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 a 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.

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 S.
- 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.
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.

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.

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

**Chemical elements are the fundamental building blocks of chemistry**

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

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**Applications and skills:**

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

**Guidance**

- 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.

**Guidance**

- 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.
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.

<table>
<thead>
<tr>
<th>Name of element</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>C</td>
</tr>
<tr>
<td>fluorine</td>
<td>F</td>
</tr>
<tr>
<td>potassium</td>
<td>K</td>
</tr>
<tr>
<td>calcium</td>
<td>Ca</td>
</tr>
<tr>
<td>mercury</td>
<td>Hg</td>
</tr>
<tr>
<td>tungsten</td>
<td>W</td>
</tr>
</tbody>
</table>

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 properties of a compound from those of the individual elements, containing a fixed ratio of atoms. The physical and chemical properties of a compound are different from those of its component elements.
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, Cl₂, 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.)

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Symbol</th>
<th>Name of compound</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium chloride</td>
<td>NaCl</td>
<td>water</td>
<td>H₂O</td>
</tr>
<tr>
<td>potassium oxide</td>
<td>K₂O</td>
<td>glucose</td>
<td>C₆H₁₂O₆</td>
</tr>
<tr>
<td>calcium bromide</td>
<td>CaBr₂</td>
<td>ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
</tr>
</tbody>
</table>

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

\[ \text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}_2 \]

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

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>hydrogen atoms</th>
<th>oxygen atoms</th>
<th>total on left side</th>
<th>total on right side</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Note that when the coefficient is 1, this does not need to be explicitly stated.
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 hydrogen carbonate (NaHCO₃) into sodium carbonate (Na₂CO₃), water (H₂O), and carbon dioxide (CO₂).

**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.

\[
\text{NaHCO₃} \rightarrow \text{Na₂CO₃} + \text{H₂O} + \text{CO₂}
\]

<table>
<thead>
<tr>
<th>Total on left side</th>
<th>Total on right side</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium atoms</td>
<td>1</td>
</tr>
<tr>
<td>hydrogen atoms</td>
<td>1</td>
</tr>
<tr>
<td>carbon atoms</td>
<td>1</td>
</tr>
<tr>
<td>oxygen atoms</td>
<td>3</td>
</tr>
</tbody>
</table>

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

\[
2\text{NaHCO₃} \rightarrow \text{Na₂CO₃} + \text{H₂O} + \text{CO₂}
\]

Finally check that it is balanced for each element.

**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.

**Exercises**

1. Write balanced chemical equations for the following reactions:
   - (a) The decomposition of copper carbonate (CuCO₃) into copper(II) oxide (CuO) and carbon dioxide (CO₂).
   - (b) The combustion of magnesium (Mg) in oxygen (O₂) to form magnesium oxide (MgO).
   - (c) The neutralization of sulfuric acid (H₂SO₄) with sodium hydroxide (NaOH) to form sodium sulfate (Na₂SO₄) and water (H₂O).
   - (d) The synthesis of ammonia (NH₃) from nitrogen (N₂) and hydrogen (H₂).
   - (e) The combustion of methane (CH₄) to produce carbon dioxide (CO₂) and water (H₂O).

2. Write balanced chemical equations for the following reactions:
   - (a) K + H₂O → KOH + H₂
   - (b) C₂H₅OH + O₂ → CO₂ + H₂O
   - (c) Cl₂ + KI → KCl + I₂
   - (d) CrO₃ → Cr₂O₃ + O₂
   - (e) Fe₂O₃ + C → CO + Fe
Exercises

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) \( \text{Cu} + \text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + \text{NO} + \text{H}_2\text{O} \)

(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 \textbf{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.

Mixtures form when substances combine without chemical interaction

Air is described as a \textbf{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.
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.

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

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

From our everyday experience, we know that all matter (elements, compounds, and mixtures) can exist in different forms depending on the temperature and the 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.

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.
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 °C  
B. H₂ at 200 °C  
C. O₂ at 300 °C  
D. H₂O at 400 °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 or speed (v) of a substance, according to the relationship:

\[
KE = \frac{1}{2}mv^2
\]

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. 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.

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.

<table>
<thead>
<tr>
<th>State</th>
<th>Symbol</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>(s)</td>
<td>Mg(s)</td>
</tr>
<tr>
<td>liquid</td>
<td>(l)</td>
<td>Br₂(l)</td>
</tr>
<tr>
<td>gas</td>
<td>(g)</td>
<td>N₂(g)</td>
</tr>
<tr>
<td>aqueous (dissolved in water)</td>
<td>(aq)</td>
<td>HCl(aq)</td>
</tr>
</tbody>
</table>

For example:

\[
2Na(s) + 2H₂O(l) \rightarrow 2NaOH(aq) + H₂(g)
\]

**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

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Exercises

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) \( \text{Pb(NO}_3)_2 + \text{NaCl} \rightarrow \text{PbCl}_2 + \text{NaNO}_3 \) (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.

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.

\[ \text{solid} \quad \text{melting} \quad \text{sublimation} \quad \text{evaporating/boiling} \quad \text{freezing} \quad \text{condensing} \quad \text{deposition} \quad \text{gas} \]

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.
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.

![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, C₄H₁₀, 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 the butane to boil, releasing a gas that can be burned.

**CHALLENGE YOURSELF**

1. Propane (C₃H₈) and butane (C₄H₁₀) are both commonly used in portable heating devices. Their boiling points are butane -1 °C and propane -42 °C. Suggest why butane is less suitable for use in very cold climates.

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.
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.

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.

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.
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 SI (Systeme International d’Unites) refers to the metric system of measurement based on seven base units. These are metre (m) for length, kilogram for mass (kg), 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.

The generally used unit of molar mass (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.

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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 16 times greater than an atom of hydrogen, and an atom of oxygen has a mass approximately 32 times that of an atom of hydrogen. 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.

<table>
<thead>
<tr>
<th>mass of 1 atom (arbitrary units)</th>
<th>1</th>
<th>16</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>ratio of mass</td>
<td>1 : 16 : 32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mass of 100 atoms</th>
<th>100</th>
<th>1600</th>
<th>3200</th>
</tr>
</thead>
<tbody>
<tr>
<td>ratio of mass</td>
<td>1 : 16 : 32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

... and so on for any fixed number of atoms.

Now 32 g of gold contain

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.02 x 10^{23} atoms H</td>
<td>6.02 x 10^{23} atoms O</td>
<td>6.02 x 10^{23} atoms S</td>
</tr>
<tr>
<td>1g</td>
<td>16g</td>
<td>32g</td>
</tr>
</tbody>
</table>

Figure 1.5 100 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.)

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.

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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).

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?

Avogadro’s number is so large that we cannot comprehend its scale. For example:

- \(6.02 \times 10^{23}\) pennies distributed equally 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.

**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

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

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

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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:

- from water $\text{H}_2\text{O}$: number of H atoms = $2 \times (2.10 \times 10^{23})$ = $4.20 \times 10^{23}$
- from ammonia $\text{NH}_3$: number of H atoms = $3 \times (8.00 \times 10^{21})$ = $0.240 \times 10^{23}$

∴ total H atoms = $(4.20 \times 10^{23}) + (0.240 \times 10^{23})$ = $4.44 \times 10^{23}$

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

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

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.
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 \(1.66 \times 10^{-27} \text{ kg}\).

Relative atomic mass, \(A_r\), is the weighted average of one atom of an element relative to one-twelfth of an atom of carbon-12.

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

\[
A_r = \frac{\text{weighted average of one atom of the element}}{\text{mass of one atom of carbon-12}}
\]

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.

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative atomic mass ((A_r))</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen, H</td>
<td>1.01</td>
</tr>
<tr>
<td>carbon, C</td>
<td>12.01</td>
</tr>
<tr>
<td>oxygen, O</td>
<td>16.00</td>
</tr>
<tr>
<td>sodium, Na</td>
<td>22.99</td>
</tr>
<tr>
<td>sulfur, S</td>
<td>32.07</td>
</tr>
<tr>
<td>chlorine, Cl</td>
<td>35.45</td>
</tr>
</tbody>
</table>

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.

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.

One mole of different compounds, each showing the molar mass. The chemical formulas of these ionic compounds are, clockwise from lower left: NaCl, FeCl₃, CuSO₄, KI, Co(NO₃)₂, and KMnO₄.
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 g mol\(^{-1}\), which is a derived SI unit. Using the examples discussed already in this chapter, we can now deduce the following:

<table>
<thead>
<tr>
<th>Element or compound</th>
<th>Molar mass (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen, H</td>
<td>1.01 g mol(^{-1})</td>
</tr>
<tr>
<td>oxygen, O</td>
<td>16.00 g mol(^{-1})</td>
</tr>
<tr>
<td>sulfur, S</td>
<td>32.07 g mol(^{-1})</td>
</tr>
<tr>
<td>chlorine, Cl(_2)</td>
<td>70.90 g mol(^{-1})</td>
</tr>
<tr>
<td>ammonium nitrate, NH(_4)NO(_3)</td>
<td>80.06 g mol(^{-1})</td>
</tr>
<tr>
<td>aluminium sulfate, Al(_2)(SO(_4))(_3)</td>
<td>342.17 g mol(^{-1})</td>
</tr>
</tbody>
</table>

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 (g mol\(^{-1}\))

\[
\begin{align*}
\text{number of moles} (n) & \rightarrow \text{mass} (m) \\
\text{divide by molar mass, } M & \\
\end{align*}
\]

\[
\begin{align*}
\text{multiply by molar mass, } M \\
\end{align*}
\]
Stoichiometric relationships

**Worked example**

What is the mass of the following?

(a) 6.50 moles of NaCl
(b) 0.10 moles of OH\(^{-}\) ions

**Solution**

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

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

\[n\) (NaCl) = 6.50 mol\]

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

(b) OH\(^{-}\) ions carry a charge because electrons have been transferred, but the change to the mass is negligible and so can be ignored in calculating \(M\).

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

\[n\) (OH\(^{-}\)) = 0.10 mol\]

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

**Worked example**

What is the amount in moles of the following?

(a) 32.50 g \((\text{NH}_4\)\)_2SO\(_4\)
(b) 273.45 g N\(_2\)O\(_5\)

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

\[m\) ((NH\(_4\))\(_2\)SO\(_4\)) = 32.50 g\]

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

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

\[m\) (N\(_2\)O\(_5\)) = 273.45 g\]

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

These simple conversions show that:

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

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.

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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 Ar.

16 Calculate the molar mass of the following compounds:
   (a) magnesium phosphate, Mg₃(PO₄)₂
   (b) ascorbic acid (vitamin C), C₆H₈O₆
   (c) calcium nitrate, Ca(NO₃)₂
   (d) hydrated sodium thiosulfate, Na₂S₂O₃·5H₂O

17 Calcium arsenate, Ca₃(AsO₄)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, CO₂?

19 How many moles of chloride ions, Cl⁻, are there in 0.50 g of copper(II) chloride, CuCl₂?

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, C₁₂H₂₂O₁₁?

22* Which contains the greater number of particles, 10.0 g of water (H₂O) or 10.0 g of mercury (Hg)?

23* Put the following in descending order of mass?
   1.0 mol N₂H₄
   2.0 mol N₂
   3.0 mol NH₃
   25.0 mol H₂

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 : 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.
Experiment to determine the empirical formula of MgO

Full details of how to carry out this experiment with a worksheet are available online.

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

<table>
<thead>
<tr>
<th>Mass / g ± 0.001</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of crucible + lid</td>
<td>19.777</td>
</tr>
<tr>
<td>mass of crucible + lid + Mg</td>
<td>19.820</td>
</tr>
<tr>
<td>mass of crucible + lid + white solid product</td>
<td>19.849</td>
</tr>
</tbody>
</table>

Processed data

<table>
<thead>
<tr>
<th></th>
<th>Magnesium, Mg</th>
<th>Oxygen, O</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass /g ± 0.002</td>
<td>0.043</td>
<td>0.029</td>
</tr>
<tr>
<td>M / g mol⁻¹</td>
<td>24.31</td>
<td>16.00</td>
</tr>
<tr>
<td>moles / mol</td>
<td>0.00177</td>
<td>0.00181</td>
</tr>
</tbody>
</table>

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  C₆H₆
II  C₃H₈
III N₂O₄
IV Pb(NO₃)₂
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 NO₂.

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 1.120 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass / g</th>
<th>M / g mol⁻¹</th>
<th>Number of moles / mol</th>
<th>Divide by Smallest</th>
<th>Nearest Whole Number Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1.120</td>
<td>14.01</td>
<td>0.0799</td>
<td>2.00</td>
<td>2</td>
</tr>
<tr>
<td>H</td>
<td>0.161</td>
<td>1.01</td>
<td>0.159</td>
<td>3.98</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>0.480</td>
<td>12.01</td>
<td>0.0400</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>0.640</td>
<td>16.00</td>
<td>0.0400</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

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

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 \( \text{CaCl}_2\cdot4\text{H}_2\text{O} \).

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.
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 phosphorus pentoxide, P₂O₅, and percentage by mass potassium oxide, K₂O. The percentage data for P₂O₅ and K₂O 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.

**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 subtraction of the total given masses from 100.

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

<table>
<thead>
<tr>
<th>Strontium, Sr</th>
<th>Sulfur, S</th>
<th>Oxygen, O</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by mass</td>
<td>47.70</td>
<td>17.46</td>
</tr>
<tr>
<td>M / g mol⁻¹</td>
<td>87.62</td>
<td>32.07</td>
</tr>
<tr>
<td>number of moles/mol</td>
<td>0.5443</td>
<td>0.5444</td>
</tr>
<tr>
<td>divide by smallest</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

So the empirical formula of the mineral is SrSO₄.

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, Na₂B₄O₇·5H₂O 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, NH₄NO₃?

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.

$$\% \text{ N} = \frac{14.01 \times 2}{80.06} \times 100 = 35.00\% \text{ by mass}$$

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

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

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

Finally check the numbers add up to 100%. Note that rounding here means that the total is 100.01%.

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, CH₂ 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 C₂H₄, C₃H₆, 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.

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

Worked example

Calomel is a compound once used in the treatment of syphilis. It has the empirical formula HgCl and a molar mass of 472.08 g mol⁻¹. What is its molecular formula?
Solution

First calculate the mass of the empirical formula:

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

\[
(236.04) \times x = M = 472.08
\]

\[
\therefore x = 2
\]

Thus, the molecular formula is \( \text{Hg}_2\text{Cl}_2 \).

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.

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

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

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, \( M \).

\[
\begin{align*}
\text{mass C} &= 0.02361 \text{ mol } \times 12.01 \text{ g mol}^{-1} = 0.2836 \text{ g} \\
\text{mass H} &= 0.07068 \text{ mol } \times 1.01 \text{ g mol}^{-1} = 0.07139 \text{ g} \\
\therefore \text{mass O} &= 0.5438 \text{ g} - (0.2836 + 0.07139) = 0.1888 \text{ g} \\
\text{mol O atoms} &= \frac{0.1888 \text{ g}}{16.00 \text{ g mol}^{-1}} = 0.01180 \text{ mol}
\end{align*}
\]

Now we can proceed as with the previous examples, converting mass of O to moles and then comparing the mole ratios.
You are asked to write your name on a suitable surface, using a piece of chalk that is pure calcium carbonate, CaCO₃. How could you calculate the number of carbon atoms in your signature?

A compound has a formula M₃N where M is a metal element and N is nitrogen. It contains 0.673 g of nitrogen. Determine the empirical formula.

A weak acid has a molar mass of 162 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 was O. Determine its empirical and molecular formulas.

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 H₂O. Determine its empirical formula.

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

Give the empirical formulas of the following compounds:
(a) ethyne, C₂H₂
(b) glucose, C₆H₁₂O₆
(c) sucrose, C₁₂H₂₂O₁₁
(d) octane, C₈H₁₈
(e) oct-1-yne, C₅H₁₄
(f) ethanoic acid, CH₃COOH

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.

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 its empirical and molecular formulas.

A compound has a molar mass of 181 g mol⁻¹. Analysis of a 0.979 g sample showed the composition by mass is 0.1927 g C, 0.02590 g H, 0.1124 g N, and 0.1491 g P. The remainder was O. Determine its empirical and molecular formulas.

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 its empirical formula of ATP. Its formula mass was found to be 507 g mol⁻¹. Determine its molecular formula.

Exercises

<table>
<thead>
<tr>
<th>Sample</th>
<th></th>
<th>Carbon, C</th>
<th>Hydrogen, H</th>
<th>Oxygen, O</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass / g</td>
<td></td>
<td>0.1888</td>
<td></td>
<td></td>
</tr>
<tr>
<td>moles</td>
<td>0.02361</td>
<td>0.07068</td>
<td>0.01180</td>
<td></td>
</tr>
<tr>
<td>divide by smallest</td>
<td>2.001</td>
<td>5.999</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>nearest whole number ratio</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

So the empirical formula is C₂H₆O.
Stoichiometric relationships

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, and 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: g dm\(^{-3}\), 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, CH\(_4\), burns in air, we can conclude the following, all from the balanced chemical equation:

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

Reacting ratio by mole:
- \(1\) mole \(\rightarrow\) \(2\) moles
- \(1\) mole \(\rightarrow\) \(2\) moles

Reacting ratio by mass:
- 16.05 g \(\rightarrow\) 64.00 g
- 44.01 g \(\rightarrow\) 36.04 g

\[
80.05 \text{ g reactant} \quad 80.05 \text{ g product}
\]

(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.)
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, here they are marked in red; these are the species where we need to convert moles to grams.

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

Reacting ratio by mole: \(1\) mole \(1\) mole

Reacting ratio by mass / g: \(16.05\) \(44.01\)

For 1.00 g methane: \(1.00\)

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

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

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

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.

**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 \(\text{CO}_2\text{e}\), 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.

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 \(m = \frac{n}{M}\);
- insert the data from the question and solve the ratio.

**Worked example**

Iodine chloride, \(\text{ICl}\), can be made by the following reaction:

\[
2\text{I}_2 + \text{KIO}_3 + 6\text{HCl} \rightarrow 5\text{ICl} + \text{KCl} + 3\text{H}_2\text{O}
\]

Calculate the mass of iodine, \(\text{I}_2\), needed to prepare 28.60 g of ICl by this reaction.

**Solution**

The relevant terms from the question are \(\text{I}_2\) and ICl, so these are our focus.

Reacting ratio by mole: \(2\) moles \(5\) moles

Reacting ratio by mass: \(2 \times (126.90 \times 2) = 507.60 \text{ g}\)

For 28.60 g ICl:

\[
x = \frac{28.60}{811.75} \times 507.60 = 17.88 \text{ g I}_2
\]
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.

**Worked example**

Nitrogen gas (N₂) can be prepared from this reaction:

\[ 2\text{NH}_3(g) + 3\text{CuO}(s) \rightarrow \text{N}_2(g) + 3\text{Cu}(s) + 3\text{H}_2\text{O}(g) \]

If 18.1 g NH₃ are reacted with 90.40 g CuO, determine the mass of N₂ 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.

\[
\begin{align*}
\text{n(NH}_3\text{)} &= \frac{18.1 \text{ g}}{14.01 \text{ g mol}^{-1} + (3 \times 1.01) \text{ g mol}^{-1}} = 1.06 \text{ mol NH}_3 \\
\text{n(CuO)} &= \frac{90.40 \text{ g}}{63.55 \times 16.00 \text{ g mol}^{-1}} = 1.14 \text{ mol CuO}
\end{align*}
\]

Mole ratio from equation: \( \frac{\text{NH}_3}{\text{CuO}} = \frac{2}{3} \approx 0.667 \)

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 NH₃ is in excess and CuO is the limiting reactant.

This means that the amount of N₂ that can form will be determined by the amount of CuO. This is now similar to the earlier questions, where we write out the equation and focus on the terms identified in the question.

\[
\begin{align*}
2\text{NH}_3(g) + 3\text{CuO}(s) &\rightarrow \text{N}_2(g) + 3\text{Cu}(s) + 3\text{H}_2\text{O}(g) \\
\text{reacting ratio by mole:} &\quad 3 \text{ moles} \quad 1 \text{ mole} \\
\text{for 1.14 moles CuO:} &\quad 1.14 \quad x \\
\text{mole ratio } &\quad \frac{\text{CuO}}{\text{N}_2} = \frac{3}{1} = \frac{1.14}{x} \quad \therefore x = \frac{1.14 \times 1}{3} = 0.380 \text{ mol N}_2 \\
\text{mass N}_2 &\quad = 0.380 \text{ mol} \times \text{M(N}_2\text{)} \text{ g mol}^{-1} = 0.380 \text{ mol} \times 28.02 \text{ g mol}^{-1} = 10.7 \text{ g N}_2
\end{align*}
\]
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 CH₄ when 1 mole of CH₄ and 1 mole of O₂ are supplied.

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

reacting ratio by mole:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
</table>

reactant ratio given:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
</table>

⇒ O₂ is limiting reactant

mole ratio at the end of reaction:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>0.5</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
</tr>
</thead>
</table>

So 0.5 moles CH₄ will be un-reacted 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 N₂ is known as the theoretical yield, because it assumes that all of the CuO was converted to N₂ 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 to determine 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.
**CHALLENGE YOURSELF**

3. 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.

---

**Stoichiometric relationships**

**Worked example**

The previous Worked example on the synthesis of N₂ from NH₃ and CuO had a theoretical yield of 10.7 g N₂ from the starting amounts of reactants. Under the same conditions, an experiment produced 8.35 g N₂. 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:

\[
\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}(l)
\]

(a) How many moles of Fe can be made from 1.25 moles of Fe₂O₃?
(b) How many moles of H₂ are needed to make 3.75 moles of Fe?
(c) If the reaction yields 12.50 moles of H₂O, what mass of Fe₂O₃ was used up?

37. Lighters commonly use butane, C₄H₁₀, as the fuel.
(a) Formulate the equation for the combustion of butane.
(b) Determine the mass of butane that burned when 2.46 g of water were produced.

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

\[
3\text{Al}(s) + 3\text{NH}_4\text{ClO}_4(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{AlCl}_3(s) + 3\text{NO}(g) + 6\text{H}_2\text{O}(g)
\]

Calculate the mass of NH₄ClO₄ that should be added to this fuel mixture to react completely with every kilogram of Al.

39. Limestone is mostly calcium carbonate, CaCO₃, but also contains other minerals. When heated, the CaCO₃ decomposes into CaO and CO₂. A 1.605 g sample of limestone was heated and gave off 0.657 g of CO₂.
(a) Formulate the equation for the thermal decomposition of calcium carbonate.
(b) Determine the percentage mass of CaCO₃ in the limestone.
(c) State the assumptions that you are making in this calculation.

40. Methanol, CH₃OH, is a useful fuel that can be made as follows:

\[
\text{CO(g)} + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l)
\]

(a) Determine the theoretical yield of CH₃OH.
(b) Calculate the amount of the excess reactant that remains unchanged at the end of the reaction.

41. The dry-cleaning solvent 1,2-dichloroethane, C₂H₄Cl₂, is prepared from the following reaction:

\[
\text{C}_2\text{H}_4(g) + \text{Cl}_2(g) \rightarrow \text{C}_2\text{H}_4\text{Cl}_2(l)
\]

Determine the mass of product that can be formed from 15.40 g of C₂H₄ and 3.74 g of Cl₂.

42. Calcium carbonate, CaCO₃, is able to remove sulfur dioxide, SO₂, from waste gases by a reaction in which they react in a 1:1 stoichiometric ratio to form equimolar amounts of CaSO₄. When 255 g of CaCO₃ reacted with 135 g of SO₂, 198 g of CaSO₄ were formed. Determine the percentage yield of CaSO₄.

43. Pentyl ethanoate, CH₃COOC₅H₁₁, which smells like bananas, is produced from the esterification reaction:

\[
\text{CH}_3\text{COOH}(aq) + \text{C}_5\text{H}_11\text{OH}(aq) \rightarrow \text{CH}_3\text{COOC}_5\text{H}_{11}(aq) + \text{H}_2\text{O}(l)
\]

A reaction uses 3.58 g of CH₃COOH and 4.75 g of C₅H₁₁OH 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, C₆H₅Cl, from the following reaction:

\[
\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}
\]

Determine the minimum quantity of benzene, C₆H₆, 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 (H₂) in flask A and bromine (Br₂) 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 cm³ of carbon monoxide are reacted with 40 cm³ of oxygen in the reaction:

\[ 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \]

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

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 airbag.

![Diagram of balloons](image)

Figure 1.12 These four balloons are all filled with 1 dm\(^3\) 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?

**Solution**

First identify the mole ratios in the equation:

\[
2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)
\]

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

\[
\frac{2\text{moles}}{1\text{mole}} = \frac{40\text{cm}^3}{20\text{cm}^3}
\]

Therefore 40 cm\(^3\) of carbon dioxide are produced. (Oxygen is in excess by 20 cm\(^3\).)

**Worked example**

When 10 cm\(^3\) of a gaseous hydrocarbon (a compound containing only carbon and hydrogen) is burned in excess oxygen, the products consist of 30 cm\(^3\) of carbon dioxide and 30 cm\(^3\) 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.

\[
\text{C}_x\text{H}_y + \text{excess } \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

volumes:

\[
\begin{align*}
10\text{cm}^3 & \quad 30\text{cm}^3 \\
30\text{cm}^3 & \quad 30\text{cm}^3 \\
\end{align*}
\]

ratio of volumes / mole ratio:

\[
\begin{align*}
1 & \quad 3 \\
3 & \quad 3 \\
\end{align*}
\]

∴ 1 molecule hydrocarbon \(\rightarrow\) 3 molecules \(\text{CO}_2\) + 3 molecules \(\text{H}_2\text{O}\)

3 C atoms + 6 H atoms

The molecular formula is \(\text{C}_3\text{H}_6\).

**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\(^{-2}\) m\(^3\) mol\(^{-1}\) (=22.7 dm\(^3\) mol\(^{-1}\)). The conditions at STP are:

* a temperature of 0 °C (273 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.

\[ 2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 10\text{H}_2\text{O}(g) \]

mole / volume ratio: \( \frac{1}{6.5} \)

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.

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

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 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, dm^3 and cm^3 are commonly used, so it is important to be able to interconvert these.

\[
\begin{align*}
1 \text{ dm}^3 &= 10^{-3} \text{ m}^3 \\
1 \text{ cm}^3 &= 10^{-4} \text{ dm}^3
\end{align*}
\]

\[
\begin{align*}
1000 \text{ dm}^3 &= 1 \text{ m}^3 \\
1000 \text{ cm}^3 &= 1 \text{ dm}^3
\end{align*}
\]

\[
\begin{align*}
\text{divide by 1000} & \quad \text{divide by 1000} \\
\text{dm}^3 & \quad \text{m}^3
\end{align*}
\]

\[
\begin{align*}
\text{multiply by 1000} & \quad \text{multiply by 1000} \\
\text{cm}^3 & \quad \text{dm}^3
\end{align*}
\]

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

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

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.
**Stoichiometric relationships**

### Exercises

45 How many moles are present in each of the following at STP?
   - (a) 54.5 dm³ CH₄
   - (b) 250.0 cm³ CO
   - (c) 1.0 m³ O₂

46 What is the volume of each of the following at STP?
   - (a) 44.00 g N₂
   - (b) 0.25 mol NH₃

47 Pure oxygen gas was first prepared by heating mercury(II) oxide, HgO.

   \[ 2\text{HgO(s)} \rightarrow \text{2Hg(l)} + \text{O₂(g)} \]

   What volume of oxygen at STP is released by heating 12.45 g of HgO?

48 Which sample contains more molecules, 3.14 dm³ of bromine, Br₂, or 11.07 g of chlorine, Cl₂ when measured at the same temperature and pressure?

49 Calcium reacts with water to produce hydrogen.

   \[ \text{Ca(s)} + 2\text{H₂O(l)} \rightarrow \text{Ca(OH)₂(aq)} + \text{H₂(g)} \]

   Calculate the volume of gas at STP produced when 0.200 g of calcium reacts completely with water.

50 Dinitrogen oxide, N₂O, is a greenhouse gas produced from the decomposition of artificial nitrate fertilizers. Calculate the volume at STP of N₂O produced from 1.0 g of ammonium nitrate, when it reacts according to the equation:

   \[ \text{NH₄NO₃(s)} \rightarrow \text{N₂O(g)} + \text{2H₂O(l)} \]

### 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 was 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.

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

The kinetic theory of matter, summarized on page 9, 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 below.
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 °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).

\[
temperature (K) = temperature (°C) + 273.15
\]

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 N m\(^{-2}\). Pressure is now commonly given in bars, where 10\(^5\) Pa = 1 bar, as this is conveniently close to 1 atmospheric 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^{-18} \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. Superconductivity is discussed further in Chapter 12.

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.

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**Stoichiometric relationships**

1. **Boyle’s law**
   - As the pressure on a gas is increased, its volume decreases proportionately.
   - Pressure $P$ varies inversely with volume $V$: $P \propto \frac{1}{V}$
   - Product of pressure and volume $PV = \text{constant}$
   - 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.
   - $V \propto T$
   - $\frac{V}{T} = \text{constant}$

   - **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.

---

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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.

\[ P \propto T \]

\[ \frac{P}{T} = \text{a constant} \]

Figure 1.17 Gas pressure is proportional to the absolute temperature.

Always be certain to use temperature in Kelvin only when applying these relationships.

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

**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.
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:

\[ P \propto \frac{1}{V} \quad \text{at constant temperature} \]
\[ V \propto T \quad \text{at constant pressure} \]
\[ P \propto T \quad \text{at constant volume} \]

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

\[ \frac{PV}{T} = \text{a constant} \]

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 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

\[ \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \]

\[ P_2 = 2 \times P_1 \text{ and } T_2 = 2 \times T_1 \text{, so these can be substituted into the equation:} \]

\[ \frac{P_1 V_1}{T_1} = \frac{2P_1 V_2}{2T_1} \]

We can cancel \( P_1 \) and \( T_1 \) from both sides and 2s on the right side, leaving

\[ V_1 = V_2 \]

The volume does not change.

Worked example

The molar volume of a gas at STP is 22.7 dm\(^3\) mol\(^{-1}\). Calculate the molar volume at 25°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 °C to K.

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

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]

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

\[ V_2 = \frac{298 \times 22.7 \text{ dm}^3}{273} = 24.8 \text{ dm}^3 \]
The ideal gas equation is derived from the combined gas equation and Avogadro’s law

The combined gas equation tells us that

\[ \frac{PV}{T} = \text{constant} \]

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

So \( \frac{PV}{T} \propto n \)

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

\[ \therefore \frac{PV}{n} = R \]

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

\[ \text{density} = \frac{\text{mass}}{\text{volume}} \]

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 (N m\(^{-2}\)); if kPa are given, multiply by 10\(^3\).
- **Volume, \( V \):** must be in m\(^3\); if dm\(^3\) are given, divide by 10\(^3\), if 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 °C is given, add 273.15.

**Worked example**

A helium party balloon has a volume of 18.0 dm\(^3\). At 25 °C the internal pressure is 108 kPa. Calculate the mass of helium in the balloon.

**Solution**

First ensure all data are in SI units:

\[ P = 108 \text{ kPa} = 108 \times 10^3 \text{ Pa} \]
\[ V = 18.0 \text{ dm}^3 = 18.0 \times 10^{-3} \text{ m}^3 \]
\[ T = 25 \text{ °C} = 298 \text{ K} \]
\[ PV = nRT \]

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

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

\[ \therefore \text{mass (He)} = n \times \frac{4.00 \text{ g mol}^{-1}}{\text{mol}} = 3.14 \text{ g} \]

**Worked example**

A sample of gas has a volume of 445 cm\(^3\) and a mass of 1.500 g at a pressure of 95 kPa and a temperature of 28 °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:

\[ P = 95 \text{ kPa} = 95 \times 10^3 \text{ Pa} \]
\[ V = 445 \text{ cm}^3 = 445 \times 10^{-6} \text{ m}^3 \]
\[ T = 28 ^\circ \text{C} = 301 \text{ K} \]

\[ \therefore M = \frac{1.500 \text{ g} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 301 \text{ K}}{95 \times 10^3 \text{ Pa} \times 445 \times 10^{-6} \text{ m}^3} = 88.8 \text{ g mol}^{-1} \]

**Worked example**

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

**Solution**

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

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

\[ \therefore 1.65 \text{ g} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \]
\[ \therefore 92.0 \times 10^3 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3 = 44.7 \text{ g mol}^{-1} \]
Experiment to calculate the molar mass of carbon dioxide by application of the ideal gas equation

Full details with a worksheet are available online.

A known mass of CuCO₃(s) is heated and the gas evolved collected by displacement of water. The volume of the gas, the room temperature, and pressure are recorded.

\[ \text{CuCO}_3(s) \rightarrow \text{CuO(s)} + \text{CO}_2(g) \]

**Sample results**

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of boiling tube + CuCO₃ before heating / g ± 0.001</td>
<td>33.910</td>
</tr>
<tr>
<td>mass of boiling tube + CuCO₃ after heating / g ± 0.001</td>
<td>33.822</td>
</tr>
<tr>
<td>mass change (mass CO₂) / g ± 0.002</td>
<td>0.088</td>
</tr>
<tr>
<td>volume of gas collected / cm³ ± 0.1</td>
<td>38.1</td>
</tr>
<tr>
<td>temperature / K ± 0.1</td>
<td>293.0</td>
</tr>
<tr>
<td>pressure / Pa ± 0.1</td>
<td>101.3 kPa</td>
</tr>
</tbody>
</table>

**Processed data**

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

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

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

\[ \therefore \% \text{ error } = 26.1\% \]

The percentage error can be analysed in consideration of systematic errors such as:
- gas collected may not be pure CO₂;
- CO₂ 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.
For one mole of an ideal gas, the relationship $PV/RT$ is a constant at all pressures.

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 1. 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).

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

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 $PV/RT < 1$.

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.
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 (H₂O), bromine (Br₂), and hexane (C₆H₁₄), but more commonly liquids are solutions containing two or more components.

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 mol dm⁻³.

\[
\text{concentration of solution (mol dm}^{-3}\text{)} = \frac{\text{amount of solute (mol)}}{\text{volume of solution (dm}^3\text{)}}
\]

or

\[
c = \frac{n}{V}
\]

\[
\therefore \text{amount of solute (mol) } = \text{conc. (mol dm}^{-3}\text{)} \times \text{volume (dm}^3\text{)}
\]

Square brackets are often used to represent ‘concentration of’ a particular substance; such as [HCl] = 1.0 mol dm⁻³.
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.

![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.](image)

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.

**Worked example**

Explain how you would prepare 100 cm³ of a 0.100 mol dm⁻³ solution of NaCl.

**Solution**

Ensure that cm³ are converted to dm³ 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 g NaCl(s) to a 100 cm³ volumetric flask, and make up to the mark with distilled water.

Concentration can also be expressed in mass (g dm⁻³).

**Worked example**

Calculate the concentration of a 0.0400 mol dm⁻³ solution of sodium carbonate, Na₂CO₃, in g dm⁻³.

**Solution**

\[ M(\text{Na₂CO₃}) = (22.99 \times 2) + 12.01 + (16.00 \times 3) = 105.99 \text{ g mol}^{-1} \]

\[ m = n M \therefore m = 0.0400 \text{ mol} \times 105.99 \text{ g mol}^{-1} = 4.24 \text{ g} \]

\[ \therefore [\text{Na₂CO₃}] = 4.24 \text{ g dm}^{-3} \]
A different unit of concentration is known as **ppm**, parts per million. It denotes one part per 10^6 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\(^{-3}\), 1 ppm also means that each dm\(^3\) 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.

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, \(n\), is a constant, and as \(n = cV \Rightarrow cV\) must be constant through dilution.

\[c_1 V_1 = c_2 V_2\]

where \(c_1\) and \(V_1\) refer to the initial concentration and volume and \(c_2\) and \(V_2\) refer to the diluted concentration and volume.

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

\[
c_1 V_1 = c_2 V_2
\]

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

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

\[
c_2 \text{ dilute concentration} = 0.10 \text{ mol dm}^{-3}
\]

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.

\[
\begin{align*}
\text{HCl(aq)} & + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)} \\
\text{mole ratio:} & \quad 1 : 1 \\
\text{volume:} & \quad \text{known} : \text{known (by titration)} \\
\text{conc.:} & \quad \text{unknown} = x : \text{known (standard solution)}
\end{align*}
\]

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

Note that in the equation \(c_1 V_1 = c_2 V_2\), 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.

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

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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. This is explained more fully in Chapter 8.

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

Worked example

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

$$2\text{NaHCO}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$$

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

Solution

We can calculate the amount of 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:

$$2n(\text{NaHCO}_3) = n(\text{H}_2\text{SO}_4)$$

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

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

Here is a summary of the steps in volumetric analysis calculations:

Back titration

- 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 $c = \frac{n}{V}$.

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 NaHCO₃ was added to 25.00 cm³ of 0.125 mol dm⁻³ hydrochloric acid. After the reaction was complete, the excess hydrochloric acid required 3.50 cm³ of 0.200 mol dm⁻³ NaOH to reach the equivalence point in a titration. Calculate the percentage of NaHCO₃ in the tablet.

Solution

original reaction:  
\[ \text{NaHCO}_3(s) + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l}) + \text{CO}_2(g) \]

mole ratio: 1 : 1

First calculate the total amount of HCl added, which is a known excess.

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

titration reaction:  
\[ \text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l}} \]

mole ratio: 1 : 1

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

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

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

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

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

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

percentage by mass in tablet = \[
\frac{0.204}{0.300} \times 100 = 68.0\%
\]

Note that there are several assumptions made in this calculation. These include the fact that all the NaHCO₃ did react with the acid, and that the only component of the tablet that reacted with HCl is NaHCO₃. 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, KOH, required to prepare 250 cm³ of a 0.200 mol dm⁻³ solution.

65 Calculate the mass of magnesium sulfate heptahydrate, MgSO₄·7H₂O, required to prepare 0.100 dm³ of a 0.200 mol dm⁻³ solution.

66 Calculate the number of moles of chloride ions in 0.250 dm³ of 0.0200 mol dm⁻³ zinc chloride, ZnCl₂, solution.

67 250 cm³ of a solution contains 5.85 g of sodium chloride. Calculate the concentration of sodium chloride in mol dm⁻³.

68 Concentrated nitric acid, HNO₃, is 16.0 mol dm⁻³. What volume would you need to prepare 100 cm³ of 0.50 mol dm⁻³ HNO₃?

69 In a titration a 15.00 cm³ sample of H₂SO₄ required 36.42 cm³ of 0.147 mol dm⁻³ NaOH solution for complete neutralization. What is the concentration of the H₂SO₄?

70 Gastric juice contains hydrochloric acid, HCl. A 5.00 cm³ sample of gastric juice required 11.00 cm³ of 0.0100 mol dm⁻³ KOH for neutralization in a titration. What was the concentration of HCl in this fluid? If we assume a density of 1.00 g cm⁻³ for the fluid, what was the percentage by mass of HCl?
Stoichiometric relationships

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

\[
\text{Na}_2\text{SO}_4(\text{aq}) + \text{Pb(NO}_3\text{)}_2(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{NaNO}_3(\text{aq})
\]

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

**Challenge problems**

72 The fertilizer tri-ammonium phosphate is made from ‘phosphate rock’ by:

1. reacting the phosphate rock with sulfuric acid, \( \text{H}_2\text{SO}_4 \), to produce phosphoric acid, \( \text{H}_3\text{PO}_4 \);
2. reacting the phosphoric acid with ammonia, \( \text{NH}_3 \), to give tri-ammonium phosphate, \( (\text{NH}_4)_3\text{PO}_4 \);
3. reacting the phosphate rock with sulfuric acid, \( \text{H}_2\text{SO}_4 \), to produce phosphoric acid, \( \text{H}_3\text{PO}_4 \);
4. reacting the phosphate rock with sulfuric acid, \( \text{H}_2\text{SO}_4 \), to produce phosphoric acid, \( \text{H}_3\text{PO}_4 \);

If the phosphate rock contains 90% by mass \( \text{Ca}_3(\text{PO}_4)_2 \) from which the overall yield of tri-ammonium phosphate is 95%, calculate the mass of phosphate rock required to make 1000 tonnes of tri-ammonium phosphate.

73 The combustion of both ammonia, \( \text{NH}_3 \), and hydrazine, \( \text{N}_2\text{H}_4 \), in oxygen gives nitrogen and water only. When a mixture of ammonia and hydrazine is burned in pure oxygen, the volumetric \( \text{N}_2 : \text{H}_2\text{O} \) ratio in the product gas is 0.40. Calculate the % by mass of ammonia in the original mixture. What assumptions are being made here?

74 Sulfuric acid, \( \text{H}_2\text{SO}_4 \), is produced from sulfur in a three-step process:

1. \( \text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \)
2. \( 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g}) \)
3. \( \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{l}) \)

Assuming 100% conversion and yield for each step, what is the minimum mass of sulfur in kg needed to produce 980 tonnes of \( \text{H}_2\text{SO}_4 \)?

75 The concentration of hydrogen peroxide, \( \text{H}_2\text{O}_2 \), in excess aqueous sulfuric acid, \( \text{H}_2\text{SO}_4 \), can be determined by redox titration using potassium permanganate, \( \text{KMnO}_4 \), as follows:

\[
2\text{KMnO}_4(\text{aq}) + 5\text{H}_2\text{O}_2(\text{l}) + 3\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{MnSO}_4(\text{aq}) + 5\text{H}_2\text{O}(\text{l}) + 8\text{H}_2\text{O}(\text{g})
\]

A 10.00 cm\(^3\) sample of \( \text{H}_2\text{O}_2 \) solution requires 18.00 cm\(^3\) of a 0.05 mol dm\(^{-3}\) solution of \( \text{KMnO}_4 \) to reach the equivalence point in a titration. Calculate the concentration of \( \text{H}_2\text{O}_2 \) in the solution.

76 Mixtures of sodium carbonate, \( \text{Na}_2\text{CO}_3 \), and sodium hydrogencarbonate, \( \text{NaHCO}_3 \), in aqueous solution are determined by titration with hydrochloric acid, \( \text{HCl} \), in a two-step procedure.

1. Titrate to the phenolphthalein end-point:
   \[
   \text{Na}_2\text{CO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{NaHCO}_3(\text{aq}) + \text{NaCl}(\text{aq})
   \]
2. Continue titration to the methyl orange end-point:
   \[
   \text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2
   \]

For an \( X \) cm\(^3\) sample of a sodium carbonate / sodium hydrogencarbonate mixture titrated with \( Y \) mol dm\(^{-3}\) \( \text{HCl} \), the respective end-points are Step 1 = \( P \) cm\(^3\) \( \text{HCl} \). Step 2 = \( Q \) cm\(^3\) \( \text{HCl} \). Derive relationships between \( X \), \( Y \), \( P \), and \( Q \) to obtain the concentrations of sodium carbonate and sodium hydrogencarbonate in the original mixture.

77 A sealed vessel with fixed total internal volume 2.00 m\(^3\) contains 0.720 kg pentane, \( \text{C}_5\text{H}_{12} \), and oxygen only. The pentane is ignited and undergoes 100% conversion to carbon dioxide and water. Subsequently the temperature and pressure in the vessel are respectively 740 K, 400 kPa. Calculate the initial amount and mass in kg of oxygen in the vessel.

**Practice questions**

1. How many oxygen atoms are in 0.100 mol of \( \text{CuSO}_4.5\text{H}_2\text{O} \)?
   
   A \( 5.42 \times 10^{22} \)  \hspace{1cm} B \( 6.02 \times 10^{22} \)  \hspace{1cm} C \( 2.41 \times 10^{23} \)  \hspace{1cm} D \( 5.42 \times 10^{23} \)

2. What is the sum of the coefficients when the following equation is balanced using whole numbers?

\[
\text{Fe}_2\text{O}_3(\text{s}) + \_ \text{CO(g)} \rightarrow \_ \text{Fe(s)} + \_ \text{CO}_2(\text{g})
\]

   A 5  \hspace{1cm} B 6  \hspace{1cm} C 8  \hspace{1cm} 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?

- A: nitrogen
- B: oxygen
- C: ethane
- D: neon

4 1.0 dm³ of an ideal gas at 100 kPa and 25 °C is heated to 50 °C at constant pressure. What is the new volume in dm³?
   - A: 0.50
   - B: 0.90
   - C: 1.1
   - D: 2.0

5 What is the amount, in moles, of sulfate ions in 100 cm³ of 0.020 mol dm⁻³ FeSO₄(aq)?
   - A: 2.0 × 10⁻³
   - B: 2.0 × 10⁻²
   - C: 2.0 × 10⁻¹
   - D: 2.0

6 1.7 g of NaNO₃ (Mₐ = 85) is dissolved in water to prepare 0.20 dm³ of solution. What is the concentration of the resulting solution in mol dm⁻³?
   - A: 0.100
   - B: 0.1
   - C: 0.2
   - D: 1.0

7 What mass, in g, of hydrogen is formed when 3 mol of aluminium react with excess hydrochloric acid according to the following equation?
   
   2Al(s) + 6HCl(aq) → 2AlCl₃(aq) + 3H₂(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 CH₂. What is the molecular formula of the gas?
   - A: CH₂
   - B: C₃H₆
   - C: C₆H₆
   - D: C₄H₈

9 What is the sum of all coefficients when the following equation is balanced using the smallest possible whole numbers?
   
   2C₂H₂ + ___ O₂ → ___ CO₂ + ___ H₂O

   - A: 5
   - B: 7
   - C: 11
   - D: 13

10 What is the total number of hydrogen atoms in 1.0 mol of benzamide, C₆H₅CONH₂?
   - A: 7
   - B: 6.0 × 10²³
   - C: 3.0 × 10²⁴
   - D: 4.2 × 10²⁴

11 Chloroethene, C₂H₃Cl, reacts with oxygen according to the equation below:

   2C₂H₃Cl(g) + 5O₂(g) → 4CO₂(g) + 2H₂O(g) + 2HCl(g)

   What is the amount, in mol, of H₂O produced when 10.0 mol of C₂H₃Cl and 10.0 mol of O₂ 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 mol dm⁻³, when 10.0 cm³ of 0.200 mol dm⁻³ NaCl solution is added to 30.0 cm³ of 0.600 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 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: CH₂O
   - B: CH₂O
   - C: C₂H₂O
   - D: C₂H₄O₂
14 300 cm$^3$ of water is added to a solution of 200 cm$^3$ of 0.5 mol dm$^{-3}$ sodium chloride. What is the concentration of sodium chloride in the new solution?

A 0.05 mol dm$^{-3}$  B 0.1 mol dm$^{-3}$  C 0.2 mol dm$^{-3}$  D 0.3 mol dm$^{-3}$

15 What is the approximate molar mass, in g mol$^{-1}$, of MgSO$_4$·7H$_2$O?

A 120  B 130  C 138  D 246

16 Which is both an empirical and a molecular formula?

A C$_2$H$_12$  B C$_3$H$_{10}$  C C$_4$H$_8$  D C$_5$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.

\[ 2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g) \]

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

<table>
<thead>
<tr>
<th>Temperature (T) / °C</th>
<th>Mass of NaN$_3$(s) / kg</th>
<th>Pressure (p) / atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.00</td>
<td>0.0650</td>
<td>1.08</td>
</tr>
</tbody>
</table>

(a) Stage the number of significant figures for the temperature, mass, and pressure data.

(b) Calculate the amount, in mol, of sodium azide present.

(c) Determine the volume of nitrogen gas, in dm$^3$, produced under these conditions based on this reaction.

(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 CO$_2$ and 0.089 g H$_2$O.

Precipitation reaction with AgNO$_3$(aq):

0.535 g of J gave 1.75 g AgCl precipitate.

(a) Determine the percentage by mass of carbon and hydrogen in J, using the combustion data.

(b) Determine the percentage by mass of chlorine in J, using the precipitation data.

(c) The molar mass was determined to be 131.38 g mol$^{-1}$. Deduce the molecular formula of J.

(Total 7 marks)

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

\[ 4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(l) \]

30.0 dm$^3$ of ammonia reacts with 30.0 dm$^3$ of nitrogen monoxide at 100 °C. Identify which gas is in excess and by how much and calculate the volume of nitrogen produced.
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 cm$^3$ of 0.200 mol dm$^{-3}$ HCl to 0.188 g of eggshell. Calculate the amount, in mol, of HCl added. (1)

(b) The excess acid requires 23.80 cm$^3$ of 0.100 mol dm$^{-3}$ NaOH for neutralization. Calculate the amount, in mol, of acid that is in excess. (1)

(c) Determine the amount, in mol, of HCl that reacted with the calcium carbonate in the eggshell. (1)

(d) State the equation for the reaction of 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 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, AgNO$_3$(aq). The precipitated silver chloride, AgCl(s), was collected, washed and dried. The mass of the dried silver chloride was 6.127 g. Calculate the percent by mass of the sodium chloride and calcium chloride in the original mixture. (2)

22 A hydrate of potassium carbonate has the formula K$_2$CO$_3$.xH$_2$O. A 10.00 g sample of the hydrated solid is heated, and forms 7.93 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$^3$ of ammonia, NH$_3$, at 42°C and 160 kPa is combined with 740 cm$^3$ of hydrogen chloride at 57°C and 113.3 kPa. The reaction produces ammonium chloride as follows: NH$_3$(g) + HCl(g) → NH$_4$Cl(s)

(a) Which reactant is in excess? (1)

(b) Which reactant is limiting? (1)

(c) What mass of ammonium chloride forms? (1)

(Total 3 marks)