.820	magnesium metal has grey, shiny appearance
mass of crucible + lid + white solid product	19.849	metal burned with bright flame, leaving grey-white powder

## Processed data

	Magnesium, Mg	Oxygen, O
mass / g $\pm$ 0.002	0.043	0.029
M / g mol <sup>-1</sup>	24.31	16.00
moles / mol	0.00177	0.00181

ratio moles Mg : moles O = 1 : 1.02

So the ratio atoms Mg : atoms O approximates to 1 : 1

So the formula of magnesium oxide is MgO.

The fact that the experimental result is not exactly 1 : 1 indicates there are some errors in the experiment. We can consider possible systematic errors here, such as:

- the Mg weighed is not all pure;
- not all the Mg weighed reacted;
- the product was not magnesium oxide only;
- loss of Mg or of product occurred;
- change in the mass of the crucible occurred during handling and heating.

Modifications to the experimental design can be considered, which help to reduce the experimental error.

From the result of this experiment, we conclude that the formula of magnesium oxide is MgO. This is known as an **empirical formula**, which gives the simplest whole-number ratio of the elements in a compound.

## Worked example

Which of the following are empirical formulas?

- I C<sub>6</sub>H<sub>6</sub>
- II C<sub>3</sub>H<sub>8</sub>
- III N<sub>2</sub>O<sub>4</sub>
- IV Pb(NO<sub>3</sub>)<sub>2</sub>

## Solution

Only II and IV are empirical formulas, as their elements are in the simplest whole-number ratio. I has the empirical formula CH; III has the empirical formula NO<sub>2</sub>.

The formulas of all ionic compounds, made of a metal and a non-metal such as magnesium oxide, are empirical formulas. This is explained when we look at ionic bonding in Chapter 4. But as we see in the worked example above, the formulas of covalently bonded compounds, usually made of different non-metal elements, are not always empirical formulas. This is explained in the next section on molecular formulas.

Empirical formulas can be deduced from experimental results, usually involving combustion, that give the masses of each of the elements present in a sample. It is a similar process to the one we used for magnesium oxide.

### Worked example

A sample of urea contains 1.210 g N, 0.161 g H, 0.480 g C, and 0.640 g O. What is the empirical formula of urea?

### Solution

- Convert the mass of each element to moles by dividing by its molar mass,  $M$ .
- Divide by the smallest number to give the ratio.
- Approximate to the nearest whole number.

	Nitrogen, N	Hydrogen, H	Carbon, C	Oxygen, O
mass / g	1.210	0.161	0.480	0.640
$M / \text{g mol}^{-1}$	14.01	1.01	12.01	16.00
number of moles / mol	0.086	0.159	0.0399	0.0400
divide by smallest	2.15	3.98	1.00	1.00
nearest whole number ratio	2	4	1	1

So the empirical formula of urea is  $\text{N}_2\text{H}_4\text{CO}$ , usually written as  $\text{CO}(\text{NH}_2)_2$ .

A modification of this type of question is to analyse the composition of a **hydrated salt**. These are compounds that contain a fixed ratio of water molecules, known as **water of crystallization**, within the crystalline structure of the compound. The water of crystallization can be driven off by heating, and the change in mass used to calculate the ratio of water molecules to the **anhydrous salt**. The formula of the hydrated salt is shown with a dot before the number of molecules of water, for example  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ .

It is common for the composition data to be given in the form of percentages by mass, and we use these figures in the same way to deduce the ratio of atoms present. Percentage data effectively give us the mass present in a 100 g sample of the compound.



### Experiment to determine the formula of hydrated barium chloride, $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$

Full details of how to carry out this experiment with a worksheet are available on your eBook.

Hydrated copper(II) sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is blue due to the presence of water of crystallization within the structure of the crystals. The anhydrous form is white, as shown in the lower part of the tube. Heating removes the water molecules, leading to the colour being lost. The process is reversible, and the addition of water to the anhydrous crystals restores their blue colour.



Fertilizers contain nutrients that are added to the soil, usually to replace those used by cultivated plants. The elements needed in the largest quantities, so-called **macronutrients**, include nitrogen, phosphorus and potassium. Fertilizers are often labelled with an N-P-K rating, such as 30-15-30, to show the quantities of each of these three elements. The numbers indicate respectively the percentage by mass N, percentage by mass diphosphorus pentoxide,  $P_2O_5$ , and percentage by mass potassium oxide,  $K_2O$ . The percentage data for  $P_2O_5$  and  $K_2O$  represent the most oxidized forms of elemental phosphorus and potassium present in the fertilizer. Ammonium salts are the most common source of nitrogen used in fertilizers.



**GENERAL PURPOSE 20-10-20**  
(For continuous liquid feed programs)

Guaranteed analysis	F1143
Total nitrogen (N)	20%
7.77% ammoniacal nitrogen	
12.23% nitrate nitrogen	
Available phosphate ( $P_2O_5$ )	10%
Soluble potash ( $K_2O$ )	20%
Magnesium (Mg)(Total)	0.05%
0.05% Water soluble magnesium (Mg)	
Boron (B)	0.0068%
Copper (Cu)	0.0036%
0.0036% Chelated copper (Cu)	
Iron (Fe)	0.05%
0.05% Chelated iron (Fe)	
Manganese (Mn)	0.025%
0.025% Chelated manganese (Mn)	
Molybdenum (Mo)	0.0009%
Zinc (Zn)	0.0025%
0.0025% Chelated zinc (Zn)	

Derived from: ammonium nitrate, potassium phosphate, potassium nitrate, magnesium sulfate, boric acid, copper EDTA, manganese EDTA, iron EDTA, zinc EDTA, sodium molybdate. Potential acidity: 487 lbs. calcium carbonate equivalent per ton.

**Figure 1.9** The label on a fertilizer bag shows the percentage by mass of macro- and micro-nutrients that it contains.

## CHALLENGE YOURSELF

- 3** A fertilizer has an N-P-K rating of 18-51-20. Use the information in the box above to determine the percentage by mass of nitrogen, phosphorus and potassium present.

When working with percentage figures, always check that they add up to 100. Sometimes an element is omitted from the data and you are expected to deduce its identity and percentage from information given.



## Worked example

The mineral celestine consists mostly of a compound of strontium, sulfur and oxygen. It is found by combustion analysis to have the composition 47.70% by mass Sr, 17.46% S, and the remainder is O. What is its empirical formula?

### Solution

Here we need first to calculate the percentage of oxygen by subtracting the total given masses from 100.

$$\% \text{ O} = 100 - (47.70 + 17.46) = 34.84$$

	Strontium, Sr	Sulfur, S	Oxygen, O
% by mass	47.70	17.46	34.84
$M / g \text{ mol}^{-1}$	87.62	32.07	16.00
number of moles / mol	0.5443	0.5444	2.178
divide by smallest	1.000	1.000	4.001

So the empirical formula of the mineral is  $SrSO_4$ .

An understanding of percentage by mass data helps us to evaluate information that we commonly see on products such as foods, drinks, pharmaceuticals, household cleaners as well as fertilizers. For example, a common plant fertilizer is labelled as pure sodium tetraborate pentahydrate,  $Na_2B_4O_7 \cdot 5H_2O$  and claims to be 15.2% boron. How accurate is this claim?



## Percentage composition by mass can be calculated from the empirical formula

We can see in the example above that, even though the mineral celestine has only one atom of strontium for every four atoms of oxygen, strontium nonetheless accounts for 47.70% of its mass. This, of course, is because an atom of strontium has significantly greater mass than an atom of oxygen, and the percentage by mass of an element in a compound depends on the *total* contribution of its atoms. We can calculate this as follows.

### Worked example

What is the percentage by mass of N, H, and O in the compound ammonium nitrate,  $\text{NH}_4\text{NO}_3$ ?

### Solution

First calculate the molar mass  $M$

$$M(\text{NH}_4\text{NO}_3) = 14.01 + (1.01 \times 4) + 14.01 + (16.00 \times 3) = 80.06 \text{ g mol}^{-1}$$

Then for each element total the mass of its atoms, divide by  $M$  and multiply by 100:

$$\% \text{ N} = \frac{14.01 \times 2}{80.06} \times 100 = 34.99\% \text{ by mass}$$

$$\% \text{ H} = \frac{1.01 \times 4}{80.06} \times 100 = 5.05\% \text{ by mass}$$

$$\% \text{ O} = \frac{16.00 \times 3}{80.06} \times 100 = 59.96\% \text{ by mass}$$

(alternatively, this last term can be calculated by subtraction from 100)

Finally check the numbers add up to 100%.

## The molecular formula of a compound gives the actual number of atoms in a molecule

The empirical formula gives us the simplest ratio of atoms present in a compound, but this often does not give the full information about the actual *number* of atoms in a molecule. For example,  $\text{CH}_2$  is an empirical formula. There is no molecule that exists with just one atom of carbon and two atoms of hydrogen, but there are many molecules with multiples of this ratio, such as  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$  and so on. These formulas, which show all the atoms present in a molecule, are called **molecular formulas**.

The molecular formula can be deduced from the empirical formula if the molar mass is known.

$$x (\text{mass of empirical formula})_x = M \text{ where } x \text{ is an integer}$$

### Worked example

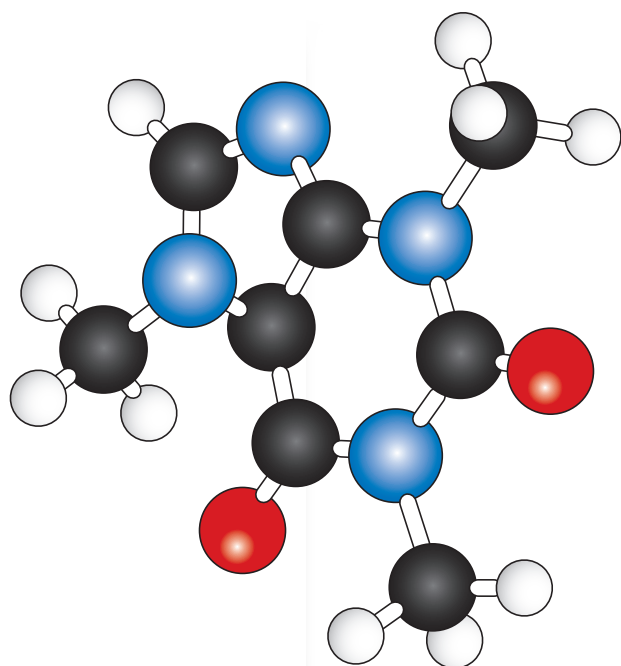
Calomel is a compound once used in the treatment of syphilis. It has the empirical formula  $\text{HgCl}$  and a molar mass of  $472.08 \text{ g mol}^{-1}$ . What is its molecular formula?



The molecular formula shows all the atoms present in a molecule. It is a multiple of the empirical formula.

### TOK

Assigning numbers to the masses of elements has allowed chemistry to develop into a physical science. To what extent is mathematics effective in describing the natural world?



**Figure 1.10** A molecular model of the stimulant caffeine. The atoms are colour coded as follows: black = carbon, grey = hydrogen, red = oxygen, blue = nitrogen. Can you deduce the molecular formula, the empirical formula, and the molar mass of caffeine?

### Solution

First calculate the mass of the empirical formula:

$$\text{mass}(\text{HgCl}) = 200.59 + 35.45 = 236.04 \text{ g mol}^{-1}$$

$$\text{So } (236.04)_x = M = 472.08$$

$$\therefore x = 2$$

$$\text{molecular formula} = \text{Hg}_2\text{Cl}_2$$

### Combustion analysis usually gives data on the mass of compounds formed

The data presented so far may suggest that combustion analysis directly gives information on the relative masses of individual elements in a compound. In fact this is rarely the case, but instead elements are converted into new compounds, typically their oxides, by reaction with oxygen. So the primary data obtained are the masses of carbon dioxide, water, sulfur dioxide, and so on, which are measured by infra-red absorption, as described in Chapter 11. Processing these data simply involves an extra step.

### Worked example

A 0.5438 g sample of a compound known to contain only carbon, hydrogen, and oxygen was burned completely in oxygen. The products were 1.0390 g  $\text{CO}_2$  and 0.6369 g  $\text{H}_2\text{O}$ . Determine the empirical formula of the compound.

### Solution

First we must convert the mass of each compound to moles in the usual way. From the number of moles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  we can deduce the number of moles of C atoms and H atoms.

$$n(\text{CO}_2) = \frac{1.0390 \text{ g}}{12.01 + (16.00 \times 2) \text{ g mol}^{-1}} = 0.02361 \text{ mol CO}_2 \Rightarrow 0.02361 \text{ mol C atoms}$$

$$n(\text{H}_2\text{O}) = \frac{0.6369 \text{ g}}{(1.01 \times 2) + 16.00 \text{ g mol}^{-1}} = 0.03534 \text{ mol H}_2\text{O} \Rightarrow 0.03534 \times 2 = 0.07068 \text{ mol H atoms}$$

In order to know the mass of O in the original sample, we must convert the number of moles of C and H atoms to mass by multiplying by their molar mass, M:

$$\text{mass C} = 0.02361 \text{ mol} \times 12.01 \text{ g mol}^{-1} = 0.2836 \text{ g}$$

$$\text{mass H} = 0.07068 \text{ mol} \times 1.01 \text{ g mol}^{-1} = 0.07139 \text{ g}$$

$$\therefore \text{mass O} = 0.5438 - (0.2836 + 0.07139) = 0.1888 \text{ g}$$

$$\text{mol O atoms} = 0.1888 \text{ g} / 16.00 \text{ g mol}^{-1} = 0.01180 \text{ mol}$$

Now we can proceed as with the previous examples, converting mass of O to moles and then comparing the mole ratios.

	Carbon, C	Hydrogen, H	Oxygen, O
mass / g			0.1888
number of moles / mol	0.02361	0.07068	0.01180
divide by smallest	2.001	5.999	1.000
nearest whole-number ratio	2	6	1

So the empirical formula is  $\text{C}_2\text{H}_6\text{O}$ .

## Exercises

**24** Give the empirical formulas of the following compounds:

- (a) ethyne,  $\text{C}_2\text{H}_2$       (b) glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$       (c) sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$   
 (d) octane,  $\text{C}_8\text{H}_{18}$       (e) oct-1-yne,  $\text{C}_8\text{H}_{14}$       (f) ethanoic acid,  $\text{CH}_3\text{COOH}$

**25** A sample of a compound contains only the elements sodium, sulfur and oxygen. It is found by analysis to contain 0.979 g Na, 1.365 g S and 1.021 g O. Determine its empirical formula.

**26** A sample of a hydrated compound was analysed and found to contain 2.10 g Co, 1.14 g S, 2.28 g O and 4.50 g  $\text{H}_2\text{O}$ . Determine its empirical formula.

**27** A street drug has the following composition: 83.89% C, 10.35% H, 5.76% N. Determine its empirical formula.

**28** The following compounds are used in the production of fertilizers. Determine which has the highest percentage by mass of nitrogen:  $\text{NH}_3$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ .

**29** A compound has a formula  $\text{M}_3\text{N}$  where M is a metal element and N is nitrogen. It contains 0.673 g of N per gram of the metal M. Determine the relative atomic mass of M and so its identity.

**30** Compounds of cadmium are used in the construction of photocells. Deduce which of the following has the highest percentage by mass of cadmium: CdS, CdSe, CdTe.

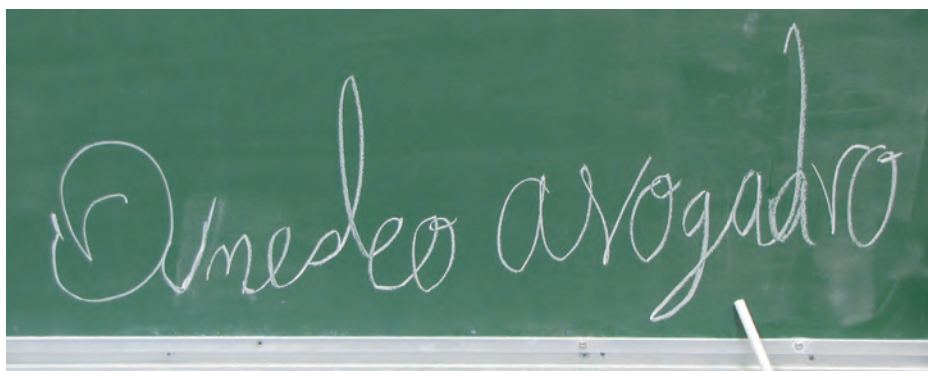
**31** Benzene is a hydrocarbon, a compound of carbon and hydrogen only. It is found to contain 7.74% H by mass. Its molar mass is  $78.10 \text{ g mol}^{-1}$ . Determine its empirical and molecular formula.

**32** A weak acid has a molar mass of  $162 \text{ g mol}^{-1}$ . Analysis of a 0.8821 g sample showed the composition by mass is 0.0220 g H, 0.3374 g P and the remainder is O. Determine its empirical and molecular formulas.

**33** ATP is an important molecule in living cells. A sample with a mass of 0.8138 g was analysed and found to contain 0.1927 g C, 0.02590 g H, 0.1124 g N, and 0.1491 g P. The remainder was O. Determine the empirical formula of ATP. Its formula mass was found to be  $507 \text{ g mol}^{-1}$ . Determine its molecular formula.

**34** A 0.30 g sample of a compound that contains only carbon, hydrogen and oxygen was burned in excess oxygen. The products were 0.66 g of carbon dioxide and 0.36 g of water. Determine the empirical formula of the compound.

**35** You are asked to write your name on a suitable surface, using a piece of chalk that is pure calcium carbonate,  $\text{CaCO}_3$ . How could you calculate the number of carbon atoms in your signature?



How many atoms of calcium are in Avogadro's name written in chalk?

## 1.3 Reacting masses and volumes

### Understandings:

- Reactants can be either limiting or excess.
- The experimental yield can be different from the theoretical yield.
- Avogadro's law enables the mole ratio of reacting gases to be determined from volumes of the gases.
- The molar volume of an ideal gas is a constant at specified temperature and pressure.

#### Guidance

Values for the molar volume of an ideal gas are given in the IB data booklet in section 2.

- The molar concentration of a solution is determined by the amount of solute and the volume of solution.

#### Guidance

The use of square brackets to denote molar concentration is required.

- A standard solution is one of known concentration.

### Applications and skills:

- Solution of problems relating to reacting quantities, limiting and excess reactants, theoretical, experimental and percentage yields.
- Calculation of reacting volumes of gases using Avogadro's law.
- Solution of problems and analysis of graphs involving the relationship between temperature, pressure and volume for a fixed mass of an ideal gas.
- Solution of problems relating to the ideal gas equation.

#### Guidance

The ideal gas equation,  $PV = nRT$ , and the value of the gas constant ( $R$ ), are given in the IB data booklet in sections 1 and 2.

- Explanation of the deviation of real gases from ideal behaviour at low temperature and high pressure.
- Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.
- Solution of problems involving molar concentration, amount of solute and volume of solution.

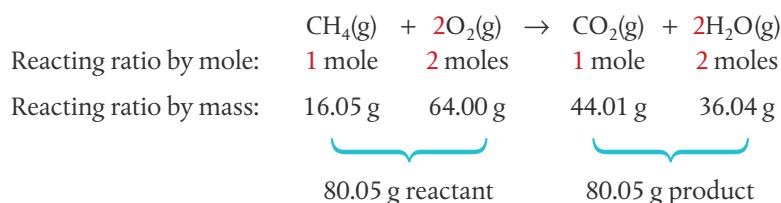
#### Guidance

Units of concentration to include  $\text{g dm}^{-3}$ ,  $\text{mol dm}^{-3}$  and parts per million (ppm).

- Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution.

### Chemical equations show reactants combining in a fixed molar ratio

Chemical change, as summarized in chemical equations, is simply an expression of reactants combining in fixed ratios to form products. The most convenient means to express this ratio is as moles, as that gives us a means of relating the number of particles that react to the mass that we can measure. So, for example, when methane,  $\text{CH}_4$ , burns in air, we can conclude the following, all from the balanced chemical equation.



(The figures for total mass of reactant and product are just a check, as we know something would be wrong if they did not equate.)



The Bunsen burner controls the combustion of methane,  $\text{CH}_4$ , and is often used as a source of heat in the laboratory.



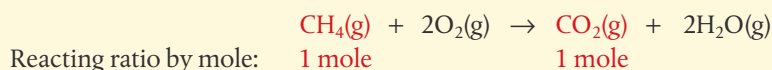
This simple interpretation of equations, going directly from coefficients to molar ratios, opens the door to a wide range of calculations involving reacting masses.

### Worked example

Calculate the mass of carbon dioxide produced from the complete combustion of 1.00 g of methane.

### Solution

Write the balanced equation and deduce the mole ratio as above. Then pick out from the question the terms that we need to analyse – these are marked in red, and are the species where we need to convert moles to grams.



Reacting ratio by mass / g: 16.05 44.01

For 1.00 g methane: 1.00 x

Now solve the ratio, shown here using cross-multiplication, to determine the value of x.

$$\frac{\text{g CH}_4}{\text{g CO}_2} = \frac{16.05}{44.01} = \frac{1.00}{x}$$

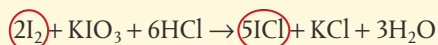
$$x = \frac{1.00 \times 44.01}{16.05} \text{ g CO}_2 = 2.74 \text{ g CO}_2$$

All questions on reacting ratios involve a variation of this approach:

- write the balanced equation;
- work out the mole ratio for the species identified in the question;
- work out the reacting ratio by mass for these species, using  $m = nM$ ;
- insert the data from the question and solve the ratio.

### Worked example

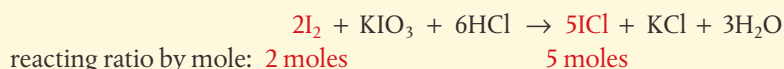
Iodine chloride, ICl, can be made by the following reaction:



Calculate the mass of iodine, I<sub>2</sub>, needed to prepare 28.60 g of ICl by this reaction.

### Solution

The relevant terms from the question are I<sub>2</sub> and ICl, so these are our focus.



reacting ratio by mass:  $2 \times (126.90 \times 2)$   $5 \times (126.90 + 35.45)$   
 $= 507.60 \text{ g}$   $= 811.75 \text{ g}$

For 28.60 g ICl: x 28.60 g

$$\frac{\text{g I}_2}{\text{g ICl}} = \frac{507.60}{811.75} = \frac{x}{28.60}$$

$$x = \frac{507.60 \times 28.60}{811.75} \text{ g I}_2 = 17.88 \text{ g I}_2$$



The term **carbon footprint** refers to the mass of carbon dioxide and other greenhouse gases such as methane that an individual emits in a 1-year period. It is often expressed as the carbon dioxide equivalent, or CO<sub>2</sub>e, to represent the total climate change impact of all the greenhouse gases caused by an item or activity. It includes emissions from fuels used in transport, services such as heating, production and consumption of food, and the direct and indirect emissions from manufactured goods and construction. It is extremely difficult to measure all sources accurately, but the fundamental concept uses the type of calculation shown here. The carbon footprint is a measure of an individual's consumption of resources, and suggests the link between this and the enhanced greenhouse effect. There is further discussion of carbon footprints in Chapter 12.



Remember to convert between mass and moles by using  $n = \frac{m}{M}$  or  $m = nM$ .



It is common for people to waste time solving questions like this by doing the mole to gram conversions for all the species represented in the equation. You can save yourself a lot of trouble by focusing only on the terms indicated in the question, as shown in this example.

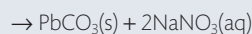
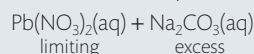
## The theoretical yield is determined by the limiting reactant

Imagine that you are following a recipe to make 12 cookies. It calls for you to mix two eggs with four cups of flour. The problem is that you only have one egg. You will quickly realize that this means you can use only two cups of flour and end up with only six cookies. We could say that the number of eggs *limited* the amount of product.

In many chemical reactions the relative amounts of reactants available to react together will similarly affect the amount of product. The reactant that determines the quantity of product is known as the **limiting reactant**. Other reactants will therefore not be fully used, and are said to be in **excess**. Identifying the limiting reactant is therefore a crucial step before we can calculate the expected quantity of product. The **theoretical yield**, which is usually expressed in grams or moles, refers to the maximum amount of product obtainable, assuming 100% of the limiting reactant is converted to product.

Note that identification of the limiting reactant depends on the *mole ratios* in the balanced chemical equation for the reaction. This means that if reactant quantities are given in grams, they must first be converted to moles.

The concept of limiting reactant is often useful in the design of experiments and synthetic processes. By deliberately making one reactant available in an amount greater than that determined by its mole ratio in the balanced equation, it ensures that the other reactant is limiting and so will be fully used up. For example, in order to remove lead ions in lead nitrate from a contaminated water supply, sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is added to precipitate lead carbonate as shown in the equation:



By using excess  $\text{Na}_2\text{CO}_3$ , this ensures that *all* the lead ions react and so are removed from the water supply.



### Worked example

Nitrogen gas,  $\text{N}_2$ , can be prepared from this reaction:



If 18.1 g  $\text{NH}_3$  are reacted with 90.40 g  $\text{CuO}$ , determine the mass of  $\text{N}_2$  that can be formed.

### Solution

First we must determine the limiting reactant. We convert the mass of reactants to moles, and then compare the mole ratio in the balanced equation with the mole ratio of reactants given.

$$n(\text{NH}_3) = \frac{18.1 \text{ g}}{14.01 + (3 \times 1.01) \text{ g mol}^{-1}} = 1.06 \text{ mol NH}_3$$

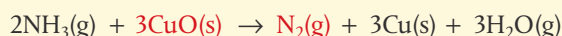
$$n(\text{CuO}) = \frac{90.40 \text{ g}}{63.55 + 16.00 \text{ g mol}^{-1}} = 1.14 \text{ mol CuO}$$

$$\text{mole ratio from equation: } \frac{\text{NH}_3}{\text{CuO}} = \frac{2}{3} = 0.667$$

$$\text{mole ratio from given masses: } \frac{\text{NH}_3}{\text{CuO}} = \frac{1.06}{1.14} = 0.930$$

As the ratio  $\text{NH}_3 : \text{CuO}$  of the given masses is *larger* than the required ratio in the equation, it means  $\text{NH}_3$  is in excess and  $\text{CuO}$  is the limiting reactant.

This means that the amount of  $\text{N}_2$  that can form will be determined by the amount of  $\text{CuO}$ . This is now similar to the earlier questions, where we write out the equation and focus on the terms identified in the question.



reacting ratio by mole: 3 moles 1 mole  
for 1.14 moles  $\text{CuO}$ : 1.14 x

$$\text{mole ratio } \frac{\text{CuO}}{\text{N}_2} = \frac{3}{1} = \frac{1.14}{x} \quad \therefore x = \frac{1.14 \times 1}{3} = 0.380 \text{ mol N}_2$$

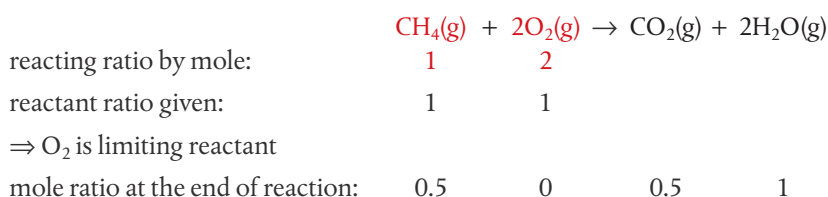
$$\therefore \text{mass N}_2 = 0.380 \text{ mol} \times M(\text{N}_2) \text{ g mol}^{-1} = 0.380 \text{ mol} \times 28.02 \text{ g mol}^{-1} = 10.7 \text{ g N}_2$$

There are alternate approaches to determining the limiting reactant, such as calculating which given amount of reactant would yield the smallest amount of product. But in essence, all questions on limiting reactant and theoretical yield involve comparing the mole ratio of given masses of reactants with the coefficients in the equation. This is a summary of the steps:

- write the balanced equation and focus on the mole ratio of reactants;
- convert the given mass of reactants to moles;
- compare the given mole ratios with the ratio of coefficients in the equation;
- identify the limiting reactant from the above ratios;
- calculate the moles of product from the given moles of limiting reactant.

Sometimes it is useful to measure how much excess reactant will remain when all the limiting reactant has been used up and the reaction stops. One example of this is a technique called **back-titration**, which analyses excess acid or alkali after a reaction is complete, and so indirectly measures the amount of a limiting reactant. This is explained on page 50.

A simple example of how to calculate the excess is shown below using an example of burning  $\text{CH}_4$ , when 1 mole of  $\text{CH}_4$  and 1 mole of  $\text{O}_2$  are supplied.



So 0.5 moles  $\text{CH}_4$  will be unreacted at the end of the reaction.

We will study more examples of this type of question in the next section.

## The percentage yield can be calculated from the experimental and theoretical yields

The answer to the Worked example above, 10.7 g  $\text{N}_2$  is known as the theoretical yield, because it assumes that *all* of the  $\text{CuO}$  was converted to  $\text{N}_2$  with no loss, impurities present, wastage or incomplete reaction. In reality, all of the above happen to different extents in most chemical reactions, and so the theoretical yield is usually different from the actual or **experimental yield**.

When we compare the experimental yield with the theoretical yield, we get a measure of the efficiency of the conversion of reactants to products. This is usually expressed as the **percentage yield**, defined as follows:

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

In your own experiments, you may often be able to calculate the percentage yield of product in evaluating the results. In industry, this is a very important calculation for determining the efficiency of a process such as the synthesis of a drug in the pharmaceutical industry. Many aspects of green chemistry focus on ways to increase the yield of product by reducing wastage.

The limiting reactant determines the amount of product that can form. The theoretical yield is the quantity of product that can form from the complete conversion of the limiting reactant.



Industrial plants such as this oil refinery need to be able to track the efficiency of the chemical reactions taking place. Measuring the yield of product is an essential part of this.

## CHALLENGE YOURSELF

- 4 Percentage yield and the atom economy are different concepts, but both can be used to assess aspects of the overall efficiency of a chemical process. See if you can find a reaction that has a high percentage yield under certain conditions, but a low atom economy.

### Worked example

The previous Worked example on the synthesis of  $\text{N}_2$  from  $\text{NH}_3$  and  $\text{CuO}$  had a theoretical yield of 10.7 g  $\text{N}_2$  from the starting amounts of reactants. Under the same conditions, an experiment produced 8.35 g  $\text{N}_2$ . Determine the percentage yield.

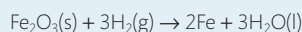
### Solution

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

$$\therefore \text{percentage yield} = \frac{8.35 \text{ g}}{10.7 \text{ g}} \times 100 = 78.0\%$$

### Exercises

- 36 Iron ore can be reduced to iron by the following reaction:

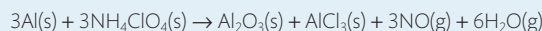


- How many moles of Fe can be made from 1.25 moles of  $\text{Fe}_2\text{O}_3$ ?
- How many moles of  $\text{H}_2$  are needed to make 3.75 moles of Fe?
- If the reaction yields 12.50 moles of  $\text{H}_2\text{O}$ , what mass of  $\text{Fe}_2\text{O}_3$  was used up?

- 37 Lighters commonly use butane,  $\text{C}_4\text{H}_{10}$ , as the fuel.

- Formulate the equation for the combustion of butane.
- Determine the mass of butane that burned when 2.46 g water were produced.

- 38 Booster rockets for the space shuttle use the following reaction:

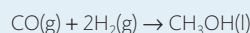


Calculate the mass of  $\text{NH}_4\text{ClO}_4$  that should be added to this fuel mixture to react completely with every kilogram of Al.

- 39 Limestone is mostly calcium carbonate,  $\text{CaCO}_3$ , but also contains other minerals. When heated, the  $\text{CaCO}_3$  decomposes into  $\text{CaO}$  and  $\text{CO}_2$ . A 1.605 g sample of limestone was heated and gave off 0.657 g of  $\text{CO}_2$ .

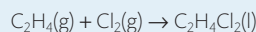
- Formulate the equation for the thermal decomposition of calcium carbonate.
- Determine the percentage mass of  $\text{CaCO}_3$  in the limestone.
- State the assumptions that you are making in this calculation.

- 40 Methanol,  $\text{CH}_3\text{OH}$ , is a useful fuel that can be made as follows:



A reaction mixture used 12.0 g of  $\text{H}_2$  and 74.5 g of CO.

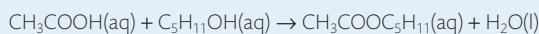
- Determine the theoretical yield of  $\text{CH}_3\text{OH}$ .
  - Calculate the amount of the excess reactant that remains unchanged at the end of the reaction.
- 41 The dry-cleaning solvent 1,2-dichloroethane,  $\text{C}_2\text{H}_4\text{Cl}_2$ , is prepared from the following reaction:



Determine the mass of product that can be formed from 15.40 g of  $\text{C}_2\text{H}_4$  and 3.74 g of  $\text{Cl}_2$ .

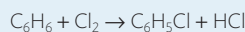
- 42 Calcium carbonate,  $\text{CaCO}_3$ , is able to remove sulfur dioxide,  $\text{SO}_2$ , from waste gases by a reaction in which they react in a 1 : 1 stoichiometric ratio to form equimolar amounts of  $\text{CaSO}_3$ . When 255 g of  $\text{CaCO}_3$  reacted with 135 g of  $\text{SO}_2$ , 198 g of  $\text{CaSO}_3$  were formed. Determine the percentage yield of  $\text{CaSO}_3$ .

- 43 Pentyl ethanoate,  $\text{CH}_3\text{COOC}_5\text{H}_{11}$ , which smells like bananas, is produced from the esterification reaction:



A reaction uses 3.58 g of  $\text{CH}_3\text{COOH}$  and 4.75 g of  $\text{C}_5\text{H}_{11}\text{OH}$  and has a yield of 45.00%. Determine the mass of ester that forms.

- 44 A chemist has to make a 100 g sample of chlorobenzene,  $\text{C}_6\text{H}_5\text{Cl}$ , from the following reaction:



Determine the minimum quantity of benzene,  $\text{C}_6\text{H}_6$ , that can be used to achieve this with a yield of 65%.



## Avogadro's law directly relates gas volumes to moles

All the examples above use mass as a way to measure amount, the number of moles. But in the laboratory we often work with liquids and gases, where *volume* is a more convenient measure. So what is the relationship between gas volume and number of moles?

Consider the following demonstration where two gas jars are each filled with different gases – hydrogen ( $\text{H}_2$ ) in flask A and bromine ( $\text{Br}_2$ ) in flask B. The flasks are at the same temperature and pressure and have equal volumes.

It is known, from many experimental measurements on gas volumes, that the number of particles in the two flasks above is the same. At first this might seem surprising – after all bromine molecules are much larger and heavier than hydrogen molecules. But we need to consider the nature of the gaseous state, and as we learned on page 9, remember that the particles in a gas are widely spaced out with only negligible forces between them. In simple terms, most of a gas volume is empty space. And for this reason the chemical nature of the gas is irrelevant to its volume. Gas volume is determined only by the number of particles, and by the temperature and pressure.

This understanding is known as Avogadro's law, which states that:

**Equal volumes of all gases, when measured at the same temperature and pressure, contain an equal number of particles.**

Alternatively, it can be stated that equal numbers of particles of all gases, when measured at the same temperature and pressure, occupy equal volumes.

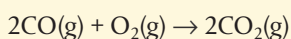
Using  $V$  for volume and  $n$  for number of moles

$$V \propto n$$

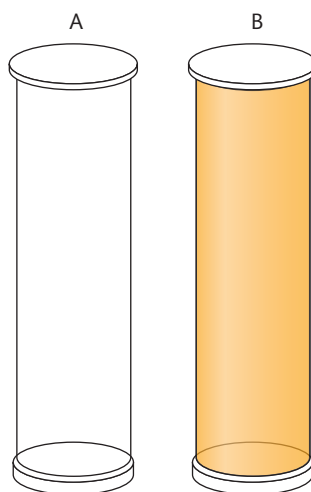
This relationship enables us to relate gas volumes (of any gas) to the number of moles, and so to reacting ratios in equations.

### Worked example

40 cm<sup>3</sup> of carbon monoxide are reacted with 40 cm<sup>3</sup> of oxygen in the reaction:



What volume of carbon dioxide is produced? (Assume all volumes are measured at the same temperature and pressure.)



**Figure 1.11** Flask A contains hydrogen molecules, flask B contains bromine molecules. The two flasks are under the same conditions of temperature and pressure.



Airbags have become a standard safety fitting in many vehicles. They are designed to act as a cushion or shock absorber by inflating rapidly on sudden impact of the vehicle during a collision. Airbags work on the principle of a chemical reaction triggered by the impact producing a gaseous product that causes a sudden volume change. The key reaction used is the conversion of sodium azide,  $\text{NaN}_3$ , to nitrogen gas,  $\text{N}_2$ . To avoid the production of dangerously reactive sodium metal, potassium nitrate,  $\text{KNO}_3$ , and silicon dioxide,  $\text{SiO}_2$ , are also included so that harmless silicates are produced instead.

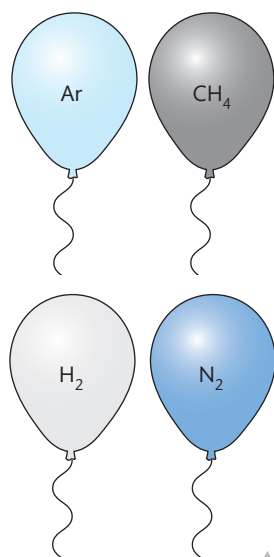


Illustration of an airbag and seatbelt in action during a car accident. On impact, the airbag inflates and the seatbelt slows the forward force of the body, protecting the driver's head and chest.

Avogadro's law states that equal volumes of all gases at the same conditions of temperature and pressure contain equal numbers of particles:  
 $V \propto n$

## CHALLENGE YOURSELF

- 5 Use the explanation on page 33 to deduce the chemical equations for the reactions taking place in a deployed air bag.



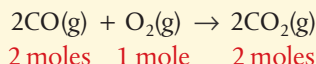
**Figure 1.12** These four balloons are all filled with 1 dm<sup>3</sup> of gas. At 25 °C and 100 kPa, they each contain 0.044 mol or  $2.65 \times 10^{22}$  atoms or molecules. Which balloon is the heaviest?

Note that STP (standard temperature and pressure) is not the same as the 'standard state', which is used in thermodynamic data and explained in Chapter 5.

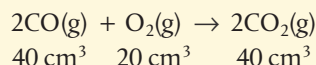
STP refers to a temperature of 273 K and a pressure of 100 kPa.

## Solution

First identify the mole ratios in the equation:



The mole ratio is equal to the ratio of reacting gas volumes, so:



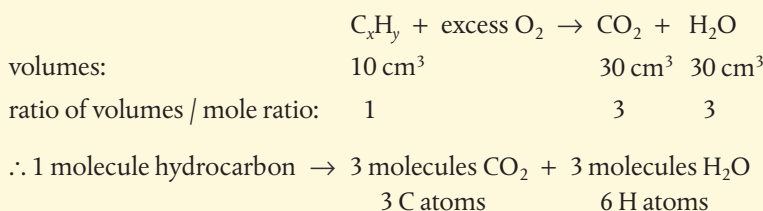
Therefore 40 cm<sup>3</sup> of carbon dioxide are produced. (Oxygen is in excess by 20 cm<sup>3</sup>.)

## Worked example

When 10 cm<sup>3</sup> of a gaseous hydrocarbon (a compound containing only carbon and hydrogen) is burned in excess oxygen, the products consist of 30 cm<sup>3</sup> of carbon dioxide and 30 cm<sup>3</sup> of water vapour, measured under the same conditions of temperature and pressure. Determine the molecular formula of the hydrocarbon.

## Solution

'Excess' oxygen indicates that the combustion reaction is complete.



The molecular formula is C<sub>3</sub>H<sub>6</sub>.

## All gases under the same conditions have the same molar volume

On the basis of Avogadro's law, the volume occupied by one mole of any gas, known as the **molar volume**, must be the same for *all* gases when measured under the same conditions of temperature and pressure.

At standard temperature and pressure (STP), one mole of a gas has a volume of  $2.27 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$  (22.7 dm<sup>3</sup> mol<sup>-1</sup>). The conditions at STP are:

- temperature of 0 °C (273.15 K);
- pressure of 100 kPa.

The molar volume can be used to calculate the amount of gas in a similar way to the use of molar mass earlier in this chapter. Here though the calculations are easier, as all gases have the same molar volume under the same conditions.

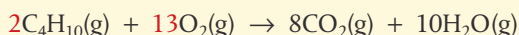
$$\text{number of moles of gas (n)} = \frac{\text{volume (V)}}{\text{molar volume}}$$

### Worked example

What volume of oxygen at standard temperature and pressure would be needed to completely burn 1 mole of butane,  $C_4H_{10}$ ?

### Solution

As always, start with the balanced equation and pick out the terms from the question.



mole / volume ratio: 1 6.5

6.5 moles of gas at STP have volume =  $6.5 \text{ mol} \times 22.7 \text{ dm}^3 \text{ mol}^{-1} = 147.6 \text{ dm}^3$

### Worked example

Calculate the volume occupied by 0.0200 g of He at standard temperature and pressure.

### Solution

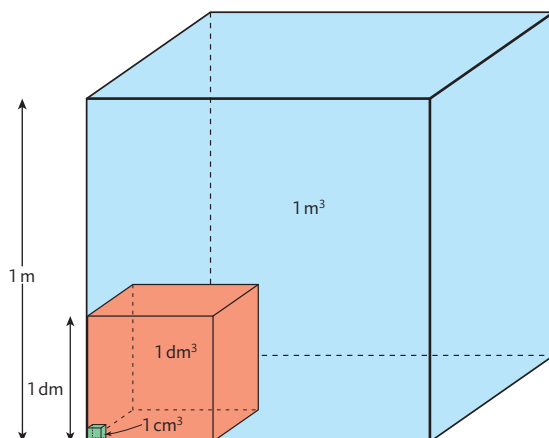
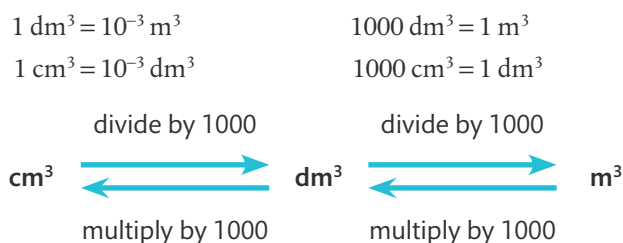
First convert the mass of He to moles:

$$n = \frac{m}{M} = \frac{0.0200 \text{ g}}{4.00 \text{ g mol}^{-1}} = 0.00500 \text{ mol}$$

$$\text{volume} = 0.00500 \text{ mol} \times 22.7 \text{ dm}^3 \text{ mol}^{-1} = 0.114 \text{ dm}^3$$

### A note about units of volume

The metric unit  $\text{m}^3$  is widely used in industrial and engineering calculations, but is too large to be convenient for many volume measurements in the laboratory. Instead,  $\text{dm}^3$  and  $\text{cm}^3$  are commonly used, so it is important to be able to interconvert these.



The litre (l or L) is widely used in place of  $\text{dm}^3$ , and millilitre (ml or mL) in place of  $\text{cm}^3$ . You will not be penalized for the use of these terms in an examination, but they will not be used in examination questions so it is essential that you know the correct use of  $\text{m}^3$ ,  $\text{dm}^3$  and  $\text{cm}^3$ .



The value of the molar volume and the conditions for STP are given in section 2 of the IB data booklet.



CODATA (Committee on Data for Science and Technology) is an interdisciplinary scientific committee of the International Council of Science. It was established in 1966 to promote the worldwide compilation and sharing of reliable numerical data, such as the molar volume of a gas.

**Figure 1.13** The three cubes shown are not to scale.  $1 \text{ m}^3 = 1000 \text{ dm}^3 = 1\,000\,000 \text{ cm}^3$ . In the laboratory, volumes are usually measured in  $\text{cm}^3$  or  $\text{dm}^3$  and often these measurements need to be converted to  $\text{m}^3$  in calculations.

## Exercises

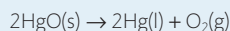
45 How many moles are present in each of the following at STP?

- (a)  $54.5 \text{ dm}^3 \text{ CH}_4$                       (b)  $250.0 \text{ cm}^3 \text{ CO}$                       (c)  $1.0 \text{ m}^3 \text{ O}_2$

46 What is the volume of each of the following at STP?

- (a)  $44.00 \text{ g N}_2$                       (b)  $0.25 \text{ mol NH}_3$

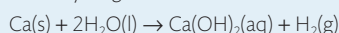
47 Pure oxygen gas was first prepared by heating mercury(II) oxide,  $\text{HgO}$ .



What volume of oxygen at STP is released by heating  $12.45 \text{ g}$  of  $\text{HgO}$ ?

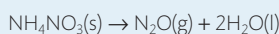
48 Which sample contains more molecules,  $3.14 \text{ dm}^3$  of bromine,  $\text{Br}_2$ , or  $11.07 \text{ g}$  of chlorine,  $\text{Cl}_2$  when measured at the same temperature and pressure?

49 Calcium reacts with water to produce hydrogen.



Calculate the volume of gas at STP produced when  $0.200 \text{ g}$  of calcium reacts completely with water.

50 Dinitrogen oxide,  $\text{N}_2\text{O}$ , is a greenhouse gas produced from the decomposition of artificial nitrate fertilizers. Calculate the volume at STP of  $\text{N}_2\text{O}$  produced from  $1.0 \text{ g}$  of ammonium nitrate, when it reacts according to the equation:



## NATURE OF SCIENCE

Early ideas on gas behaviour were suggested from the postulates of the kinetic theory, but could not advance without scientific evidence. This was provided by experimental work, mainly that of Boyle and Mariotte, Charles and Gay-Lussac who contributed quantitative data based on testable predictions of how gases would respond to changes in temperature, volume and pressure. In a fairly classic example of scientific process, the data supported the theory, and the theory explained the data. As a result there was wide acceptance of what became known as the 'gas laws' by the 18th century.

It is interesting to consider on the other hand why Avogadro's hypothesis was not widely accepted initially. Experiments led him to suggest that equal volumes of all gases at the same temperature and pressure contain the same number of molecules, but data to confirm this were somewhat lacking. In addition, his ideas conflicted with Dalton's atomic theory, which suggested that particles in gases could be only single atoms, not molecules as Avogadro proposed. It took the logical argument of Cannizzaro nearly 50 years later to show that Avogadro's hypothesis could be explained, and moreover used as a means to determine molecular mass. Following this, the relationship between gas volume and number of molecules became widely accepted and known as Avogadro's law. History has shown that the acceptance of scientific ideas by the scientific community is sometimes influenced by the time and manner of their presentation, as well as by their power to explain existing ideas.



An ideal gas is one that obeys the ideal gas laws.



The ideal gas equation can be deduced from a small number of assumptions of ideal behaviour. What is the role of reason, perception, intuition and imagination in the development of scientific models?

TOK

## The gas laws describe pressure, volume and temperature relationships for all gases

The kinetic theory of matter, summarized on pages 9–10, describes gases as largely empty space containing free moving particles of negligible volume having no inter-particle forces. This is often referred to as the **ideal gas** model. In effect it is an approximation, as no gas fits this description exactly, but it is nonetheless a useful means for predicting and interpreting the physical properties of gases under typical conditions of temperature and pressure. Later in this section we will explore situations when gas behaviour deviates from this ideal model.

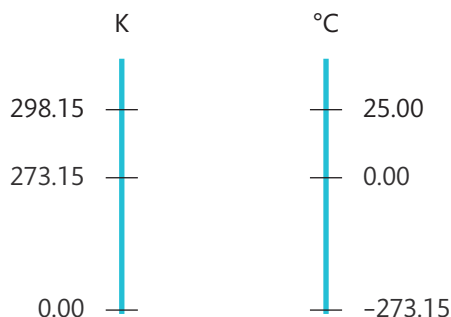
You will be familiar with some behaviour of gases through everyday experiences such as blowing up a balloon, or inflating a bicycle tyre to increase the pressure. Perhaps you have noticed how inflated balloons shrivel in colder conditions and expand when it is warmer? The interesting thing about these simple observations of the volume, pressure and temperature of a gas is that they are not dependent on the chemical nature of the gas. In fact, all gases respond in the same way to changes in volume, pressure and temperature when the mass of gas is fixed. These relationships are summarized as the **gas laws** and are discussed on the following pages.



## A note about units of temperature

In all work on gases, it is essential to use values for temperature recorded in kelvin (K), not in Celsius (°C). Temperature in kelvin is known as the **absolute temperature**, and is based on a scale where absolute zero, 0 K, is the point of zero kinetic energy of particles. This coincides with  $-273.15^{\circ}\text{C}$ . As the interval on the Kelvin scale is the same as that on the Celsius scale, conversion between the two simply involves addition or subtraction of 273.15 (commonly approximated to 273).

$$\text{temperature (K)} = \text{temperature (}^{\circ}\text{C)} + 273.15$$



William Thomson (1824–1907), who became known as Lord Kelvin later in life, completed most of his work at the University of Glasgow, Scotland. His concept of the absolute temperature scale followed from his recognition of the relationship between heat energy and the ability to do work. The existence of a minimum possible temperature at which no heat can be extracted from the system and so no work done, led him to the definition of absolute zero in 1848. This in turn led to the formulation of the laws of thermodynamics. Kelvin is considered one of the great scientists of the 19th century, and is buried next to Isaac Newton in London.

## A note about units of pressure

The SI unit of pressure is the Pascal (Pa), which is equal to  $\text{N m}^{-2}$ . Pressure is now commonly given in bars, where  $10^5 \text{ Pa} = 1 \text{ bar}$ , as this is conveniently close to 1 atmosphere pressure.

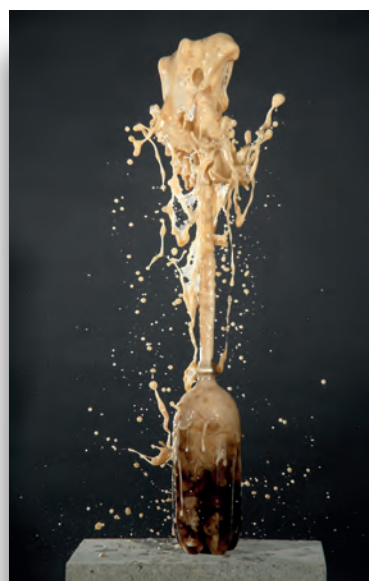
### NATURE OF SCIENCE

The definition of absolute zero (0 K) as the temperature where a substance has no kinetic energy suggests it is the point at which all motion in particles ceases. It is the lowest possible temperature. Zero kelvin has not been achieved, although modern technologies, which improve cooling methods and use magnets to contain the gas, are helping scientists to reach values ever closer to this. Researchers in Finland have achieved temperatures as low as 100 pK ( $1 \times 10^{-10} \text{ K}$ ) in a piece of rhodium metal. Ultra-low temperature research has led to observations of phenomena such as quantum fluid behaviour and superconductivity, and could lead to improvements in precision measurements such as those used in atomic clocks and sensors for gravity and rotation. Science progresses as improvements in technology give access to new information, and studies in one field open up possibilities in another.

## 1 Relationship between volume and pressure

The volume of a gas is always the volume of its container as the particles spread out fully. Its pressure is the result of the particles colliding with the walls of the container, and will increase when the frequency or energy of these collisions increases.

If the temperature is held constant, it is found that increasing the pressure on a fixed mass of gas decreases its volume. In other words, the pressure of a gas is inversely proportional to its volume, and the product of pressure and volume is a constant.



▲ The so-called mentos-soda fountain reaction. Dissolved carbon dioxide in the soda changes quickly into gas in the presence of the candy mint mentos. The sudden pressure change causes the soda to be ejected in a fountain of foam.

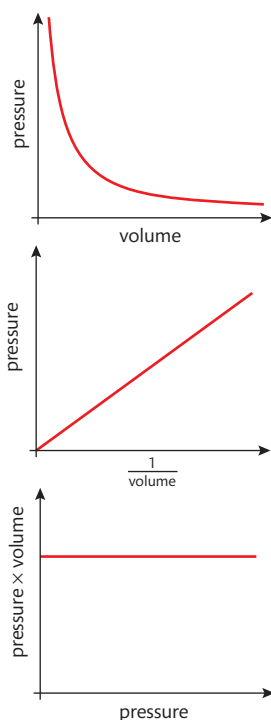


Different countries continue to use a variety of units for pressure, including millimetres of mercury (mmHg), torr, pounds per square inch (psi), and atmosphere (atm).



In all the examples here, use of the term 'pressure' assumes 'absolute pressure', which is referenced against a perfect vacuum. This is in contrast to 'gauge pressure', which is measured relative to atmospheric pressure.

**Figure 1.14** As the pressure on a gas is increased, its volume decreases proportionately.



**Figure 1.15** Boyle's law. Gas pressure is inversely proportional to its volume.

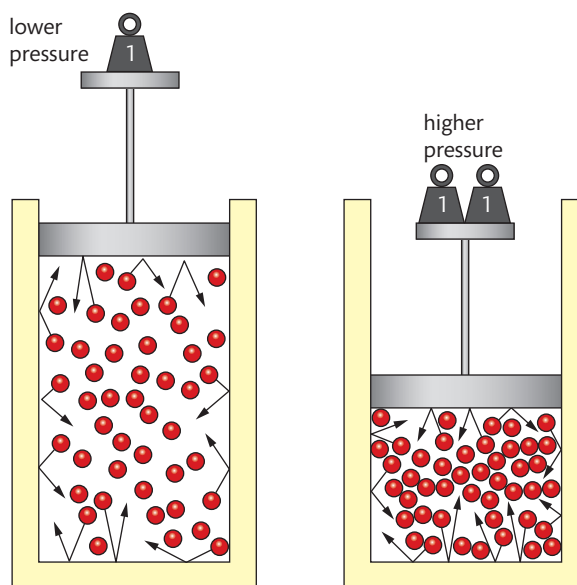
$$P \propto \frac{1}{V}$$

$$PV = \text{a constant}$$

**Figure 1.16** Charles' law. Gas volume is proportional to the absolute temperature. Note the dotted line represents an extrapolation, as data at temperatures down to 0 K are not obtainable.

$$V \propto T$$

$$\frac{V}{T} = \text{a constant}$$



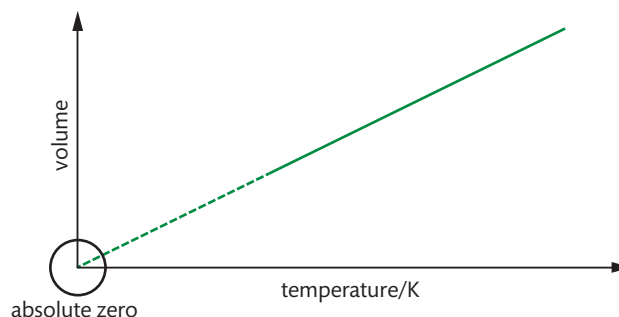
$$P \propto \frac{1}{V}$$

$$PV = \text{a constant}$$

This relationship is often known as **Boyle's law**, as it was first established by Robert Boyle in 1662. Application of this relationship is found in the compression of gases under pressure, often useful in transport and storage.

## 2 Relationship between volume and temperature

An increase in temperature represents an increase in the average kinetic energy of the particles. If the pressure is held constant, it is found that increasing the temperature of a fixed mass of gas increases its volume. In other words, the volume of a gas is directly proportional to its absolute temperature, and volume divided by absolute temperature is a constant.



$$V \propto T$$

$$\frac{V}{T} = \text{a constant}$$

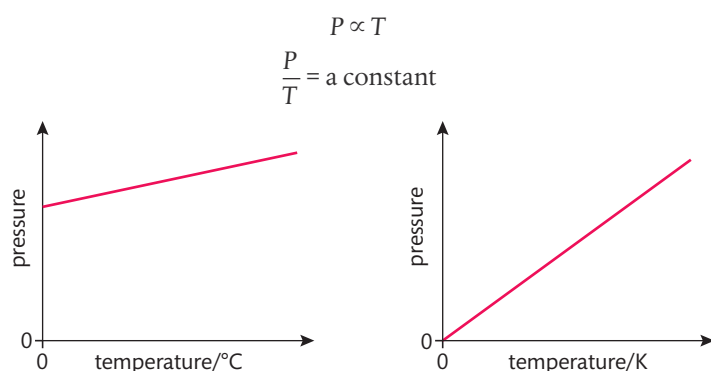
**TOK**

The SI base unit of temperature is the kelvin, which has a natural basis for its definition of zero. By contrast, zero in the imperial scale of degrees Celsius is arbitrarily defined. What are the implications of using a scale based on natural or arbitrary values?

This relationship is often known as **Charles' law**, as it was first established by Frenchman Jacques Charles in the late 18th century. You can demonstrate this relationship by immersing dented table tennis balls in warm water. As the air inside the ball equilibrates to the temperature of the water, it expands, pushing the dents out on the surface.

### 3 Relationship between pressure and temperature

An increase in temperature increases the average kinetic energy of the particles. The particles move faster and collide with the walls of the container with more energy and more frequency, raising the pressure. If the volume is held constant, it is found that increasing the temperature of a fixed mass of gas proportionately raises its pressure. In other words, the pressure of a gas is directly proportional to the absolute temperature, and pressure divided by temperature is a constant.



#### NATURE OF SCIENCE

Scientists work to contribute to a common body of knowledge. Results are shared through publication, considered and used as the basis for further studies by other scientists. Although many scientific discoveries, such as the gas laws, are named after the key scientist involved, in reality the theories and laws of science stand apart from the individual discoverers. Without Charles and Boyle, the relationships between pressure, volume and temperature of a gas would still exist. This is very different from the arts. Without Shakespeare, there would have been no Hamlet, without Picasso, no Guernica.



Balloons dipped in a mixture of dry ice (solid  $\text{CO}_2$ ) and water rapidly deflate as the air inside contracts at low temperature.

**Figure 1.17** Gas pressure is proportional to the absolute temperature.



Be certain to use temperature in kelvin only when applying these relationships.



$$P \propto T$$

$$\frac{P}{T} = \text{a constant}$$

The label on the aerosol can warns of the dangers of exposing the pressurised contents to high temperature.



Pressurized cans, such as soda or beer, often carry a warning to be stored in a cool place. This is because at higher temperatures, the pressure inside the can at fixed volume is able to rise to the point of causing the can to explode.

These three gas laws applied to a fixed mass of gas can be summarized as follows:

$$P \propto 1/V \text{ at constant temperature}$$

$$V \propto T \text{ at constant pressure}$$

$$P \propto T \text{ at constant volume}$$

These can be combined to give one equation for a fixed mass of gas:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$



$$\frac{PV}{T} = \text{a constant or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

where 1 and 2 refer to initial and final conditions respectively.

Application of this enables gas volume, pressure and temperature to be calculated as conditions change.

### Worked example

What happens to the volume of a fixed mass of gas when its pressure and its absolute temperature are both doubled?

#### Solution

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$P_2 = 2 \times P_1$  and  $T_2 = 2 \times T_1$ , so these can be substituted into the equation:

$$\frac{P_1 V_1}{T_1} = \frac{2P_1 V_2}{2T_1}$$

cancelling  $P_1$  and  $T_1$  from both sides, and 2s on the right side:

$$V_1 = V_2$$

The volume does not change.

Note that temperature must be in kelvin in these calculations, but the units of volume and pressure are not specified, so long as they are consistent on both sides of the equation.



### Worked example

The molar volume of a gas at STP is  $22.7 \text{ dm}^3 \text{ mol}^{-1}$ . Calculate the molar volume at  $25^\circ \text{C}$  at the same pressure.

#### Solution

As the pressure is not changing, we do not need to insert  $P_1$  and  $P_2$  into the combined gas equation. Temperature must be converted from  $^\circ \text{C}$  to K.

$$T_1 = 273 \text{ K}, T_2 = 25 + 273 = 298 \text{ K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{22.7 \text{ dm}^3}{273 \text{ K}} = \frac{V_2}{298 \text{ K}}$$

$$V_2 = \frac{298 \times 22.7 \text{ dm}^3}{273} = 24.8 \text{ dm}^3$$



## The ideal gas equation is derived from the combined gas equation and Avogadro's law

The combined gas equation tells us that

$$\frac{PV}{T} = \text{a constant}$$

The value of the constant is directly proportional to the fixed mass of gas, or the number of moles,  $n$ .

$$\text{So } \frac{PV}{T} \propto n$$

This can be made into an equation by introducing a constant,  $R$ , known as the **universal gas constant**.

$$\therefore \frac{PV}{T} = nR, \text{ usually written as } PV = nRT$$

This equation is known as the **ideal gas equation**, and is given in section 1 of the IB data booklet. The value of  $R$  can be calculated by substituting known values into the equation, such as those for the molar volume of a gas at STP. In this case:

$$P = 10^5 \text{ Pa (N m}^{-2}\text{)}, V = 2.27 \times 10^{-2} \text{ m}^3, T = 273 \text{ K}, n = 1$$

$$\therefore 10^5 \text{ N m}^{-2} \times 2.27 \times 10^{-2} \text{ m}^3 = 1 \text{ mol} \times R \times 273 \text{ K}$$

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

This value for  $R$ , the gas constant, is given in section 2 in the IB data booklet, and should be used for all calculations involving the ideal gas equation.

Use of the ideal gas equation enables us to calculate how systems respond to changes in pressure, volume and temperature, and to calculate molar mass. Gas density can also be derived by applying the relationship, density = mass/volume. These calculations usually involve simply substituting values into the equation, but the use of units needs special attention here. The guidelines below, based on the use of SI units only, should help you avoid some of the common mistakes that arise.

- **Pressure  $P$ :** must be in Pa ( $\text{N m}^{-2}$ ); if kPa are given, multiply by  $10^3$ .
- **Volume  $V$ :** must be in  $\text{m}^3$ ; if  $\text{dm}^3$  are given divide by  $10^3$ , if  $\text{cm}^3$  are given divide by  $10^6$ .
- **Number of moles  $n$ :** this is often derived by application of  $n = \frac{m}{M}$ .
- **Temperature  $T$ :** must be in kelvin; if  $^{\circ}\text{C}$  is given, add 273.15.

### Worked example

A helium party balloon has a volume of  $18.0 \text{ dm}^3$ . At  $25^{\circ}\text{C}$  the internal pressure is 108 kPa. Calculate the mass of helium in the balloon.

### Solution

First ensure all data are in SI units:

$$P: 108 \text{ kPa} = 108 \times 10^3 \text{ Pa}$$

$$V: 18.0 \text{ dm}^3 = 18.0 \times 10^{-3} \text{ m}^3$$

$$T: 25^{\circ}\text{C} = 298 \text{ K}$$

$$PV = nRT$$

$$108 \times 10^3 \text{ Pa} \times 18.0 \times 10^{-3} \text{ m}^3 = n \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$\therefore n(\text{He}) = 0.785 \text{ mol}$$

$$\therefore \text{mass (He)} = nM = 0.785 \text{ mol} \times 4.00 \text{ g mol}^{-1} = 3.14 \text{ g}$$



**The ideal gas equation is  $PV = nRT$**



Many sources give data for ideal gas law questions in non-SI units such as atmospheres, which require a mathematical conversion. You will not be expected to be familiar with these conversions in IB examinations.



As this example shows, if pressure is given in kPa and volume is given in  $\text{dm}^3$ , the same answer is obtained if these values are used directly in the ideal gas equation in place of Pa and  $\text{m}^3$ .

Blowing up a balloon increases its volume as the number of particles increases. What do you think would happen to this inflated balloon on the top of a very high mountain?



### Worked example

A sample of gas has a volume of  $445 \text{ cm}^3$  and a mass of  $1.500 \text{ g}$  at a pressure of  $95 \text{ kPa}$  and a temperature of  $28^\circ\text{C}$ . Calculate its molar mass.

### Solution

Substitute  $n = \frac{m}{M}$  into the ideal gas equation, and rearrange to solve for  $M$ .

$$M = \frac{mRT}{PV}$$

Ensure all data are in SI units:

$$P: 95 \text{ kPa} = 95 \times 10^3 \text{ Pa}$$

$$V: 445 \text{ cm}^3 = 445 \times 10^{-6} \text{ m}^3$$

$$T: 28^\circ\text{C} = 301 \text{ K}$$

$$\therefore M = \frac{1.500 \text{ g} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 301 \text{ K}}{95 \times 10^3 \text{ Pa} \times 445 \times 10^{-6} \text{ m}^3} = 89 \text{ g mol}^{-1}$$

### Worked example

A gas has a density of  $1.65 \text{ g dm}^{-3}$  at  $27^\circ\text{C}$  and  $92.0 \text{ kPa}$ . Determine its molar mass.

### Solution

density data  $\Rightarrow 1.65 \text{ g}$  occupies  $1.00 \text{ dm}^3$

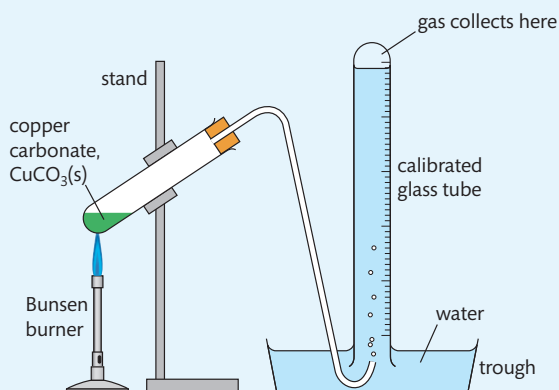
As in the example above, substitute data with correct units into  $M = \frac{mRT}{PV}$

$$\therefore M = \frac{1.65 \text{ g} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{92.0 \times 10^3 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3} = 44.7 \text{ g mol}^{-1}$$

### Experiment to calculate the molar mass of carbon dioxide by application of the ideal gas equation

Full details with a worksheet are available on your eBook.

A known mass of  $\text{CuCO}_3(\text{s})$  is heated and the gas evolved collected by displacement of water. The volume of the gas, the room temperature and pressure are recorded.



**Figure 1.18** Experiment to calculate the molar mass of carbon dioxide.

#### Sample results

	Trial 1	Observations
mass of boiling tube + $\text{CuCO}_3$ before heating / $\text{g} \pm 0.001$	33.910	$\text{CuCO}_3$ is a green powder
mass of boiling tube + $\text{CuCO}_3$ after heating / $\text{g} \pm 0.001$	33.822	the contents of the tube are black after heating
mass change (mass $\text{CO}_2$ ) / $\text{g} \pm 0.002$	0.088	
volume of gas collected / $\text{cm}^3 \pm 0.1$	38.1	the gas collected is colourless
temperature / $\text{K} \pm 0.1$	293.0	
pressure / $\text{kPa} \pm 0.1$	101.3	

#### Processed data

$$M(\text{CO}_2) = \frac{mRT}{PV} = \frac{0.088 \text{ g} \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.0 \text{ K}}{101.3 \text{ kPa} \times 0.0381 \text{ dm}^3}$$

experimental value  $M(\text{CO}_2) = 55.5 \text{ g mol}^{-1}$

theoretical value  $M(\text{CO}_2) = 44.01 \text{ g mol}^{-1}$

$\therefore$  % error = 26.1%

The percentage error can be analysed in consideration of systematic errors such as:

- gas collected may not be pure  $\text{CO}_2$ ;
- $\text{CO}_2$  may be soluble in water;
- air in the tube is collected with the gas;
- gas collected has not equilibrated to room temperature.

Modifications to the experimental design should suggest ways to reduce the impact of these errors. Note that repeat trials and error propagation are not shown here.

## Exercises

- 51 A  $2.50 \text{ dm}^3$  container of helium at a pressure of  $85 \text{ kPa}$  was heated from  $25^\circ\text{C}$  to  $75^\circ\text{C}$ . The volume of the container expanded to  $2.75 \text{ dm}^3$ . What was the final pressure of the helium?
- 52 After a sample of nitrogen with a volume of  $675 \text{ cm}^3$  and a pressure of  $1.00 \times 10^5 \text{ Pa}$  was compressed to a volume of  $350 \text{ cm}^3$  and a pressure of  $2.00 \times 10^5 \text{ Pa}$ , its temperature was  $27.0^\circ\text{C}$ . Determine its initial temperature.
- 53 The absolute temperature of  $4.0 \text{ dm}^3$  of hydrogen gas is increased by a factor of three and the pressure is increased by a factor of four. Deduce the final volume of the gas.
- 54 To find the volume of a flask, it was first evacuated so that it contained no gas at all. When  $4.40 \text{ g}$  of carbon dioxide was introduced, it exerted a pressure of  $90 \text{ kPa}$  at  $27^\circ\text{C}$ . Determine the volume of the flask.
- 55 An unknown noble gas has a density of  $5.84 \text{ g dm}^{-3}$  at STP. Calculate its molar mass, and so identify the gas.
- 56 A  $12.1 \text{ mg}$  sample of a gas has a volume of  $255 \text{ cm}^3$  at a temperature of  $25.0^\circ\text{C}$  and a pressure of  $1300 \text{ Pa}$ . Determine its molar mass.
- 57 Which has the greater density at STP, hydrogen or helium?
- 58 Calculate the volume of oxygen at STP required for the complete combustion of  $125 \text{ g}$  of octane,  $\text{C}_8\text{H}_{18}$ , to form carbon dioxide and water.
- 59 A sample of an unknown gas with a mass of  $3.620 \text{ g}$  occupied a volume of  $1120 \text{ cm}^3$  at a pressure of  $99 \text{ kPa}$  and a temperature of  $25.0^\circ\text{C}$ . The sample contained  $2.172 \text{ g O}$  and  $1.448 \text{ g S}$ . Determine the empirical and molecular formula of the gas.
- 60 A road cyclist pumps his tyres up very hard before a trip over a high mountain pass at high altitude. Near the summit one of his tyres explodes. Suggest why this may have occurred.



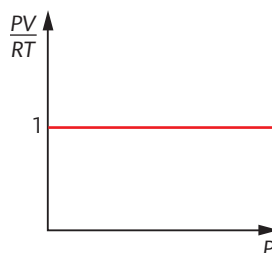
## NATURE OF SCIENCE

Scientists often use models, which may be simple or complex, to explain concepts that are not observable. By their nature, models are thinking tools and so they all have limitations. Models are often tested against experimental results, and should be able to explain phenomena that are seemingly different from the ones used to develop the model. Sometimes, when a model does not seem consistent with data or observations, it may need to be modified or replaced. At other times it can be retained, with limitations to its usefulness agreed.

The ideal gas model has all of these characteristics. While it provides a useful conceptual image of gas behaviour, and is consistent with some testable predictions, there are limitations to this, as we will see below. These do not mean, however, that the model should be discarded – rather they alert us to the fact that the model is in some ways an over-simplification, and cannot apply accurately under all conditions.

## Real gases show deviation from ideal behaviour

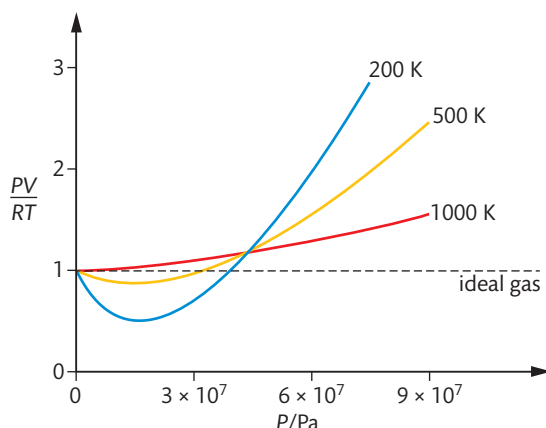
An ideal gas is defined as one that obeys the ideal gas law  $PV = nRT$  under all conditions. This means that for one mole of gas, the relationship  $PV/RT$  should be equal to one. So a graph of  $PV/RT$  against  $P$  for one mole of an ideal gas is a horizontal line of intercept 1.



**Figure 1.19** For one mole of an ideal gas, the relationship  $PV/RT$  is a constant at all pressures.

But as we noted earlier, there is no such thing as an ideal gas and all gases, known as **real gases**, deviate to some extent from ideal behaviour. So, for real gases the value of  $PV/RT$  for 1 mole will vary. An example of the extent of this variation from 1 at different conditions is shown in Figure 1.20.





**Figure 1.20** The deviation from ideal behaviour of nitrogen at different temperatures and pressures.

We can draw the following conclusions from the graph:

- the gas behaves most like an ideal gas at low pressure and shows the greatest deviation at high pressure;
- the gas behaves most like an ideal gas at high temperature and shows the greatest deviation at low temperature.

To interpret these findings, it will be helpful to question the validity of two assumptions made in describing an ideal gas in the kinetic molecular theory:

- 1 the volume of the gas particles is negligible;
- 2 there are no attractive forces between the particles.

1. At relatively low pressure, such as  $1 \times 10^5$  Pa (STP), the volume occupied by the particles of a typical gas is only about 0.05% of the total volume, so it is reasonably valid to describe this as negligible. But with increasing pressure as the space between the particles is reduced, this percentage increases and with a pressure of  $5 \times 10^5$  Pa, the volume of the particles is about 20% of the total volume – certainly not negligible. As a result, the volume of a real gas at high pressure is larger than that predicted from the ideal gas law and  $PV/nRT > 1$ .

2. When a gas is at moderately low pressure, the particles are so widely spaced that interactive forces are highly unlikely, so this assumption is valid. But at pressures up to about  $3 \times 10^7$  Pa, as the particles approach more closely, attractive forces strengthen between them. These have the effect of reducing the pressure of the gas, so  $PV/nRT < 1$ . Low temperatures increase this deviation because the lower kinetic energy of the particles increases the strength of inter-particle forces. At even higher pressures, the non-zero volume of the particles becomes more important and this effect dominates where the graph rises.

Overall, we can conclude that real gases deviate from ideal behaviour when either or both of the assumptions above are not valid. This occurs at high pressure and low temperature. It makes sense intuitively that a gas behaves in a less perfect way under these conditions, which are the closest to it changing into a liquid.

Attempts to modify the ideal gas equation to take these factors into account and make it apply accurately to real gases led to the **van der Waals' equation**, formulated in 1873. This has correction terms for both the volume of the particles and the inter-particle attractions, and these are specific to different gases. Happily, for a wide range of conditions under which gases are studied, the ideal gas equation is a sufficiently accurate expression, and has the big advantage that it is a single equation for all gases.



One form of the van der Waals' equation is:

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where  $a$  is a measure of the attraction between the particles, and  $b$  is the volume excluded by a mole of particles.



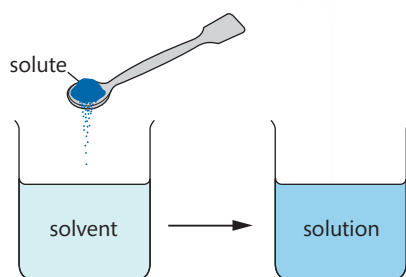
**Real gases deviate most from ideal behaviour at high pressure and low temperature.**

## Exercises

- 61** (a) List the main features of the kinetic theory for ideal gases.  
 (b) Explain the reason for the difference in behaviour between real and ideal gases at low temperature.
- 62** Ammonia,  $\text{NH}_3$ , forms a relatively strong type of intermolecular attraction known as a hydrogen bond, whereas methane,  $\text{CH}_4$ , does not. Explain the relative deviation from ideal behaviour that each gas is likely to show.
- 63** Gases deviate from ideal gas behaviour because their particles:
- |                                 |   |
|---------------------------------|---|
| <b>A</b> have negligible volume | <b>B</b> have forces of attraction between them |
| <b>C</b> are polyatomic         | <b>D</b> are not attracted to one another       |

## The concentration of a solution depends on moles of solute and volume of solution

Liquids, like gases, can conveniently be quantified by measuring their volume rather than their mass. Some liquids in common use are pure substances, such as water ( $\text{H}_2\text{O}$ ), bromine ( $\text{Br}_2$ ), and hexane ( $\text{C}_6\text{H}_{14}$ ), but more commonly liquids are **solutions** containing two or more components.



**Figure 1.21** A solution is made by dissolving a solute in a solvent.

A solution is a homogeneous mixture of two or more substances, which may be solids, liquids or gases, or a combination of these. The **solvent** is the component present in the greatest quantity, in which the **solute** is dissolved. Some examples of solutions include:

- solid/solid: metal alloy such as brass (copper and zinc);
- solid/liquid: seawater (salts and water), copper sulfate(aq) (copper sulfate and water);
- liquid/liquid: wine (ethanol and water);
- gas/liquid: fizzy drinks (carbon dioxide and water).

In this section we will be considering solutions made by dissolving a solid solute in a liquid solvent.

Unlike gases, the volume of a liquid is not directly related to its amount. Instead, for solutions, we express the amount through its **concentration**. The concentration of a solution ( $c$ ) is determined by the amount of solute ( $n$ ) and the volume of solution ( $V$ ). It is usually expressed as  $\text{mol dm}^{-3}$ .

$$\text{concentration of solution (mol dm}^{-3}\text{)} = \frac{\text{amount of solute (mol)}}{\text{volume of solution (dm}^3\text{)}} \quad \text{or} \quad c = \frac{n}{V}$$

$$\therefore \text{amount of solute (mol)} = \text{conc. (mol dm}^{-3}\text{)} \times \text{volume (dm}^3\text{)} \quad \text{or} \quad n = cV$$

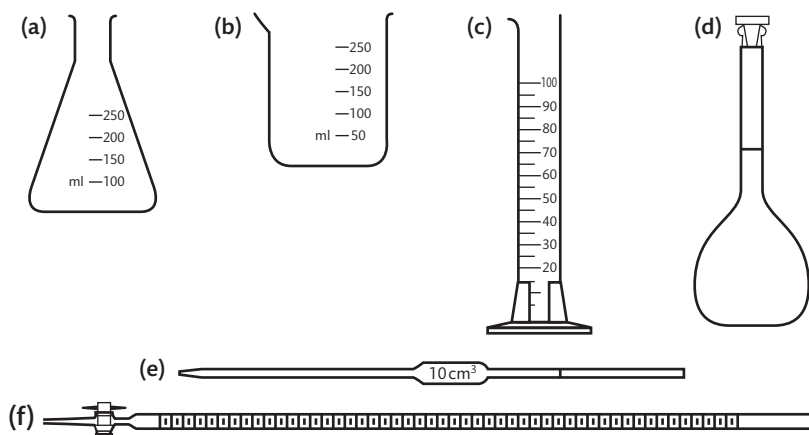


Square brackets are often used to represent 'concentration of' a particular substance, such as  $[\text{HCl}] = 1.0 \text{ mol dm}^{-3}$ .

The concentration of a solution refers to the amount of solute per volume of solution. It has the units  $\text{mol dm}^{-3}$  or  $\text{g dm}^{-3}$ .

Different types of laboratory glassware, which are identified in Figure 1.22. Note that beakers and conical flasks are generally not used for measuring volume.

Chemists routinely prepare solutions of known concentration, known as **standard solutions**. The mass of solute required is accurately measured and then transferred carefully to a volumetric flask, which is accurately calibrated for a specific volume. The solvent is added steadily with swirling to help the solute to dissolve, until the final level reaches the mark on the flask.



**Figure 1.22** Glassware commonly used in the laboratory: (a) conical or Erlenmeyer flask – its shape makes it easy to mix liquids as the flask can be easily swirled; (b) beaker; (c) measuring cylinder; (d) volumetric flask; (e) pipette; (f) burette. Standard solutions are prepared using volumetric flasks.



Note that concentration is specified per volume of final *solution*, not per volume of *solvent* added. This is because volume changes occur on dissolving the solute.

## CHALLENGE YOURSELF

- 6 When sodium hydroxide pellets (NaOH) dissolve in water, there is a *decrease* in the total volume of the solution. Explain what might cause this.



The term *molarity*,  $M$ , has been widely used to express amount concentration, but it is falling out of common usage. It will not be used in IB examination questions, so make sure you are fully familiar with the terms  $\text{mol dm}^{-3}$  and  $\text{g dm}^{-3}$ . (Note that  $M$  is used specifically to refer to molar mass.)



**A standard solution is one of accurately known concentration.**



**Number of moles of solute (mol) = concentration of solute ( $\text{mol dm}^{-3}$ )  $\times$  volume of solution ( $\text{dm}^3$ ) or  $n = cV$ .**

### Worked example

Explain how you would prepare  $100 \text{ cm}^3$  of a  $0.100 \text{ mol dm}^{-3}$  solution of NaCl.

#### Solution

Ensure that  $\text{cm}^3$  are converted to  $\text{dm}^3$  by dividing by 1000.

$$n = cV$$

$$n = 0.100 \text{ mol dm}^{-3} \times \frac{100}{1000} \text{ dm}^3 = 0.0100 \text{ mol}$$

$$M(\text{NaCl}) = 22.99 + 35.45 = 58.44 \text{ g mol}^{-1}$$

$$\therefore \text{mass required} = 0.0100 \text{ mol} \times 58.44 \text{ g mol}^{-1} = 0.584 \text{ g}$$

Add  $0.584 \text{ g NaCl(s)}$  to a  $100 \text{ cm}^3$  volumetric flask, and make up to the mark with distilled water.

Concentration can also be expressed in mass ( $\text{g dm}^{-3}$ ).

### Worked example

Calculate the concentration of a  $0.0400 \text{ mol dm}^{-3}$  solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , in  $\text{g dm}^{-3}$ .

#### Solution

$$M(\text{Na}_2\text{CO}_3) = (22.99 \times 2) + 12.01 + (16.00 \times 3) = 105.99 \text{ g mol}^{-1}$$

$$m = nM \therefore m = 0.0400 \text{ mol} \times 105.99 \text{ g mol}^{-1} = 4.24 \text{ g}$$

$$\therefore [\text{Na}_2\text{CO}_3] = 4.24 \text{ g dm}^{-3}$$



Label on sparkling water listing the mineral content in milligrams per dm<sup>3</sup>.



The increased popularity in many countries of bottled water over tap water for drinking has raised several concerns, including the environmental costs of transport and packaging, and the source of the water and its solute (dissolved mineral) content. Significant differences exist in the regulation of the bottled water industry in different countries. In the USA, the FDA (Food and Drug Administration) requires that mineral waters contain between 500 and 1500 mg dm<sup>-3</sup> of total dissolved solids. In Europe, mineral water is defined by its origin rather than by content, and the EU (European Union) prohibits the treatment of any water bottled from a source. The global cost of bottled water exceeds billions of dollars annually. As the United Nations General Assembly has explicitly recognized that access to safe, clean and affordable drinking water is a human right, there is an urgent need for money and technology to be diverted to improving tap water supplies globally to help make this a reality for all.

A different unit of concentration is known as **ppm**, parts per million. It denotes one part per 10<sup>6</sup> by mass, and is useful in describing very low concentrations such as found in air and water pollution.

$$\text{parts per million (ppm)} = \frac{\text{mass of component}}{\text{total mass of solution}} \times 10^6$$

A concentration of 1 ppm for a substance means that each kilogram of solution contains 1 milligram of solute. Assuming a density of 1 g cm<sup>-3</sup>, 1 ppm also means that each dm<sup>3</sup> of solution contains 1 mg of solute. An advantage of these values based on mass is that they are not temperature dependent.

## Dilutions of solutions reduce the concentration

A common practice in laboratory work is to make a **dilution** from a more concentrated starting solution called the **stock solution**, by adding solvent. For all aqueous solutions, distilled water, rather than tap water, must be used.



Series of dilutions of cobalt(II) chloride solutions. In coloured solutions such as these, the effect of lowering the concentration of the solution can be observed.

As a solution is diluted, the number of moles of solute remains the same, but as they become spread through a larger volume, the concentration is decreased. In other words, the number of moles  $n$  equals a constant, and as  $n = cV \Rightarrow cV$  must be constant through dilution.

$$\therefore c_1V_1 = c_2V_2$$

where  $c_1V_1$  refer to the initial concentration and volume and  $c_2V_2$  refer to the diluted concentration and volume.

This equation provides an easy way to calculate concentration changes on dilution.



### Worked example

Determine the final concentration of a  $75\text{ cm}^3$  solution of HCl of concentration  $0.40\text{ mol dm}^{-3}$ , which is diluted to a volume of  $300\text{ cm}^3$ .

#### Solution

$$c_1V_1 = c_2V_2$$

$$c_1 = 0.40\text{ mol dm}^{-3}, \quad V_1 = 75\text{ cm}^3, \quad V_2 = 300\text{ cm}^3$$

$$\therefore (0.40\text{ mol dm}^{-3})(75\text{ cm}^3) = c_2(300\text{ cm}^3)$$

$$c_2 \text{ diluted concentration} = 0.10\text{ mol dm}^{-3}$$

A quick check shows that the volume has increased four times, so the concentration must have decreased four times.

In precise work, dilution should be carried out using volumetric flasks so the final volume of the solution is measured, taking account of volume changes that may occur on dilution.

## The concentration of a solution can be determined by volumetric analysis

Suppose we have an unlabelled bottle of hydrochloric acid, HCl, and want to know its concentration. We can find this out by reacting the acid with a standard solution of an alkali such as NaOH, and determining the exact volumes that react together. From the stoichiometry of the reaction, when we know the volumes of both solutions and the concentration of one of them, we can use the mole ratio to calculate the unknown concentration as follows.

	HCl(aq)	+	NaOH(aq)	$\rightarrow$	NaCl(aq)	+ H <sub>2</sub> O(l)
mole ratio:	1	:	1			
volume:	known		known (by titration)			
conc.:	unknown = x		known (standard solution)			

- moles NaOH can be calculated as follows:  
 $n(\text{NaOH}) = c(\text{NaOH}) \times V(\text{NaOH})$
- from the mole ratio in the equation:  
 $n(\text{NaOH}) = n(\text{HCl})$
- $\therefore$  concentration of HCl,  $x$ , can be calculated from:  
 $n(\text{HCl}) = x \times V(\text{HCl})$

This is an example of a process called **volumetric analysis**. Most commonly, a technique called **titration** is used to determine the reacting volumes precisely. A **pipette** is used to measure a known volume of one of the solutions into a **conical flask**. The other solution is put into a **burette**, a calibrated glass tube that can deliver precise volumes into the conical flask through opening the tap at the bottom. The point at which the two solutions have reacted completely, the **equivalence point**, is usually determined by an **indicator** that is added to the solution in the conical flask and changes colour at its **end point**. Different indicators are chosen for specific titrations, so that their end point corresponds to the equivalence point of the titration.



Note that in the equation  $c_1V_1 = c_2V_2$ , volume terms appear on both sides of the equation and so their units will cancel. This means that any units of volume can be used directly (there is no need to convert them to  $\text{dm}^3$ ), so long as they are consistent on both sides of the equation.



Redox titration experiment. The burette tap controls the flow of the orange potassium dichromate(VI) solution into the conical flask containing iron(II) ions. The equivalence point occurs when the exact volumes of the two solutions have reacted completely.



Titration is widely used in acid-base chemistry (Chapter 8), and in redox chemistry (Chapter 9). Its applications include industrial chemical processing, chemical research, quality control checks in the food and pharmaceutical industries and aspects of environmental monitoring.

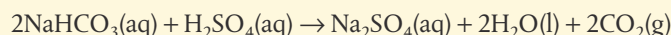
Burettes generally read to  $\pm 0.05 \text{ cm}^3$ , so be sure to record your results to this precision. Readings such as 0, 12.0 or 3.5 are not acceptable but should be recorded as 0.00, 12.00 and 3.50 respectively.



Titration usually involves multiple trials to obtain a more accurate result of the volume required to reach the equivalence point known as the **titre**. A good titration result is one that gives consistent results within  $0.05 \text{ cm}^3$  of each other.

### Worked example

$25.00 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  sodium hydrogencarbonate,  $\text{NaHCO}_3$ , solution were titrated with dilute sulfuric acid,  $\text{H}_2\text{SO}_4$ .



$15.20 \text{ cm}^3$  of the acid were needed to neutralize the solution. Calculate the concentration of the acid.

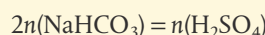
### Solution

We can calculate the amount of  $\text{NaHCO}_3$  as we are given both the volume and the concentration.

$$n = cV$$

$$n(\text{NaHCO}_3) = 0.100 \text{ mol dm}^{-3} \times \frac{25.00}{1000} \text{ dm}^3 = 2.500 \times 10^{-3} \text{ mol}$$

Look at the mole ratio in the equation:



$$\therefore n(\text{H}_2\text{SO}_4) = 0.5 \times 2.500 \times 10^{-3} \text{ mol} = 1.250 \times 10^{-3} \text{ mol}$$

$$c = \frac{n}{V} = \frac{1.250 \times 10^{-3} \text{ mol}}{15.20/1000 \text{ dm}^3} = 0.0822 \text{ mol dm}^{-3}$$

$$\therefore [\text{H}_2\text{SO}_4] = 0.0822 \text{ mol dm}^{-3}$$

Here is a summary of steps in volumetric analysis calculations:



- first write the equation for the reaction;
- look for the reactant whose volume and concentration are given and calculate its number of moles from  $n = cV$ ;
- use this answer and the mole ratio in the equation to determine the number of moles of the other reactant;
- use the number of moles and volume of the second reactant to calculate its concentration from  $c = \frac{n}{V}$ .

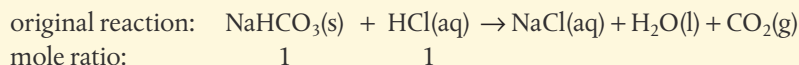
### Back titration

As the name implies, a back titration is done in reverse by returning to the end point after it is passed. It is used when the end point is hard to identify or when one of the reactants is impure. A known excess of one of the reagents is added to the reaction mixture, and the unreacted excess is then determined by titration against a standard solution. By subtracting the amount of unreacted reactant from the original amount used, the reacting amount can be determined.

### Worked example

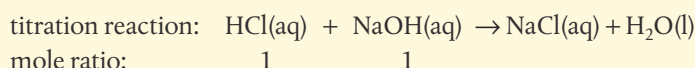
An antacid tablet with a mass of 0.300 g and containing  $\text{NaHCO}_3$  was added to  $25.00 \text{ cm}^3$  of  $0.125 \text{ mol dm}^{-3}$  hydrochloric acid. After the reaction was complete, the excess hydrochloric acid required  $3.50 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$   $\text{NaOH}$  to reach the equivalence point in a titration. Calculate the percentage of  $\text{NaHCO}_3$  in the tablet.

### Solution



First calculate the total amount of  $\text{HCl}$  added, which is a known excess.

$$n(\text{HCl total}) = \frac{25.00}{1000} \text{ dm}^3 \times 0.125 \text{ mol dm}^{-3} = 0.00313 \text{ mol HCl total}$$



$$n(\text{NaOH}) = 0.00350 \text{ dm}^3 \times 0.200 \text{ mol dm}^{-3} = 0.000700 \text{ mol}$$

$$n(\text{NaOH}) = n(\text{HCl unreacted}) = 0.000700 \text{ mol HCl unreacted}$$

$$\therefore n(\text{HCl reacted}) = 0.00313 - 0.000700 = 0.00243 \text{ mol}$$

$$\therefore \text{from the mole ratio in the first equation } n(\text{NaHCO}_3) = 0.00243 \text{ mol}$$

$$M(\text{NaHCO}_3) = 22.99 + 1.01 + 12.01 + (16.00 \times 3) = 84.01 \text{ g mol}^{-1}$$

$$m = nM = 0.00243 \text{ mol} \times 84.01 \text{ g mol}^{-1} = 0.204 \text{ g}$$

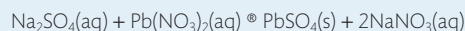
$$\text{percentage by mass in tablet} = \frac{0.204 \text{ g}}{0.300 \text{ g}} \times 100 = 68.0\%$$

Note that there are several assumptions made in this calculation. These include the fact that all the  $\text{NaHCO}_3$  did react with the acid, and that the only component of the tablet that reacted with  $\text{HCl}$  is  $\text{NaHCO}_3$ . You may like to think how you could test the validity of these assumptions in the laboratory.

### Exercises

- 64 Calculate the mass of potassium hydroxide,  $\text{KOH}$ , required to prepare  $250 \text{ cm}^3$  of a  $0.200 \text{ mol dm}^{-3}$  solution.
- 65 Calculate the mass of magnesium sulfate heptahydrate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , required to prepare  $0.100 \text{ dm}^3$  of a  $0.200 \text{ mol dm}^{-3}$  solution.
- 66 Calculate the number of moles of chloride ions in  $0.250 \text{ dm}^3$  of  $0.0200 \text{ mol dm}^{-3}$  of zinc chloride,  $\text{ZnCl}_2$ , solution.
- 67  $250 \text{ cm}^3$  of a solution contains 5.85 g of sodium chloride. Calculate the concentration of sodium chloride in  $\text{mol dm}^{-3}$ .
- 68 Concentrated nitric acid,  $\text{HNO}_3$ , is  $16.0 \text{ mol dm}^{-3}$ . What volume would you need to prepare  $100 \text{ cm}^3$  of  $0.50 \text{ mol dm}^{-3}$   $\text{HNO}_3$ ?
- 69 In a titration a  $15.00 \text{ cm}^3$  sample of  $\text{H}_2\text{SO}_4$  required  $36.42 \text{ cm}^3$  of  $0.147 \text{ mol dm}^{-3}$   $\text{NaOH}$  solution for complete neutralization. What is the concentration of the  $\text{H}_2\text{SO}_4$ ?
- 70 Gastric juice contains hydrochloric acid,  $\text{HCl}$ . A  $5.00 \text{ cm}^3$  sample of gastric juice required  $11.00 \text{ cm}^3$  of  $0.0100 \text{ mol dm}^{-3}$   $\text{KOH}$  for neutralization in a titration. What was the concentration of  $\text{HCl}$  in this fluid? If we assume a density of  $1.00 \text{ g cm}^{-3}$  for the fluid, what was the percentage by mass of  $\text{HCl}$ ?

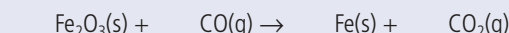
- 71** Sodium sulfate,  $\text{Na}_2\text{SO}_4$ , reacts in aqueous solution with lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , as follows:



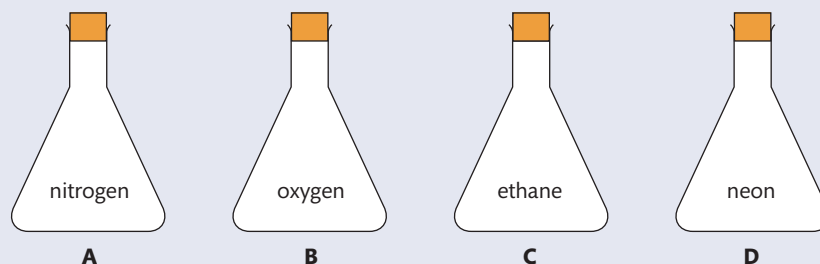
In an experiment,  $35.30 \text{ cm}^3$  of a solution of sodium sulfate reacted exactly with  $32.50 \text{ cm}^3$  of a solution of lead nitrate. The precipitated lead sulfate was dried and found to have a mass of  $1.13 \text{ g}$ . Determine the concentrations of the original solutions of lead nitrate and sodium sulfate. State what assumptions are made.

### Practice questions

- 1** How many oxygen atoms are in  $0.100 \text{ mol}$  of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ?
- A**  $5.42 \times 10^{22}$       **B**  $6.02 \times 10^{22}$       **C**  $2.41 \times 10^{23}$       **D**  $5.42 \times 10^{23}$
- 2** What is the sum of the coefficients when the following equation is balanced using whole numbers?



- A** 5      **B** 6      **C** 8      **D** 9
- 3** Four identical containers under the same conditions are filled with gases as shown below. Which container and contents will have the highest mass?



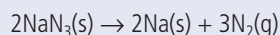
- 4**  $1.0 \text{ dm}^3$  of an ideal gas at  $100 \text{ kPa}$  and  $25^\circ\text{C}$  is heated to  $50^\circ\text{C}$  at constant pressure. What is the new volume in  $\text{dm}^3$ ?
- A** 0.50      **B** 0.90      **C** 1.1      **D** 2.0
- 5** What is the amount, in moles, of sulfate ions in  $100 \text{ cm}^3$  of  $0.020 \text{ mol dm}^{-3} \text{ FeSO}_4(\text{aq})$ ?
- A**  $2.0 \times 10^{-3}$       **B**  $2.0 \times 10^{-2}$       **C**  $2.0 \times 10^{-1}$       **D** 2.0
- 6**  $1.7 \text{ g}$  of  $\text{NaNO}_3$  ( $M_r = 85$ ) is dissolved in water to prepare  $0.20 \text{ dm}^3$  of solution. What is the concentration of the resulting solution in  $\text{mol dm}^{-3}$ ?
- A** 0.01      **B** 0.1      **C** 0.2      **D** 1.0
- 7** What mass, in  $\text{g}$ , of hydrogen is formed when  $3 \text{ mol}$  of aluminium react with excess hydrochloric acid according to the following equation?
- $$2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$$
- A** 3.0      **B** 4.5      **C** 6.0      **D** 9.0
- 8** The relative molecular mass of a gas is 56 and its empirical formula is  $\text{CH}_2$ . What is the molecular formula of the gas?
- A**  $\text{CH}_2$       **B**  $\text{C}_2\text{H}_4$       **C**  $\text{C}_3\text{H}_6$       **D**  $\text{C}_4\text{H}_8$



- 9 What is the sum of all coefficients when the following equation is balanced using the smallest possible whole numbers?



- A 5                      B 7                      C 11                      D 13
- 10 What is the total number of hydrogen atoms in 1.0 mol of benzamide,  $\text{C}_6\text{H}_5\text{CONH}_2$ ?  
A 7                      B  $6.0 \times 10^{23}$                       C  $3.0 \times 10^{24}$                       D  $4.2 \times 10^{24}$
- 11 Chloroethene,  $\text{C}_2\text{H}_3\text{Cl}$ , reacts with oxygen according to the equation below:  
$$2\text{C}_2\text{H}_3\text{Cl(g)} + 5\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)} + 2\text{HCl(g)}$$
  
What is the amount, in mol, of  $\text{H}_2\text{O}$  produced when 10.0 mol of  $\text{C}_2\text{H}_3\text{Cl}$  and 10.0 mol of  $\text{O}_2$  are mixed together, and the above reaction goes to completion?  
A 4.00                      B 8.00                      C 10.0                      D 20.0
- 12 What is the concentration of NaCl, in  $\text{mol dm}^{-3}$ , when 10.0  $\text{cm}^3$  of 0.200  $\text{mol dm}^{-3}$  NaCl solution is added to 30.0  $\text{cm}^3$  of 0.600  $\text{mol dm}^{-3}$  NaCl solution?  
A 0.450                      B 0.300                      C 0.500                      D 0.800
- 13 On analysis, a compound with molar mass  $60 \text{ g mol}^{-1}$  was found to contain 12 g of carbon, 2 g of hydrogen, and 16 g of oxygen. What is the molecular formula of the compound?  
A  $\text{CH}_2\text{O}$                       B  $\text{CH}_4\text{O}$                       C  $\text{C}_2\text{H}_4\text{O}$                       D  $\text{C}_2\text{H}_4\text{O}_2$
- 14 300  $\text{cm}^3$  of water is added to a solution of 200  $\text{cm}^3$  of 0.5  $\text{mol dm}^{-3}$  sodium chloride. What is the concentration of sodium chloride in the new solution?  
A 0.05  $\text{mol dm}^{-3}$                       B 0.1  $\text{mol dm}^{-3}$                       C 0.2  $\text{mol dm}^{-3}$                       D 0.3  $\text{mol dm}^{-3}$
- 15 What is the approximate molar mass, in  $\text{g mol}^{-1}$ , of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ?  
A 120                      B 130                      C 138                      D 246
- 16 Which is both an empirical and a molecular formula?  
A  $\text{C}_5\text{H}_{12}$                       B  $\text{C}_5\text{H}_{10}$                       C  $\text{C}_4\text{H}_8$                       D  $\text{C}_4\text{H}_{10}$
- 17 Airbags are an important safety feature in vehicles. Sodium azide, potassium nitrate, and silicon dioxide have been used in one design of airbag.  
Two students looked at data in a simulated computer-based experiment to determine the volume of nitrogen generated in an airbag.  
Sodium azide, a toxic compound, undergoes the following decomposition reaction under certain conditions.



Using the simulation program, the students entered the following data into the computer.

Temperature (T) / $^{\circ}\text{C}$	Mass of $\text{NaN}_3\text{(s)}$ (m) / kg	Pressure (p) / atm
25.00	0.0650	1.08

- (a) State the number of significant figures for the temperature, mass, and pressure data. (1)  
(b) Calculate the amount, in mol, of sodium azide present. (1)  
(c) Determine the volume of nitrogen gas, in  $\text{dm}^3$ , produced under these conditions based on this reaction. (4)

(Total 6 marks)

- 18** An important environmental consideration is the appropriate disposal of cleaning solvents. An environmental waste treatment company analysed a cleaning solvent, **J**, and found it to contain the elements carbon, hydrogen, and chlorine only. The chemical composition of **J** was determined using different analytical chemistry techniques.

Combustion reaction:

Combustion of 1.30 g of **J** gave 0.872 g  $\text{CO}_2$  and 0.089 g  $\text{H}_2\text{O}$ .

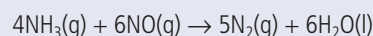
Precipitation reaction with  $\text{AgNO}_3(\text{aq})$ :

0.535 g of **J** gave 1.75 g  $\text{AgCl}$  precipitate.

- (a) Determine the percentage by mass of carbon and hydrogen in **J**, using the combustion data. (3)
- (b) Determine the percentage by mass of chlorine in **J**, using the precipitation data. (1)
- (c) The molar mass was determined to be  $131.38 \text{ g mol}^{-1}$ . Deduce the molecular formula of **J**. (3)

(Total 7 marks)

- 19** Nitrogen monoxide may be removed from industrial emissions via a reaction with ammonia as shown by the equation below:



$30.0 \text{ dm}^3$  of ammonia reacts with  $30.0 \text{ dm}^3$  of nitrogen monoxide at  $100^\circ\text{C}$ . Identify which gas is in excess and by how much and calculate the volume of nitrogen produced. (2)

- 20** The percentage by mass of calcium carbonate in eggshell was determined by adding excess hydrochloric acid to ensure that all the calcium carbonate had reacted. The excess acid left was then titrated with aqueous sodium hydroxide.

- (a) A student added  $27.20 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$   $\text{HCl}$  to  $0.188 \text{ g}$  of eggshell. Calculate the amount, in mol, of  $\text{HCl}$  added. (1)
- (b) The excess acid requires  $23.80 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$   $\text{NaOH}$  for neutralization. Calculate the amount, in mol, of acid that is in excess. (1)
- (c) Determine the amount, in mol, of  $\text{HCl}$  that reacted with the calcium carbonate in the eggshell. (1)
- (d) State the equation for the reaction of  $\text{HCl}$  with the calcium carbonate in the eggshell. (2)
- (e) Determine the amount, in mol, of calcium carbonate in the sample of the eggshell. (2)
- (f) Calculate the mass and the percentage by mass of calcium carbonate in the eggshell sample. (3)
- (g) Deduce one assumption made in arriving at the percentage of calcium carbonate in the eggshell sample. (1)

(Total 11 marks)

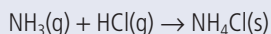
- 21** A  $2.450 \text{ g}$  sample of a mixture of sodium chloride and calcium chloride was dissolved in distilled water. The chloride solution was treated with excess silver nitrate solution,  $\text{AgNO}_3(\text{aq})$ . The precipitated silver chloride,  $\text{AgCl}(\text{s})$ , was collected, washed, and dried. The mass of the dried silver chloride was  $6.127 \text{ g}$ . Calculate the per cent by mass of the sodium chloride and calcium chloride in the original mixture. (2)

- 22** A hydrate of potassium carbonate has the formula  $\text{K}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ . A  $10.00 \text{ g}$  sample of the hydrated solid is heated, and forms  $7.93 \text{ g}$  of anhydrous salt.

- (a) Calculate the number of moles of water in the hydrated sample. (1)
- (b) Calculate the number of moles of anhydrous salt that form. (1)
- (c) Determine the formula of the hydrate. (1)
- (d) How could you determine when all the hydrated salt has been converted into anhydrous form? (1)

(Total 4 marks)

- 23** 625 cm<sup>3</sup> of ammonia, NH<sub>3</sub>, at 42 °C and 160 kPa is combined with 740 cm<sup>3</sup> of hydrogen chloride at 57 °C and 113.3 kPa. The reaction produces ammonium chloride as follows:



- (a) Which reactant is in excess? (1)
- (b) Which reactant is limiting? (1)
- (c) What mass of ammonium chloride forms? (1)

(Total 3 marks)

- 24** Sulfur dioxide, SO<sub>2</sub>, is one of the gases associated with the formation of acidic deposition. It is released during the process of extracting lead from lead ore, when lead sulfide, PbS, is roasted to form lead oxide, PbO.

- (a) Write an equation for the reaction of roasting lead sulfide. (1)
- (b) What mass of sulfur dioxide is produced when one tonne of lead sulfide is used in this reaction? (2)
- (c) What assumption have you made in this calculation? (2)

(Total 5 marks)

- 25** Aluminium metal reacts with copper(II) sulfate solution, CuSO<sub>4</sub>(aq), to produce aluminium sulfate solution, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(aq), and copper metal.

- (a) Write an equation for this reaction. (1)
- (b) How many moles of aluminium are needed to react with 10.38 moles of copper(II) sulfate? (1)
- (c) How many moles of copper are produced if 3.95 moles of copper(II) sulfate react with aluminium? (1)
- (d) What changes might be observed during this reaction? (2)

(Total 5 marks)



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