

# CHAPTER1 | A PARTICLE VIEW OF MATTER



**FIGURE 1** The **Earth's atmosphere** is a gaseous solution, ie a homogeneous mixture of gases. The major gases are, **O<sub>2</sub>** (21%), **N<sub>2</sub>** (78%) and **Ar** (1%) with variable amounts of **water vapour** and traces of other gases such as **CO<sub>2</sub>**.

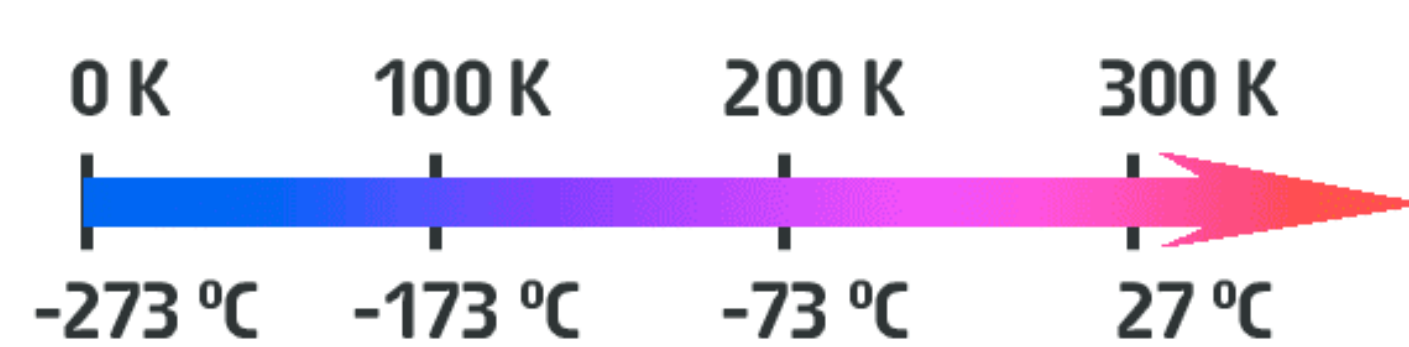
At sea level, normal air pressure due to these atmospheric gases is:

**1 atm** (one atmosphere).

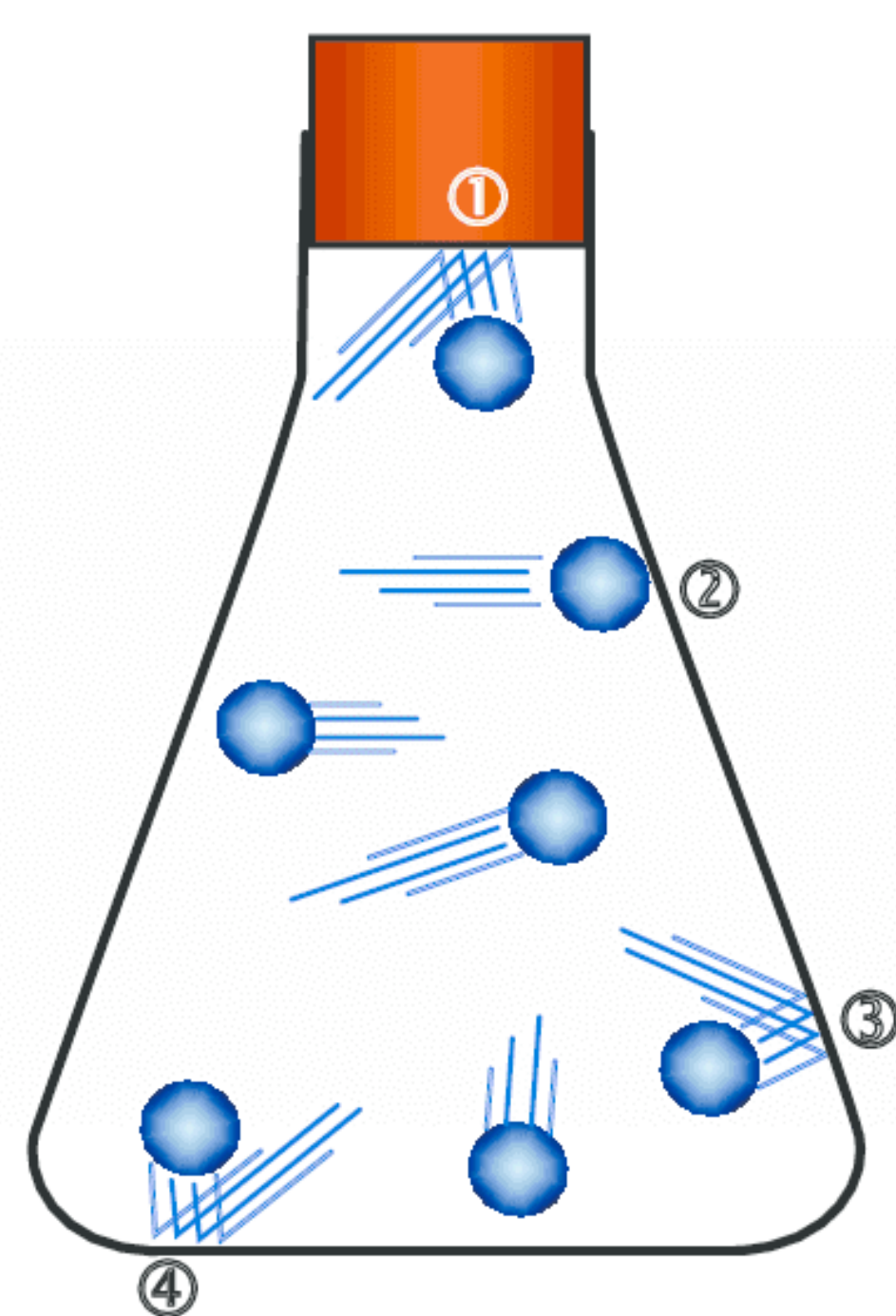
**1 atm = 101.3 kPa** (101.3 kilopascals).

These gases, as with all gases have very similar physical properties despite having very different chemical properties. The **kinetic theory** is a model that accounts for the physical properties common to all gases.

**FIGURE 3** **Temperature** is used to describe how hot or cold an object is. By definition, it's a measure of the average kinetic energy of the particles of a substance. Absolute zero, **0 K** (or **-273.15 °C**) is the lowest temperature that can be achieved. It is the temperature at which particles of matter are motionless, ie have zero kinetic energy.



Attempt Set 1 # 1 and 2.



**FIGURE 4** The particles of a gas move freely within the entire volume of their container. At 27 °C for example, the molecules in a sample of **H<sub>2</sub>(g)** move at an average speed of about 5650 km hr<sup>-1</sup>. Gas **pressure** is a result of random elastic collisions between such gas particles and their **container walls**. See ①, ②, ③ and ④ above.

## 1.1 Phases of matter

Matter is described as anything that takes up space and has mass. Everything in our environment that we can touch or see is made of matter. It can exist in any of the three physical phases; **solid**, **liquid** or **gas**. A fourth phase of matter, **plasma** can only exist under extreme conditions such as occurs in lightning or stars. Chemistry is the study of matter and its interactions.

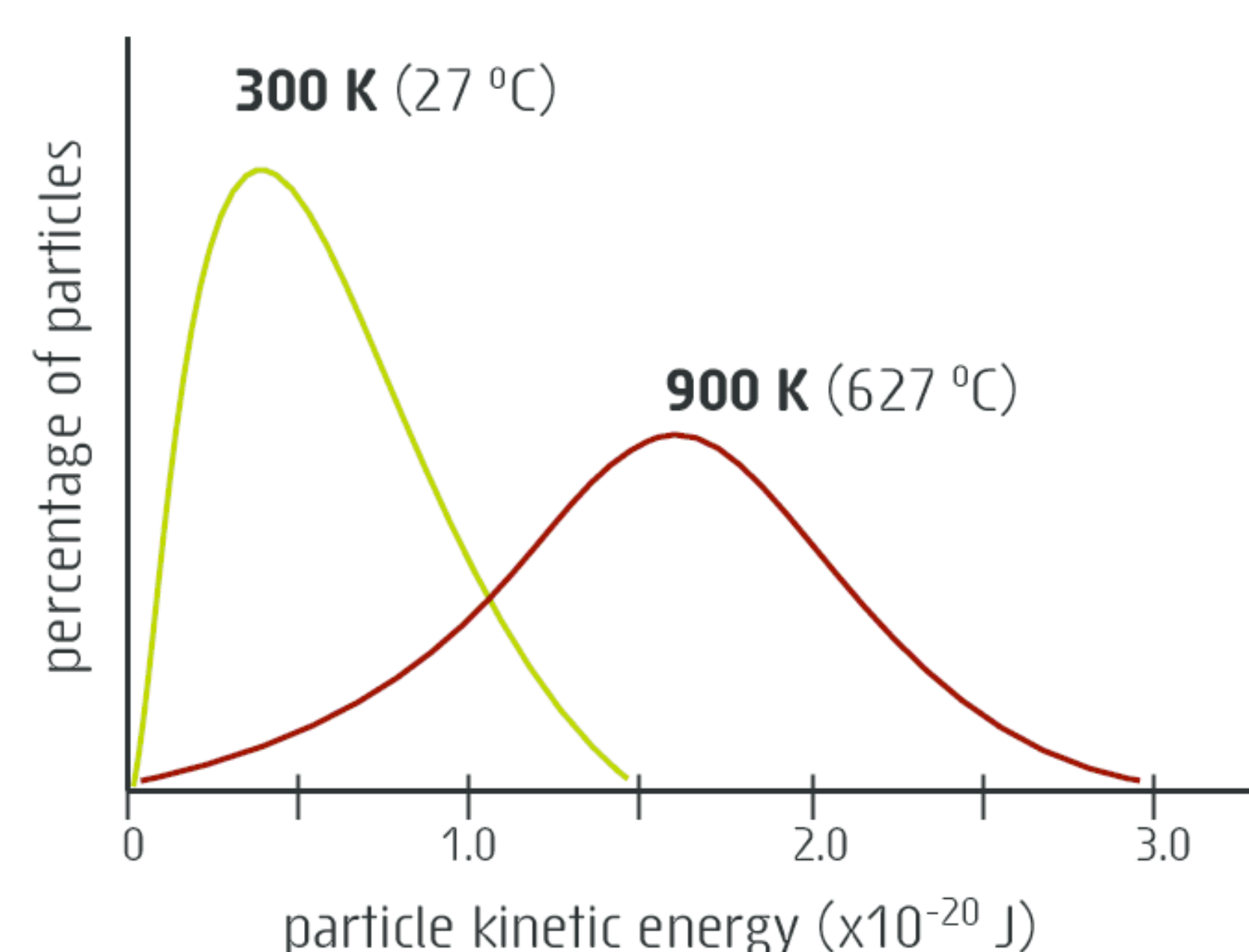
## 1.2 The kinetic theory of gases

The atmosphere we live in and breathe is a mixture of gases. (Fig 1) While the chemical properties of these gases are quite varied their physical behaviours are very similar. All gases for example exert pressure, they always take the shape of their container completely filling it and will escape from an open container to mix uniformly with other gases. The **kinetic theory** is a model about the structure of gases that is used to explain some of these common physical properties and behaviours. The first comprehensive version of this theory was printed in 1857 by Rudolf Clausius. The current model states:

- Gases are composed of particles that are in rapid continuous random motion.
- Attraction and repulsion between particles in gases is negligible.
- The particles of a gas are widely spaced such that the total volume of all of the particles is negligible compared to the volume the gas occupies.
- The particles of a gas have kinetic energy (**E<sub>k</sub>**) given by, **E<sub>k</sub>(particle) = ½mv<sup>2</sup>**, where the particles have a speed of motion, **v** and mass, **m**.
- The average kinetic energy of the particles of a gas is proportional to its temperature (Fig 2 and 3) and is the same for all gases at the same temperature.
- Particle collisions are elastic, ie over time as particles collide they do not lose speed or slow down thus particles do not lose **E<sub>k</sub>** (ie do not cool down) due to their collisions.

**FIGURE 2** The **kinetic energy distribution** for gas particles at 300K and 900K. Notice more particles have a higher kinetic energy at the higher temperature but in each case the kinetic energies are spread or distributed over a wide range. The **average kinetic energy**, however, will always be higher at a higher temperature.

It is important to realise the shape of these graphs is identical for all gases, ie it is independent of their chemical make up. Thus, as described in the kinetic theory, the average kinetic energy of the gas particles depends only upon temperature.



## 1.3 Gas behaviour: Applying the kinetic theory

Gases, irrespective of their particular chemical make up, all have a number of common physical properties. They always take the **shape** of their container, have a very **low density**, **exert pressure**, can be **compressed** and readily **diffuse** through other gases. The kinetic theory, as outlined above, can be used to account for these properties. (See Table 1.)

**TABLE 1** Understanding the **physical properties** common to all gases

**Take the shape of their container and have a low density** (density = mass ÷ volume): The particles of a gas show negligible forces of attraction and are in constant random motion. As a result, instead of clumping together, gas particles spread out as far as possible occupying the entire volume and shape of their container (ie low density).

**Can be compressed:** The particles of a gas have negligible volume and they are widely spaced so there is room for them to be compressed into a smaller volume. (See Fig 4.)

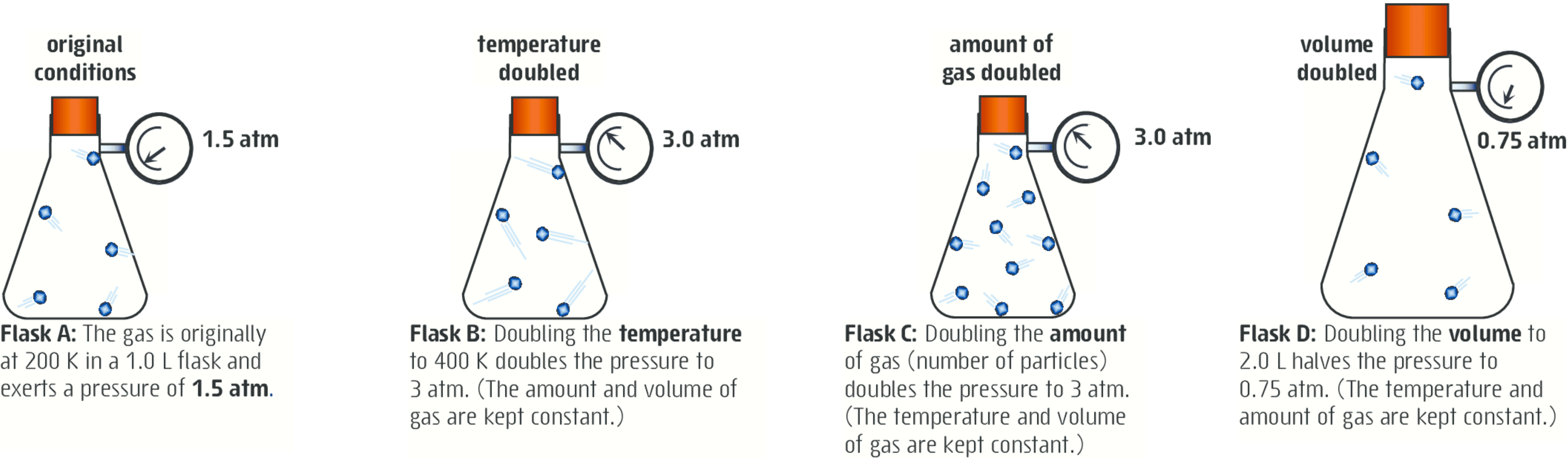
**Readily diffuse through other gases:** The particles of a gas are in constant random motion, have negligible forces of attraction and are widely spaced. For these reasons, the molecules of any gas can diffuse, ie spread out, between the molecules of any other gas.

**Exert pressure:** Particles in the gas phase do not attract one another but move randomly in straight lines. When they collide with their container walls they exert pressure on the walls. The pressure increases with the **frequency** and **force** of these collisions. (See Fig 5.)



As described in Table 1, the ability of gases to exert pressure is the result of multiple random collisions of its particles with their container walls. The pressure exerted by the gas increases with the **frequency** and **force** of these collisions. For this reason gas pressure is affected by the amount of gas in a container (ie number of gas particles), the container volume and the temperature of the gas inside the container. (See Fig 5 and Table 2.)

**FIGURE 5** Changes in gas temperature, amount of gas or container volume result in changes in the pressure exerted by the gas.



**TABLE 2** Understanding gas pressure

Property	Effect on pressure	Explanation
<b>Temperature</b> of gas ( <b>Flask B</b> )	Pressure increases with increasing gas temperature.	As gas temperature increases so does the average kinetic energy of its particles. This means greater average particle speed which results in a <b>greater rate</b> and <b>force</b> of particle collisions with the <b>container walls</b> . The increased <b>force</b> and <b>rate</b> of collisions with the container walls results in an increased pressure.
<b>Amount</b> of gas ( <b>Flask C</b> )	Pressure increases with amount of gas.	More gas means more gas particles in the container, hence there will be a <b>greater rate of collisions</b> between gas particles and their <b>container walls</b> . This causes the increased pressure.
<b>Volume</b> of container ( <b>Flask D</b> )	Pressure decreases with increasing gas volume.	Increasing the container volume means particles on average have a greater distance to travel before colliding with their <b>container walls</b> . This leads to a <b>decreased rate of collisions</b> and hence a decreased pressure. The force of particle collisions with the container walls remains unchanged.

Attempt Set 1 # 3, 4 and 5.

### 1.4 The kinetic theory applies to ideal gases

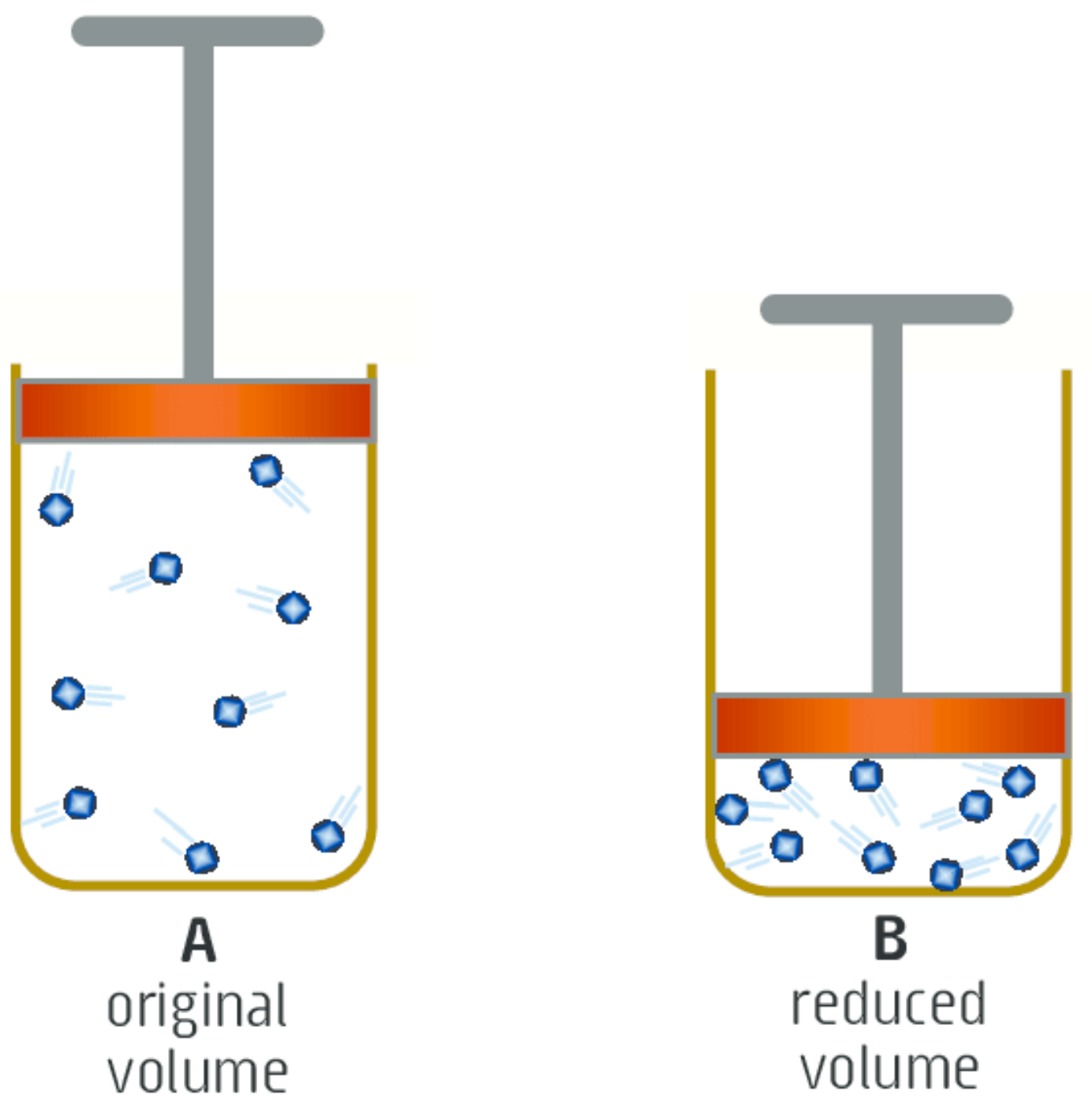
In reality the kinetic theory is a model that describes a hypothetical or idealised gas we call an **ideal gas**. The differences between an ideal gas and **real gases** like  $\text{H}_2(\text{g})$ ,  $\text{N}_2(\text{g})$  or  $\text{HCl}(\text{g})$  are:

- Particles of an ideal gas have negligible volume (like a geometric point) whereas the particles of a real gas do occupy space and their volume is sometimes significant when compared to the volume occupied by the gas as a whole. (See Fig 6.)
- Particles of an ideal gas have negligible attraction for one another whereas the particles of real gases do have forces of attraction for one another and these forces of attraction can become significant.

These differences are usually of no consequence when using the kinetic theory to explain the behaviour of real gases. In some extreme situations however, we can see differences in real gas behaviour versus that predicted for an ideal gas by the kinetic theory, eg:

- At a temperature of zero kelvin ( $-273\text{ }^\circ\text{C}$ ) an ideal gas would have zero volume. A real gas will never have zero volume as its particles do occupy space, ie have some volume.
- If a real gas is cooled and/or compressed sufficiently it will condense to form a liquid. This is due to the weak interparticle attraction that exists in real gases. An ideal gas would never condense as its particles always have negligible attraction for one another.

Apart from these extreme situations and a few other minor variations, the kinetic theory is a useful model for explaining many of the physical properties common to real gases.



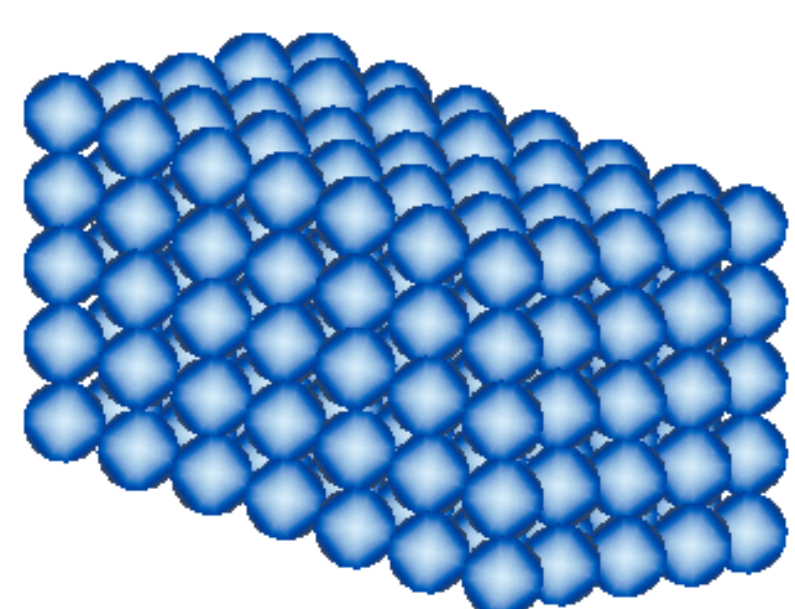
**FIGURE 6** Significantly reducing the volume occupied by a **real gas** (by increasing the pressure applied) can cause a situation where the volume of the particles of the gas become a significant factor in determining the volume occupied by the gas. When this happens, as in situation **B**, the gas volume will be a little greater than if the gas behaved as an ideal gas.

Attempt Set 1 # 6 and 7.

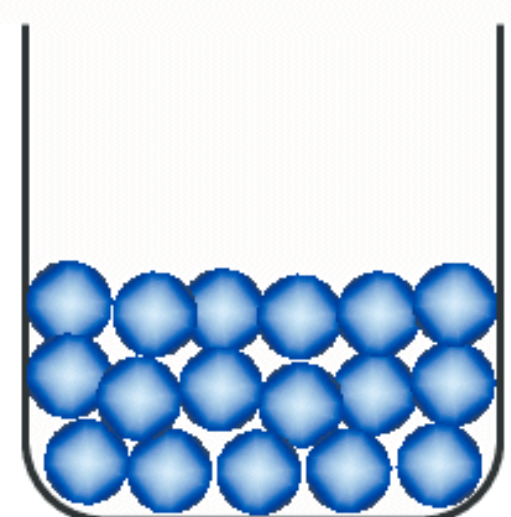
### 1.5 The kinetic theory and condensed phases of matter

The kinetic theory of gases can be extended to explain the physical properties of the condensed phases of matter, ie solids and liquids. Unlike gases, where ideally there are negligible forces of attraction between particles, in solids and liquids these forces of attraction are quite significant.





**FIGURE 7** Particle movement in the **solid** phase is restricted to vibrating about fixed positions within the solid. The particles are packed very tightly and so there is little opportunity for the solid to be compressed.

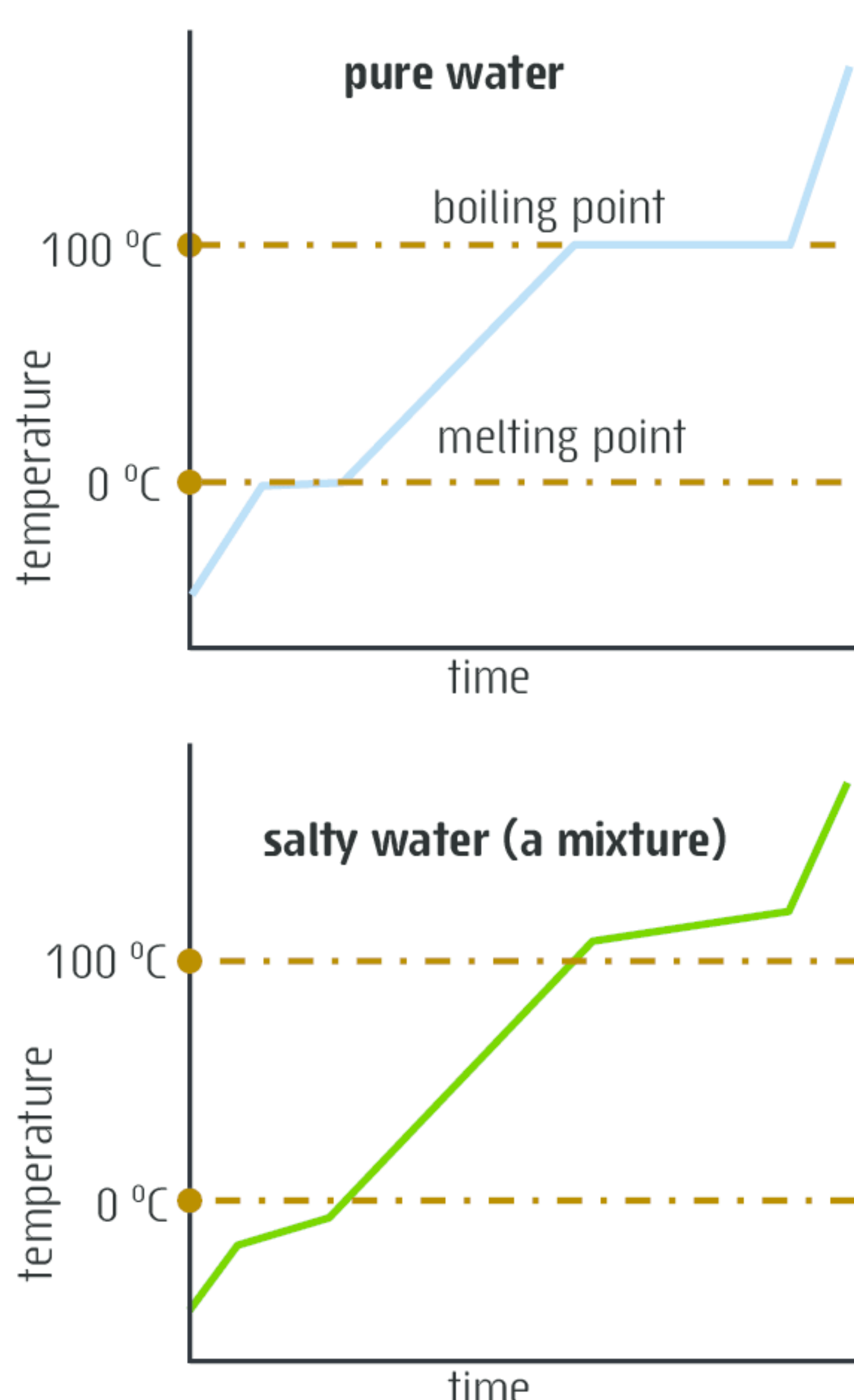


**FIGURE 8** Particles in a **liquid** are free to move and randomly jostle amongst one another within the volume of the liquid.

**Freeze drying** is a technique for preserving food by dehydrating it (removing water) without using high temperatures that can alter the food's taste. Instead a combination of low pressure (around 0.06 atm) and freezing temperatures is used to remove water by **sublimation**.

This involves solid water (ice) changing directly to a vapour. A **vapour** being the gaseous state of a substance that normally exists as a solid or liquid. All sorts of food products from coffee to roast dinners can be preserved this way. To regenerate the food, just add hot water.

**FIGURE 10** A **heating curve** shows how the temperature of a substance rises as it is **steadily** heated. The heating curve for **pure water**, (blue curve) at normal conditions shows steady temperatures at 0 °C and 100 °C. These temperatures correspond to melting and boiling of pure water. Well defined melting points and boiling points are a characteristic of all pure substances. Notice how the melting point and boiling point of salty water, a **mixture** (green curve) are not well defined. This is typical of all mixtures.



Complete Set 1.

Within **solids**, the attraction between particles is very strong. As a result the particles become packed so tightly that they are only able to vibrate about fixed positions within the solid structure. This explains why solids have a fixed shape and volume and are virtually incompressible. (See Fig 7.)

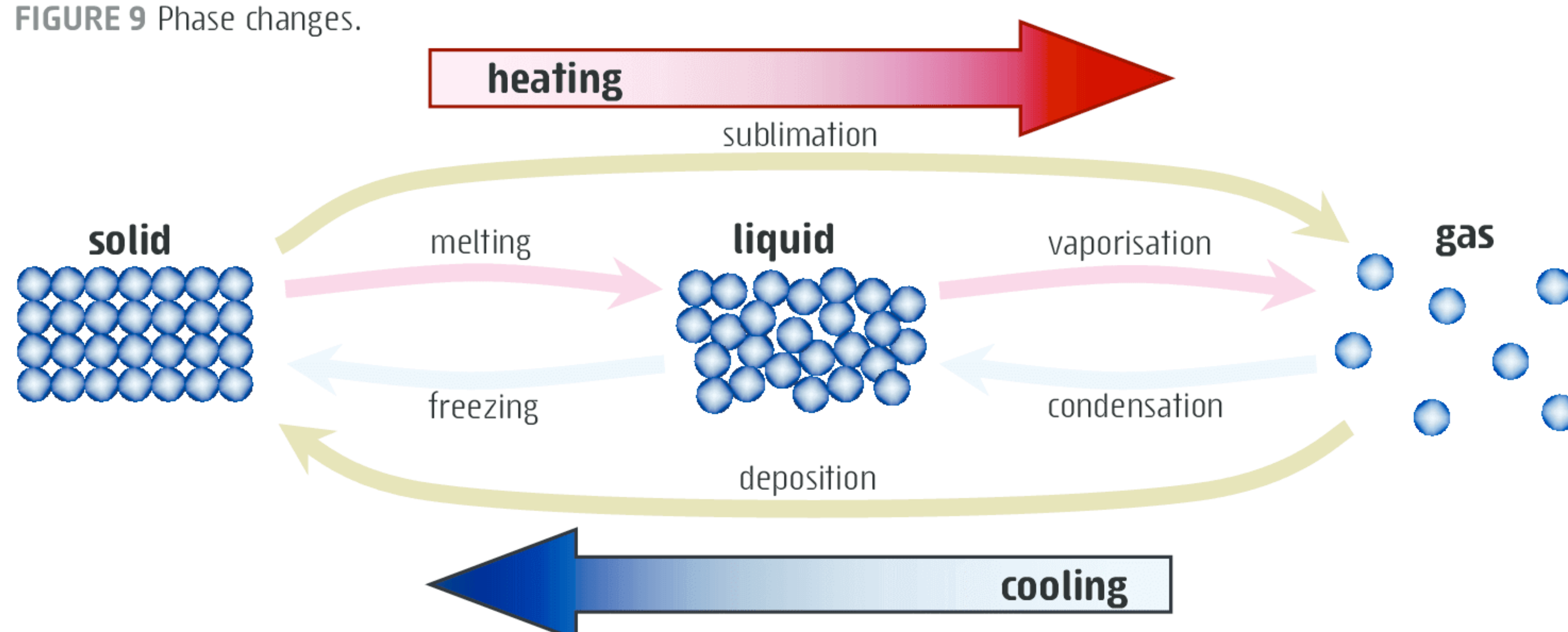
In **liquids**, the strong attractive forces between particles also cause them to pack closely. Here however, the particles are able to jostle past one another within the liquid volume. This arrangement of particles explains why liquids can flow to fill the bottom of a container but have a fixed volume and are essentially incompressible. (See Fig 8.)

Attempt Set 1 # 8.

## 1.6 Temperature, energy and phase change

Phase changes are physical processes and are readily reversible. Some examples include melting, sublimation, vaporisation (ie evaporation or boiling), condensation and freezing. (See Fig 9.) Heating a substance can cause it to change phase from solid to liquid to gas. Cooling will reverse these changes.

**FIGURE 9** Phase changes.



According to the kinetic theory, heating a substance (ie allowing heat to flow into the substance from its surroundings) will cause an increase in the kinetic energy (temperature) of its particles. At some temperature, the increased movement energy ( $E_k$ ) enables particles in the solid phase to overcome their attractive forces thus allowing them to escape their fixed positions within the solid phase. As a result the solid melts and its particles move freely within the liquid volume. The temperature at which this phase change happens is known as the **melting point**.

While a substance is in the process of melting its temperature and average particle kinetic energy remain constant. Instead, the energy absorbed during melting results in a one-off rearrangement of particles from their closely packed fixed positions in the solid phase to the random slightly more spaced positions of the liquid phase. This new arrangement of particles results in the added energy being stored in the liquid phase as increased **potential energy**.

Once fully melted, further heating will again lead to increasing particle kinetic energy. At some temperature, called the **boiling point**, particles within the liquid phase change into a gas phase by forming bubbles of gas throughout the liquid. Again, during the phase change, temperature and average particle kinetic energy remain constant. Instead, the energy absorbed during boiling is stored as increased potential energy of the very widely spaced particles in the gas phase. A **heating curve** (Fig 10) shows how the temperature of a substance changes with time as the substance melts then boils.

Phase changes like these are physical processes and as such are easily reversible. Cooling the gas phase for example, reduces particle kinetic energy and thus reverses these changes, returning the gas to a liquid then solid phase. It must also be noted that a substance's **freezing point** is the same temperature as its melting point. Freezing however, occurs when the liquid phase is cooled (ie heat is made to flow out of the liquid and into its surroundings) and its temperature falls to its freezing point and below.



## Set 1 Kinetic theory and phases of matter

- Use the list of terms given to correctly complete the following passage. Note that some of these terms are distractors and will not be needed.

The kinetic theory of gases is a model that helps us explain the common (a) \_\_\_\_\_ properties of gases. The theory states that:

- Gases are composed of tiny (b) \_\_\_\_\_ that are in constant (c) \_\_\_\_\_.
- Particles in the gas phase have negligible (d) \_\_\_\_\_ for one another and their (e) \_\_\_\_\_ is negligible compared to that of the gas as a whole.
- The temperature of a gas is a measure of the (f) \_\_\_\_\_ of its particles.
- When particles collide they do so (g) \_\_\_\_\_, ie without loss of (h) \_\_\_\_\_.

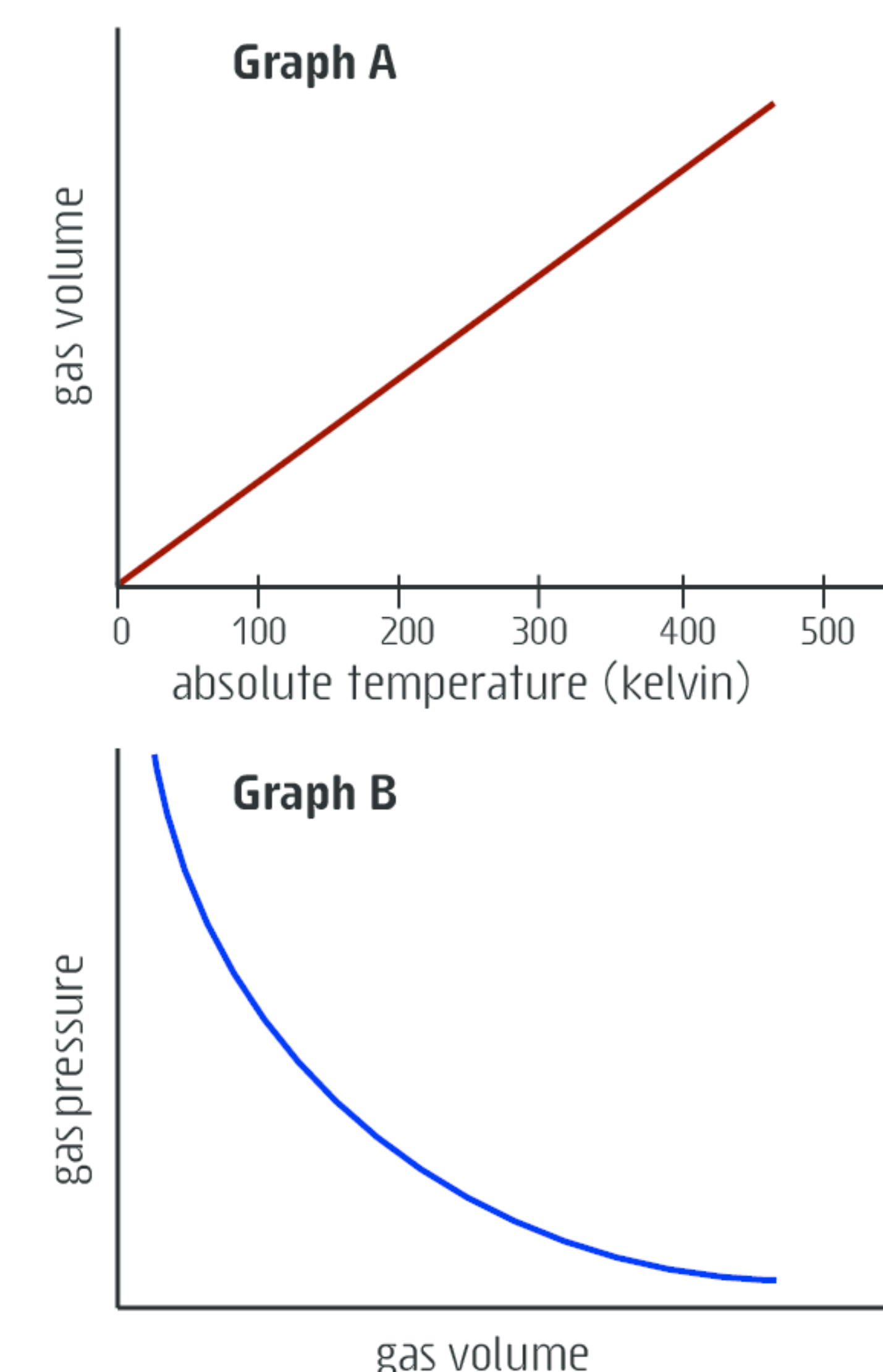
According to the kinetic theory, the particles of all gases have the same average kinetic energy at the same (i) \_\_\_\_\_. However at any given temperature the particles in a sample of gas don't have the same kinetic energy, instead their kinetic energies are (j) \_\_\_\_\_ over a wide range of values.

- According to the kinetic theory the particles of any gas have the same **average kinetic energy** when at the same temperature.
  - What is meant by average kinetic energy in this context?
  - How does **temperature** affect particle **average kinetic energy** and particle **speed**?
- If a laboratory gas tap is accidentally leaking gas into the room it will soon be possible to notice the smell of gas throughout the laboratory. This happens even if the air in the laboratory is still and no breezes are mixing the room air.
  - What is the **name** of the process by which the leaking gas spreads throughout the room?
  - Use the **kinetic theory** to describe at a particle level how this mixing process occurs.
  - Although it may not be noticeable, this process will happen more quickly on a **hot** day than it would on a very **cold** day. Why should this be the case? Explain.
- Use the **kinetic theory** to explain why gases exert pressure.
- What will happen to the **pressure** inside a car tyre in each of the following situations? Give a brief explanation of each answer with reference to the kinetic theory of matter.
  - The car tyre becomes quite **hot** during a long journey.
  - A faulty tyre valve allows some air to **leak** out. (Assume tyre volume doesn't change.)
- Refer to the graphs in Fig 11 and answer the following questions.
  - What does **Graph A** show about the volume of an ideal gas and its absolute temperature?
  - Use the kinetic theory to account for the volume of an ideal gas at zero kelvin.
  - What does **Graph B** show about the relationship between the volume and pressure of an ideal gas? Use the kinetic theory to account for this relationship.
- The kinetic theory is a model used to explain the properties of an ideal gas.
  - Describe two assumptions in the kinetic theory apply to an ideal gas but are only approximations for a real gas.
  - State **one** physical property that applies to a real gas but not to an ideal gas.
- A burning candle will have wax in all three phases, **solid**, **liquid** and **gas** (called wax vapour). The liquid wax can be seen forming in a depression at the base of the candle wick while the colourless wax vapour (gas) is produced from the surface of the wick. The luminous red region of the flame is where combustion of the wax vapour occurs.
  - Why is the gas phase of wax referred to as a **vapour**?
  - Which of the processes occurring on a burning candle; melting, vaporising or combustion, are easily **reversible**?
  - Use your knowledge of the Kinetic theory to **describe** the **processes** that occur at a particle level as the candle wax **melts** and then **vaporises** (evaporates) from the wick of a burning candle.
  - If some wax is melted in a test tube and then allowed to cool, a **depression** always forms on the surface of the solidified wax. (See Fig 12.) Consider the density of liquid and solid wax and use your knowledge of the kinetic theory to explain why the density of wax changes when it solidifies and thus why the depression forms.

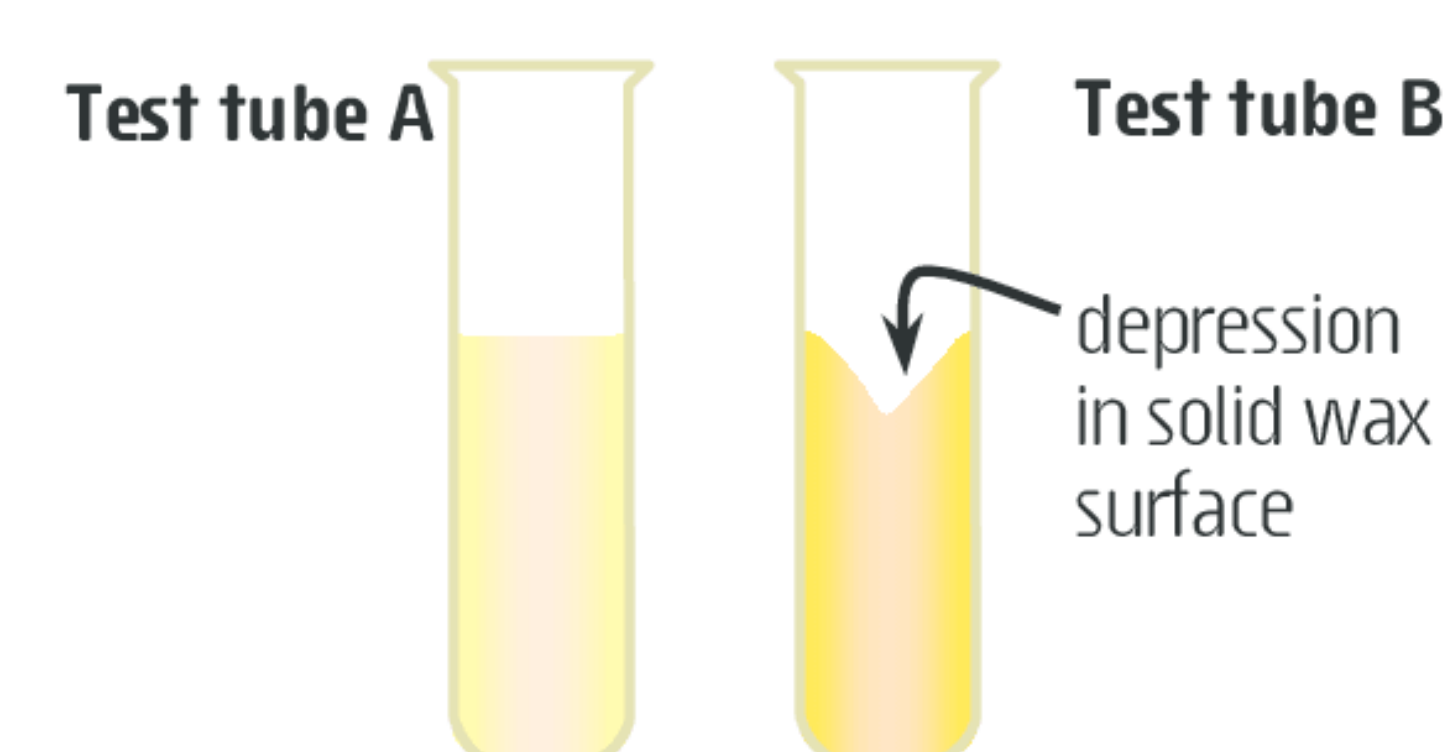
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random motion  
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attraction  
kinetic energy  
average kinetic energy  
particles  
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**FIGURE 11 Graph A** shows the relationship of gas volume to absolute temperature for an ideal gas. (Pressure and mass of gas are held constant.)

**Graph B** shows the relationship of pressure to volume for an ideal gas. (Temperature and mass of gas are held constant.)

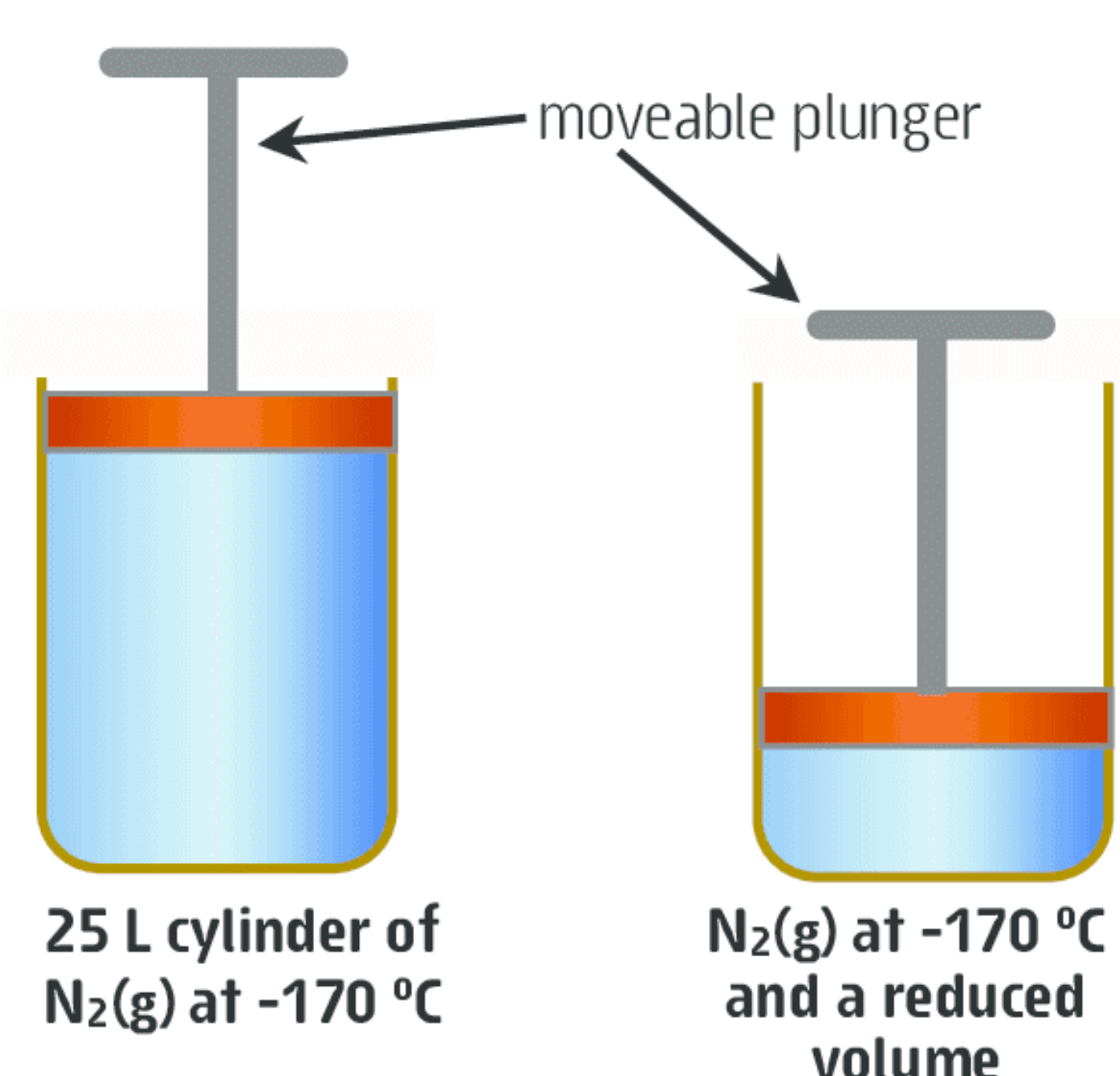


**FIGURE 12** Test tube A contains molten wax. Test tube B contains the same wax after solidification. Notice the surface depression that forms as the wax solidifies.





**FIGURE 13** Cream, milk, sugar and vanilla are the main ingredients in **ice cream**. One way to convert this mixture into ice cream is to mix in liquid nitrogen.



**FIGURE 14** Pushing the plunger in reduces the volume of the 25 L cylinder of nitrogen gas. The temperature is kept at  $-170\text{ }^{\circ}\text{C}$ .



**FIGURE 15** A scuba diver can breathe freely underwater using pressurised air contained in a steel or aluminium tank.



**FIGURE 16** These three **mylar** balloons and the one **latex** balloon (purple) all float as their buoyancy exceeds their weight. Balloon **buoyancy** depends upon its **volume**. A balloon gains about 1.2 g buoyancy for every 1.0 L of volume; 1.2 g being the mass of each 1.0 L of air that is pushed aside by the balloon's own volume. If the balloon's buoyancy exceeds its weight then it floats.

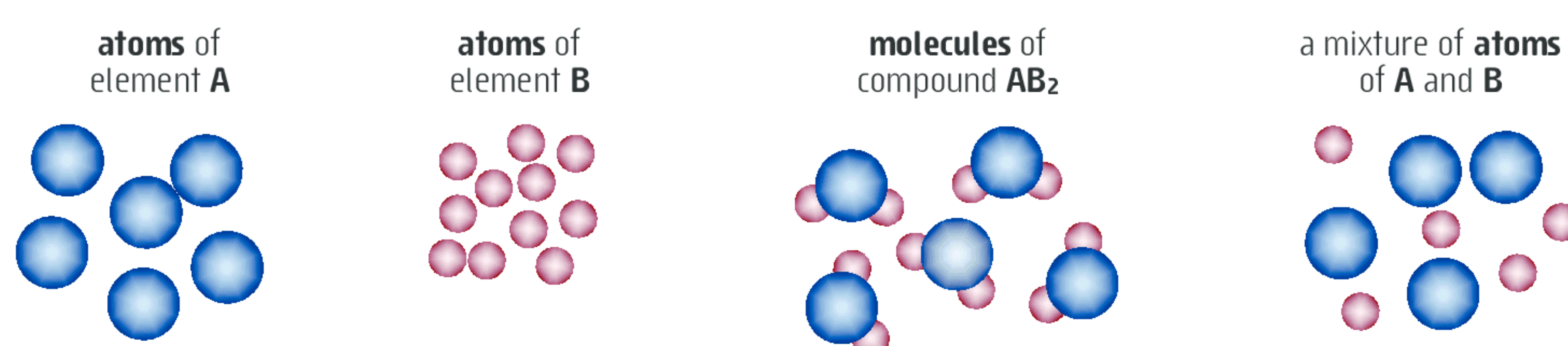
9. **Liquid nitrogen** is sometimes used in the laboratory for producing very low temperatures or for making ice cream! (See Fig 13.)
  - a. At normal laboratory conditions, a **1.0 L** sample of liquid nitrogen,  $\text{N}_2(\text{l})$  can boil to fill an **860 L** balloon. **Account** for the large increase in volume.
  - b. Although liquid nitrogen is quite cold (it boils at  $-196\text{ }^{\circ}\text{C}$ ), most of its cooling effect is produced when it boils. **Explain** how this happens.
  
10. The following questions refer to a sample of nitrogen gas sealed inside a 25 L cylinder. The cylinder is kept at a **constant temperature** of  $-170\text{ }^{\circ}\text{C}$  with the gas inside at a standard pressure of 100 kPa. A moveable plunger can be used to reduce the cylinder's internal volume. (See Fig 14.) The plunger is now steadily pushed in reducing the nitrogen gas volume while its temperature is **kept constant** at  $-170\text{ }^{\circ}\text{C}$ .
  - a. What will happen to the **pressure** of the nitrogen gas inside the cylinder as its volume is reduced? Use your knowledge of the kinetic theory of gases to help **explain** why this happens.
  - b. What will happen to the **average kinetic energy** of the nitrogen molecules (particles) inside the flask? **Explain**.
  - c. As the volume of the cylinder is reduced so the pressure inside the flask continues to rise until it reaches around 1.5 MPa pressure. Any further reduction in volume simply causes the nitrogen to **liquefy** and the pressure no longer increases. This would not happen to an ideal gas. How is nitrogen different to an ideal gas and why does this cause it to liquefy?
  
11. Air is a **homogeneous** mixture of gases. (See Fig 1.) What is a homogeneous mixture and why are **gas mixtures** always homogeneous?
  
12. Normal air pressure at sea level is **1 atm** (101.3 kPa). When scuba diving, a diver experiences a considerable increase in pressure, approximately 1 atm pressure increase for each **10 m of depth**. Scuba divers (Fig 15) are able to breathe from a pressurised tank that contains air at around 180 atm pressure (180 times normal atmospheric pressure). The diver breathes through a regulator which ensures the inhaled air coming from the high pressure tank is at a reduced pressure that matches the diver's surrounding water pressure.
  - a. In order to breathe comfortably, inhaled air must be at a similar pressure to the surrounding pressure on a person's body/lungs. With this in mind, what is the appropriate breathing air pressure at **sea level** and for an ocean depth of **20 m**?
  - b. What would happen if the inhaled air was at a **lower or higher** pressure than the surrounding water pressure exerted on the diver's body/lungs?
  - c. A typical scuba tank may contain 15 L of air at 180 atm pressure. Use the kinetic theory to **account** for the high air pressure inside the tank.
  - d. At sea level (1 atm pressure) a scuba tank of 15 L volume containing air at 180 kPa pressure may be sufficient to last a diver for around 2 hours. However, this same amount of air will only last 1 hour at a depth of 10 m or around 40 minutes at a depth of 20 m. Why does the air run out more quickly at a **greater depth**?
  - e. Why is it absolutely essential to vigorously exhale if making an emergency **rapid ascent** from a 15 m dive? Caution: Rapid ascents like this can be very dangerous leading to a potentially fatal condition known as the 'bends'.
  
13. Party balloons (Fig 16) can be filled with balloon gas (a mixture of helium and air) to make them float. **Latex** balloons are strong and stretchy so as more gas is added to a latex balloon its volume increases. **Foil** balloons, however, are made of **mylar** which is strong but doesn't stretch, so once filled, adding more gas doesn't further increase the volume of a foil balloon. When filled with sufficient gas and tied off, both types of balloons will float. Answer the following questions making reference to the kinetic theory of matter.
  - a. Why does a stretchy latex balloon inflate (increase in volume) as more gas is added?
  - b. A foil or mylar balloon is fully inflated and then extra gas is added. What happens to the pressure inside the balloon? (Remember a mylar balloon won't stretch.) **Explain**.
  - c. A **latex balloon** (Fig 16) loses its buoyancy after about 12-16 hours. This happens as helium consists of very small fast moving particles that readily leak through (diffuse) the latex membrane and out of the balloon. One such balloon has just lost its buoyancy and begins to sink to the floor. When brought out into the sunshine for a while it warms up and regains its buoyancy and once again floats upwards. How does the sunshine affect the **balloon** and its **contents**?



## 1.7 Composition of matter: Introducing the particles

**Atoms** are understood to be the basic particles from which matter is made. Substances like iron (Fe), carbon (C) and oxygen (O) are unique forms of matter known as **elements**. Each element is composed of its own unique atoms. At present 116 elements have been identified, 28 of these are either extremely rare or not known to occur naturally on earth. Unique chemical **symbols** are used to represent each of the different atoms and the elements they form. (See the periodic table on the inside back cover.)

**Compounds** are forms of matter that consist of two or more different elements that are chemically combined in a definite whole number atomic ratio. The components of a **mixture**, by contrast are not chemically combined and may occur in the mixture in any ratio. (See Fig 17.)



**FIGURE 17** Dalton's atomic theory tells us that each type of element is composed of its own unique atoms. (See p13.) When atoms of different elements chemically combine in a definite atomic ratio they form a **compound**. In a **mixture** the components are not chemically combined and may be present in any ratio.

Both elements and compounds are **pure substances**. This means they have a definite and fixed composition. Elements cannot be separated into other substances while compounds can only be separated into their component elements by chemical means.

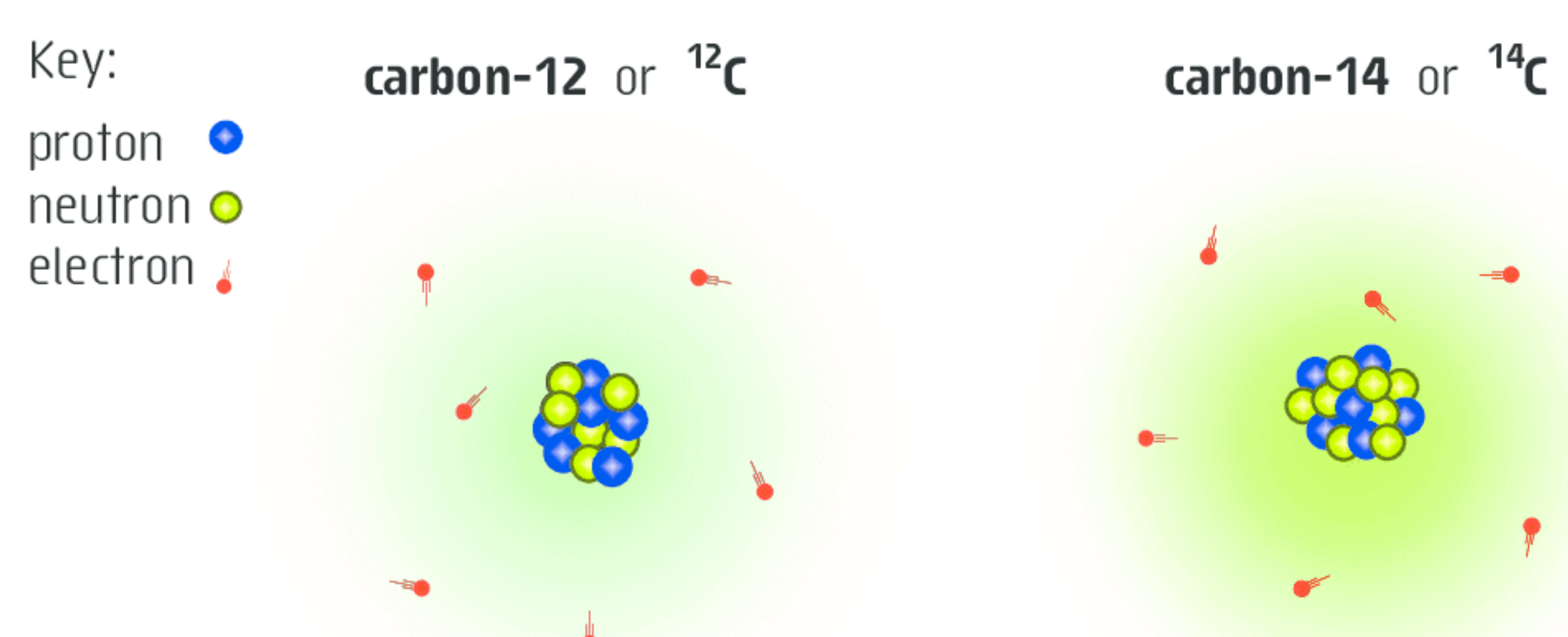
The most common type of material in our environment are mixtures. These are not pure substances. A mixture is a physical combination of elements or compounds where the parts of the mixture are not chemically combined and so are able to be separated by physical techniques like filtration, distillation or chromatography. (See Chapter 3 and 19.) The different particles of a mixture may be mixed evenly as in a **homogeneous** mixture or unevenly as in a **heterogeneous** mixture. (See border note.) Homogeneous mixtures like air ( $N_2$ ,  $O_2$  and Ar, Fig 1), seawater (mainly  $H_2O$ , NaCl,  $MgCl_2$ ,  $CaCl_2$  and  $K_2SO_4$ , see p141), soft drink (mainly  $H_2O$ ,  $C_{12}H_{22}O_{11}$ ,  $CO_2$  and flavours) and brass (Cu and Zn) are known as **solutions**. All other mixtures are heterogeneous, eg concrete, orange juice, clay and wood.

## 1.8 Atoms and isotopes

Atoms are the smallest particles of an element. They consist of a **nucleus** containing **protons** and **neutrons** and an **electron cloud** where **electrons** are found. (See Table 3 and Fig 19.) The number of protons in an atom's nucleus is its most significant feature and is known as the **atomic number (Z)**. Although atoms contain electrically charged particles, they are normally **neutral**. This happens because atoms contain as many electrons; negatively charged particles, as protons; positively charged particles. The equal numbers of oppositely charged particles result in the atom having zero overall charge.

While every atom of a given element must have the same number of protons they sometimes vary in the number of neutrons they contain. Atoms like this are known as **isotopes**, ie atoms with the same number of protons but a different number of neutrons. (See Fig 19.) Some elements such as sodium and aluminium exist as a single type of isotope while most elements have several stable isotopes. The isotopes of a given element always have identical chemical properties but differ slightly in their relative atomic mass and density. They also differ in nuclear stability causing some to be radioactive. (See Fig 18.)

**FIGURE 19** Atoms can be visualised as consisting of a positively charged nucleus of protons and neutrons and a negatively charged electron cloud. Although the nucleus is the smallest part of the atom it contains more than 99.95 % of its mass. These two **isotopes** of carbon both have six protons and six electrons but their number of neutrons differ.



The particles referred to in the kinetic theory of matter, we now know to be **atoms, ions or molecules**.

A **chemical formula** shows the ratio of each type of atom in a compound. For example:

**Water** ( $H_2O$ ) contains **two H atoms** to every **one O atom**.

**Ammonia** ( $NH_3$ ) contains **one N atom** to every **three H atoms**.

**Mixtures** do not normally have a chemical formula as their composition is not fixed.

**Homogeneous** matter has a uniform composition throughout. This means the particles of the material (atoms, ions or molecules) are spread evenly throughout its entire volume.

**Heterogeneous** mixtures are those with a variable composition throughout. This means the different particles that make up the mixture are distributed in distinct **clumps** within the substance. The substance is considered heterogeneous even if the clumps are microscopic in size. Blood, for example, may appear homogeneous to the unaided eye, however, it is considered heterogeneous as it contains a number of distinct microscopic particles (clumps of matter) like red and white blood cells.

Attempt Set 2 # 1, 2, 3, 4 and 5.

**TABLE 3** Subatomic particles

particle	relative mass (u)	relative charge	location
proton	1.0	+1	nucleus
neutron	1.0	0	nucleus
electron	$\approx 0.00055$	-1	electron cloud

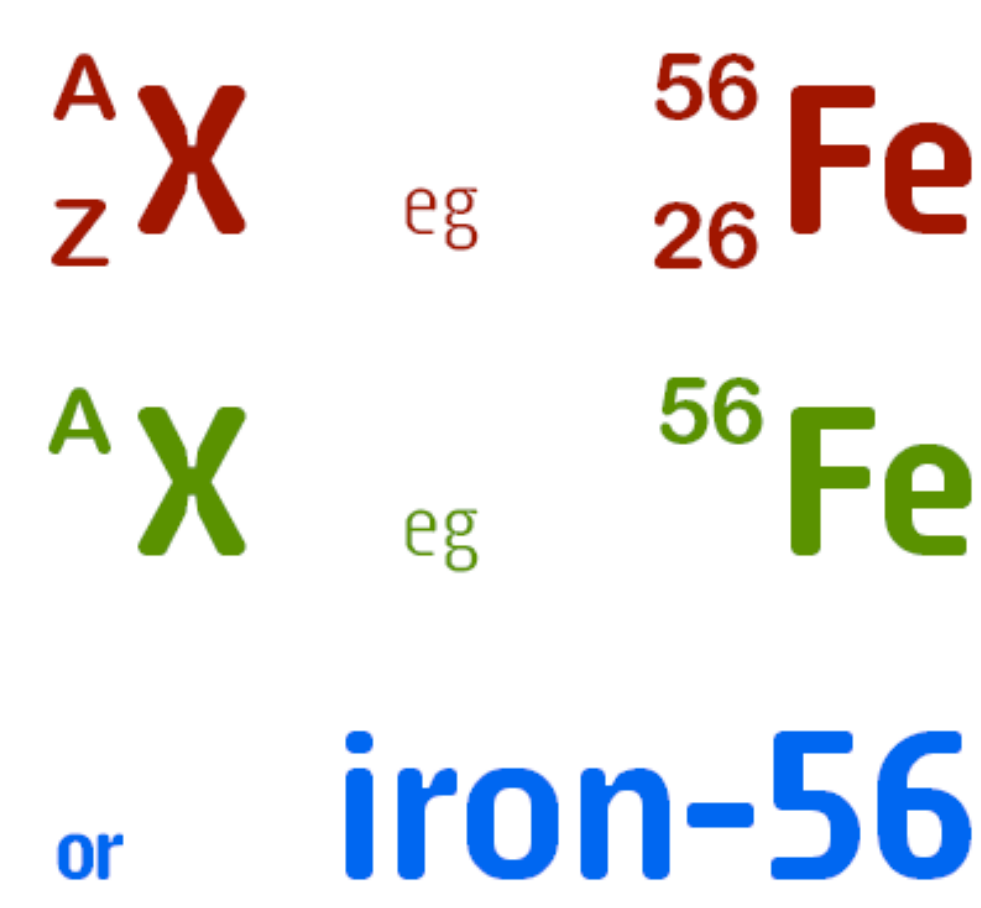


**FIGURE 18** Nuclear stability is a significant difference between isotopes of an element. Some isotopes, called **radioisotopes**, are unstable and undergo spontaneous nuclear decay to produce various types of radiation while changing into different, eventually more stable nuclei. Radioisotopes like these find important applications in industry as well as in medical diagnosis and therapeutic treatment.

The illustration above shows a canister of **radioactive iodine-131** capsules used for the diagnosis and treatment of thyroid diseases. Image courtesy of Monrol-UAE.



The **atomic number (Z)** and **mass number (A)** of an isotope are sometimes shown with the element's symbol (**X**). The current **IUPAC** notation shows only the isotope's mass number as its atomic number is implied by its symbol. Another alternative shows the isotope name followed by its mass number. Here the element iron, mass number 56 and atomic number 26 is used as an example.



Attempt Set 2 # 6, 7 and 8.

Remember, the **atomic number** gives the number of protons (positively charged particles) in the nucleus of an atom. This number never changes during any physical or chemical process. It is possible however, for an atom to lose its electrical neutrality by **gaining or losing electrons**.

Attempt Set 2 # 9.

The **relative atomic mass**,  $A_r$  of an atom is its mass compared to one twelfth ( $\frac{1}{12}$ ) the mass of a carbon-12 atom.

This quantity; ie one twelfth the mass of a carbon-12 atom, is known as a **unified atomic mass unit (u)**. It is the approximate mass of a proton or neutron. The actual rest mass of a proton, a neutron and an electron are:

$m_p=1.007276\text{ u}$  (ie  $1.67262 \times 10^{-24}\text{ g}$ )  
 $m_n=1.008665\text{ u}$  (ie  $1.67493 \times 10^{-24}\text{ g}$ )  
 $m_e=0.000549\text{ u}$  (ie  $0.00091 \times 10^{-24}\text{ g}$ )

The unified atomic mass unit is now sometimes referred to as a **dalton (Da)**.  
 $1\text{ Da} = 1\text{ u} = 1.660538782 \times 10^{-24}\text{ g}$

Another important feature of the atom is its **mass number (A)**. This is an indicator of how heavy that atom is. Mass number is equal to the number of protons plus neutrons in its nucleus. Summarising these ideas:

$Z = N_p$ 

where:  $Z$  is the atomic number of the atom.  
 $N_p$  is the number of protons in the atom.

$A = N_p + N_n$ 

$A$  is the mass number of the atom.  
 $N_n$  is the number of neutrons in the atom.

Also for **neutral** atoms:

$N_e = N_p$ 

where:  $N_e$  is the number of electrons in the atom.

**EXAMPLE 1** How many **protons**, **neutrons** and **electrons** are in an atom of the isotope  $^{15}\text{N}$ , ie nitrogen-15? (See border note at left.)

$Z = N_p = 7$ 

The atomic number of nitrogen,  $Z=7$  (see periodic table) gives the number of protons, 7. The mass number,  $A=15$  is the sum of protons and neutrons so there are 8 neutrons in this isotope of nitrogen. Also, since the atom is neutral so there is an equal number of protons and electrons.

$A = N_p + N_n$ 

$\therefore N_n = A - N_p = 15 - 7 = 8$   
and  $N_e = N_p = 7$

$\therefore$  the isotope nitrogen-15 contains **7 protons**, **8 neutrons** and **7 electrons**.

### 1.9 Ions

Although atoms are normally neutral in charge [since  $N(e) = N(p)$ ] it is possible for an atom to become charged by gaining or losing electrons. Electrically charged atoms are known as **ions**. **Negative ions** form when an atom gains one or more electrons. **Positive ions** are formed when an atom loses one or more of its electrons. The net charge of an ion depends on the number of protons (+ charges) and electrons (- charges) it has.

$\text{Ion charge} = N_p - N_e$ 

where:  $N_p$  is the number of protons in the ion.

thus  $N_e = N_p - \text{ion charge}$ 

$N_e$  is the number of electrons in the ion.

**EXAMPLE 2** How many **protons** and **electrons** are in each of the following ions?

$O^{2-}$ 

The atomic number of O is 8 (see periodic table)  
 $\therefore O^{2-}$  has **8 protons**

and  $N_e = N_p - \text{ion charge}$   
 $= 8 - (-2)$   
 $= \mathbf{10\text{ electrons}}$

$Al^{3+}$ 

The atomic number of Al is 13 (see periodic table)  
 $\therefore Al^{3+}$  has **13 protons**

and  $N_e = N_p - \text{ion charge}$   
 $= 13 - (+3)$   
 $= \mathbf{10\text{ electrons}}$

### 1.10 Relative atomic mass ( $A_r$ )

When John Dalton (1766-1844) proposed the atomic model that is still in use today, he had no means of measuring the masses of the atoms he had proposed existed. However, by accurately measuring the masses of different elements that chemically combined with one another and by making assumptions (that were sometimes incorrect) about their chemical formula he and others were able to determine the **relative atomic mass** of many elements. His experimental results, for example, might show that when calcium and oxygen combined they always did so in a **2.5 g calcium : 1.0 g oxygen** ratio by mass. By assuming these elements were combining in a **1 : 1 atomic ratio** Dalton was able to deduce that Ca atoms must be 2.5 times heavier than O atoms. In a similar way the **relative** atomic mass of many elements was determined. (See Fig 3 p13.)

Although it is now possible to measure the actual mass in grams of individual atoms we still describe the mass of atoms in relative terms (no units). In this way the **relative atomic mass ( $A_r$ )** of an atom is defined as its mass compared to  $\frac{1}{12}$  the mass of a **carbon-12 atom**. If an element has several naturally occurring isotopes then its relative atomic mass is a weighted average of the relative atomic masses of its isotopes. The weighting is based on the abundance of the individual isotopes in a naturally occurring sample of the element.

$A_r = \frac{\%_a \times A_{r(a)} + \%_b \times A_{r(b)}}{100}$ 

where:  $\%_a$  is the percentage of isotope **a** in the element  
 $A_{r(a)}$  is the relative atomic mass of isotope **a**  
 $\%_b$  is the percentage of isotope **b** in the element  
 $A_{r(b)}$  is the relative atomic mass of isotope **b**  
 $A_r$  is the average relative atomic mass of the element



**EXAMPLE 3** A natural sample of **thallium** consists of two isotopes. One isotope has an  $A_r$  of **203.0** and makes up **29.50%** of the thallium atoms. The remaining **70.50%** of the atoms have an  $A_r$  of **205.0**. Determine the **average relative atomic mass** of a natural sample of thallium.

$$A_r(\text{Tl}) = \frac{\%_a \times A_{r(a)} + \%_b \times A_{r(b)}}{100}$$

$$A_r(\text{Tl}) = \frac{29.50 \times 203.0 + 70.50 \times 205.0}{100} = 204.4$$

This formula determines the weighted average relative atomic mass of an element by incorporating the percentage abundance, ie  $\%_a$  and  $\%_b$  of each isotope along with the isotope's relative atomic mass, ie  $A_{r(a)}$  and  $A_{r(b)}$ .

Attempt Set 2 # 10, 11, 12 and 13

## 1.11 Mass spectrometry: Measuring relative atomic mass

The principle of the **mass spectrometer** was first used by Francis Aston (1877–1945) in a device he called a mass spectrograph. He had built his first mass spectrograph by 1919 and used this instrument and others to determine the presence of various atomic isotopes and their mass. Aston was awarded the Nobel Prize in Chemistry in 1922 for his work in this field.

The modern mass spectrometer is a powerful analytical tool that can be used to determine the **relative molecular mass** and **molecular structure** of complex organic compounds. In its simplest application it is used to determine the **relative atomic mass** of the isotopes of an element. (See Fig 20 and 21.)

The operation of a mass spectrometer (Fig 21) involves several key steps:

- **Vaporisation** of the sample to be analysed.
- **Ionisation** of the vaporised sample.
- **Acceleration** and separation of the resulting ions based on their mass to charge ratio, ie  $m/z$ .
- **Detection** or counting the number of each of the ions of different mass to charge ratio.

To do this, a sample of the chosen element is **vaporised** in a vacuum chamber then passed into the mass spectrometer. Here it passes through a **high energy electron beam** where collisions within the beam cause the gaseous atoms to lose one of their electrons and form +1 ions, a few +2 ions may also form. The resulting ions are then accelerated by an **electric field** to form a high speed beam of positive ions that is directed through a **strong magnetic field**. Here the individual ions become **deflected** by the field and move into circular paths of different radius depending upon their **mass** and **charge**. Ions of lower mass experience more deflection by the magnetic field, ie travel in a smaller radius. A **detector** measures the intensity and radius of deflection of each of the ion beams. This detector count is a measure of the isotope abundance while the degree of beam deflection is related to the isotopic mass (actually  $m/z$  ratio). The resulting data can be tabulated or displayed as a mass spectrum (Fig 20) of the sample.

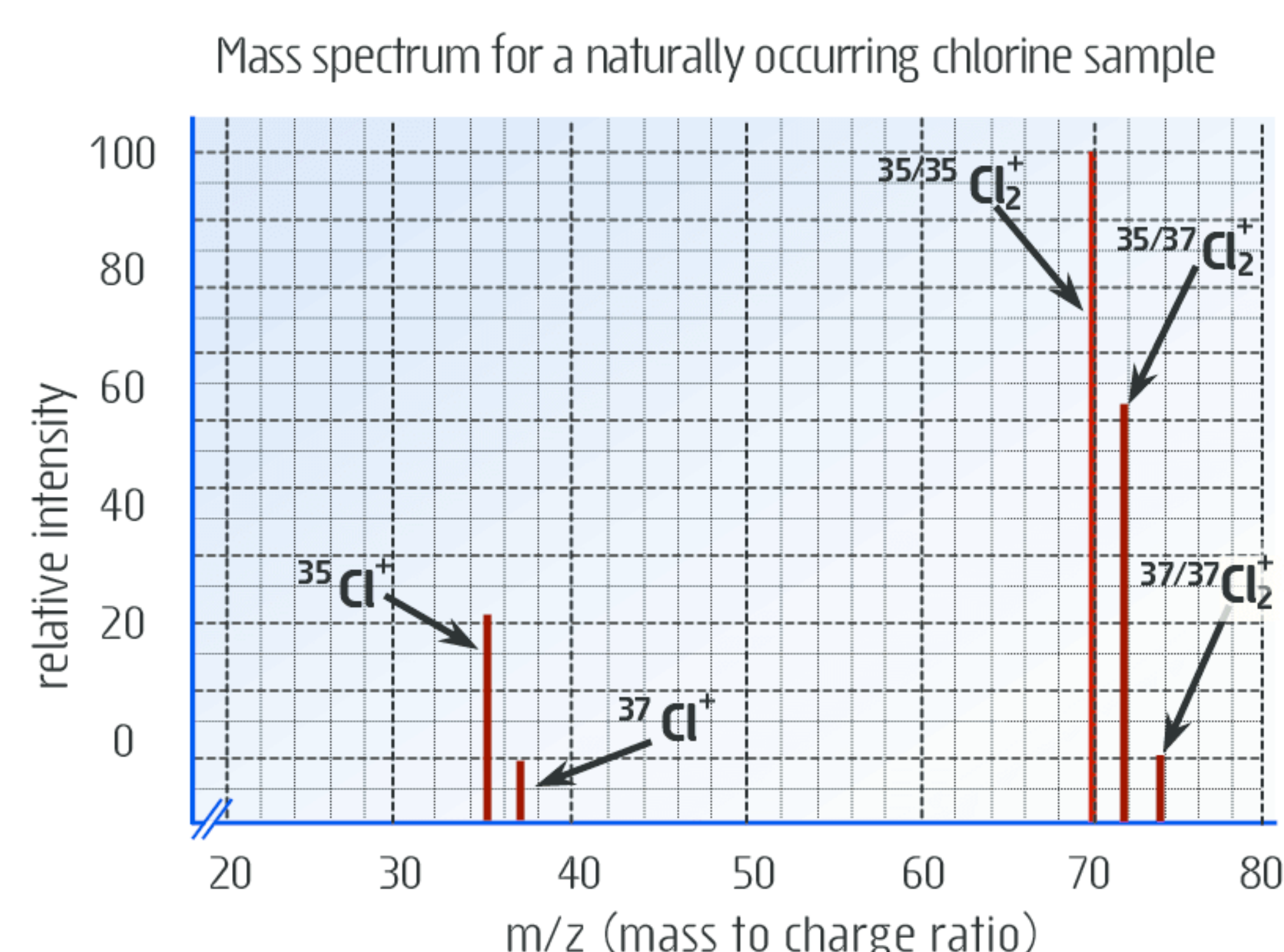
**FIGURE 20** The **mass spectrum** of a naturally occurring chlorine gas,  $\text{Cl}_2(\text{g})$  sample shows its isotopic composition. The +1 ionised atomic fragments,  $^{35}\text{Cl}^+$  and  $^{37}\text{Cl}^+$ , form as  $\text{Cl}_2$  molecules enter the mass spectrometer through a high energy electron beam. A majority of the  $\text{Cl}_2$  molecules will be ionised to  $\text{Cl}_2^+$  without being fragmented into separate atoms. These also appear in the mass spectrum and correspond to various combinations of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ .

Data from the mass spectrum shows the **relative atomic mass** and **abundance** of these two isotopes is:

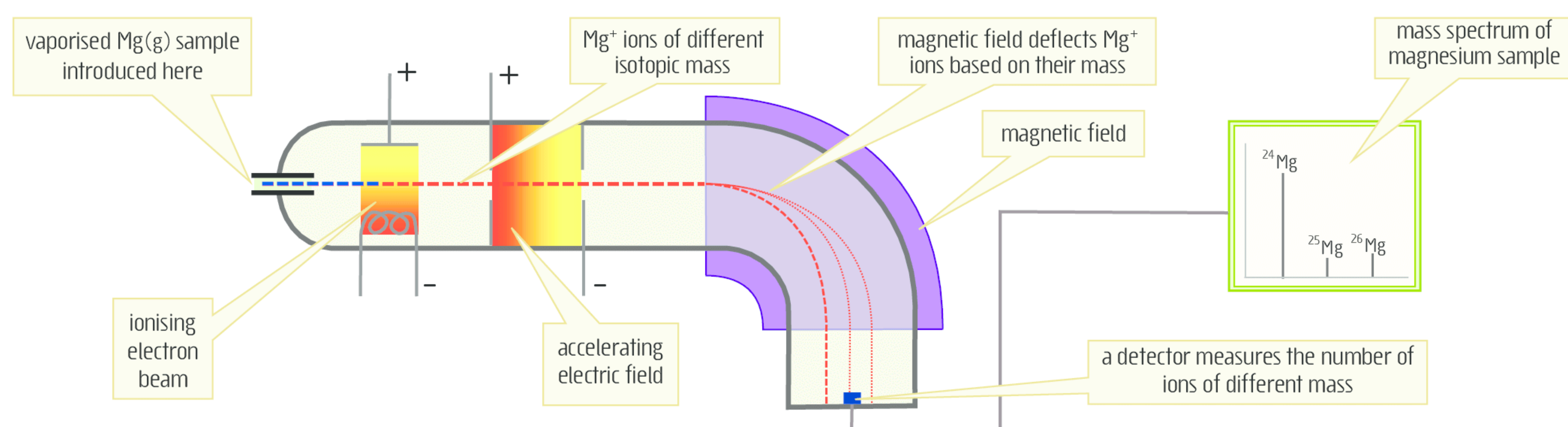
$^{35}\text{Cl}$ , 34.969 u and abundance 75.77%

$^{37}\text{Cl}$ , 36.966 u and abundance 24.23%.

Using this data the **average relative atomic mass** of chlorine is found to be 35.45 u.



**FIGURE 21** Schematic view of a **mass spectrometer** being used to analyse a sample of naturally occurring **magnesium**. Naturally occurring magnesium consists of **magnesium-24**, **magnesium-25** and **magnesium-26**. The actual mass and abundance of each isotope can be accurately measured by the mass spectrometer.



Although mass spectrometry can be used to determine an element's isotopic composition and hence its average relative atomic mass, its most important use is as an **analytical tool**. In this regard it is able to identify a great variety of compounds from within a wide range of complex mixtures. It is capable of identifying individual proteins with concentrations as low as several picomoles ( $10^{-12}$  mol) per microlitre from as little as several microlitres of solution. For this reason mass spectrometry finds great application in scientific research, industry and forensic analysis such as for the detection of performance enhancing or banned substances in the blood or urine samples of athletes. (See Fig 11 p170.)

Complete Set 2.



## Set 2 Composition of matter and atomic structure

physical  
filtration  
atom  
separated  
homogeneous  
heterogeneous  
compound  
microscopic  
pure  
mixture  
chemical  
atomic  
elements  
molecular

**Subscripts** written alongside a formula show its phase.

solid phase .....(s)  
liquid phase .....(l)  
gas phase .....(g)  
dissolved in water ....(aq)

**Remember!** For a mixture to be homogeneous its particles must be uniformly mixed. This means its atoms, molecules or ions must be evenly spread throughout the material's entire volume.

- The following passage relates to the chemical classification of the different types of matter. Use the list of terms to correctly complete the passage. Some of these terms are **used more than once** or may not be used at all.

Substances like silver, oxygen and carbon are (a) \_\_\_\_\_ substances that cannot be physically or chemically (b) \_\_\_\_\_ into other substances. Materials like this are known as (c) \_\_\_\_\_. Each element consists of its own type of (d) \_\_\_\_\_.

By comparison, compounds are substances like water and methane that consist of two or more different elements chemically combined in a definite whole number (e) \_\_\_\_\_ ratio. Although compounds consist of different elements they are considered (f) \_\_\_\_\_ as their component elements cannot be separated by (g) \_\_\_\_\_ processes. In a compound the elements can only be separated by (h) \_\_\_\_\_ means.

Mixtures are combinations of substances that can be separated by (i) \_\_\_\_\_ means like filtration, distillation or chromatography. (j) \_\_\_\_\_ mixtures are those that have the different components evenly spread at the (k) \_\_\_\_\_ or (l) \_\_\_\_\_ level throughout the mixture. If the mixture consists of clumps of the component particles, even if these are (m) \_\_\_\_\_ then the mixture is said to be (n) \_\_\_\_\_.

- Identify the following materials as **elements**, **compounds** or **mixtures**.
 

a. hydrogen gas [H <sub>2</sub> (g)]	c. salt solution [NaCl(aq)]	e. iron [Fe(s)]
b. carbon dioxide gas [CO <sub>2</sub> (g)]	d. bronze [Cu(s) + Sn(s)]	f. water [H <sub>2</sub> O(l)]
- Classify the following materials as **pure** or **mixtures**, **homogeneous** or **heterogeneous** and state which are **solutions**.
  - copper [Cu(s)]
  - sugar dissolved in water [C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(aq)]
  - vinegar, a combination of two miscible liquids [CH<sub>3</sub>COOH(l) + H<sub>2</sub>O(l)]
  - orange juice [C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(aq) + H<sub>2</sub>O(l) + pieces of orange pulp]
  - a glass of distilled water [H<sub>2</sub>O(l)]
  - a glass of mineral water [H<sub>2</sub>O(l) containing various dissolved minerals]
  - a gas jar full of clean air [N<sub>2</sub>(g) + O<sub>2</sub>(g) + Ar(g)]
  - Alka-Seltzer tablet [powdered C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>(s) combined with powdered NaHCO<sub>3</sub>(s)]
- A chef preparing a dish of salt and pepper squid, places a teaspoon of salt and a teaspoon of pepper corns into a mortar and grinds the ingredients into a fine powder.
  - Classify** each of the three substances salt (NaCl), pepper corns and the resulting fine powder, as being an element, compound or mixture. **Justify** your answer.
  - Which if any of the three substances is **homogeneous**? **Explain** your answer.
- Bronze** is a metal alloy frequently used by sculptors for making artworks like statues and plaques. (See Fig 1 p24.) Bronze has advantages over other metals as it has a particularly low melting point, is hard, resists corrosion and has an attractive colour. Bronze is produced by mixing together varying amounts of **copper** (Cu) and **tin** (Sn). Small quantities of other metals like aluminium (Al) or manganese (Mn) are sometimes added. The mixture is heated until it melts and forms a homogeneous consistency. The mixture is then cooled and solidifies.
  - Would you classify bronze as an element, compound or mixture? **Justify** your answer.
  - Justify** the statement, 'Alloys like bronze are solid solutions.'
  - Use your knowledge of the kinetic theory of matter to **explain** why the mixture of metals melts when heated and then solidifies when cooled.
  - When the mixture of metals melts it then becomes homogeneous. **Explain** at a particle level how the mixture becomes **homogeneous**.



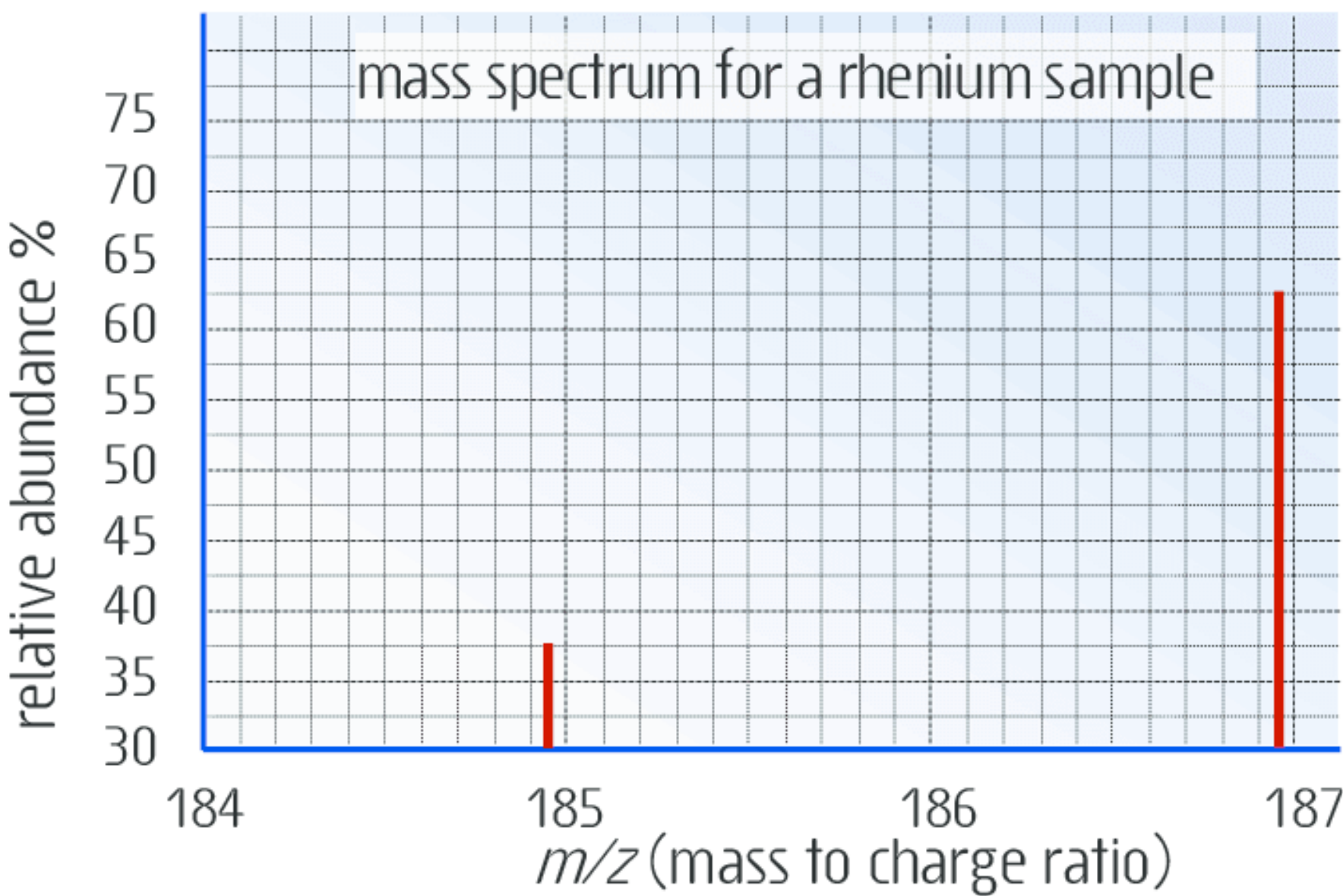
6. Give the **mass number** and **atomic number** of the following isotopes. Refer to a periodic table for atomic data where needed.
- a. nitrogen-14                      b.  $^{127}_{53}\text{I}$                       c.  $^{23}\text{Na}$
7. How many **protons**, **neutrons** and **electrons** are in one atom of the following isotopes?
- a.  $^7_3\text{Li}$                       b.  $^{35}\text{Cl}$                       c.  $^{12}\text{C}$                       d.  $^{52}\text{Cr}$
8. Most elements have more than one isotope, hydrogen for example has three isotopes,  $^1\text{H}$ ,  $^2\text{H}$  and  $^3\text{H}$ . These isotopes are known respectively as hydrogen, deuterium and tritium. With reference to the isotopes of hydrogen describe the similarities and differences in the **atomic structure** of the isotopes of an element.

9. Complete the table for each of the ions listed. See a periodic table for atomic data.

	a	b	c	d	e	f	g
ion	$\text{Mg}^{2+}$	$\text{S}^{2-}$	$\text{Cl}^-$	$\text{I}^-$	$\text{N}^{3-}$	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$
number of protons							
number of electrons							

10. How many times heavier is a carbon atom ( $A_r = 12$ ) than a hydrogen atom ( $A_r = 1$ )?
11. What is the relative atomic mass of a helium atom if it is one-third the mass of a carbon atom ( $A_r = 12$ )?
12. A natural sample of copper contains two different isotopes. The major isotope, copper-63 has a relative atomic mass of 62.9 and comprises 69.2% of the atoms in the sample. The remaining 30.8% of the atoms are copper-65 with a relative atomic mass of 64.9.
- a. In terms of subatomic particles, how are the isotopes copper-63 and copper-65 different?
- b. Determine the **average relative atomic mass** of naturally occurring copper.
13. Chlorine gas is composed of two isotopes. These are chlorine-35, comprising 75.77% with  $A_r = 34.97$  and chlorine-37, 24.23% with  $A_r = 36.97$ . What is the **average relative atomic mass** of chlorine?
14. A naturally occurring sample of copper, as described in Question 12, is analysed using a mass spectrometer. The following questions refer to this situation.
- a. **Describe** the mass spectrum of this copper sample. Include a **sketch** of relative intensity (no scale) against  $m/z$  (mass to charge ratio).
- b. What must happen to the sample of copper before it enters the mass spectrometer?
- c. For the atoms of copper to be analysed they must be **ionised**. What does this involve?
- d. Which of the two isotopes experiences the **greatest deviation** (deflection) when it **enters** the magnetic field of the mass spectrometer?

15. **Rhenium** (Fig 22) is said to be one of the rarest elements present in the Earth's crust. Of the known stable elements it was the last to be discovered in 1925. Use the data in the mass spectrum of rhenium to determine its **average relative atomic mass**.



16. The mass spectrum of a sample of an unknown metal element reveals a single peak with a mass of  $4.4804 \times 10^{-27}$  kg. What is the **relative atomic mass**,  $A_r$  of this isotope if a single carbon-12 atom has a mass of  $1.9927 \times 10^{-27}$  kg? Use your periodic table to **identify** the element.



# CHAPTER 2 | DISCOVERING THE ATOM'S STRUCTURE



**FIGURE 1** In his revolutionary 1661 publication *'The Sceptical Chymist'* **Robert Boyle** (1627-1691) outlined, amongst other things, his ideas on the composition of matter.

"I now mean by **Elements**.....certain Primitive and Simple, or perfectly **unmingled bodies**; which not being made of any other bodies, or of one another, are the Ingredients of which all those call'd perfectly mixt Bodies are immediately compounded, and into which they are ultimately resolved"

We can see in Boyle's writings the origins of our contemporary model for the division of matter into elements and compounds.

Attempt Set 3 # 1.

## 2.1 The birth of an idea: Elements and atoms (E)

The idea of fundamental or elemental forms of matter is thought to have originated with ancient Greek philosophers such as Anaximander of Miletus (about 610-546 B.C.), Plato (427-347 B.C.) and Aristotle (384-322 B.C.). They believed all matter consisted of various combinations of only four elements which they identified as the elements of fire, earth, air and water. They taught that all matter was **infinitely divisible**.

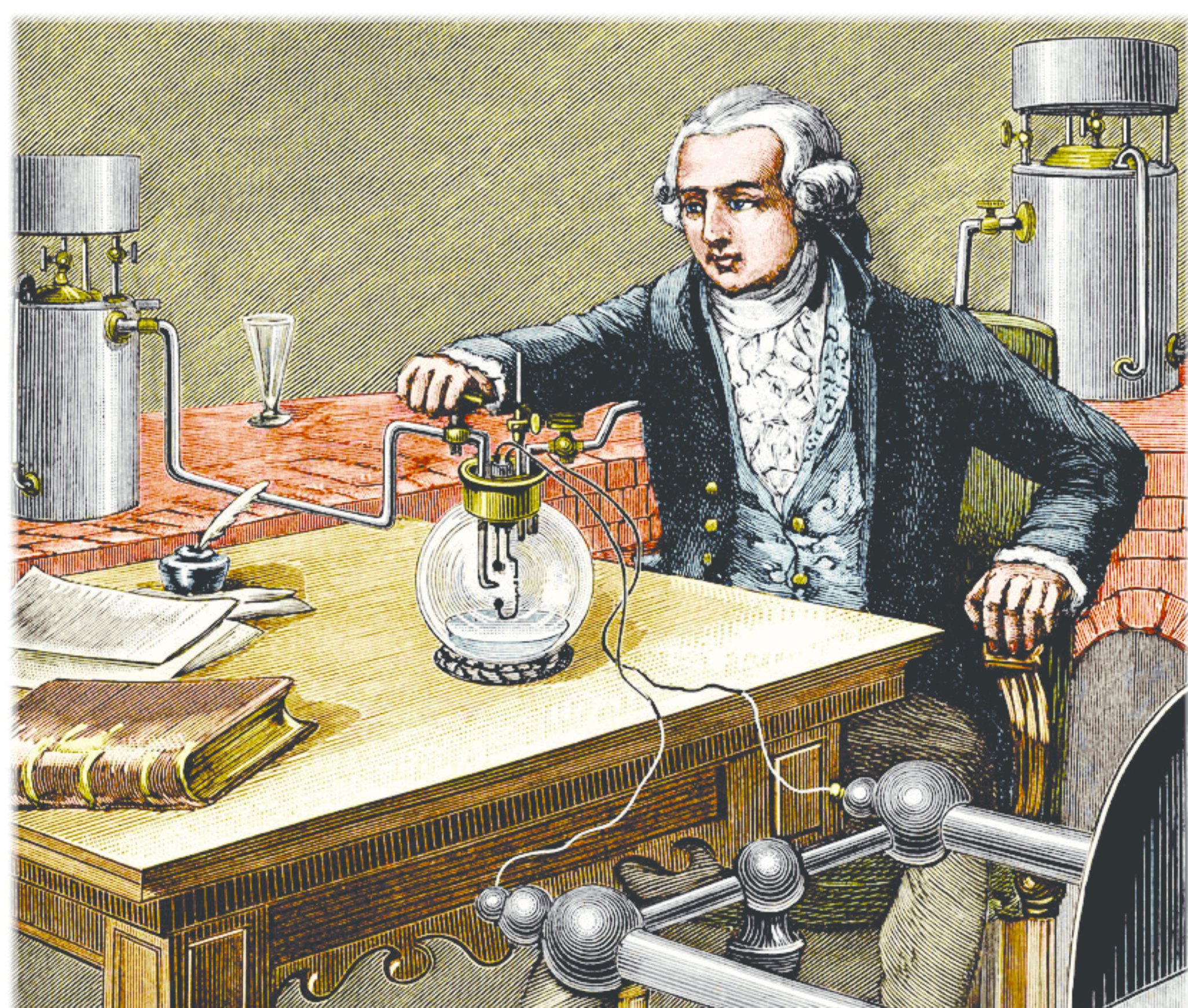
Leucippus of Miletus and Democritus (460-370 B.C.), a student of Leucippus, disagreed with the idea of infinitely divisible matter and gave us the first known written record to propose that matter consisted of tiny indivisible particles with nothing between them but empty space. Democritus called these particles **atomos**, meaning "uncuttable or indivisible".

Despite this, the influence of Anaximander, Plato and Aristotle was so great that their ideas were not seriously challenged until at least the late seventeenth century. In either case, these early ideas on the structure of matter were based on **philosophies** or **beliefs** and were not supported by evidence from experimentation or observation.

Our current understanding of the term 'element', first emerged in print in 1661 in **Robert Boyle's** (1627-1691) text, *'The Sceptical Chymist'*. (See Fig 1.) Here Boyle defined an element as a substance that could not be decomposed into simpler substances. He discounted the previously supposed elements of fire, earth, air and water and supported the idea that elements are composed of various sorts of corpuscles (atoms) which he called 'unmingled bodies'.

## 2.2 The gathering data

Despite the teachings of Greek philosophers and others, there could be no useful debate or progress towards understanding the nature of matter without **scientific evidence** as a basis. The first of this evidence began to appear very late in the eighteenth century.



**FIGURE 2** The French chemist **Antoine Laurent Lavoisier** (1743-1794) making water in 1783. The two cylinders (grey, left and right) hold oxygen and hydrogen. A static electricity generator (right) supplies a spark to the glass vessel (centre). The product of the reaction is water, proving water to be a compound of hydrogen and oxygen.

Lavoisier was one of the first to recognise the importance of accurate measurement in the analysis of chemical reactions. By careful weighing he showed that air is taken in by substances during combustion, and more generally, that any mass gained by one reactant is balanced by a loss elsewhere; the **law of conservation of mass**. He was the first to realise the role of the combustion supporting gas previously discovered by Joseph Priestley and named it **oxygen**.

Attempt Set 3 # 2, 3, and 4.

One such important breakthrough was the discovery of the **'law of conservation of mass'**. This was published in 1789 by the French Chemist **Antoine-Laurent Lavoisier** (1743-1794). Lavoisier had pioneered the use of careful numerical measurements of mass and gas volumes in his experimental work on combustion. Some of his experiments involved strongly heating substances like tin, lead or mercury in sealed containers of air to form various 'calxes' (we know these as metal oxides). His observations and measurements led him to conclude, amongst other things, that there was **no change in mass** during a chemical reaction, ie the law of conservation of mass. (See Fig 2.)

This was a major breakthrough in understanding the nature of matter as until this time there had been considerable confusion regarding what happened to mass during a chemical reaction. When burning a lump of coal or wood, for example, the mass of the coal or wood before combustion is much greater than that of the product, ash. Mass appeared to be lost during this reaction. However, if a sample of tin or lead was heated in air (burnt) the resulting ash or 'calx' (metal oxide) weighed more than the original metal. Here mass appeared to be gained during a chemical reaction. The confusion arose due to a lack of understanding of the role of gases like oxygen and carbon dioxide in the combustion process. It was Lavoisier's careful observations of combustion reactions in **sealed containers** of air that revealed mass was neither being created nor destroyed in these chemical reactions.

Another French Chemist, **Joseph Proust** (1754-1826), over a period from 1794, had conducted other experimental work that led him to later propose his **'law of definite proportions'** which states, "different samples of the same compound always contain its constituent elements in the same proportions by mass". While Proust's idea was not new he was the first to show this law **experimentally**. He was able to show for example, the compound copper carbonate always contained copper, oxygen and carbon in the constant fixed mass ratio of 5:4:1.



## 2.3 John Dalton: Proposing the atomic theory

The beginnings of our current understanding of the chemical behaviour of matter, based on the modern atomic theory, is generally attributed to the English school teacher and scientist **John Dalton** (1766-1844). (See Fig 3.) Over the period 1803-1808 Dalton presented and published a precise definition of the indivisible building blocks of matter that we now know as atoms. His **atomic theory** can be summarised as follows:

- Elements are composed of extremely small particles called atoms.
- All atoms of a given element are identical having the same size, mass and chemical properties. Atoms of different elements have a different size, mass and chemical properties.
- Atoms are not created nor destroyed or changed into different types during a chemical reaction.
- A chemical reaction involves only separation, combination or rearrangement of atoms.
- Compounds are formed when atoms of more than one element combine in a specific ratio.

In designing his atomic theory, Dalton was guided by his own **experimental observations** as well as the recent discoveries of Lavoisier and Proust. The law of definite proportions for example is accounted for in Dalton's theory as he proposes, "compounds are formed when atoms of more than one element combine in a specific ratio". Thus a compound like calcium oxide would always contain Ca atoms and O atoms in some fixed ratio. In this case the ratio of Ca atoms to oxygen atoms is 1:1 and the formula for calcium oxide would be CaO. Using this formula we can see that 40 g of Ca would combine with 16 g of O to produce 56 g of CaO. The **mass ratio** of Ca:O is 40:16 or simply **5:2**. Thus any experimental measurements of the mass of calcium that combined with oxygen would always turn out to be in the ratio of **5Ca:2O**. This ratio is different to the **atomic ratio** (**1Ca:1O**) because as Dalton's theory also states, "All atoms of a given element are identical having the same size, mass and chemical properties while atoms of different elements have different size, mass and chemical properties". Clearly in this example a Ca atom is 2.5 times the mass of an O atom.

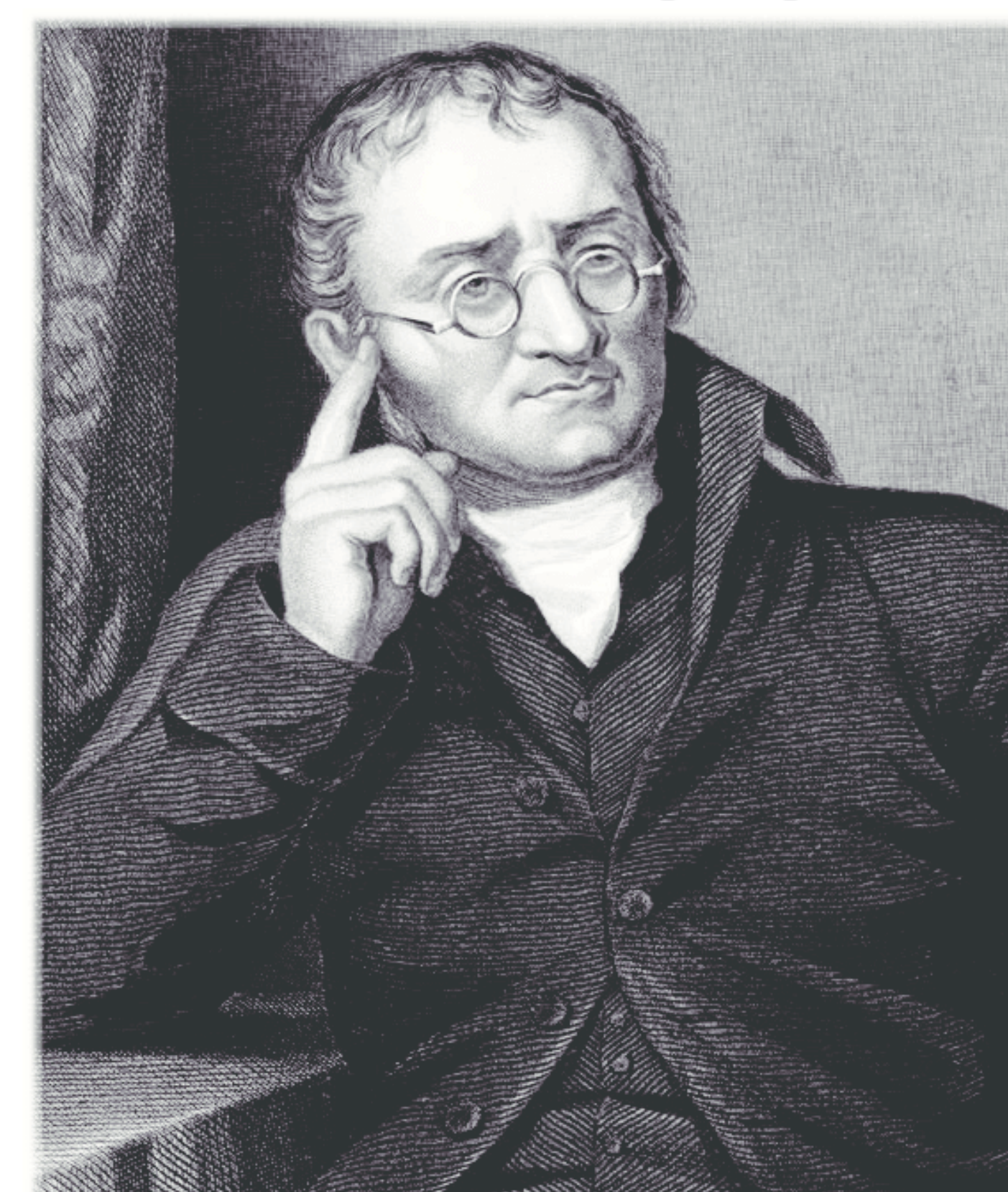
Dalton's theory also accounted for the law of conservation of mass as according to Dalton in a chemical reaction, "atoms are not created nor destroyed or changed into different types", and "a chemical reaction merely involves separation, combination or rearrangement of atoms." This means there must be as many of each type of atom before the reaction as there is after. As Dalton states, atoms have a fixed mass, then there must be as much mass present before a chemical reaction as there is after. When we balance a chemical equation we are applying Dalton's atomic theory. Using symbols to represent atoms we are ensuring there is as many atoms of each element amongst the reactants as there is amongst the products.

Further experimental work by Dalton and others showed some elements combined in different mass ratios to form two distinct compounds. In such compounds the experimental measurements consistently showed the different masses of one of the component elements always occurred in an exact whole number ratio. For example the elements carbon and oxygen form two distinct compounds, carbon monoxide, CO and carbon dioxide, CO<sub>2</sub>. In carbon monoxide the C to O mass ratio is experimentally found to be **3:4** while in carbon dioxide the C to O mass ratio is found to be **3:8**, ie for a given mass of carbon exactly twice the mass of oxygen is present in carbon dioxide. These observations led Dalton to propose the '**law of multiple proportions**' which states, "Whenever two elements form more than one compound, the different masses of one element that combines with a fixed mass of the other element is always in a whole number ratio."

This newly discovered law could be readily explained if elements existed as discrete particles of fixed mass, ie as atoms as Dalton had earlier proposed. The resulting multiple proportions by mass could then be the result of these same atoms combining in more than one atomic ratio such as we now show by writing formulas like CO and CO<sub>2</sub>. Importantly, the ability of Dalton's atomic theory to corroborate this new discovery of the law of multiple proportions, led to Dalton's atomic theory gaining much wider acceptance amongst the scientific community of the time.

Although Dalton had made great progress with his atomic theory by identifying elements as consisting of indestructible particles called atoms, he was unable to draw any conclusions as to their structure. Experimentation during the remainder of the nineteenth century would slowly shed light on the structure of the atom.

FIGURE 3 John Dalton, an engraving from 1834.



Dalton's **atomic symbols** greatly simplified the representation of elements and compounds. The table below is from Dalton's '*A New System of Chemical Philosophy*' (1808). It shows some of the atomic symbols he used for a number of 'elements' along with the **relative atomic weights** he had calculated. Notice some of his elements are now known to be compounds. Lime for example, is CaO and thus not an element.

ELEMENTS			
	Hydrogen		Strontian
	Azote		Barytes
	Carbon		Iron
	Oxygen		Zinc
	Phosphorus		Copper
	Sulphur		Lead
	Magnesia		Silver
	Lime		Gold
	Soda		Platina
	Potash		Mercury

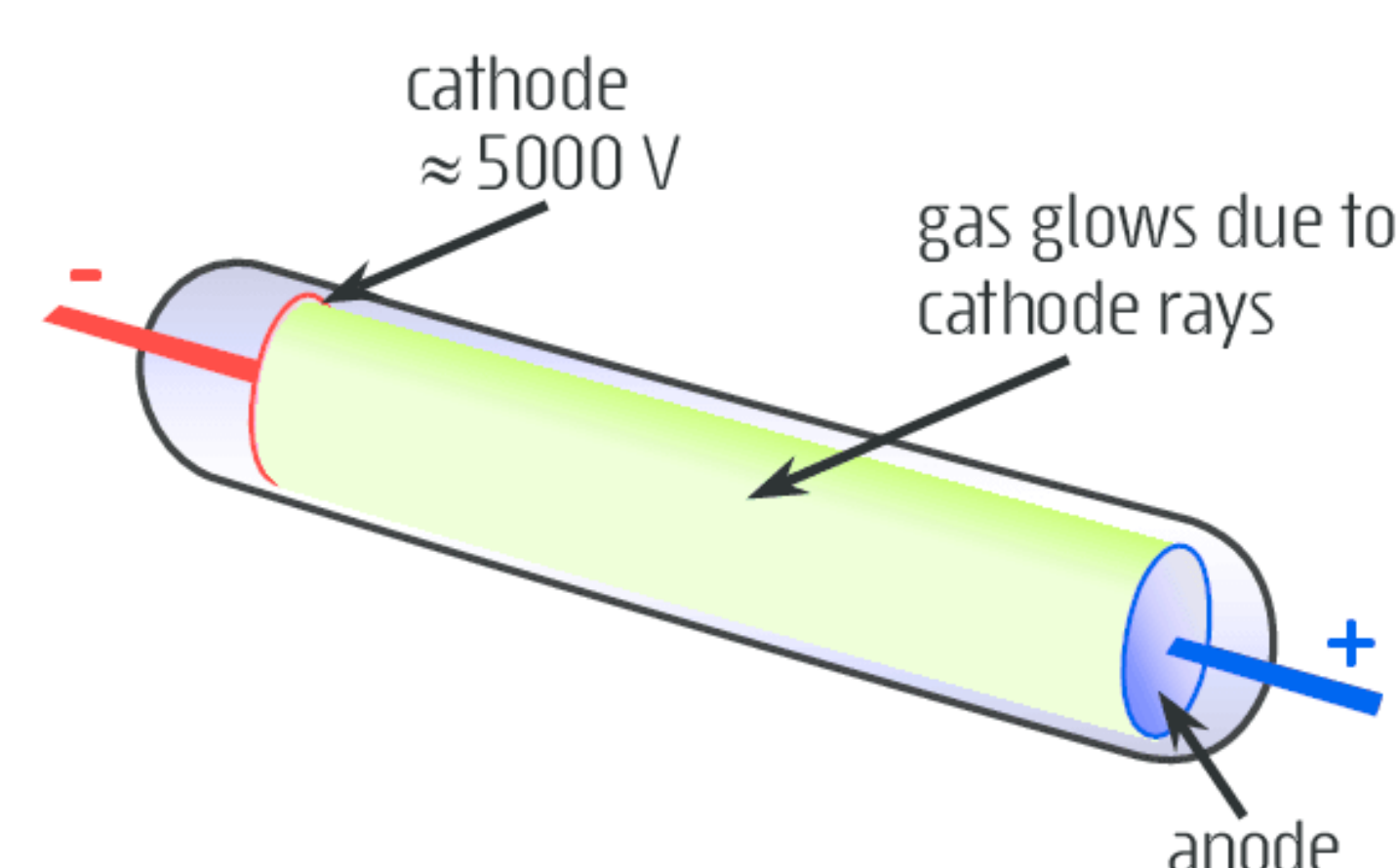
Although Dalton had the right idea about atomic theory and chemical reactions, his arbitrary rule of '**greatest simplicity**' caused him to draw some incorrect conclusions about the chemical formula of some compounds. This rule implied the simplest compound of two elements would be a **binary** compound. As a consequence Dalton believed the formula for water to be **HO**, instead of **H<sub>2</sub>O** and ammonia **NH**, instead of **NH<sub>3</sub>**. This error caused his calculations of the relative atomic weights of the elements, which were based on experimental mass measurements and these formula, to sometimes be out by factors of 2 times or 3 times and so on. On this basis, his calculation for the atomic weight of Oxygen for example was doomed to be at least half the true value. (See table above.)



Experiments conducted by Michael Faraday in about 1833 showed that passing an electric current through an aqueous solution would cause chemical changes to take place. The amount of chemical change (ie mass of products formed) was directly proportional to the current flowing and the amount of time for which it flowed. His observations indicated atoms had **electrical properties** while the discovery of **radioactivity** by Antoine Henri Becquerel (1852-1908) in 1896, challenged the idea that atoms were indestructible particles.

## 2.4 The first piece of the puzzle: Discovering the electron

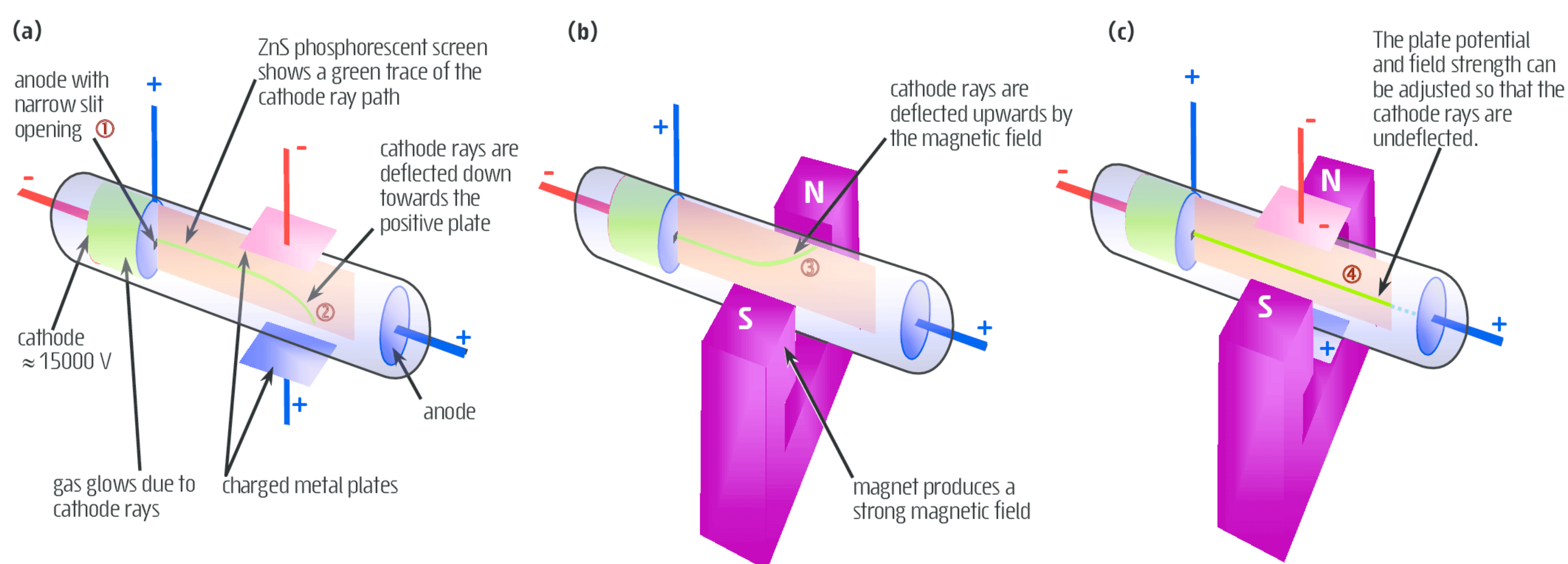
**FIGURE 4** A schematic of the cathode ray tube (CRT). The CRT consists of a partially evacuated sealed glass tube fitted with two electrodes. If a potential difference of greater than 5000 V is applied between the anode and cathode then the gas can be seen to glow due to the emission of cathode rays.



Other experimental work from the mid nineteenth century onwards focused on the use of a newly developed device called a **cathode ray tube** (CRT, see Fig 4). This device allowed scientists like Julius Plucker (1801-1868), Sir William Crookes (1832-1919), J.J.Thomson (1856-1940) and others to further explore the electrical nature of matter. Their experimental observations led to the discovery of **cathode rays**. These invisible rays are produced from the cathode (negative terminal) in a partially evacuated glass tube (a cathode ray tube). While the cathode rays themselves are invisible they could cause the gas inside the CRT to glow like the glow from a neon sign. The rays could also be detected as they caused certain materials called phosphors, eg ZnS(s) to glow. Initially it was not clear if cathode rays were a new type of radiation, like light, or if they consisted of some sort of particles. Although cathode rays were seen to travel in a straight line from the cathode to the anode of the CRT they could be deflected by charged metal plates or magnets. Negatively charged plates deflected the cathode rays away from the plate while positively charged plates would attract the rays towards the plate. (See Fig 5 a/b.)

J.J.Thomson also noted the nature of the cathode rays was independent of the material of which the cathode was made and that a metal plate exposed to cathode rays would become charged. These observations led Thomson to conclude in a paper published in 1897 that cathode rays were not a form of radiation but consisted of a stream of negatively charged particles with mass. These particles soon came to be known as **electrons** and it is **J.J.Thomson** who is generally credited with their discovery.

The first **quantitative** measurements of cathode ray particles (electrons) were produced in 1897 by Thomson using a modified CRT. (See Fig 5c.) In Thomson's CRT the cathode rays passed as a narrow beam between a pair of charged metal plates and a magnetic field. As the cathode rays passed through the magnetic field they experienced a sideways force causing the rays to move in a curved path. By adjusting the charge applied to the metal plates inside the tube it was possible to use the deflecting force of the charged plates to cancel the deflecting force of the magnetic field so that the cathode rays once again moved in a straight path.



**FIGURE 5** In the CRT, a cathode ray beam is formed using a narrow slit in a positive plate, ①. The beam can be seen as it creates a green trace on the phosphorescent ZnS coated screen. Notice how the cathode ray beam is deflected by the charged metal plates, ②. A magnetic field is also observed to deflect cathode rays, ③. These observations led scientists to conclude that cathode rays consisted of particles with a negative charge.

Thomson experimented further on cathode rays by using a pair of charged metal plates in conjunction with a magnetic field. (See Fig 5 (c).) He adjusted the conditions so that the deflecting effect of the plates cancelled out the deflecting effect of the magnetic field. As a result the cathode rays passed undeflected between the plates and field, ④. Measurements from such experiments allowed Thomson to determine the **charge to mass ratio** ( $q_e/m_e$ ) for a cathode ray particle (electron) and to make an estimate of the mass of an electron.



Measurements obtained in these experiments enabled Thomson to determine the charge,  $q_e$  to mass,  $m_e$  ratio ( $q_e/m_e$ ) for the cathode ray particles (electrons). He determined this ratio to be  $1.76 \times 10^{-8}$  coulombs per gram. Using this value and the known charge to mass ratio of various aqueous ions, Thomson was able to estimate the mass of a cathode ray particle (electron) to be less than a thousandth the mass of the lightest atom, hydrogen. This realisation presented Thomson with the revolutionary conclusion that contrary to Dalton ideas, **atoms must be divisible** into even smaller states of matter.

In 1909, not long after Thomson's measurements of the atom's charge to mass ratio another important experimental discovery about the electron was made. **Robert Millikan** (1868-1953) of the University of Chicago devised an experiment, now known as the Millikan oil-drop experiment, which enabled him to determine the charge,  $q_e$  of an electron. The experimental value he determined was amazingly within 1% of today's accepted value of  $1.602 \times 10^{-19}$  coulomb. Importantly, with Thomson's charge to mass ratio ( $q_e/m_e$ ) now known to be  $1.76 \times 10^{-8}$  and Millikan's determination of the electronic charge,  $q_e$  it was now possible to precisely calculate the mass of the electron,  $m_e$ . It turned out to be an extremely low mass particle (about half that originally estimated by Thomson) of mass  $9.11 \times 10^{-31}$  kg or approximately 1/1800 of the mass of a hydrogen atom.

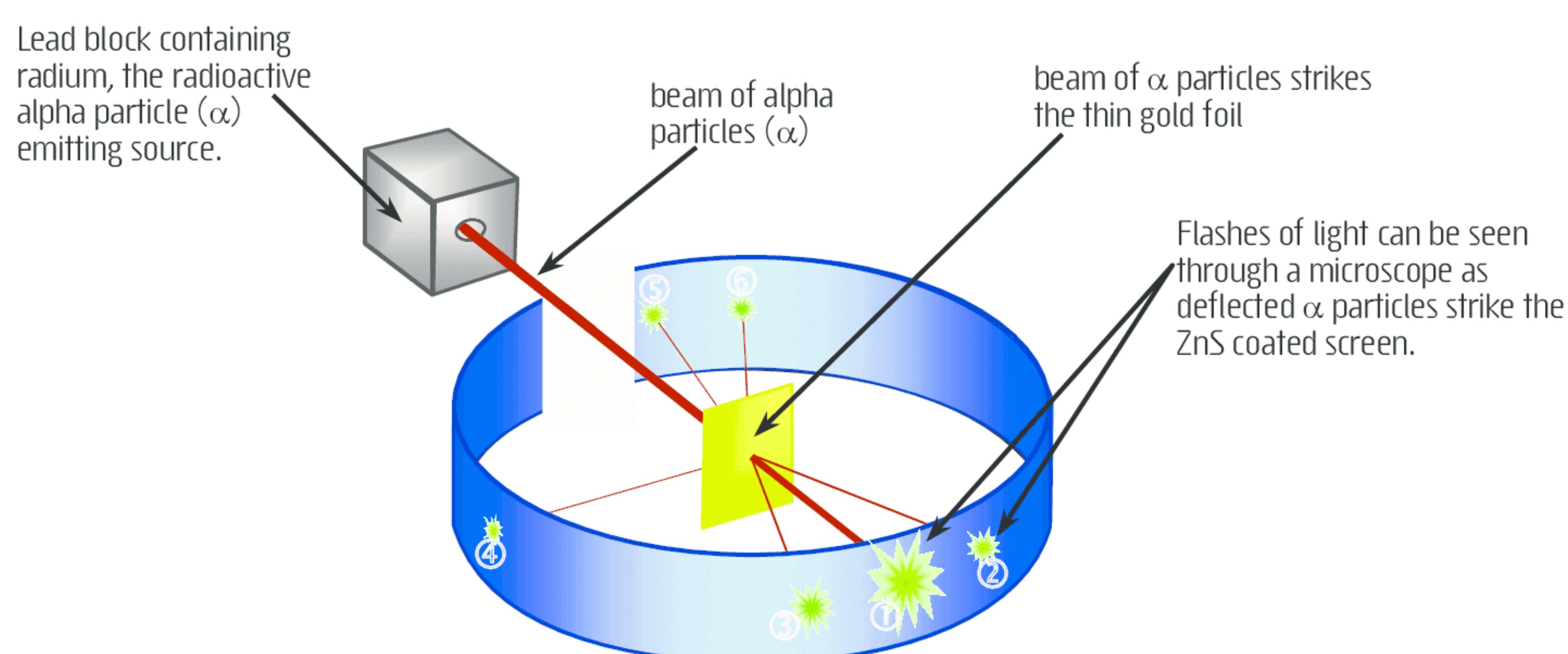
## 2.5 Thomson's model of the atom

By the end of the nineteenth century it was generally agreed amongst scientists that matter consisted of tiny particles called atoms. Matter was known to be electrically neutral and Thomson had shown that the negative particles which made up cathode rays, now known as electrons, had an estimated mass of around 1/1000<sup>th</sup> that of the smallest known atom. This led J.J. Thomson to propose a new model for the atom (Fig 7) that could account for these observations. Thomson's atomic model consisted of numerous very small negatively charged electrons imbedded within a much larger uniform positively charged sphere. The large spherical part of the atom accounted for almost all of its mass. His model, which became known as the '**plum-pudding**' model of the atom, however, would prove to be short lived due to experimental work by Ernest Rutherford (1871-1937).

## 2.6 Rutherford's model of the atom

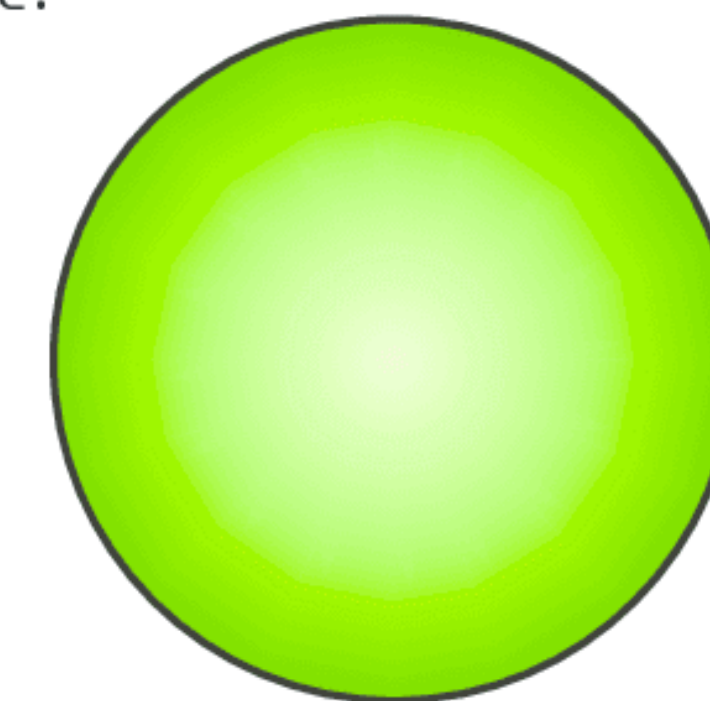
Between 1909 and 1913 **Ernest Rutherford** (Fig 9) and his co-workers, Hans Geiger and Ernest Marsden, carried out a series of experiments in which a beam of **alpha particles**,  $\alpha$  (+2 charged helium nuclei) were targeted at a very thin sheet of gold foil. (See Fig 8 below.)

**FIGURE 8** Rutherford's **gold foil experiments** involved directing a beam of  $\alpha$  particles towards a thin sheet of gold foil. The scattered  $\alpha$  particles are observed through a microscope as they cause a flash of light when they strike the ZnS coated screen. Most alpha particles in the beam pass straight through the gold foil undeflected, ①. Some show a slight deflection, ② and ③. While a very small percentage of  $\alpha$  particles are deflected backwards, ④, ⑤ and ⑥.

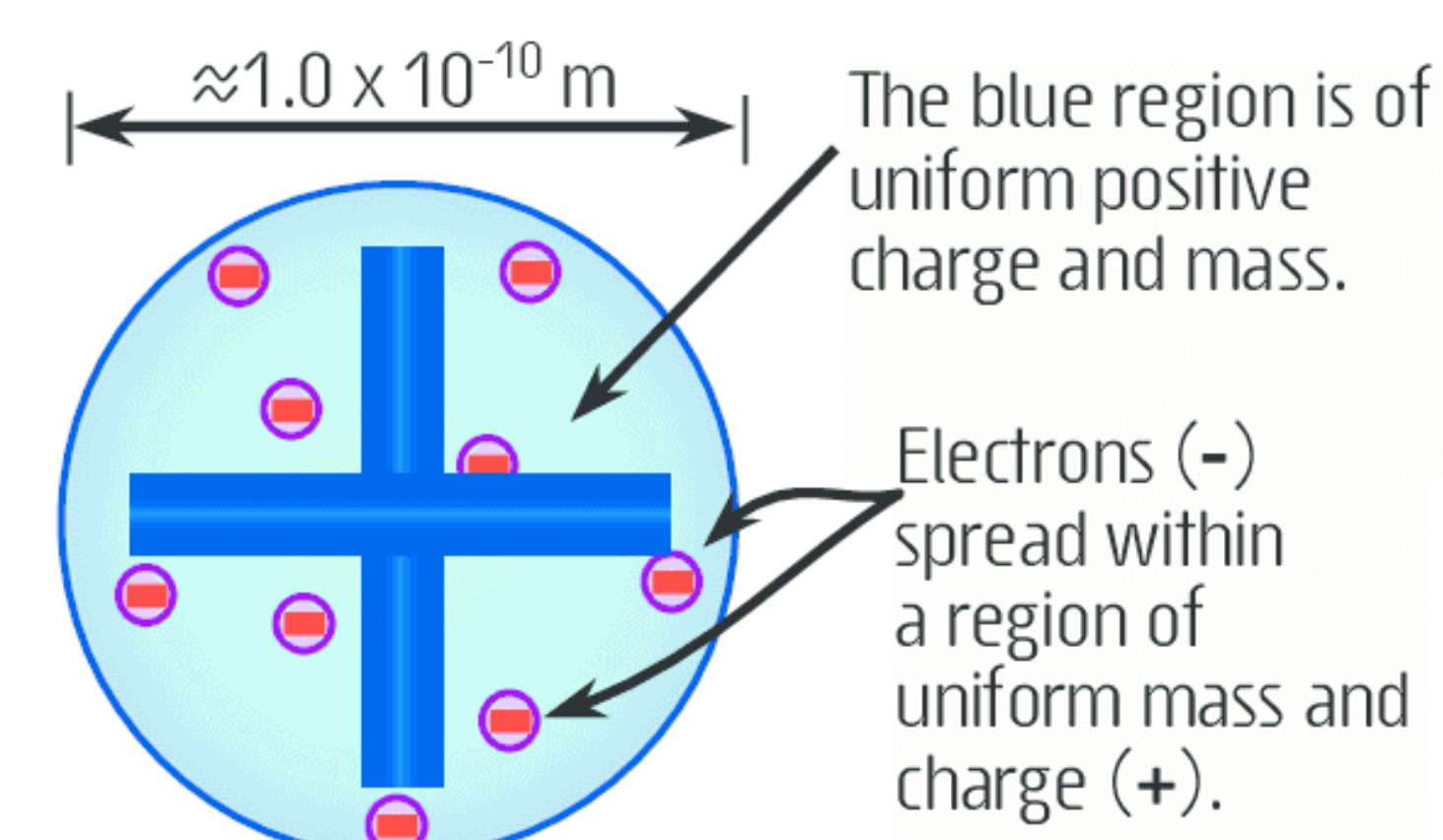


Rutherford was particularly interested in how the alpha particles would be deflected as they passed through the thin gold foil. If Thomson's 'plum-pudding' model of the atom was correct then all of the alpha particles would pass through the gold foil with little or no deflection. This he concluded as the positive charge and mass of Thomson's atomic model was thinly and uniformly spread throughout the atom.

**FIGURE 6** Dalton's original 1803 concept of the atom was that of small, hard, dense and indivisible sphere with no internal structure.

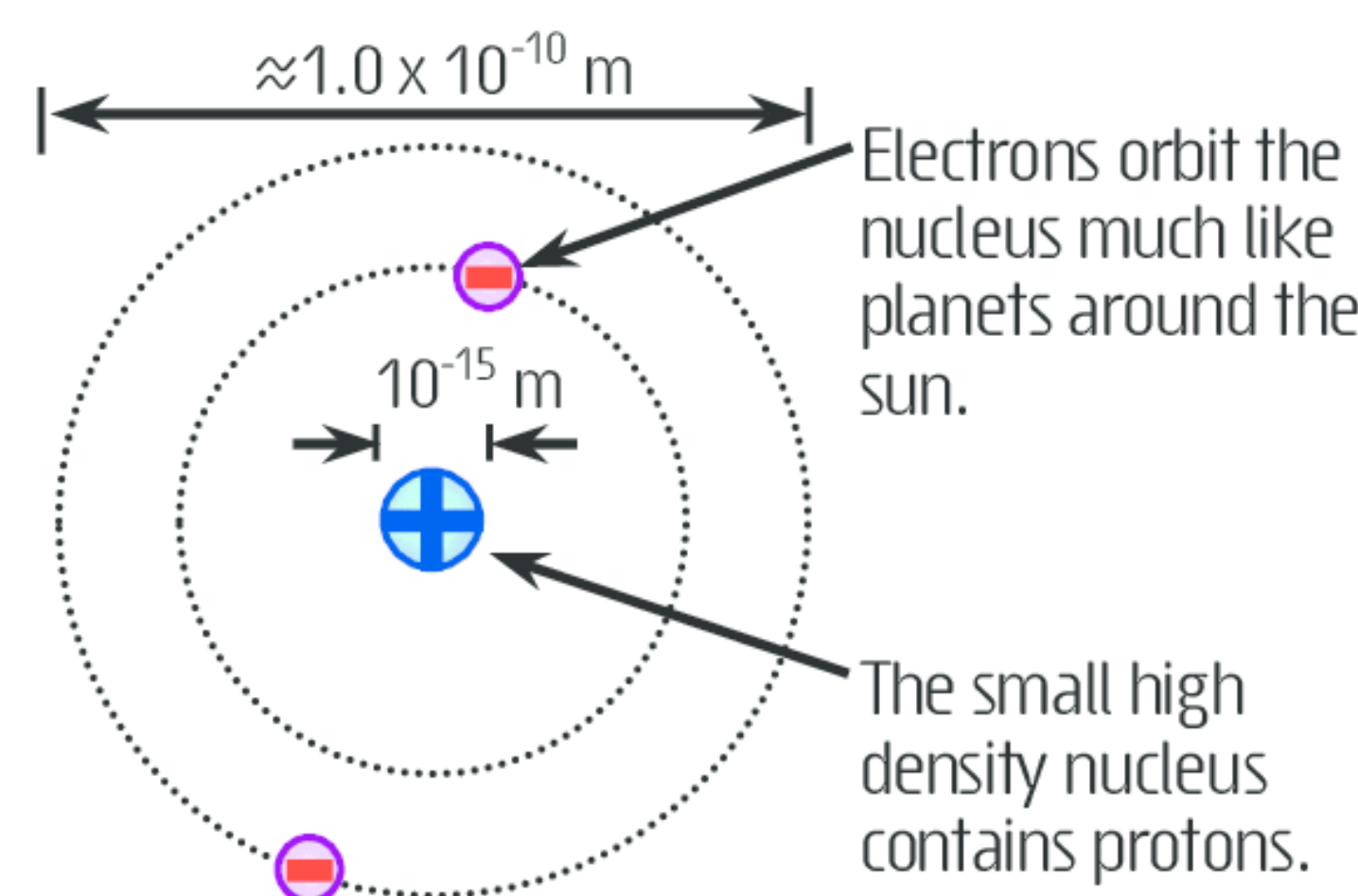


Attempt Set 3 # 6.





**FIGURE 10** In Rutherford's **planetary** (or nuclear) model of the atom over 99.9% of the mass and all of the positive charge is located in a very small central region of the atom. Small negatively charged electrons orbit the nucleus.



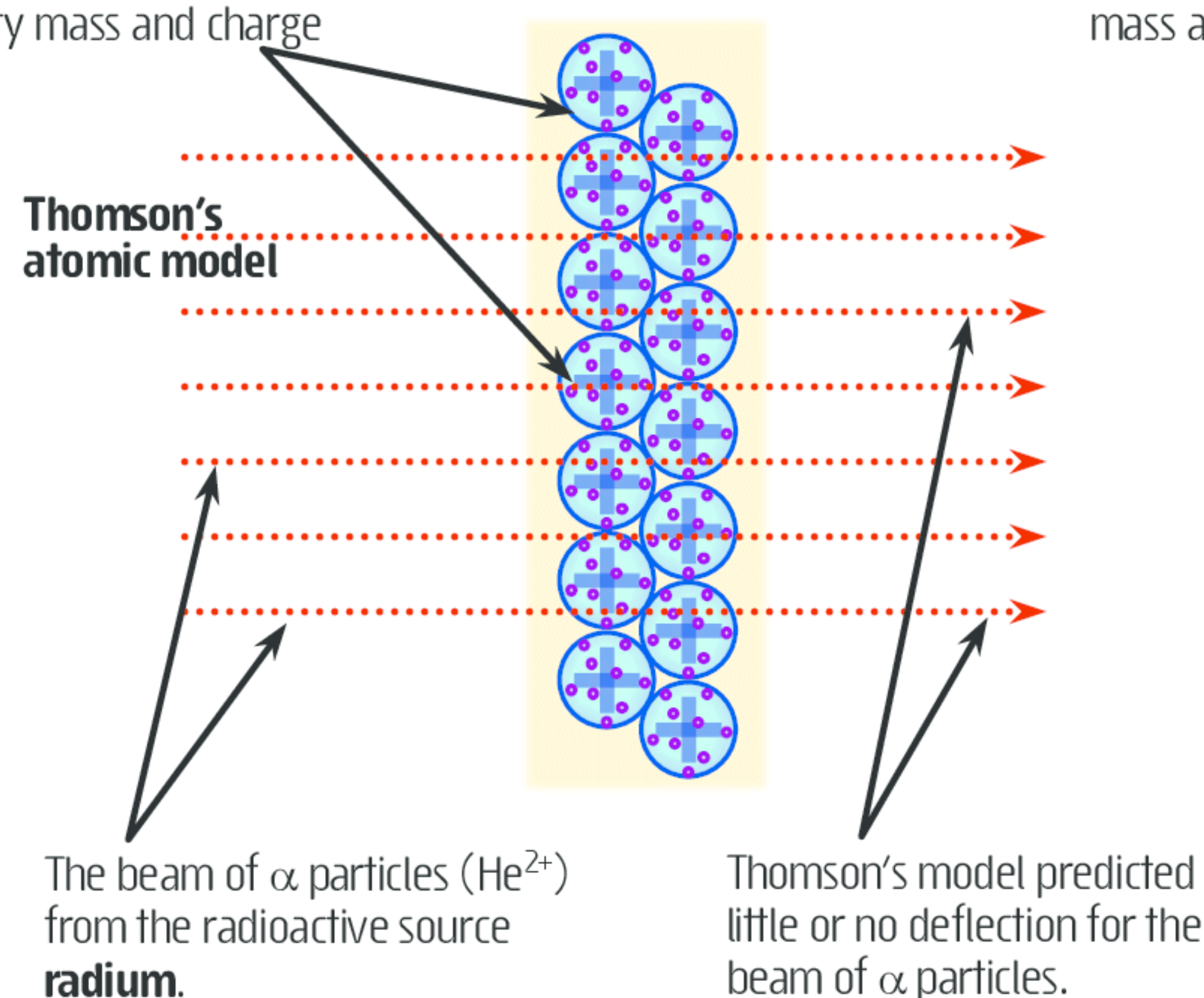
Rutherford and his co-workers did observe that almost all of the alpha particles passed straight through the gold foil unaffected. However, a very small number of alpha particles were **deflected quite significantly**, some ( $\approx 1$  in 20,000 of them) even turned back in their original direction. In Rutherford's own words this was ... "as if you fired a 15-inch ( $\approx 38$  cm) shell into a piece of tissue paper and it came back and hit you". Thomson's atomic model, with mass and charge distributed fairly evenly within the atom, could not account for the heavily deflected alpha particles. In 1911 Rutherford proposed an improved model for the atom that would account for these experimental observations. (See Fig 10.)

He proposed the atom consisted mostly of empty space occupied only by the very low mass negatively charged particles called electrons. The electrons orbited a tiny central region he called the nucleus. In Rutherford's model almost all of the atom's mass and all of its positive charge are located in the nucleus with the positive charge being carried by protons. This model explained why most of the alpha particles in Rutherford's gold foil experiment passed through the gold foil undeflected. (See Fig 11.) The undeflected alpha particles had simply passed through the relatively empty region of the atom, the region occupied only by the very low mass particles called electrons. The very few alpha particles that passed close to or directly toward the tiny but dense and positively charged gold nuclei would show significant deflection or even be deflected backwards.

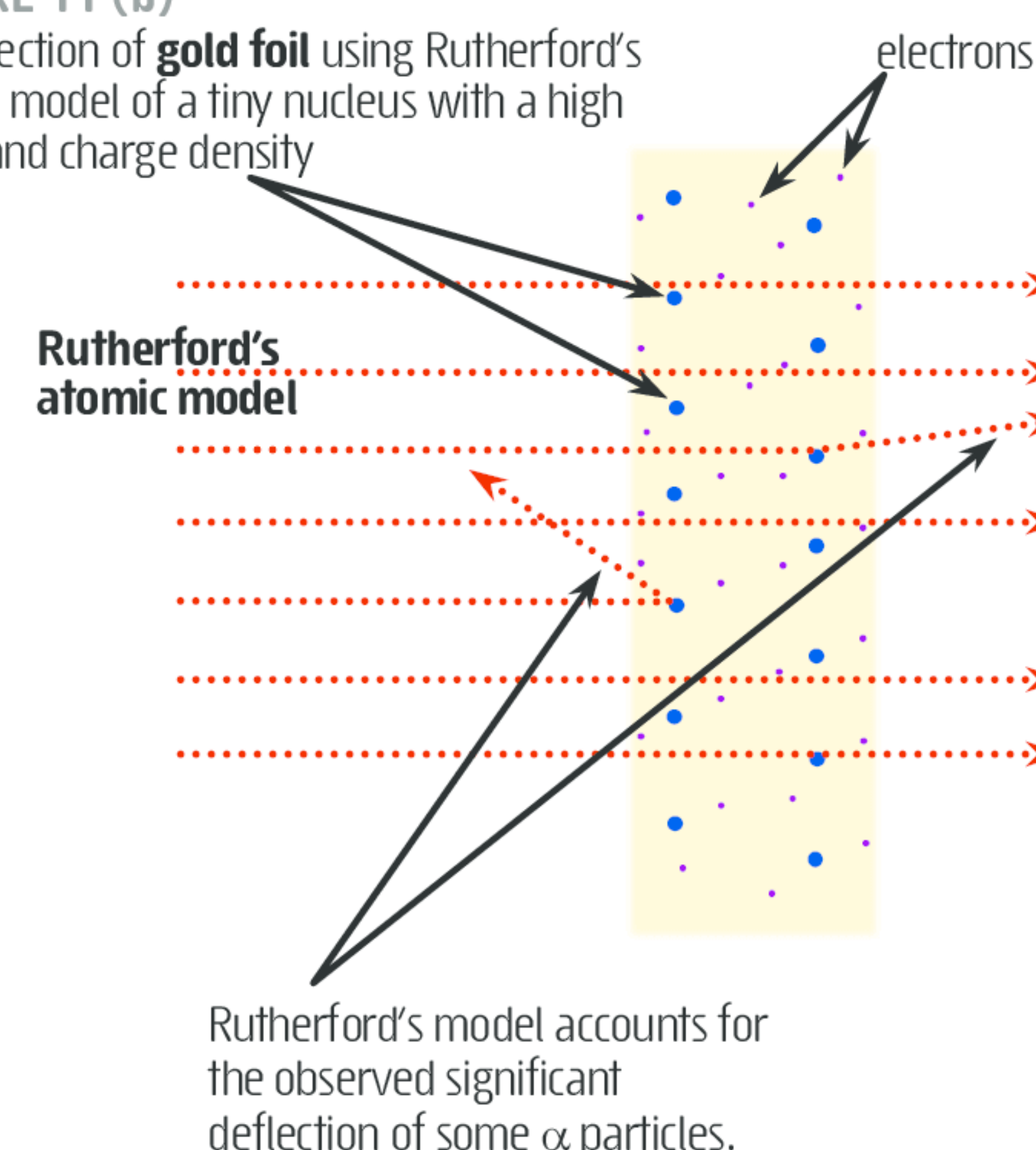
**FIGURE 11** Based on J.J.Thomson's model of the atom Rutherford predicted the alpha particles should pass through the gold foil undeflected or at most show a slight deflection. See **Fig 11 (a)**.

Rutherford's experimental observations did not match these predictions. With this in mind he proposed a **nuclear** model of the atom as a way to account for the strong deflection and rebounding of some of the alpha particles. See **Fig 11 (b)**.

**FIGURE 11 (a)** cross section of **gold foil** using Thomson's atoms of uniform low density mass and charge



**FIGURE 11 (b)** cross section of **gold foil** using Rutherford's atomic model of a tiny nucleus with a high mass and charge density



Attempt Set 3 # 7.

## 2.7 Chadwick's discovery of the neutron

Rutherford's model was consistent with the current experimental observations (1911) and gave a good account of the charge and mass distribution within the atom. The model, however, could not account for all of the atom's mass. Experimental data by Hans Geiger and Ernest Marsden on the extent and frequency of alpha particle deflection showed the number of protons in the nucleus equalled half the atom's relative mass. At best this meant the protons could only account for half of the atom's overall mass. Some other neutral particle must be present in the nucleus. A search for this particle proved difficult as detection methods at the time involved using electric or magnetic fields to deflect particles followed by their detection. The charge and mass of a particle could be inferred from the direction and extent of its deflection. These techniques worked on charged particles but were no use on neutral particles.

The search for the chargeless particle, the neutron, finally ended at the University of Cambridge Cavendish Laboratories in 1932 when **Sir James Chadwick** (1891-1974), a previous student and collaborator of Rutherford, identified neutrons as a product of the alpha particle bombardment of the metal Beryllium. For this pivotal discovery he was awarded the Hughes Medal of the Royal Society in 1932 and later the Nobel Prize for Physics in 1935.

Attempt Set 3 # 8.



## 2.8 Bohr's contribution

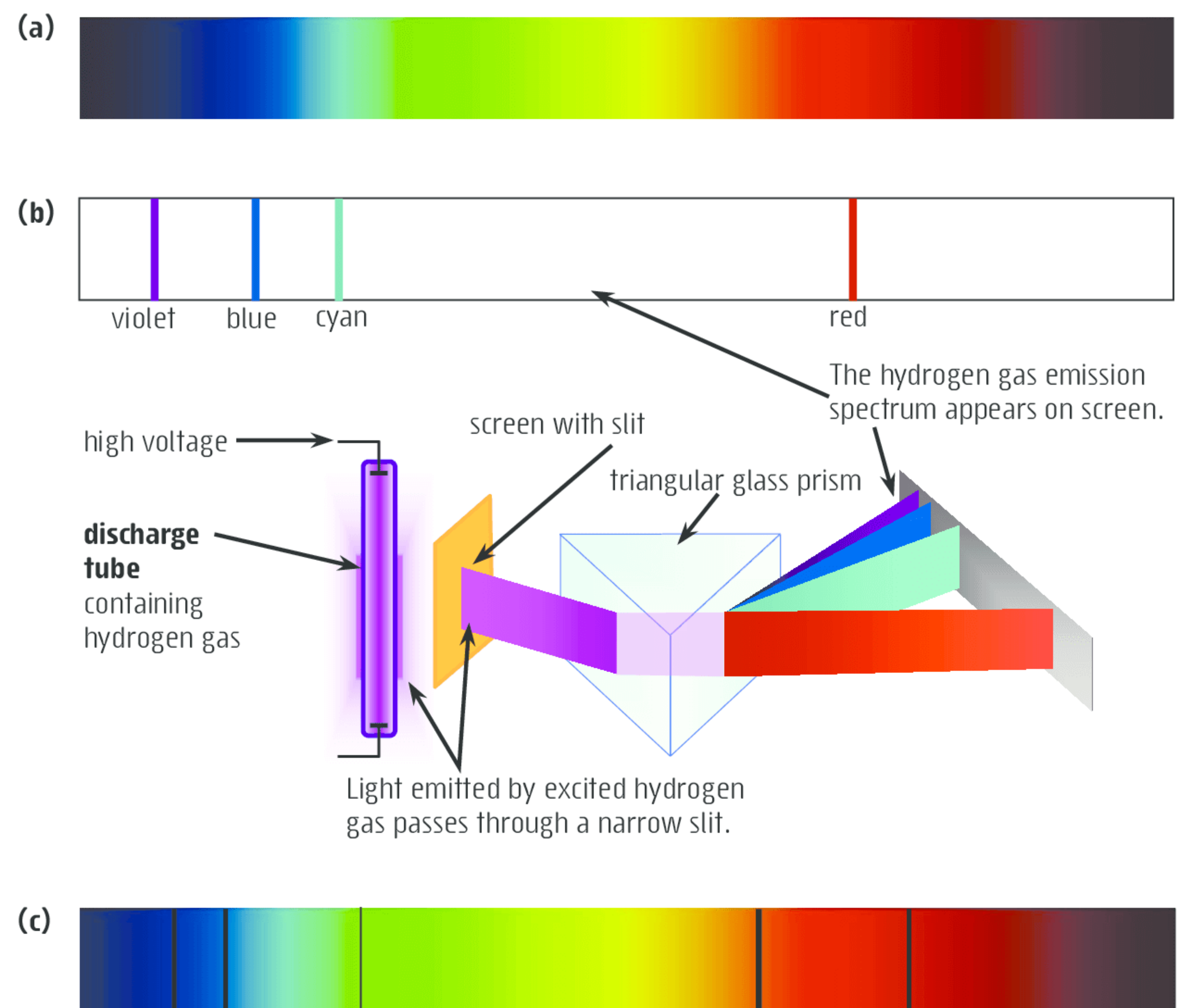
Rutherford's model of the atom had introduced the concept of a very small but dense nucleus with a large positive charge due to the protons it contained. Later, Chadwick experimentally identified neutrons as the particles with no charge that contributed around half the atom's mass. A remaining limitation of Rutherford's atomic model was its inability to provide an explanation for the then well known phenomenon of **emission spectra**, also known as **line spectra**. (See Fig 12b.) These spectra are produced by electrically excited low pressure gases and vaporised elements.

FIGURE 12

(a) The **continuous spectrum** shown at right is formed by a very hot object like the filament of an incandescent globe. This is much like the spectrum seen when a rainbow forms.

(b) The gas **discharge tube** shown here is filled with **hydrogen** gas. When a high voltage is applied to the electrodes, the gas produces a characteristic **line spectrum** (**emission spectrum**) that is unique for the gas in the tube. The atomic line spectrum of hydrogen gas, shown here, contains four distinct lines in the visible part of the electromagnetic spectrum.

(c) The **absorption spectrum** at right occurs when light consisting of a continuous spectrum, as in (a) above, passes through a gas of atomised **cadmium**. The dark lines, ie absence of light, occur as cadmium atoms absorb these specific wavelengths of light. The absorbed wavelengths match those in the element's emission spectrum.



Furthermore, Rutherford's idea of electrons orbiting the nucleus was problematic. Such orbiting electrons would, according to classical physics principles, continuously emit radiation causing the electron to lose energy and speed then presumably spiral into the nucleus. Atoms based on the Rutherford model appeared to be inherently unstable!

In 1913 the Danish physicist **Niels Bohr** applied concepts from the newly developing field of **quantum theory** to propose a modified version of Rutherford's nuclear atom. Bohr's model solved the problem of the unstable electron orbits while precisely accounting for the line spectrum of hydrogen gas. His model proposed that electrons moved about the central nucleus in circular orbits, as was first proposed by Rutherford, but that only certain orbit radii are allowed. He also postulated that the electron in each orbit had a specific amount (quanta, see Fig 13) of energy with the lowest orbital radii corresponding to the lowest possible energy. (See Fig 14.) Contrary to classical physics principles he proposed the electron could orbit without losing energy.

Bohr hypothesised a single light photon would be emitted from an excited atom when one of its electrons fell from a higher energy orbit ( $E_{\text{upper}}$ ) to a lower energy one ( $E_{\text{lower}}$ ). (See Fig 14.) The energy of the emitted photon ( $E_{\text{photon}}$ ) would equal the difference in energy of the two orbits. The frequency (and wavelength) of the emitted photon depends upon its energy ( $E_{\text{photon}} = hf$  where  $h = 6.626 \times 10^{-34}$  and  $f$  = frequency).

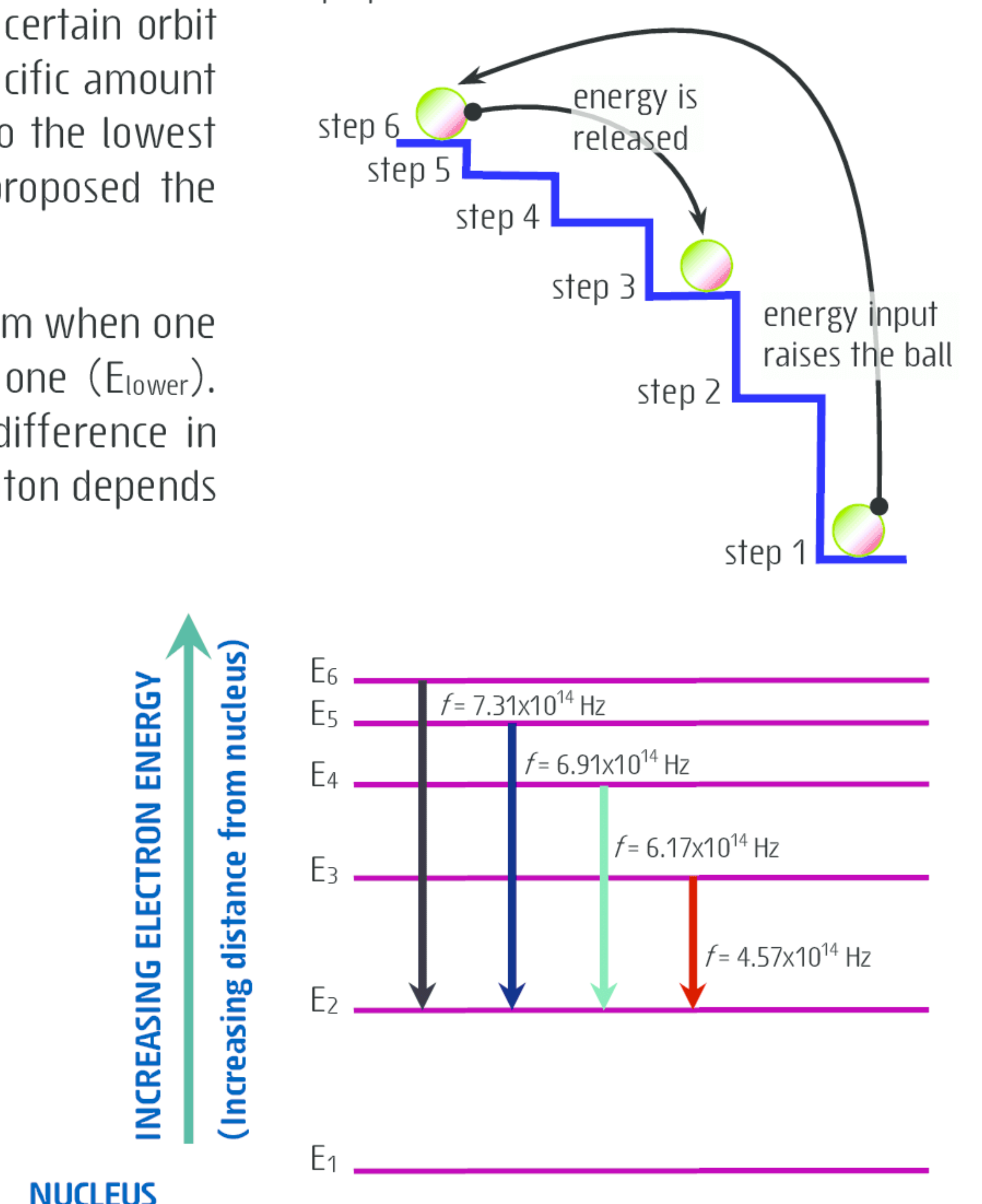
FIGURE 14 The simplified sketch at right shows some of the electron **energy levels** ( $E_1$  to  $E_6$ ) of the **hydrogen atom** as visualised by Bohr. The **electron transitions** shown here correspond to the formation of the visible part of the hydrogen emission spectrum shown in Fig 12(b).

These **emission lines** may occur once the single electron in a hydrogen atom has been excited from its ground state ( $E_1$ ), eg by electrical discharge, [Fig 12(b)], to a higher energy level like  $E_2$ ,  $E_3$ ,  $E_4$  and so on. In this example the excited electron then falls to the lower energy level  $E_2$  and releases energy in the form of a **visible light photon** where,  $E_{\text{photon}} = E_3 - E_2$  and so on. The wavelength and associated colour of the emitted light depends upon its energy, ie  $E_{\text{photon}}$ .

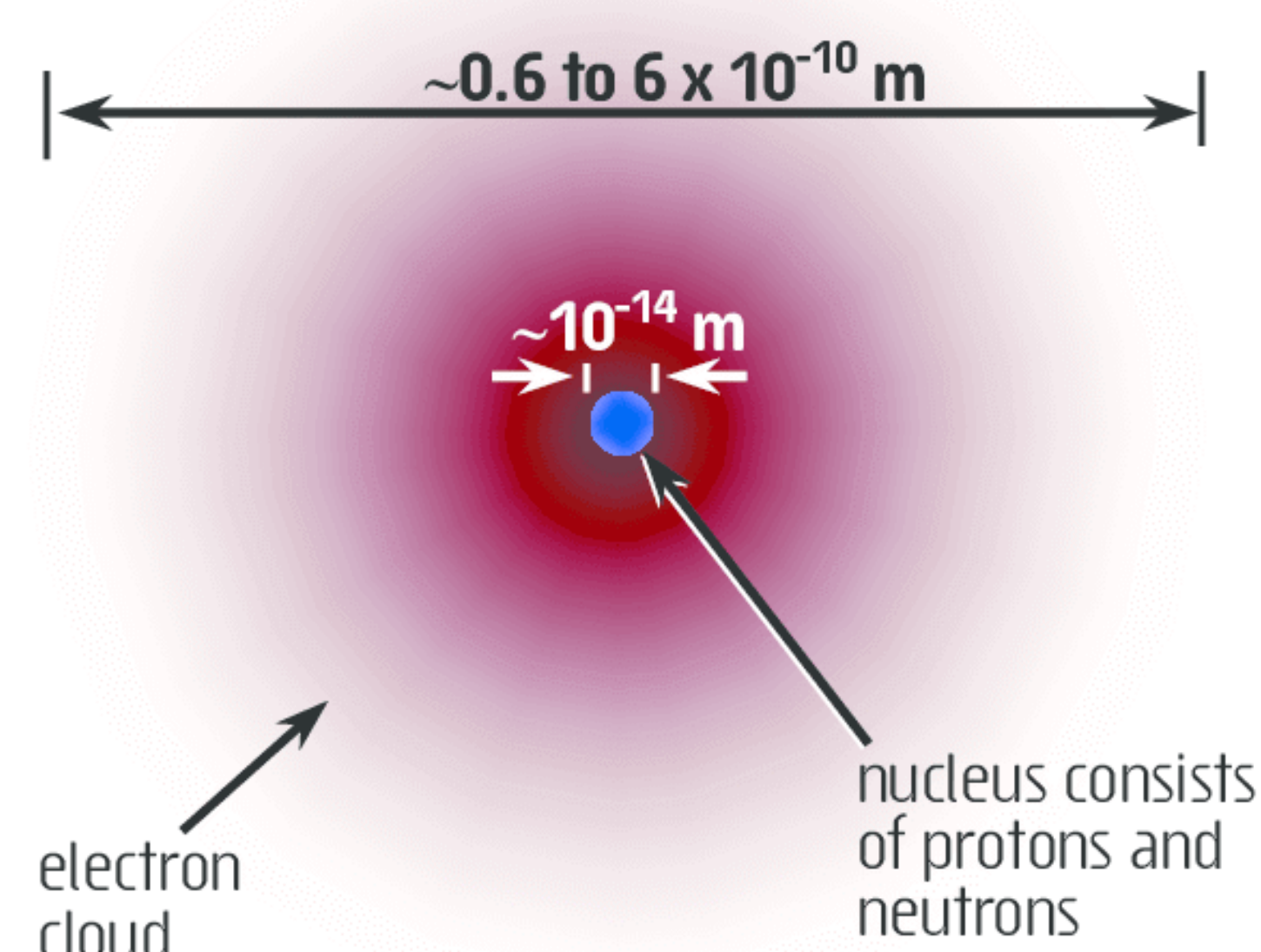
It must be noted that visible light is only produced by hydrogen if the electron falls to  $E_2$ . Ultimately the electron will emit more radiant energy when it returns to the lowest energy level, the ground state,  $E_1$ . This, however, will not be in the form of visible light.

FIGURE 13 Bohr's **quantum model** is **analogous** to a ball sitting on a **staircase**. The ball can fall from a higher step to a lower one or it can be raised up to a higher step but it won't rest in between steps. In either case the energy lost or gained by the ball is exactly the difference in potential energy of the two steps.

In this analogy the individual steps are like the electron quantum levels or radii Bohr proposed for electrons in an atom.







**FIGURE 15** The **current** atomic model has a central nucleus of protons and neutrons. The electrons, however, do not orbit the nucleus as in Bohr's model but instead move within regions of characteristic electron distribution and energy called orbitals. The lowest energy orbital for the hydrogen atom has a spherical probability distribution, much like that shown above, with the **average** electron-nucleus distance of  $5.29 \times 10^{-11} \text{ m}$ .

Although the nucleus contains all of the positive charge and over 99.95% of the atom's mass it only represents a tiny fraction of its total volume. This gives the nucleus a very high charge and mass density. The low mass and negatively charged electrons occupy the electron cloud region which comprises over 99.99999999% of the atom's total volume but almost none of its mass.

Bohr was able to determine, by a mix of quantum theory and classical mathematics, the energy associated with each of the electron energy levels of the hydrogen atom. This enabled Bohr to theoretically calculate the wavelengths of light that should be present in the line (emission) spectrum of hydrogen. (See Fig 12(b) and 14.) His results showed an excellent agreement with the experimentally measured wavelengths of light seen in hydrogen's line spectrum.

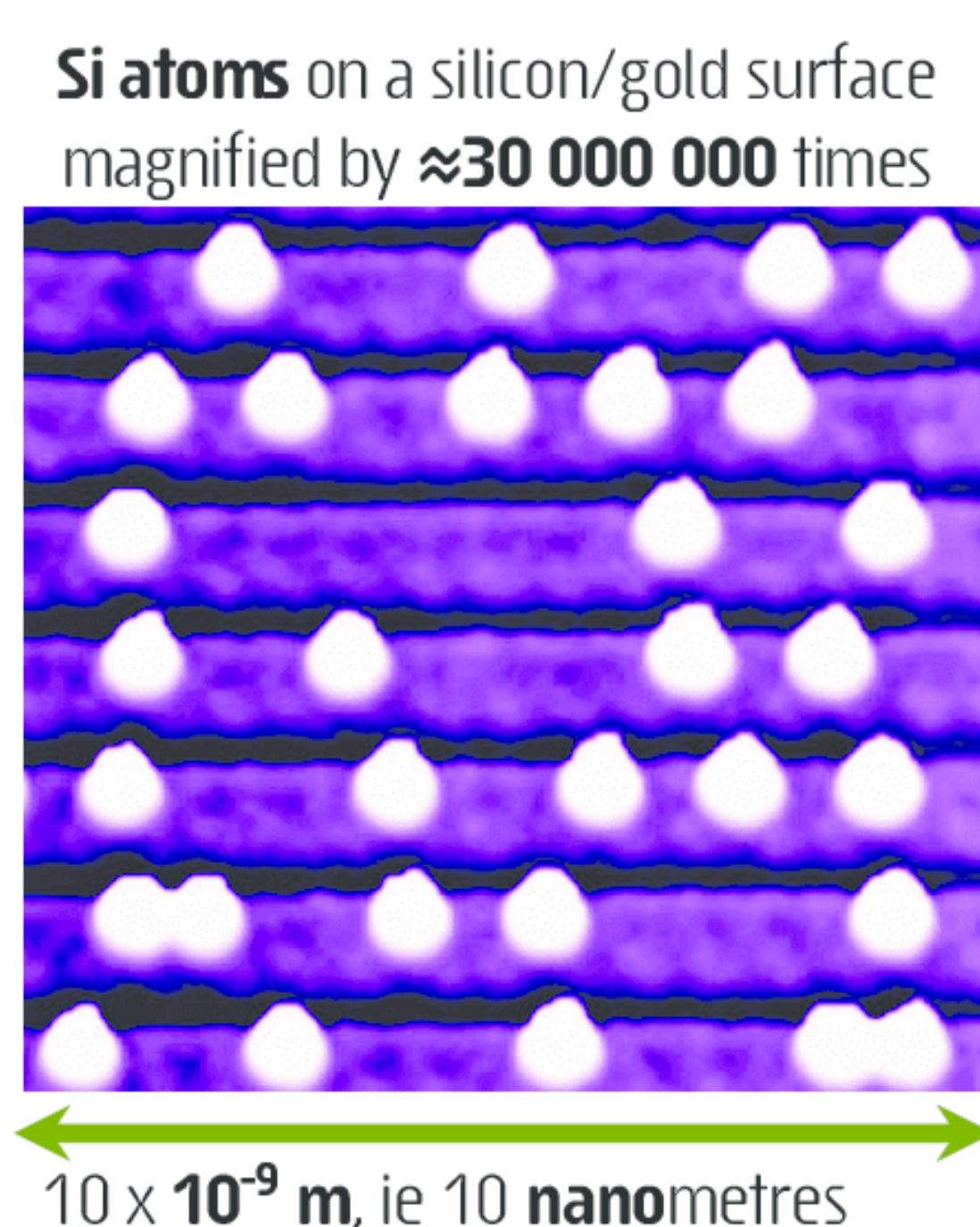
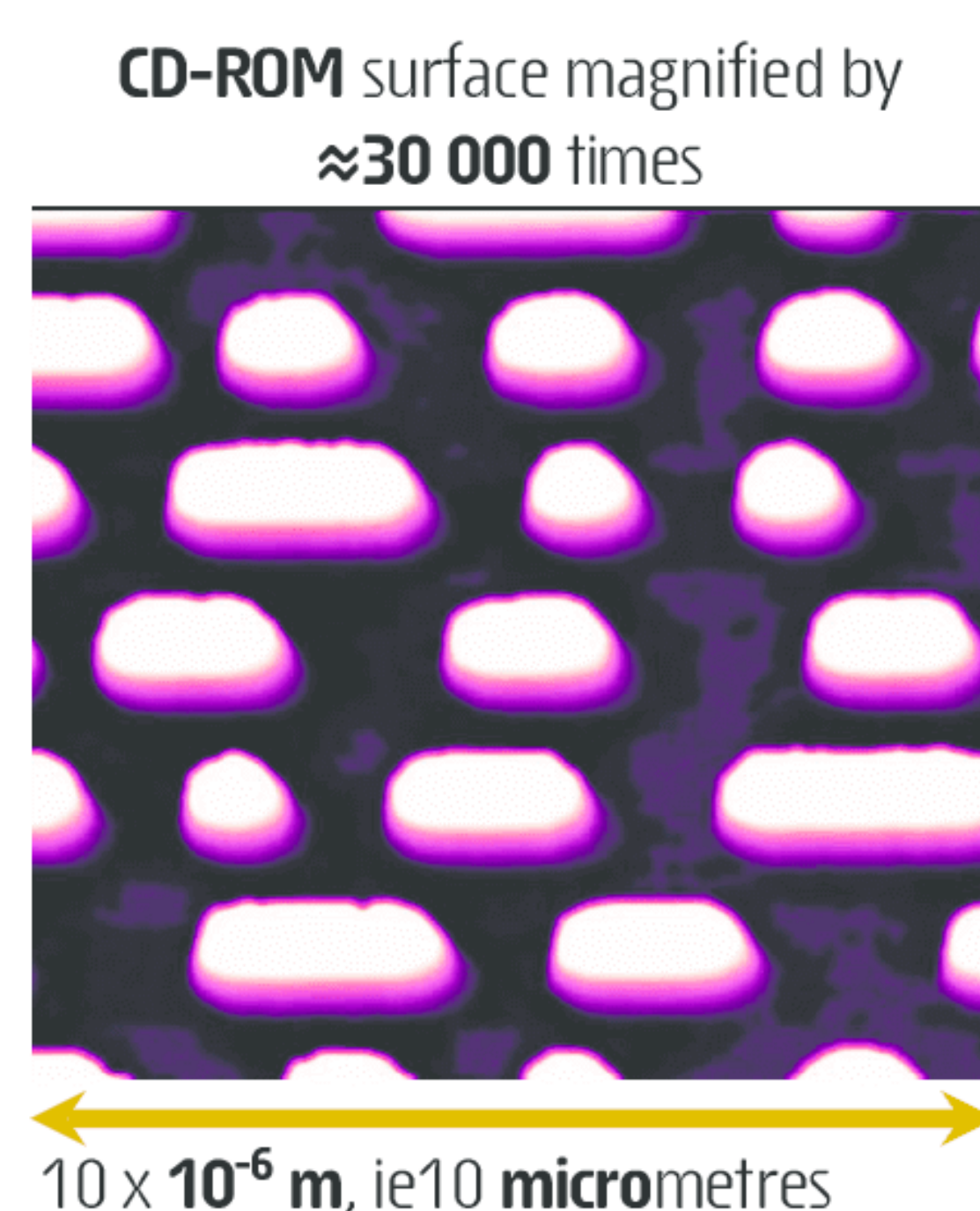
## 2.9 The current atomic model

The great success of the Bohr model was its ability to explain the experimental observations of **line spectra** and accurately predict the wavelengths of light in the line spectrum of hydrogen. The Bohr model also explained the formation of **absorption spectra**. Bohr's model allowed photons of just the right energy (ie wavelength) to excite an electron from a lower energy level to a higher one. In the process these specific wavelengths of light having the exact energy that matched the electrons transition to a higher energy orbit, could be absorbed. Wavelengths of light not exactly matching the energy difference for the electron transition were not affected. This model gave a good explanation for the observation of absorption spectra as seen in Fig 12c and Fig 19.

The Bohr model also states that the electron's orbit of smallest radius corresponds to its lowest energy level. This he called its **ground state**. In this way Bohr established the stability of the atom, ie the electron won't fall into the nucleus as this is not a lower energy state.

There were problems with the Bohr model however, as it gave no reason why the energy of electron orbits should be quantised and no reason for atomic stability, ie why the ground state orbit was the lowest energy state for the electron. Furthermore, while it accurately predicted the wavelengths of light in the emission spectrum of hydrogen and other single electron species such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  and so on, it was not able to do so for atoms or ions that had two or more electrons. Some of these problems would be solved in the early 1920s when Louis de Broglie proposed that particles of matter like electrons can be considered to have both a wave nature as well as a particle nature. This wave nature of electrons gave a basis for their discrete (quantised) orbits or energy states. Two years after de Broglie, Erwin Schrödinger and Werner Heisenberg independently developed a new comprehensive quantum mechanical theory of the electronic structure of the atom. This new theory was a more satisfactory explanation of the atom's quantum nature and is used today to account for the electron structure of the atom.

We are now at a point in our technological development where through the use of devices such as the scanning tunnelling electron microscope (STEM or STM, see p67) and the atomic force microscope (AFM) we are able to image and manipulate individual atoms. (See Fig 16.) Further research into the nature of the nucleus has revealed numerous subatomic particles exist and that protons and neutrons themselves consist of smaller particles called **quarks**.



**FIGURE 16** Comparing **micro** and **nano** data storage.

The magnified image at left shows the arrangement of micrometre sized pits on a CD-ROM surface. The arrangement of these pits is used to store digital information. At right is an image produced by a **scanning tunnelling microscope** (STM) of individual **silicon atoms** (white) arranged on a silicon-gold lattice (purple). Researchers are hoping to use such arrangements of individual atoms to store data much like the pits on a CD-ROM surface. Such data, ie the placement of individual atoms, can be written and read using an STM/AFM. (See p67-68.)

This research was conducted at the Universities of Basel, Switzerland and Madison, Wisconsin, USA.

As can be seen, our understanding of the nature of the atom and the development of the atomic theory was initially a slow process. Our written records show it had its beginnings with the ideas of various Greek philosophers who argued whether matter was continuous or particulate. It still continues today as many teams of researchers around the world probe into the nature of the subatomic particles. Along the way many individuals have been recognised for their various contributions but seldom do these researchers work in isolation. Their success has been built on the **collective endeavours of many**, their preparedness to **communicate** new findings and ideas and apply the **scientific method** in the search for an understanding of our world that matches our **experimental observations** of it.



## 2.10 Spectral analysis: Identifying atoms from spectra

While the pattern of quantised energy levels as first proposed by Bohr are exactly the same for all elements, the actual energy of each level is different for different elements. As a result, the energy absorbed or released in the electron transitions of a given element are unique for that element and hence its resulting line spectrum is also unique. (See Fig 17.) For this reason an element's **line spectrum**, also known as its **emission spectrum**, is like an **atomic fingerprint** that can be used to identify it.

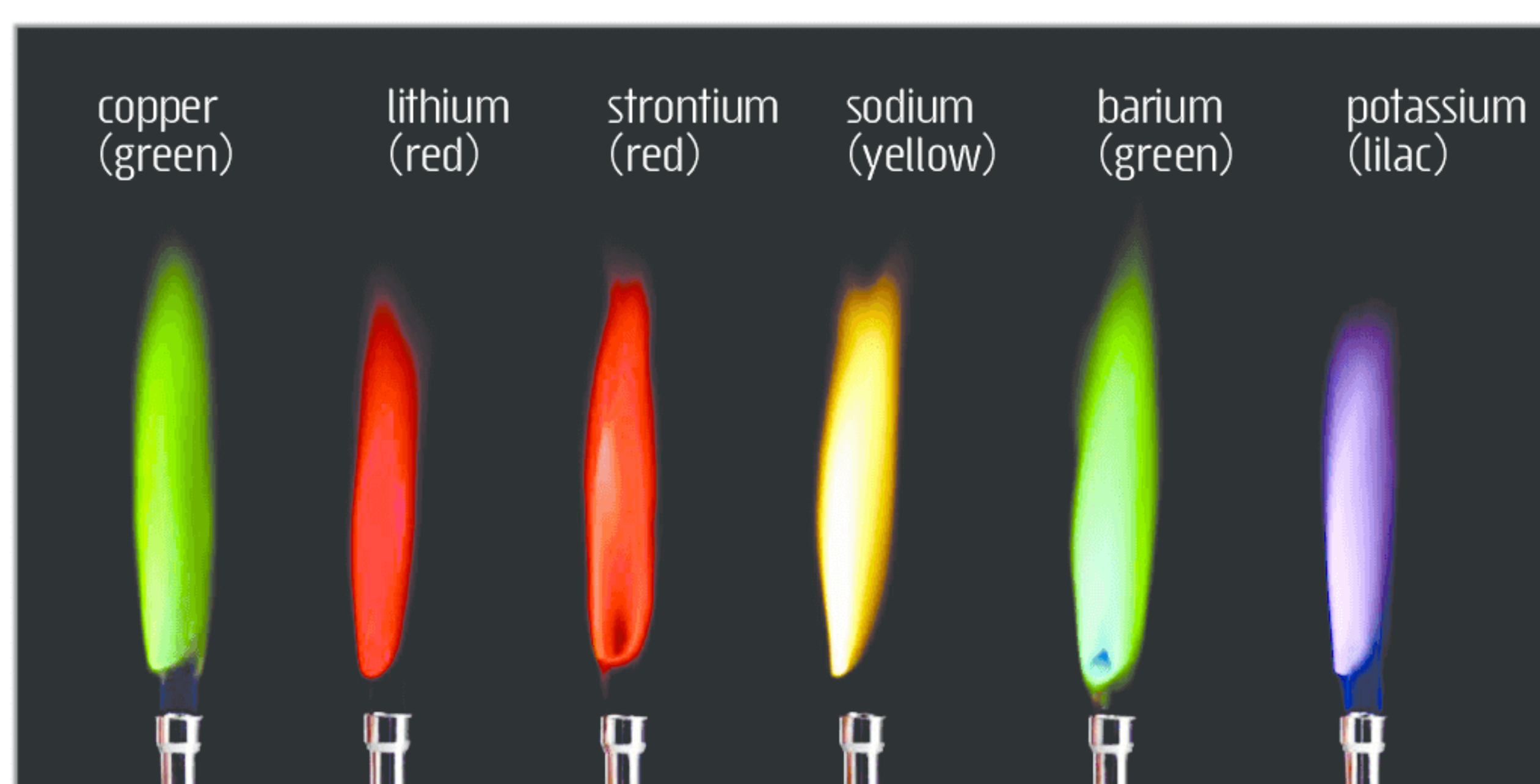
▪ **Flame test:** This analytical technique relies on the unique nature of an element's **emission spectrum** to identify its presence in a mixture or compound. The test involves placing a small sample of the unknown, usually a salt, into a hot, almost colourless Bunsen flame. A thoroughly cleaned (using hydrochloric acid and distilled water) platinum wire loop is often used for this purpose. The clean wire loop is dipped into a solution or paste of the salt. When placed into the Bunsen flame the heat of the flame excites electrons in the vaporised metal ions of the salt. When these excited electrons return to their ground state they emit light of specific wavelengths thus producing characteristic colours. The resulting **flame colour** (Fig 18b) indicates the metal element present in the salt. Some elements may be difficult to distinguish this way as they produce very similar looking flame colours. However, by viewing the flame through a **spectroscope** it is possible to see the details of the emission spectrum (Fig 17) and make a precise judgement of the element(s) present.

**FIGURE 18 (a) Fireworks over Perth water**

The brilliant display of colour seen here is largely due to the **emission spectra** produced by various metal ions present in the pyrotechnic mixture. Adding strontium salts for example produces a red colour while barium salts give the fireworks a green colour.

**FIGURE 18 (b) Flame tests**

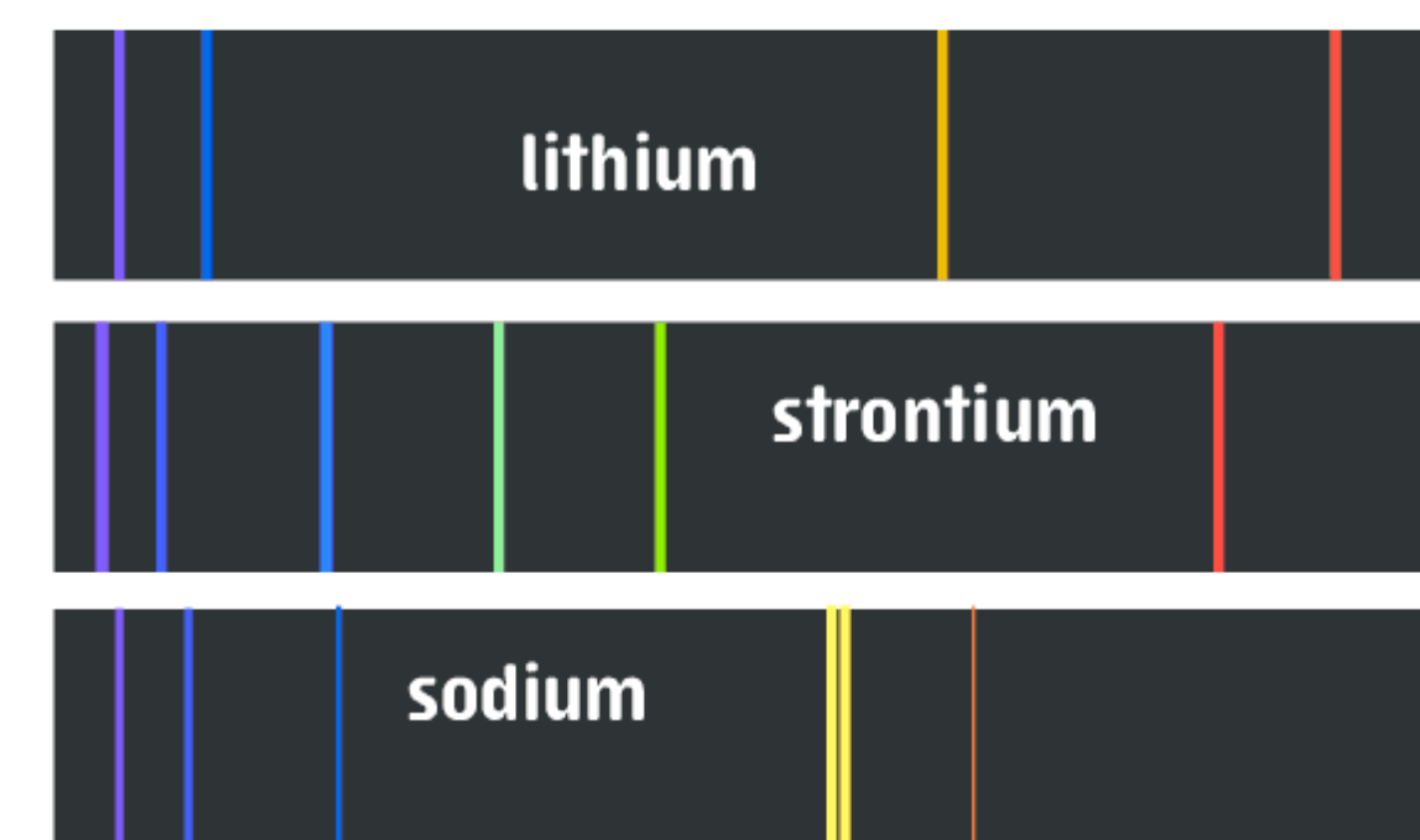
A clean platinum wire loop is used to introduce a salt solution or paste into a hot, non-luminous Bunsen flame. The heat of the flame vaporises the salt and excites electrons in the vaporised metal ions. When these excited electrons return to their ground state they emit light of specific wavelengths and produce characteristic flame colours. These colours can be used to identify the metal element present in an unknown salt.



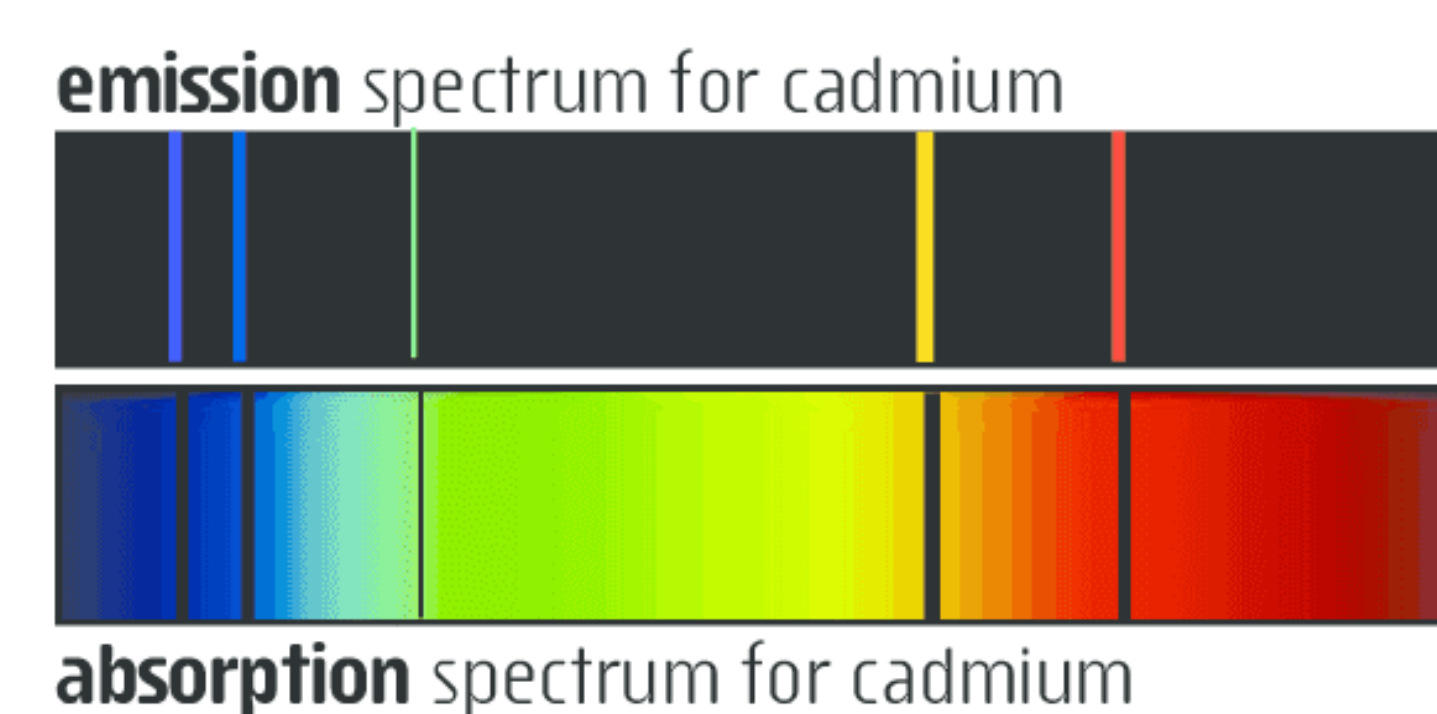
▪ **Atomic absorption spectroscopy (AAS):** This analytical technique relies on the unique nature of an element's **absorption spectrum** to identify its **presence** and **concentration** in a mixture. The technique was pioneered by an Australian, **Sir Alan Walsh** (1916–1998) and his team of co-workers in the early 1950s while working at the CSIRO. AAS is now used worldwide to routinely analyse around 70 different metal elements with concentrations as low as **1 ppb** (parts per billion).

AAS is a **highly selective** technique able to analyse the chosen element even though high concentrations of similar elements are also present in the mixture. It is ideal for analysing the concentration of toxic heavy metals or other metal ions in water samples such as from bore water, streams, lakes or drinking water. Biological tissue or fluids can be analysed for various metals such as mercury concentration in seafood or lead in blood. In the mining industry, AAS is an important technique for finding the concentration of many metals like gold, silver and copper in mineral samples.

**FIGURE 17** The **emission spectrum** for an element can be viewed with a **spectroscope**. Some of the major lines in the visible emission spectrum of lithium, strontium and sodium are shown here.



**FIGURE 19** The wavelengths of light emitted by an excited gaseous atom will depend upon the **unique energies** of its quantum levels. For this reason an element's **emission spectrum** is unique to that element. Also, the wavelengths of light a gaseous atom can **absorb** usually match the ones its excited gaseous atoms can **emit**. This is seen in the emission and absorption spectra shown below. **AAS** relies on this effect.



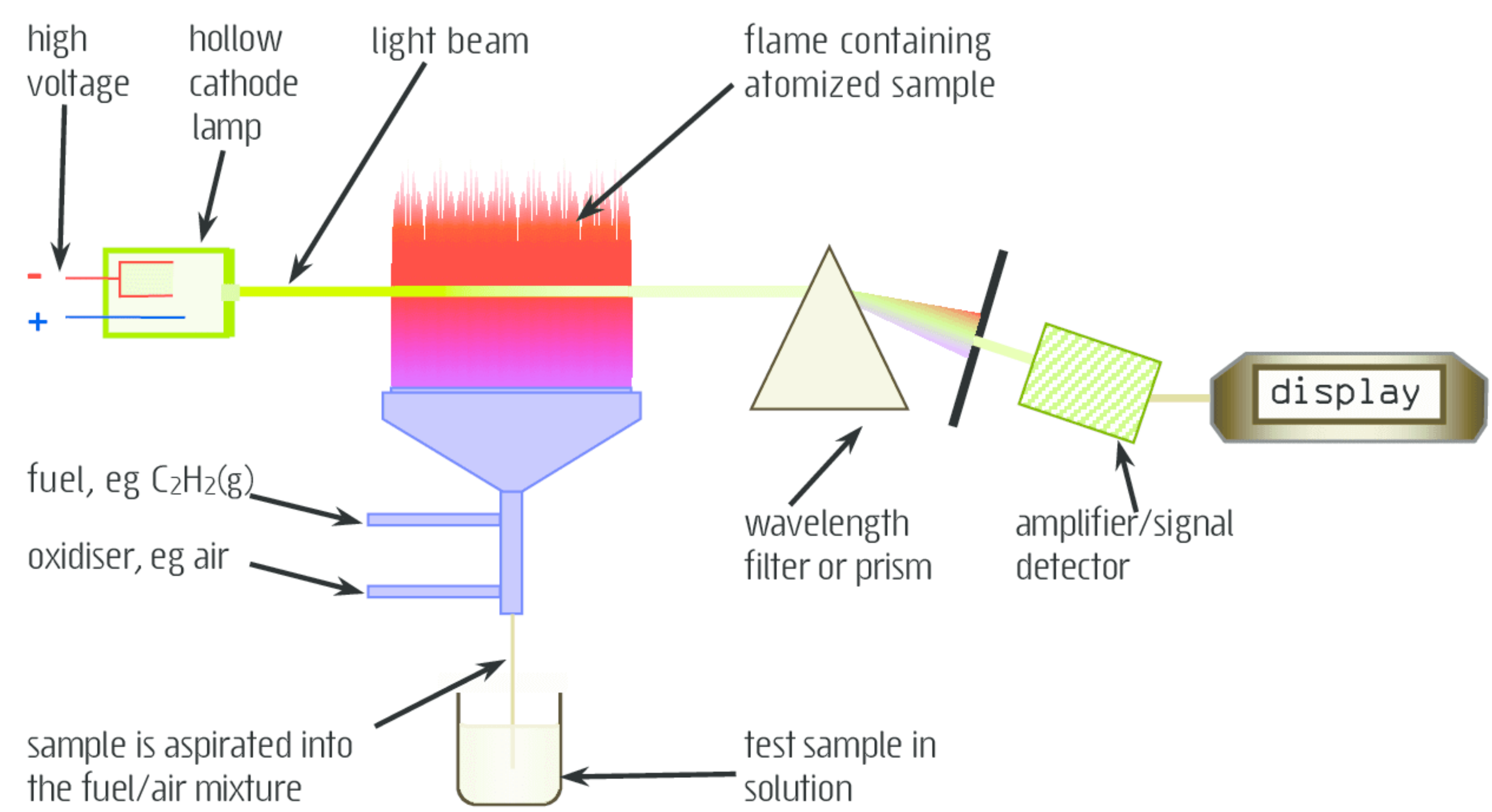


The atomic absorption spectrometer (Fig 20) operates on the principle that an element in the gaseous state can absorb only certain specific wavelengths (energy) of light, called its **absorption spectrum**. (See Fig 12c and 19.) Every element has its own characteristic absorption spectrum where the absorbed frequencies match many of the frequencies found in its emission spectrum. To analyse for a specific element using AAS a solution of the sample must first be atomised in a suitably hot flame. A beam of light of just the right wavelength(s) is then passed through the flame containing the atomised sample. By measuring the degree of light **absorption**, called **absorbance**, the concentration of the particular target metal in the sample can be found.

**FIGURE 20 Atomic absorption spectrometer** schematic. In this example of the AAS, a **hollow cathode lamp** is used as the light source. The metal of the cathode is chosen to match the target metal being analysed from the test solution. In this way the light it produces is of the precise wavelengths that can be absorbed by the target metal atoms alone.

The test sample is aspirated (sucked up) into the gas/air stream supplying the flame of the AAS. This suitably hot flame ensures the sample is decomposed and **atomised**. Any metal atoms originally present in the test sample are now present as free atoms in the flame. In this form the target metal atoms freely **absorb light** from the light beam directed through it.

A wavelength filter selects a desired wavelength of light from the exiting beam and the amplifier/signal detector determines the extent to which it has been absorbed, called the **absorbance**. Absorbance is proportional to the concentration of the target metal atoms present in the flame. It is used, along with a **calibration curve**, to determine the metals concentration in the test solution. (See Fig 21.)

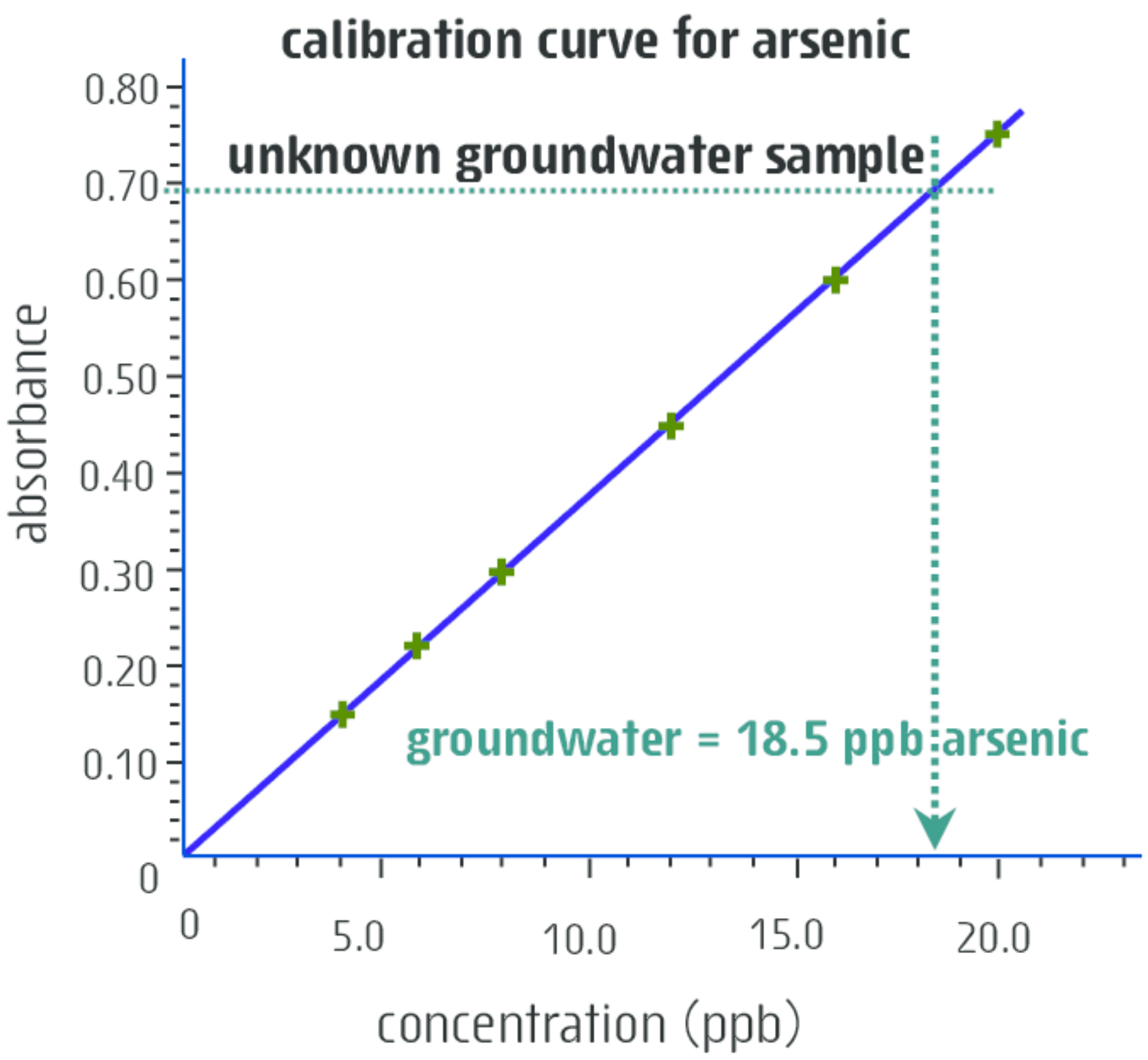


In order to determine the target metal concentration in the unknown test sample a **calibration curve** is required for that element. The calibration curve is generated by measuring the absorbance of a set of solutions of known concentration. (See Fig 21.)

**FIGURE 21** Groundwater supplies are sometimes found to be contaminated with naturally occurring arsenic. Water like this may be unsuitable for drinking. In Australia the NHMRC guideline for arsenic in drinking water recommends a threshold of 0.01 mg L<sup>-1</sup>, ie 10 ppb. AAS can be used to monitor the concentration of arsenic in such situations. To do this a **calibration curve** must be prepared by analysing a set of **standard solutions** of known arsenic concentration and graphing the absorbance of these solutions against concentration. The concentration of arsenic in the test sample is then determined by referring to its absorbance and the calibration curve. The following data in Table 1 was obtained and used to prepare the calibration curve at right. This is then used to determine the concentration of arsenic in a groundwater sample of unknown arsenic concentration.

**TABLE 1 Absorbance** data for the standard solutions and the **unknown** groundwater sample

arsenic concentration (ppb)	20.0	16.0	12.0	8.0	6.0	4.0	<b>groundwater</b>
absorbance	0.750	0.600	0.450	0.300	0.225	0.150	<b>0.695</b>



Complete Set 3.

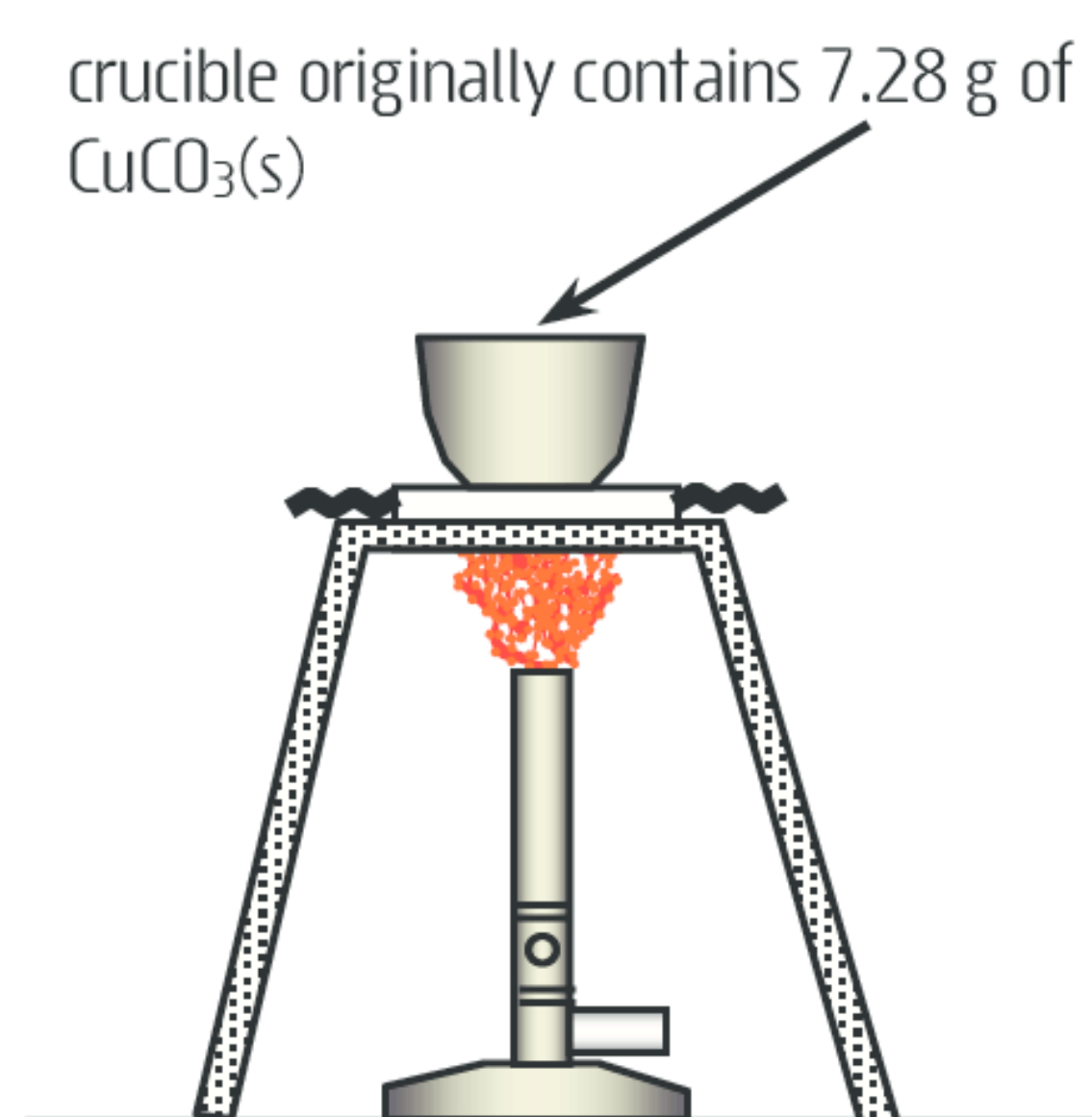
### Set 3 Discovering the atom’s structure

could  
could not  
philosophies  
beliefs  
Plato  
Democritus  
Aristotle  
nothing

1. Use the list of terms given to correctly **complete** the following passage. **(E)**
- Early Greek philosophers like (a) \_\_\_\_\_ and (b) \_\_\_\_\_ taught that matter was continuous, meaning it (c) \_\_\_\_\_ be divided endlessly into ever smaller pieces. The first known written record that talks of matter being composed of atoms is attributed to (d) \_\_\_\_\_. Leucippus and Democritus believed matter consisted of tiny particles that (e) \_\_\_\_\_ be divided into smaller pieces and that (f) \_\_\_\_\_ occupied the space between the particles of matter. These early ideas about the structure of matter were based on (g) \_\_\_\_\_ or (h) \_\_\_\_\_ rather than experimental observations.



2. The French chemist **Antoine-Laurent Lavoisier** (1743-1794) is credited with discovering the law of conservation of mass. Essentially this law states that there is no change in mass during a chemical reaction. Answer the following questions about this law.
  - a. **Complete** the following sentence which is a restatement of the law of conservation of mass. In a chemical reaction the total mass of the products formed equals \_\_\_\_\_.
  - b. In what way was the **development and proposal** of Lavoisier's law of conservation of mass **different** to Democritus, proposing that matter consisted of indivisible particles called 'atomos'.
  - c. A student carefully weighs a 1.84 g strip of magnesium ribbon,  $\text{Mg(s)}$  and burns this in air to produce 3.05 g of white powder. It appears as though there is 1.21 g more mass after the reaction than before. **Account** for the increase in mass during the chemical change.
  - d. In an experiment, 7.28 g of  $\text{CuCO}_3\text{(s)}$  is added to a crucible as shown in Fig 22. After heating, the remaining black powder has a mass of 4.37 g. **Apply** the law of **conservation of mass** to determine the mass of carbon dioxide produced.
  
3. The idea of compounds having a constant composition was not new before it had been proposed by Proust. **Why** was the 'law of constant composition' accredited to Proust?
  
4. A 3.42 g sample of magnesium was burnt in air and found to combine with 2.25 g of oxygen. Answer the following questions **without** referring to moles or stoichiometry.
  - a. How much **magnesium oxide** was formed? (Assuming it's the only product.)
  - b. What **law** did you use to answer part (a)?
  - c. How much **magnesium** would react with a 10.0 g of oxygen?
  - b. What **law** did you use to answer part (c)?
  
5. John Dalton (1766-1844) is accredited with having proposed the original atomic theory of matter. He proposed for example, "All atoms of a given element are identical having the same size, mass and chemical properties." How has our view of this point changed? **Explain**.
  
6. The invention of the cathode ray tube (**CRT**) in the mid nineteenth century ultimately resulted in J.J.Thomson's discovery of the electron. Answer the following questions about the CRT.
  - a. How are cathode rays detected in a **CRT**? ie Describe **two** ways their presence can be observed.
  - b. What **observations** led Thomson and others to conclude that cathode rays must have a negative charge?
  - c. Thomson's modified CRT (see Fig 5c) used a narrow beam of cathode rays. Very **briefly describe** how he was able to produce a beam of cathode rays.
  - d. In Thomson's modified CRT (see Fig 5c) how did he '**see**' the cathode rays?
  - e. What was Thomson able to determine about cathode rays with his modified CRT?
  
7. Ernest Rutherford and his co-workers carried out a series of experiments in which a beam of alpha particles were targeted at a very thin sheet of gold foil only a few atoms thick. (See Fig 8 p15.) The following questions refer to this experiment.
  - a. What are **alpha particles** and where did Rutherford get them?
  - b. What **physical property** of gold allowed it to be made so **thin**?
  - c. If Thomson's model of the atom was correct, what did Rutherford and his co-workers expect to observe? **Explain**.
  - d. How were the deflected alpha particles **counted** in these experiments?
  - e. Why was Rutherford and his team so surprised with their **observations**? What did Rutherford interpret this to mean about the **structure** of the atom?



**FIGURE 22** As the crucible with  $\text{CuCO}_3\text{(s)}$  is strongly heated its contents decompose leaving behind only  $\text{CuO(s)}$ . The other product,  $\text{CO}_2\text{(g)}$  escapes from the crucible.



8. Rutherford's model of the atom worked quite well as it was able to explain many of the observed properties of matter. However Rutherford and his co-workers were aware of several shortfalls. In particular it appeared his model could only account for about half the mass of the atom. **What** type of **particle** did Rutherford suggest was missing? **Why** was it so hard to detect it and **who** is credited with its discovery?
  
9. **Niels Bohr** made some important modifications to the Rutherford model of the atom. His modifications enabled the stability of the atom to be accounted for as well as explain line spectra (emission spectra). The following questions are about these aspects of the atomic model.
  - a. **Explain** why the Rutherford model meant the atom was **inherently unstable**.
  - b. What did Bohr propose about the **arrangement** and **energy** of the electrons in an atom that solved the problem of its instability?
  - c. Another limitation of the Rutherford atomic model was its inability to predict or explain the **spectra** produced when a high voltage was applied to a low pressure gas in a discharge tube. What simple **instrument** can be used to observe the various colours (spectrum) produced by a discharge tube?
  - d. **Describe** the visible part of the emission spectrum of hydrogen gas.
  - e. Using the Bohr model of the atom **explain** how a gas like hydrogen can produce a **line spectrum** (emission spectrum) that has only a few specific wavelengths of light.
  
10. A simple laboratory test called a **flame test** can be used to differentiate between salts like barium chloride, sodium chloride and strontium chloride. Consider the following.
  - a. **Describe** a method you could use to perform a flame test on these salts.
  - b. What **colour** flame would you expect for each of the salts?
  - c. **Explain** the formation of the characteristic flame colours that can be seen when metal salts are placed into a hot flame?
  
11. Why is it important to prepare the solutions of the different salts in **distilled water** rather than tap water? What might happen if tap water was used instead of distilled water?
  
12. **Sodium** is an essential element in our diets, however, excess amounts can cause health issues. Processed foods often contain significant amounts of sodium and for this reason they often carry consumer information about their salt content. A food manufacturer needs to determine the sodium content of a new brand of breakfast cereal. To do this a sample of the cereal was weighed, crushed, and brought into solution, making it up to 500.0 mL in a volumetric flask.

**Atomic absorption spectroscopy** was then used to determine its sodium content. To do this several standard solutions of known NaCl concentration were prepared. The absorbance of the standard solutions and that from the cereal solution were measured using AAS. The results are shown here:

concentration of Na <sup>+</sup> (aq) mg L <sup>-1</sup>	320	640	800	960	1150	unknown cereal solution
absorbance	0.163	0.320	0.398	0.477	0.573	0.515

- a. Construct a **calibration curve** for this data and use this to determine the **concentration** of sodium in the solution prepared from the breakfast cereal.
- b. In the AAS technique the cereal solution is aspirated into a hot flame. What is the **role** of the **flame** in the atomic absorption process?
- c. This technique is **highly specific** for the element in question, ie sodium. Even though the cereal solution may contain very similar ions like potassium or lithium they will not interfere with the measurement of the sodium ion concentration. **Account** for the ability of AAS to be so **metal specific**.



# CHAPTER 3 | IT'S A MIXED UP WORLD OF MATTER



**FIGURE 1** The alloy **bronze**, used in this statue is an homogeneous mixture of **copper** and **tin**. Use of bronze is believed to date to at least the 4th millennium B.C. It was one of the most important materials used by early civilisations. Much **harder** than pure copper or stone, it was used for tools, weapons, decorative plaques and statues. The **melting point** of bronze, like that of all mixtures, is not fixed or well defined but depends upon several factors including the % composition of the bronze. (See table.)

copper %Cu	tin %Sn	melting point of bronze (°C)
100	0	1085
90	10	945
70	30	720
30	70	530
0	100	232

This bronze statue of John Harvard (above) can be found outside the University Hall offices of the Dean of Harvard. It is visited by tourists and aspiring students from all over the world. They rub his shoe for good luck.

Attempt Set 4 # 1, 2, 3 and 4.

## 3.1 Properties of mixtures and pure substances

Almost all of the materials we encounter in our everyday lives are examples of **mixtures** of at least two or more pure substances. The air we breathe, the food we eat, the construction materials around us like glass, brick, steel and wood and even the ocean we swim in are examples of mixtures. While we rarely encounter **pure substances** some familiar examples include distilled water,  $\text{H}_2\text{O}(\text{l})$  that is used for example in a steam iron, table salt,  $\text{NaCl}(\text{s})$  for cooking or gold,  $\text{Au}(\text{s})$  and diamonds,  $\text{C}(\text{s})$  used in jewellery.

Chemists define a pure substance as one having a fixed or constant composition and not being able to be separated into other substances by physical means such as filtration or distillation. Pure substances can be distinguished from mixtures by observing their physical or chemical properties. A pure substance will always have a well defined and **constant boiling point** and **melting point**. If you tested a clear liquid and found that it froze at  $0\text{ }^{\circ}\text{C}$  and boiled at  $100\text{ }^{\circ}\text{C}$  you could be confident (though not certain) the substance was pure water,  $\text{H}_2\text{O}(\text{l})$ . By comparison, sea water, a mixture of water and various soluble salts will boil at some temperature above  $100\text{ }^{\circ}\text{C}$ , and freeze at some temperature below  $0\text{ }^{\circ}\text{C}$ . (See Fig 10 p4.) The actual temperature at which sea water starts to boil or freeze depends upon the amount of each of the salts present in the sea water. Thus samples of sea water from different marine environments do not have the same boiling point or freezing point.

Similarly the **density** (see p41) of a pure substance is fixed, while that of a mixture will vary. At standard laboratory conditions pure water has a density of  $1.0\text{ g mL}^{-1}$  whereas the density of sea water may be as high as  $1.24\text{ g mL}^{-1}$ ; as in sea water from the 'Dead Sea'. These and other physical properties like **hardness**, **electrical conductivity** and even **colour** can be used to distinguish a pure substance from a mixture. In each case a sample of a pure substance always has a constant and well defined set of physical properties irrespective of where the sample originated from. In mixtures, such properties vary and depend upon the actual percentage composition of its components. (See Fig 1.)

As with physical properties, the **chemical properties** of a pure substance are also well defined and constant irrespective of their source. Pure iron,  $\text{Fe}(\text{s})$  for example, has a tendency to slowly corrode when exposed to water and oxygen to form a new substance called rust. Mixtures of iron with other metals like chromium and nickel, called alloys, show varying tendencies to corrode. Some like stainless steel show almost no tendency to rust.

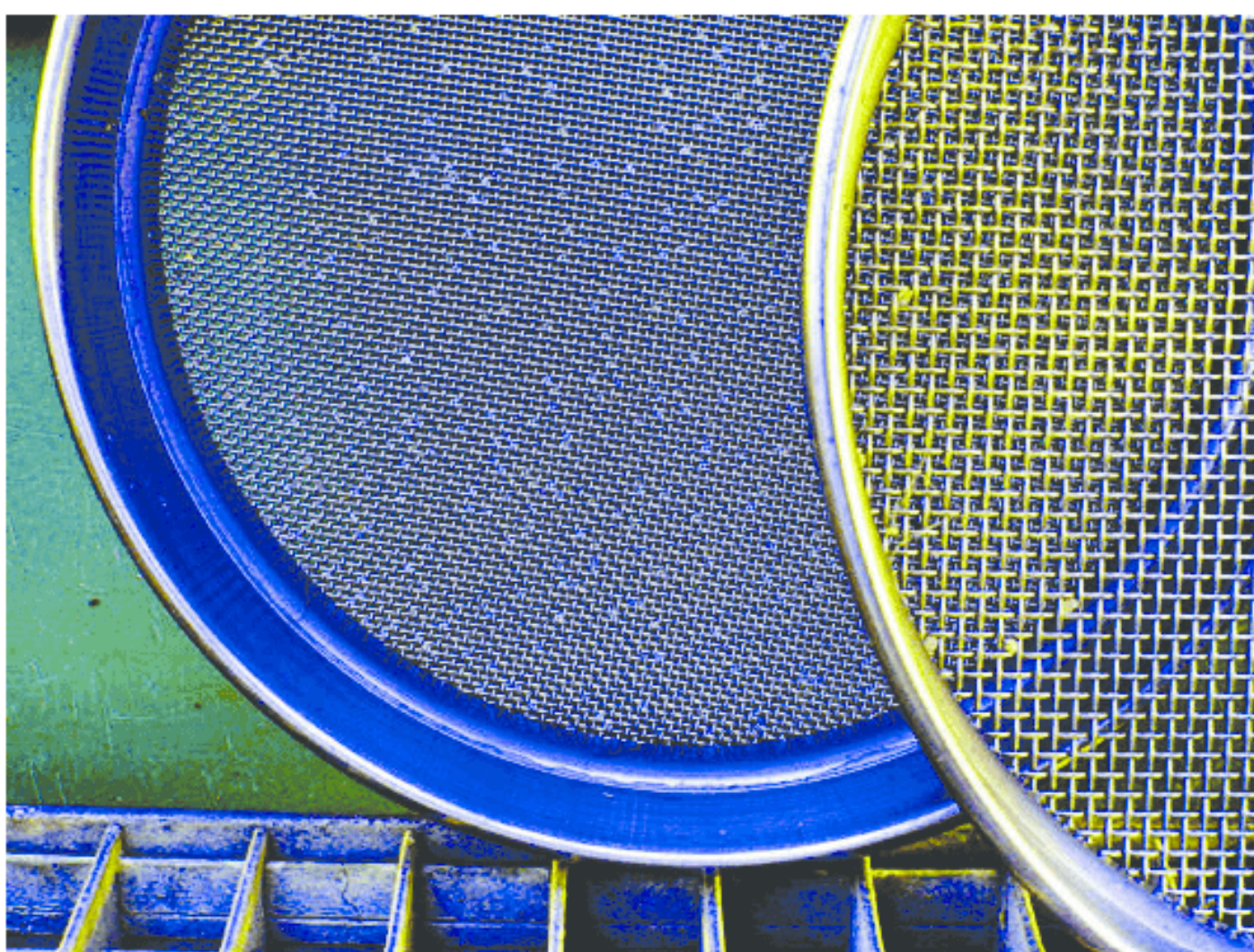
## 3.2 Mixture separation using physical properties

One of the great endeavours of scientists, and chemists in particular, has been to learn about and understand the nature and properties of matter. This however, is extremely difficult to achieve when studying matter in the form of mixtures, as mixtures don't have a fixed composition and their properties vary with their composition. Our progress in understanding the properties of matter has relied greatly upon our ability to extract and isolate individual pure substances from the naturally occurring mixtures around us.

While the overall properties of a mixture are influenced by all of its constituents, the individual pure substances making up a mixture always retain their own unique physical properties. This feature of a mixture allows substances whose properties are significantly different to others in the mixture to be separated from the mixture. Thus if any pure substance in a mixture has a significantly different **solubility**, **density**, **boiling point** or even **particle size** compared to the other components then it may be able to be separated from the mixture by physical means.

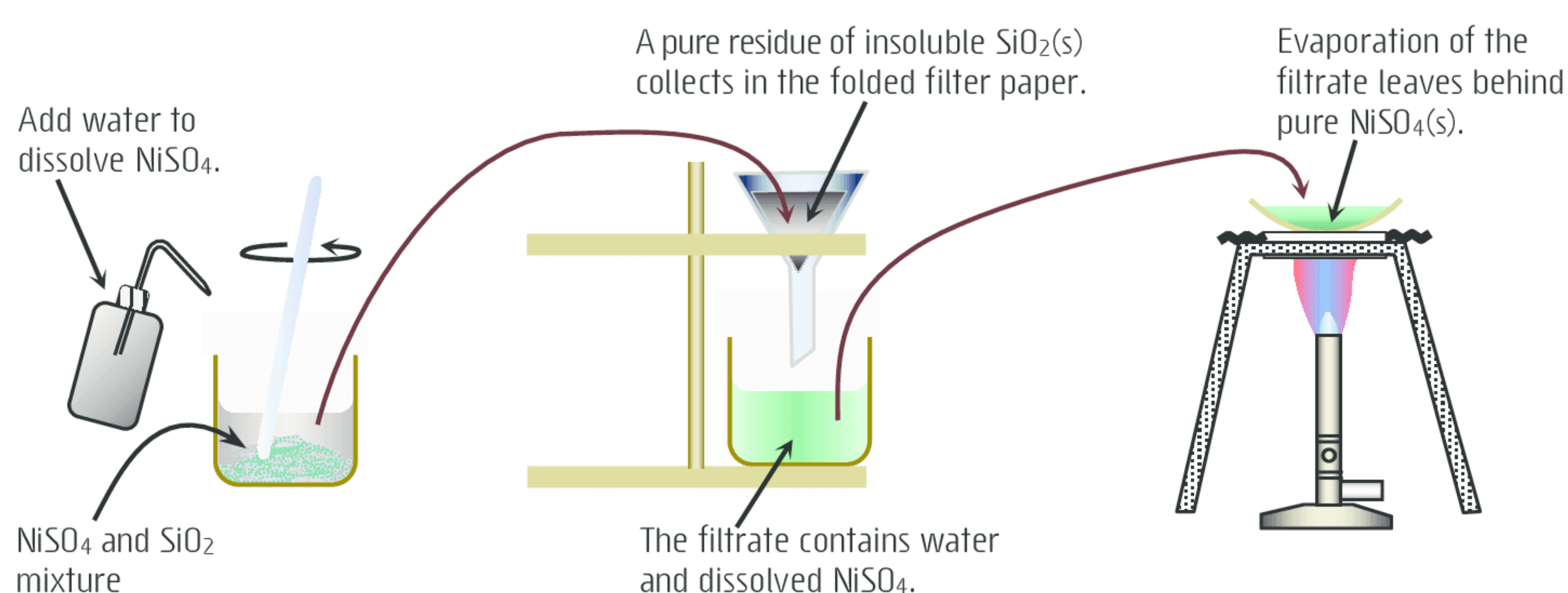
- **Sieving:** Can be used to separate the components of a mixture based on **particle size**. The mixture is passed through a sieve of suitable mesh size (hole size) that allows the smaller particles to pass through while leaving coarser grains behind. Sand used for making concrete is often screened by sieving to remove rubble and ensure the sand grains are of a suitable size. Although sieving is unlikely to produce pure substances from a mixture it can concentrate a desired component. (See Fig 2.)

**FIGURE 2** Metal sieves like these are often used in laboratories for separating crushed mineral samples according to particle size.





▪ **Filtration and evaporation:** These techniques can be used to separate the substances in a mixture based on their differing solubility and volatility. (See Fig 3.)



**FIGURE 3 Filtration and evaporation**  
A mixture of NiSO<sub>4</sub> (soluble) and powdered quartz granules, SiO<sub>2</sub>(s) (insoluble) can be separated using **filtration** and **evaporation**.

Adding distilled water to this mixture dissolves only the soluble component, ie NiSO<sub>4</sub>(s). The insoluble, undissolved solid, SiO<sub>2</sub> can be separated by passing the mixture through a folded **filter paper** placed inside a **filter funnel**. Insoluble SiO<sub>2</sub> collects in the filter paper while the solution of NiSO<sub>4</sub>, the **filtrate**, passes through tiny pores in the filter paper and collects in a beaker below the filter funnel.

**Evaporation** of water (volatile) from the filtrate yields pure NiSO<sub>4</sub>(s) crystals.

In the mixture from Fig 3, nickel sulfate, NiSO<sub>4</sub>(s) can be separated from the powdered quartz granules, SiO<sub>2</sub>(s) as NiSO<sub>4</sub>(s) is soluble in water while SiO<sub>2</sub>(s) is not. Adding water to this mixture dissolves only NiSO<sub>4</sub>(s) leaving SiO<sub>2</sub>(s) as an undissolved residue. The resulting NiSO<sub>4</sub>(aq) solution is then **filtered** to separate it from the undissolved SiO<sub>2</sub>(s). Pure NiSO<sub>4</sub>(s) is then separated from the filtrate by **evaporation**. (See Fig 3.) Evaporation is useful for separating **non-volatile** substances (ones that don't evaporate), in this case NiSO<sub>4</sub>(s), from **volatile** ones (do evaporate) in this case water.

The process of filtration can be seen as a form of **sieving**. Ions and molecular sized particles in solution pass through the filter paper pores, typically 2-25  $\mu\text{m}$  in size. (See border note.) Larger solid particles can't and are retained in the folded filter paper as a residue. Other forms of filtration such as **microfiltration**, **ultrafiltration** and **nanofiltration** use membranes with pore sizes as small as  $1 \times 10^{-10}$  m to filter fine particles, microorganisms and even molecules or ions from solution.

Microfiltration membranes, for example, are sometimes used in remote locations for the treatment of drinking water. These membranes have pore sizes of 100 to 1000 nanometres (see border note) which are sufficiently small to filter very fine muddy particles from water as well as a variety of microorganisms such as protozoa and bacteria. Smaller particles like viruses, molecules or salt ions are able to pass through these membranes. Ultrafiltration and nanofiltration (pore size 0.5-5 nm) can be used to filter progressively smaller particles like viruses, molecules and some of the ions that may be present in water. Reverse osmosis is the ultimate in membrane filtration (0.1-1 nm pore size) and is used to produce pure water from sea water and other brackish or polluted water sources. (See 16.10 p146-147.)

▪ **Gravity separation:** Is suitable for separating (or concentrating) components in a mixture based on their **densities**. This is especially effective when the components in the mixture have significantly different densities, eg for separating gold particles (density  $19.3 \text{ g mL}^{-1}$ ) from within quartz rock (density  $2.6 \text{ g mL}^{-1}$ ). Typically the mixture needs to be crushed and ground to a suitably fine particle size. Agitating or shaking the mixture will then cause the much denser particles (eg gold) to settle towards the bottom of the mixture and the less dense particles (eg quartz grains) to accumulate towards the top, hence separating the components of the mixture. The process may be repeated several times to produce a better separation. Some gold mining operations use 'panning' or various gravity separation devices like the 'sluice box', 'spiral concentrator' (Fig 4) or 'shaking table' to concentrate various minerals based on density differences. These techniques are typically inexpensive and sufficiently effective where the density differences are large enough.

▪ **Distillation:** Can be used to separate a mixture based on **boiling point** differences in the individual components of the mixture. (See Fig 5.) In the laboratory, a simple distillation process is most effective in separating a **volatile** component (eg water) from a **non-volatile** one (eg salt). This process can be used to produce distilled water (pure H<sub>2</sub>O) from sea water. Distillation can also be used to separate a **mixture of volatile substances** if their boiling points are significantly different (eg differ by around 70 °C or more). A mixture of hydrocarbons like toluene (BP=110.6 °C) and cyclopentane (BP=49.3 °C) could be separated this way. When the mixture is heated, the lower boiling point substance, cyclopentane, boils first resulting in a vapour consisting mainly of cyclopentane. Cooling and condensing this vapour gives a distillate of cyclopentane. The higher boiling point liquid, toluene remains in the boiling flask.

**Note:** 1 micrometre = **1  $\mu\text{m}$**  =  $1 \times 10^{-6}$  metres  
also  
1 nanometre = **1 nm** =  $1 \times 10^{-9}$  metres



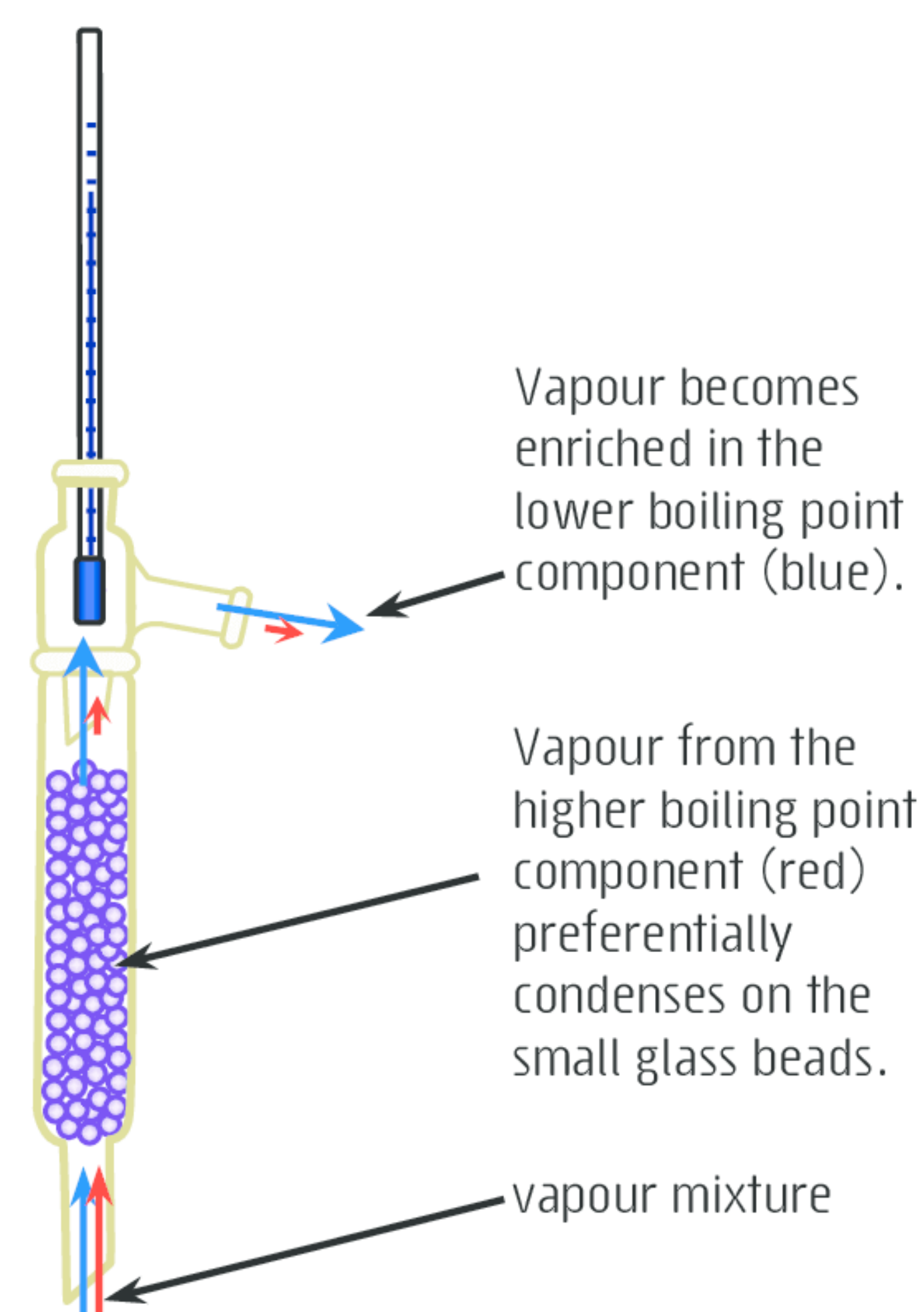
**FIGURE 4** The **spiral concentrator** shown here is used at various Australian mine sites to **concentrate** a variety of dense minerals such as gold ( $19.3 \text{ g mL}^{-1}$ ), iron ore ( $5.2 \text{ g mL}^{-1}$ ), tantalum ( $5.2 \text{ g mL}^{-1}$ ), heavy mineral sands and chromite.

The ore to be concentrated (partially separated) is crushed then mixed with water to form a slurry that flows down the spirals (green). Higher density minerals in the mixture accumulate to the inside of the spirals and are siphoned off from here. The lower density minerals travel faster and accumulate on the outside edges of the spirals. Image courtesy of Mulotech Australia.

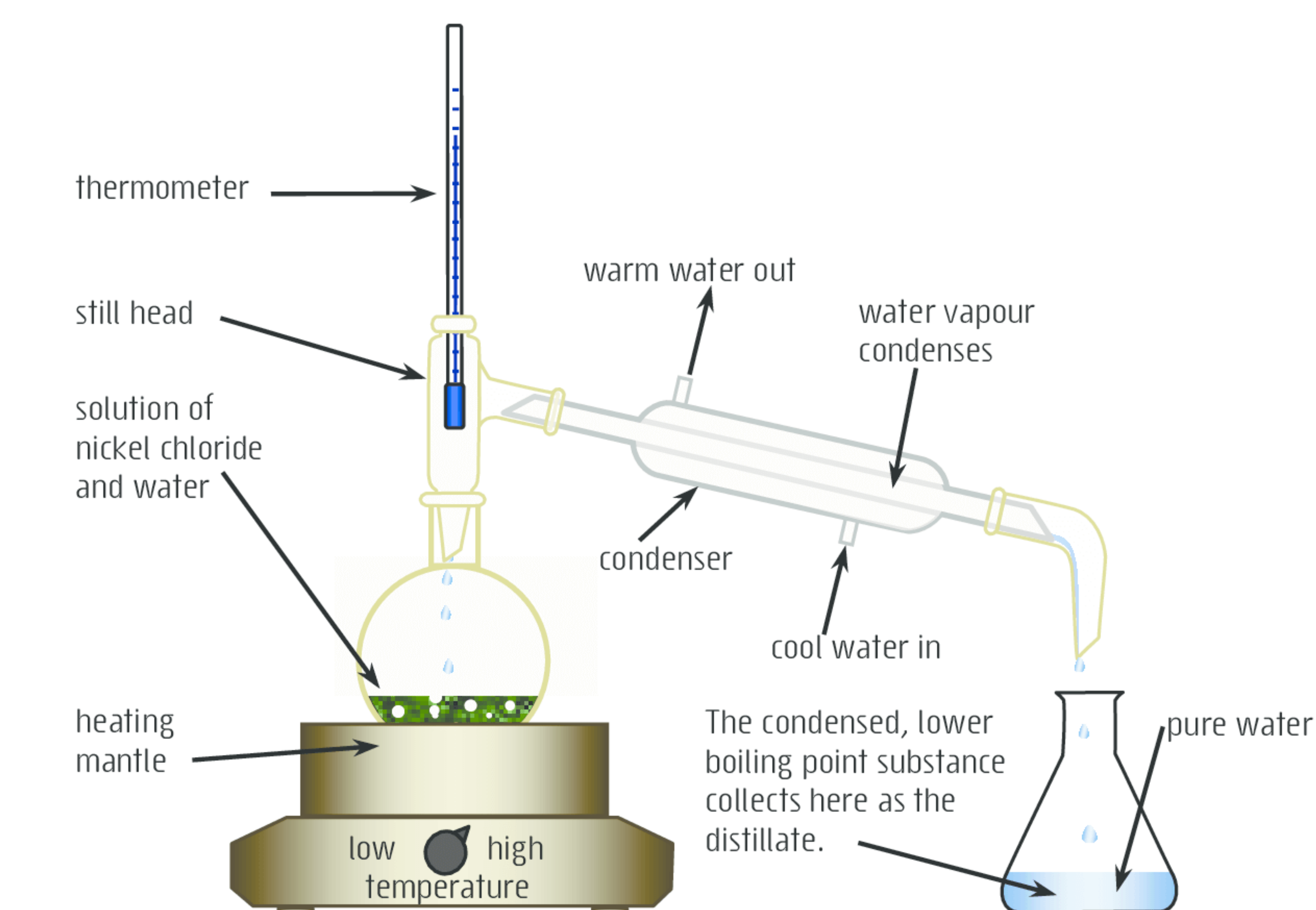


In practice, however, some of the higher boiling point substance, in this example toluene, will also evaporate along with the lower boiling point substance and so the distillate isn't exactly pure. A second distillation of this distillate will give a higher purity product. If the boiling points of the components in the mixture are too similar, as in say an ethanoic acid (BP = 117.9 °C) and water (BP = 100.0 °C) mixture, then simple distillation is ineffective as a separation technique.

**FIGURE 5** Distillation is most effective for separating a mixture of **volatile** and **non-volatile** components. The distillation apparatus at right is being used to separate water (shown as pale blue) from a nickel chloride solution (green). Nickel chloride,  $\text{NiCl}_2$  is the non-volatile component and remains in the round bottom flask while the volatile water boils then condenses and is collected as the **distillate** in the conical flask. This apparatus can be used to separate a mixture of volatile liquids as long as their boiling points are significantly different.



**FIGURE 6** Including a **fractionating column** (shown above) below the distillation still head (Fig 5) greatly improves the efficiency of separation of volatile components. This is especially important if the components have similar boiling points.



- **Fractional distillation:** This technique can be used to separate two or more volatile components like toluene and cyclopentane from a mixture. In fractional distillation the vapour passes upwards through a **fractionating column** (Fig 6) that is packed with glass beads. Within the column the higher boiling point component has a greater tendency to condense on the surface of the glass beads and drip back into the flask. Thus, as the vapour mixture moves up the fractionating column it becomes richer in the more volatile lower boiling point substance. Condensing the fractionated vapour produces a much more pure distillate of the lower boiling point substance.

Complete Set 4.

## Set 4 Mixtures, pure substances and separation techniques

- Classify the following materials as pure substances or mixtures.
 

a. a solid cube of zinc, Zn	c. the mineral calcite, $\text{CaCO}_3$	e. a glass of milk
b. sweat on an athlete's skin	d. the air in a balloon	f. a glass of water
- The boiling point and freezing point of **pure water** can be found in any chemical data book or by researching the internet. However, the boiling point and freezing point of seawater won't be so easy to find. Why don't books generally record this data for **sea water**?
- Elemental gold** is yellow in colour with a density of  $19.3 \text{ g mL}^{-1}$ . It does not tarnish when exposed to air and does not dissolve in most acids. Although elemental gold is quite soft, 2.5 on the Moh's scale, it has a high melting point of 1063 °C. One type of gold frequently used in jewellery is 18 carat **rose gold**. It is quite a bit harder than elemental gold and typically has a melting point in the range 895 °C to 930 °C. Unlike elemental gold, rose gold has a rose colour and can discolour when exposed to air.
  - Classify** the quoted properties of elemental gold as physical or chemical.
  - What does the **well defined melting point** of 1063 °C indicate about elemental gold?
  - Suggest** a reason why rose gold has a melting point range rather than a specific melting point as does elemental gold.
  - Other than having a different melting point what are three other physical properties and one chemical property that is likely to be different for rose gold?



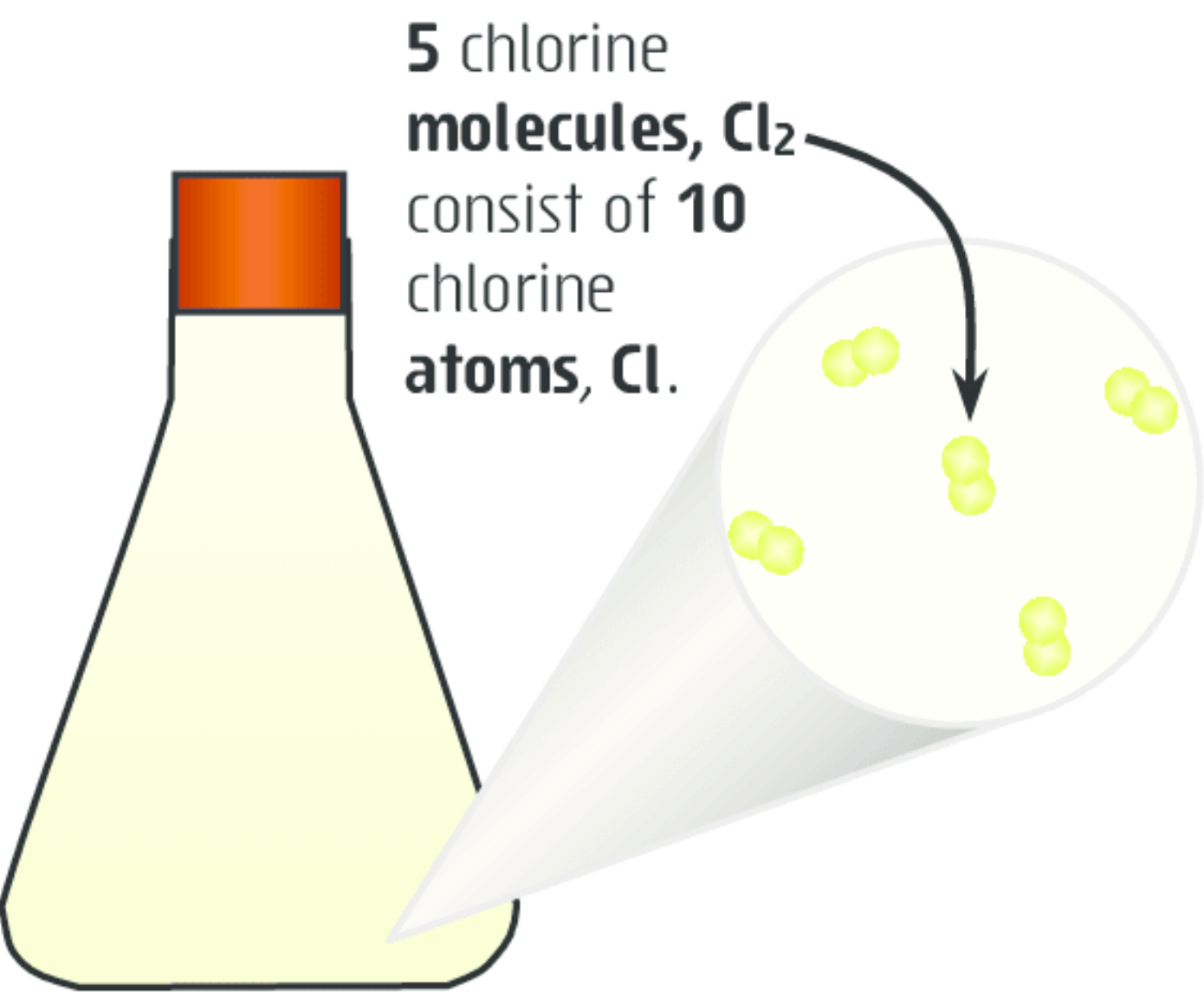
4. Ethanoic acid,  $\text{CH}_3\text{COOH}$  is the active component in vinegar. It has a boiling point of **118 °C** and a melting point of **16.7 °C**. A student measured the boiling point of a liquid that she was sure was ethanoic acid as it had its characteristic sharp pungent odour. She found the test liquid started boiling at **102 °C** and as it boiled the boiling temperature slowly increased. Was the liquid she tested **pure** ethanoic acid? Explain your answer and give a possible explanation for her observations of odour and boiling point.
  
5. A mixture contains three solids, **copper chloride**,  $\text{CuCl}_2(\text{s})$ , **sodium chloride**,  $\text{NaCl}(\text{s})$  and **graphite**,  $\text{C}(\text{s})$ . Their respective solubilities in water are, 61 g  $\text{CuCl}_2$  per 100 g of water, 36 g  $\text{NaCl}$  per 100 g of water and C is insoluble.
  - a. Based on the physical properties given, outline a method you could use in the laboratory to isolate graphite,  $\text{C}(\text{s})$  from the mixture. You will need to include a labelled sketch of the apparatus you would use.
  - b. Explain why filtration can't be used to separate  $\text{CuCl}_2(\text{s})$  and  $\text{NaCl}(\text{s})$  from the remaining filtrate mixture.
  
6. It is possible to use filtration to separate pure **sodium chloride**,  $\text{NaCl}(\text{s})$  from a mixture of **copper chloride**,  $\text{CuCl}_2(\text{s})$  and **sodium chloride**,  $\text{NaCl}(\text{s})$ . To do this the solvent ethanol must be used instead of water. The solubilities of sodium chloride and copper chloride in **ethanol** are, 0.065 g  $\text{NaCl}$  per 100 g of ethanol and 67 g  $\text{CuCl}_2$  per 100 g of ethanol.  
 The procedure involves placing the  $\text{CuCl}_2(\text{s})/\text{NaCl}(\text{s})$  mixture into a 250 mL beaker and adding sufficient ethanol to just dissolve the mixture. The resulting saturated solution is placed onto an electric hot plate and gently heated. Heating is stopped once crystals start to appear in the mixture. The mixture is then filtered in the usual way.
  - a. Gently heating the solution causes some ethanol to evaporate and crystals to appear. What are the crystals composed of and why do they form?
  - b. Why is the solution heated on an electric hot plate instead of using a Bunsen flame? You may need to research (online) the SDS (safety data sheet) for ethanol.
  - c. The crystals in the filter paper are washed with some ethanol and then left to dry. What is the reason for washing these with ethanol and what observation would indicate they had been sufficiently washed?
  - d. Evaporating all of the ethanol from the filtrate does not necessarily leave a residue of pure copper chloride. Explain.
  
7. In a laboratory exercise a student produced some methyl methanoate by reacting methanol with excess methanoic acid. The final reaction mixture contained the product, **methyl methanoate** (BP 31.5 °C), some **water** (BP=100 °C) which is a by-product of the reaction and some excess **methanoic acid** (BP=100.8 °C).
  - a. The student decided to use distillation to separate the desired product, methyl methanoate from the reaction mixture. **Explain** how this process works.
  - b. Is the resulting distillate completely pure methyl methanoate? **Explain**.
  - c. Using **physical means** only, **describe** how the student could verify the purity or otherwise of the methyl methanoate distillate?
  - d. Once all of the methyl methanoate is distilled off, a mixture of methanoic acid and water remains in the flask. Is it possible to use distillation to separate these two compounds? **Explain**.
  
8. Mineral sand deposits contain several valuable 'heavy minerals' such as **ilmenite**, ( $\text{Fe.TiO}_3$ ), **rutile**, ( $\text{TiO}_2$ ), and **zircon** ( $\text{ZrSiO}_4$ ). (See Fig 6.) These deposits usually occur in ancient sand dunes where they have become concentrated by the action of wind or water. The density of this group of minerals ranges from 4.2 g  $\text{mL}^{-1}$  to 5.0 g  $\text{mL}^{-1}$ . A major impurity occurring along with heavy minerals is **quartz sand**,  $\text{SiO}_2(\text{s})$  which has a much lower density, 2.7 g  $\text{mL}^{-1}$ . Separating the heavy minerals from the mineral sands involves mining, washing and screening followed by several stages of physical concentration to ultimately produce a 98 % heavy mineral concentrate. One of the concentration processes involves a number of **spiral gravity separation** circuits that ultimately remove most of the quartz sand from the heavy mineral ore. Briefly explain the basis of this process and how it might operate.



**FIGURE 6 Naturally occurring zircon crystals**  
 Small crystals of zircon recently recovered from the Jack Hills region of the Yilgarn, 800 km north of Perth, are currently believed to be the oldest mineral on Earth. The zircon sample was dated at around 4.4 billion years.



# CHAPTER 4 | CHEMICAL FORMULAS



**FIGURE 1** A 250 mL flask of the gaseous element chlorine at normal laboratory conditions contains around  $6.2 \times 10^{21}$  chlorine **molecules** of formula  $\text{Cl}_2$ . Each molecule is a single cluster of **two** strongly bonded chlorine **atoms**.

## 4.1 Symbols and formulas for elements

The chemical **symbol** of an element represents a single atom of that element. With the exception of a few non-metal elements, the **formula** of an element is the same as its symbol. (See Tables 1 and 2.) Most non-metal elements have a **covalent molecular** structure. The formula of these elements shows the number of atoms in one molecule of the element. (See Fig 1.)

**TABLE 1** Symbol and formula of common metal elements

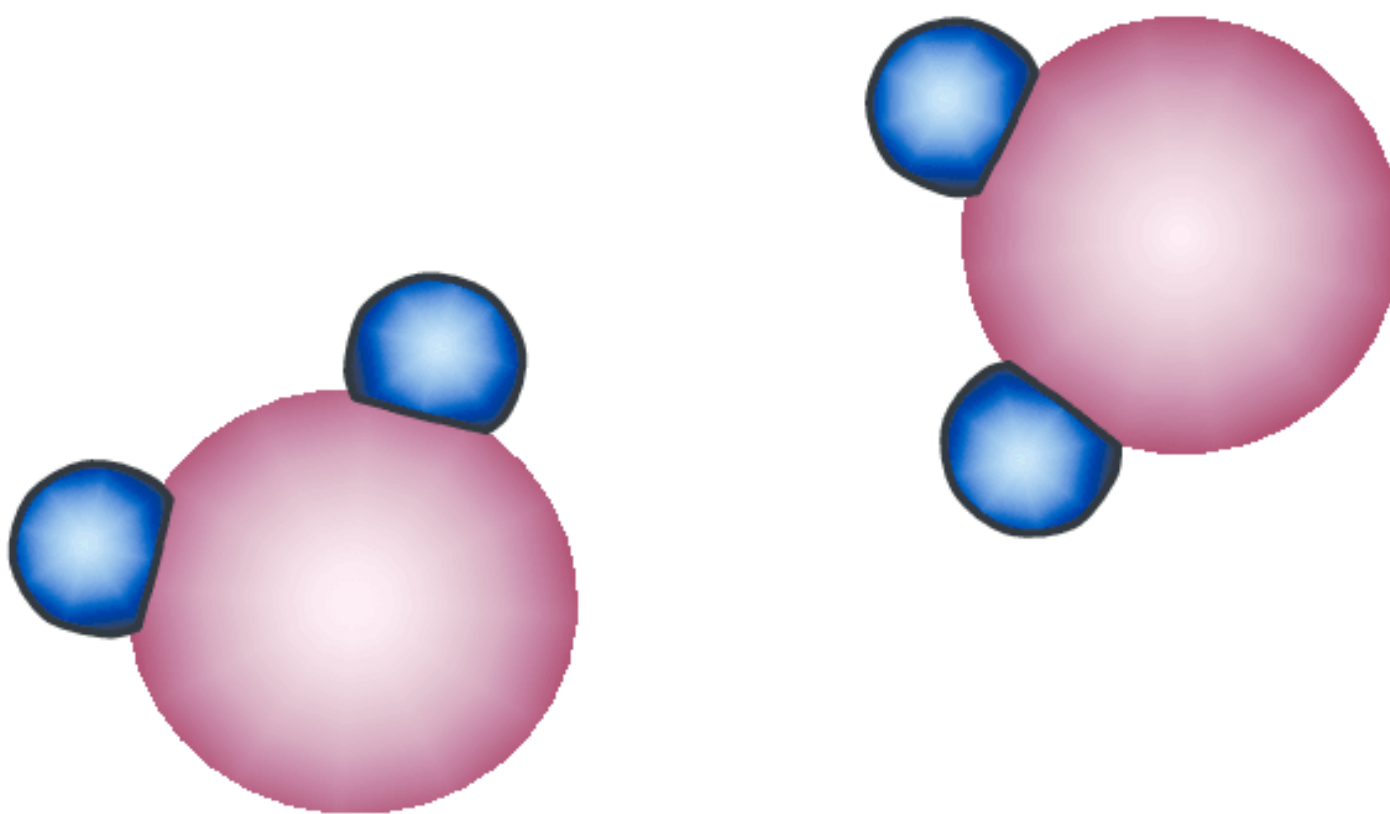
Element	Symbol and formula	Element	Symbol and formula	Element	Symbol and formula
lithium	Li	chromium	Cr	gold	Au
sodium	Na	manganese	Mn	zinc	Zn
potassium	K	iron	Fe	cadmium	Cd
magnesium	Mg	cobalt	Co	mercury	Hg
calcium	Ca	nickel	Ni	aluminium	Al
strontium	Sr	copper	Cu	tin	Sn
barium	Ba	silver	Ag	lead	Pb

**TABLE 2** Symbol and formula of common non-metal elements

Element	Symbol	Formula	Element	Symbol	Formula
hydrogen	H	$\text{H}_2$	fluorine	F	$\text{F}_2$
carbon	C	C	chlorine	Cl	$\text{Cl}_2$
silicon	Si	Si	bromine	Br	$\text{Br}_2$
nitrogen	N	$\text{N}_2$	iodine	I	$\text{I}_2$
phosphorus *	P	$\text{P}_4$	helium	He	He
oxygen	O	$\text{O}_2$	argon	Ar	Ar
sulfur *	S	$\text{S}_8$	neon	Ne	Ne

\* It is generally accepted to write the **formula P** for **P<sub>4</sub>** and **S** for **S<sub>8</sub>**.

Attempt Set 5 # 1.



**FIGURE 2** This sketch shows two water molecules. Each molecule consists of two hydrogen atoms (small blue spheres) and one oxygen atom (large brown sphere). The chemical formula  $\text{H}_2\text{O}$  shows this.

Many covalent molecular substances have **common** or **non-systematic** names.

- $\text{H}_2\text{O}(\text{l})$  ..... water
- $\text{H}_2\text{O}_2(\text{l})$  ..... hydrogen peroxide
- $\text{NH}_3(\text{g})$  ..... ammonia
- $\text{NO}(\text{g})$  ..... nitric oxide
- $\text{H}_2\text{CO}_3(\text{aq})$  ..... carbonic acid
- $\text{CH}_3\text{COOH}(\text{aq})$  ..... acetic acid
- $\text{HCl}(\text{aq})$  ..... hydrochloric acid
- $\text{H}_2\text{SO}_4(\text{aq})$  ..... sulfuric acid
- $\text{H}_3\text{PO}_4(\text{aq})$  ..... phosphoric acid
- $\text{HNO}_3(\text{aq})$  ..... nitric acid
- $\text{C}_2\text{H}_2(\text{g})$  ..... acetylene

## 4.2 Molecular formulas

Substances with a **covalent molecular** structure consist of particles called molecules. A **molecule** is a group of two or more atoms strongly bonded together by covalent bonds to form a single cluster. (See Fig 1, 2 and 7.) The **molecular formula** of these substances shows the number of atoms of each element present in one molecule of the substance.

As a general rule, a substance containing a combination of **non-metal elements only** will form molecules. These are known as **covalent molecular** substances. Well known exceptions to this rule are the **covalent network** materials, eg silicon carbide ( $\text{SiC}$ ), silicon dioxide ( $\text{SiO}_2$ ), carbon (diamond and graphite) and silicon ( $\text{Si}$ ). Other exceptions are compounds containing **ammonium**, eg  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ . These form **ionic compounds**. (See Chapter 8.)

**EXAMPLE 1** What information is conveyed by the following formulas?

<b><math>\text{H}_2\text{O}</math></b> (water)	Since H and O are non-metal elements then $\text{H}_2\text{O}$ is a molecular compound. It has two H atoms and one O atom in each water molecule. (See Fig 2.)
<b><math>\text{NH}_3</math></b> (ammonia)	$\text{NH}_3$ is a molecular compound (contains non-metal elements only) with one N atom and three H atoms in each ammonia molecule.
<b><math>\text{C}_2\text{H}_6</math></b> (ethane)	$\text{C}_2\text{H}_6$ is a molecular compound (contains non-metal elements only) with two C atoms and six H atoms in each of its molecules.
<b><math>\text{SiC}</math></b> (silicon carbide)	Although $\text{SiC}$ consists of non-metal elements only it is not a molecular compound. This particular compound along with a few other exceptions (see notes above) is a <b>covalent network</b> material. It contains Si and C atoms in a 1:1 ratio.

Most covalent molecular compounds are carbon based (organic). These have a specialised IUPAC naming system (Chapter 12) and many others have accepted common names. (See border note.) Systematic naming uses prefixes such as **mono** = 1, **di** = 2, **tri** = 3, **tetra** = 4, **penta** = 5, **hexa** = 6 to indicate the number of each atom in one molecule of the compound.



For oxygen, mon, di, tri, tetr, pent and hex are used. Mono is never used for the first named element, thus CO is carbon monoxide rather than monocarbon monoxide. The last named element has the suffix **-ide**.

**EXAMPLE 2** Write systematic names for these molecular compounds.

<b>NO<sub>2</sub></b>	Each molecule has one N atom (no prefix) and two O atoms (prefix di) in every molecule of NO <sub>2</sub> . Add the suffix ide. Thus the systematic name is <b>nitrogen dioxide</b> .
<b>N<sub>2</sub>O<sub>4</sub></b>	Each molecule has two N atoms (prefix di) and four O atoms (tetr) in every molecule of N <sub>2</sub> O <sub>4</sub> . Add the suffix ide. Thus the systematic name is <b>dinitrogen tetroxide</b> .
<b>SO<sub>3</sub></b>	Each molecule has one S atom (no prefix) and three O atoms (prefix tri) in every molecule of SO <sub>3</sub> . Add the suffix ide. Thus the systematic name is <b>sulfur trioxide</b> .

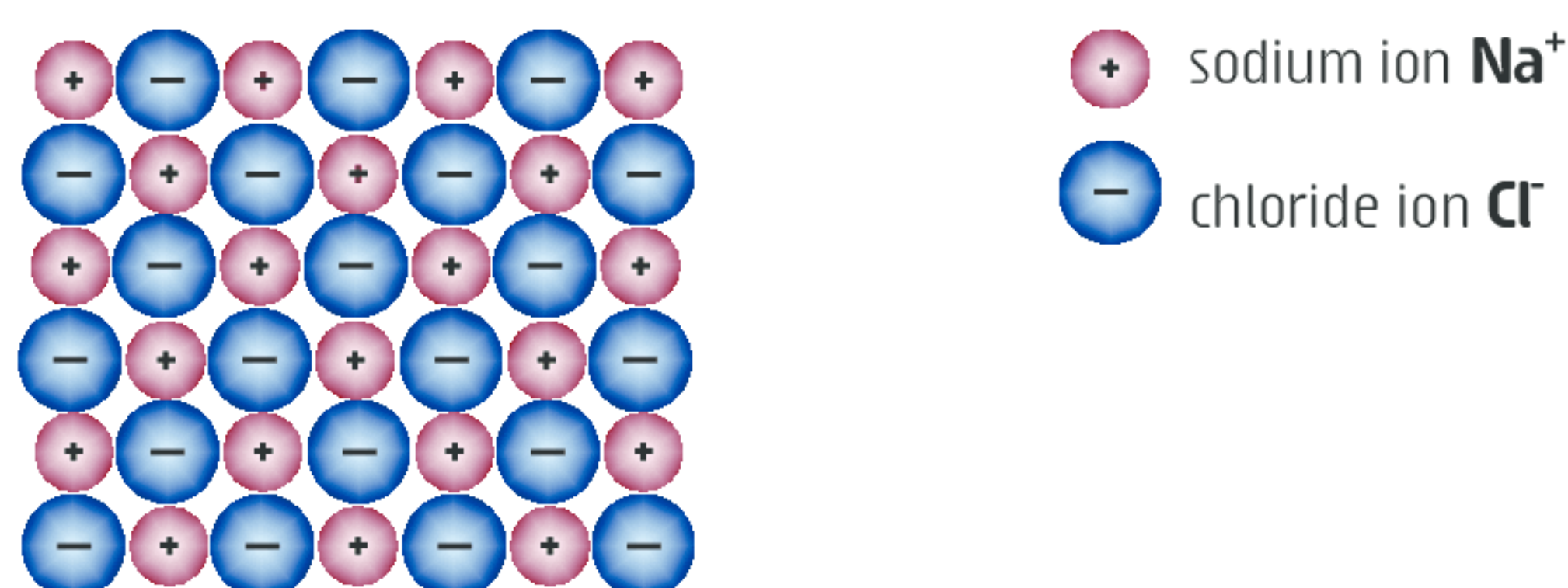
Attempt Set 5 # 2 and 3.

## 4.3 Ionic formulas

As a general rule, an **ionic compound** is formed from a combination of **metal** and **non-metal** elements. (See border note.) These compounds consist of an array of oppositely charged ions. The ions may be **monatomic** like Na<sup>+</sup>, Br<sup>-</sup>, Mg<sup>2+</sup> or N<sup>3-</sup> or they may be **polyatomic** like OH<sup>-</sup>, NH<sub>4</sub><sup>+</sup> or SO<sub>4</sub><sup>2-</sup>. (See Appendix Table 1 and 2 for ion formulas.) Remember, an **ion** is an electrically charged atom. **Negative ions** form when an atom gains one or more electrons. **Positive ions** are formed when an atom loses one or more of its electrons. (See 1.9 p8.) **Polyatomic ions** are combinations of atoms that behave as a single cluster with an overall positive or negative charge. (See Fig 4.)

Within an ionic compound the metal element is in the form of a positive ion, an atom that has lost one or more electrons. The non-metal element is present as a negative ion, an atom that has gained one or more electrons. (See Fig 3.)

**FIGURE 3** Ionic substances consist of a continuous **three-dimensional array** of ions. The **ratio of ions** depends upon the ion charges. This simplified two-dimensional view shows the NaCl(s) structure. Its lattice contains one sodium ion for every one chloride ion.

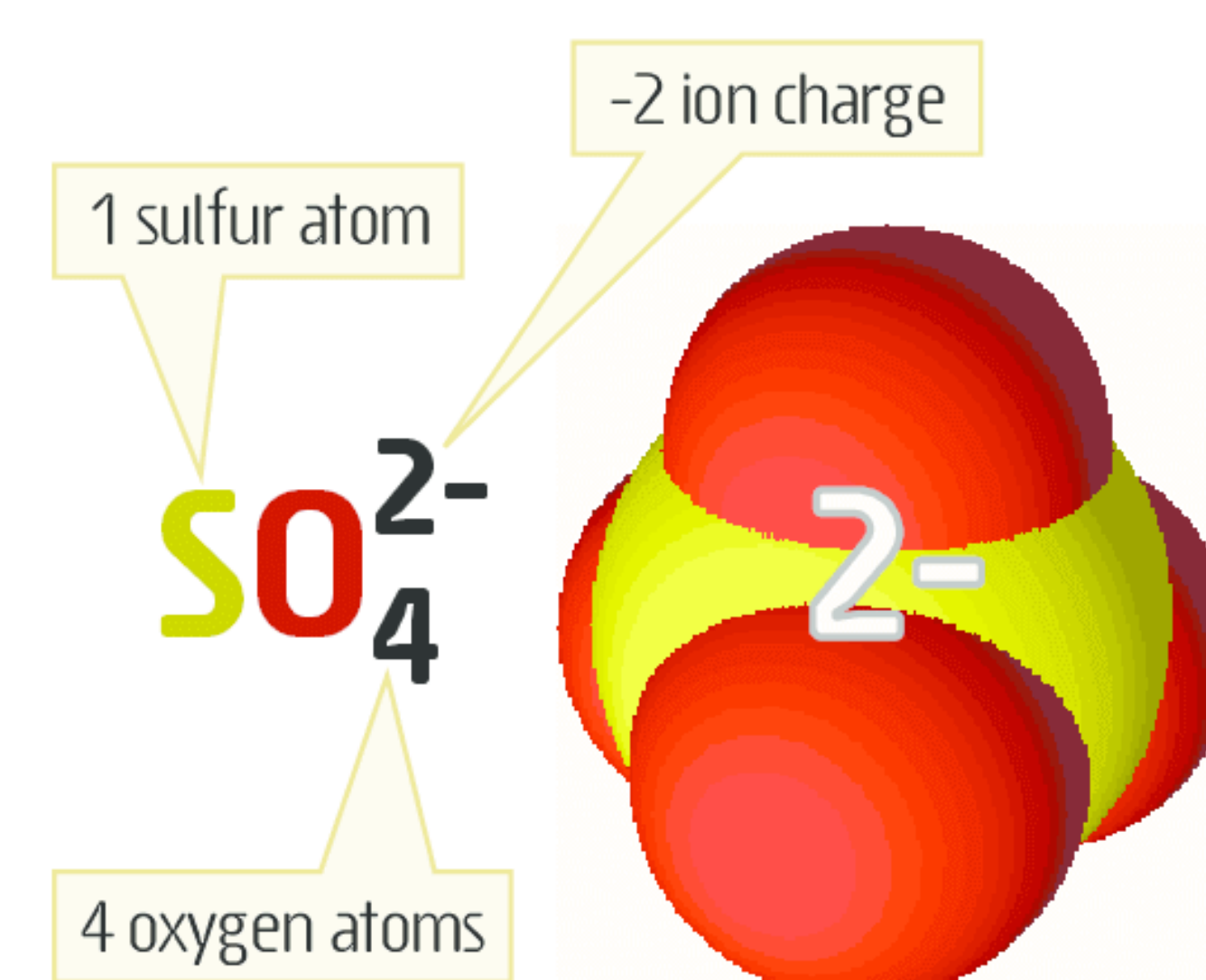


An **ionic formula** represents one **formula unit** of the compound. It shows the simplest whole number ratio of the ions present in the compound. To write an ionic formula from the name of a compound:

- ① Ensure the compound is ionic, that is it contains both metal and non-metal elements in its formula. (See two special cases above right.)
- ② Write the formula for the positive ion first followed by the negative ion.
- ③ Determine the least number of positive and negative ions that gives a neutral combination.
- ④ Write these numbers as subscripts to the ions. Remove the ion charges and do not alter any subscripts already present in the ion formula. Use brackets if a subscript is needed for a polyatomic ion.

**Metal or non-metal? Two special cases.** Although the **ammonium ion**, NH<sub>4</sub><sup>+</sup> consists of non-metal elements only, it behaves like a **metal ion** by forming ionic compounds with non-metal elements. Thus compounds like **NH<sub>4</sub>NO<sub>3</sub>** and **NH<sub>4</sub>Cl** are **ionic** even though they contain non-metal elements only.

Also, **hydrogen** is a **non-metal**, so when combined with other **non-metals** it forms **covalent molecular** compounds not ionic ones, eg H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub>. Interestingly the formula of these compounds can be found as if the compound were ionic.



**FIGURE 4** A **polyatomic ion** is a **charged cluster** of two or more atoms. The sulfate polyatomic ion, pictured above, consists of a cluster of 5 atoms that includes 1 sulfur atom and 4 oxygen atoms. The ion has a total of 50 electrons, 8 from each of the O atoms (32) plus 16 from the S atom and 2 extra electrons to give an overall ion charge of **-2**.

**EXAMPLE 3** Determine the **ionic formula** for each of the following compounds.

	<b>sodium sulfide</b>	<b>ammonium chloride</b>	<b>iron(III) hydroxide</b>	<b>aluminium sulfate</b>
<b>Step ①</b>	This is ionic as Na is a metal and S is a non-metal.	This is ionic as NH <sub>4</sub> <sup>+</sup> behaves as a metal ion and Cl is a non-metal.	This is ionic as Fe is a metal and H and O are non-metals.	This is ionic as Al is a metal and S and O are non-metals.
<b>Step ②</b>	<b>Na<sup>+</sup> S<sup>2-</sup></b>	<b>NH<sub>4</sub><sup>+</sup> Cl<sup>-</sup></b>	<b>Fe<sup>3+</sup> OH<sup>-</sup></b>	<b>Al<sup>3+</sup> SO<sub>4</sub><sup>2-</sup></b>
<b>Step ③</b>	Two Na <sup>+</sup> ions and one S <sup>2-</sup> ion have a charge of 2+ and 2- which together give a charge of zero.	One NH <sub>4</sub> <sup>+</sup> ion and one Cl <sup>-</sup> ion have a charge of 1+ and 1- which together give a charge of zero.	One Fe <sup>3+</sup> ion and three OH <sup>-</sup> ions have a charge of 3+ and 3- which together give a charge of zero.	Two Al <sup>3+</sup> ions and three SO <sub>4</sub> <sup>2-</sup> ions have a charge of 6+ and 6- which gives a net charge of zero.
<b>Step ④</b>	<b>Na<sub>2</sub>S</b>  Remove all ion charges. The formula shows a ratio of two Na <sup>+</sup> ions for every one S <sup>2-</sup> ion.	<b>NH<sub>4</sub>Cl</b>  ( ) are not used as the polyatomic ion NH <sub>4</sub> <sup>+</sup> has no added subscript. This formula shows a ratio of one NH <sub>4</sub> <sup>+</sup> ion for every one Cl <sup>-</sup> ion.	<b>Fe(OH)<sub>3</sub></b>  ( ) are used as the polyatomic ion OH <sup>-</sup> has a subscript of 3. The formula shows a ratio of one Fe <sup>3+</sup> ion for every three OH <sup>-</sup> ions.	<b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b>  ( ) are used as the polyatomic ion SO <sub>4</sub> <sup>2-</sup> has a subscript of 3. The formula shows a ratio of two Al <sup>3+</sup> ions for every three SO <sub>4</sub> <sup>2-</sup> ions.



**Note:** Sections identified in this text with an (E) may be considered an extension to the Chemistry Course Units 1 and 2. These cover content considered desirable for developing a good understanding of the Chemistry Course Units 1 or 2 or they lead into content covered later in Chemistry Course Units 3 or 4. Their inclusion is for the convenience of teachers and students.



**FIGURE 5 Water of crystallization** consists of water molecules weakly bonded within the framework of the crystal structure. This water is responsible for the colour and shape of the crystalline form.

The photograph shows a sample of crystalline copper sulfate. If the crystals are gently heated the water of crystallisation is expelled leaving the salt as a white non crystalline powder.

**Ammonia** ( $\text{NH}_3$ ), **ethanoic acid** ( $\text{CH}_3\text{COOH}$ ) and **glucose** ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) are three common household substances. Glucose is used as a sweetener in many food products, ethanoic acid is the active ingredient in vinegar and ammonia is found in many floor cleaners.

Note:  $\Sigma A_r$  is the  $A_r$  for the element multiplied by the number of times it appears in the formula, eg:

$$\Sigma A_r(\text{H}) \text{ in } \text{H}_2\text{O} = 2 \times A_r(\text{H}) = 2 \times 1.008 = 2.016$$

$$\Sigma A_r(\text{H}) \text{ in } \text{CH}_4 = 4 \times A_r(\text{H}) = 4 \times 1.008 = 4.032$$

$$\Sigma A_r(\text{H}) \text{ in } \text{Al}(\text{OH})_3 = 3 \times A_r(\text{H}) = 3 \times 1.008 = 3.024$$

**EXAMPLE 4** What **information** is conveyed by the following formulas?

<b>ZnCl<sub>2</sub></b> (zinc chloride)	<b>ZnCl<sub>2</sub></b> is an ionic compound (Zn is a metal and Cl a non-metal) containing the ions $\text{Zn}^{2+}$ and $\text{Cl}^-$ in a ratio of one $\text{Zn}^{2+}$ ion for every two $\text{Cl}^-$ ions.
<b>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b> (iron(III) sulfate)	<b>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></b> is an ionic compound (Fe is a metal, S and O are non-metals) containing the ions $\text{Fe}^{3+}$ and $\text{SO}_4^{2-}$ in a ratio of two $\text{Fe}^{3+}$ ions for every three $\text{SO}_4^{2-}$ ions.
<b>(NH<sub>4</sub>)<sub>2</sub>S</b> (ammonium sulfide)	<b>(NH<sub>4</sub>)<sub>2</sub>S</b> is an ionic compound ( $\text{NH}_4^+$ behaves as a metal ion and S is a non-metal) containing the ions $\text{NH}_4^+$ and $\text{S}^{2-}$ in a ratio of two $\text{NH}_4^+$ ions for every one $\text{S}^{2-}$ ion.

## 4.4 Hydrated formulas (E, see border note at left.)

Some solid compounds contain **water of crystallisation** within the crystal structure of the substance. (See Fig 5.) A **hydrated formula** shows the number of water molecules per molecule or formula unit of the compound.

**EXAMPLE 5** Determine the **formula** and **name** of each compound described below.

Description	Formula	Name
Copper sulfate with five molecules of $\text{H}_2\text{O}$ for every formula unit of $\text{CuSO}_4$ .	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	copper sulfate-5-water or copper sulfate pentahydrate
Oxalic acid containing two molecules of $\text{H}_2\text{O}$ for every molecule of $\text{H}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	oxalic acid-2-water or oxalic acid dihydrate

## 4.5 Empirical formulas (E, as above.)

An **empirical formula** shows the simplest whole number ratio of the atoms of each element in a compound. The empirical formula is found by dividing the subscripts of each element in the formula by the lowest common denominator (LCD).

**EXAMPLE 6** Determine the **empirical formula** for each of the compounds shown.

Compound	Formula	Divide by LCD	Empirical formula
dinitrogen tetroxide	$\text{N}_2\text{O}_4$	÷ by 2	$\text{NO}_2$
3-octenedioic acid	$\text{C}_8\text{H}_{12}\text{O}_4$	÷ by 4	$\text{C}_2\text{H}_3\text{O}$
potassium oxalate	$\text{K}_2\text{C}_2\text{O}_4$	÷ by 2	$\text{KCO}_2$
glucose	$\text{C}_6\text{H}_{12}\text{O}_6$	÷ by 6	$\text{CH}_2\text{O}$
ammonia	$\text{NH}_3$	÷ by 1	$\text{NH}_3$
ethanoic acid	$\text{CH}_3\text{COOH}$	÷ by 2	$\text{CH}_2\text{O}$

## 4.6 Percentage composition

The **percentage composition** of a compound gives the **percentage by mass** of each element in the compound. Since a compound has a definite and fixed atomic composition, as shown by its formula, then its percentage composition by mass is also fixed. Percentage composition can be found from a compound's formula (Example 7) or it can be determined from experimental measurements (Example 9). The percentage composition of water in a hydrated compound (Example 8) can also be found from its formula.

- Finding percentage composition from a compound's **formula**:

$$\% \text{ element in compound} = \frac{\Sigma A_r \text{ for the element in the formula} \times 100}{A_r(\text{compound})}$$

- Finding percentage composition from **experimental** measurements:

$$\% \text{ element in compound} = \frac{\text{mass of element in sample} \times 100}{\text{total mass of sample}}$$

**EXAMPLE 7** Determine the **percentage composition** of  $\text{Na}_2\text{CO}_3$ .

$$\% \text{Na} = \frac{\Sigma A_r(\text{Na}) \times 100}{A_r(\text{Na}_2\text{CO}_3)} = \frac{2 \times 22.99 \times 100}{105.99} = 43.38\%$$

$$\% \text{C} = \frac{\Sigma A_r(\text{C}) \times 100}{M(\text{Na}_2\text{CO}_3)} = \frac{12.01 \times 100}{105.99} = 11.33\%$$

$$\% \text{O} = \frac{\Sigma A_r(\text{O}) \times 100}{A_r(\text{Na}_2\text{CO}_3)} = \frac{3 \times 16.00 \times 100}{105.99} = 45.29\%$$

Thus  $\text{Na}_2\text{CO}_3$  contains 43.38% Na, 11.33% C and 45.29% O by mass.



**EXAMPLE 8** Determine the **percentage composition** of **water** in crystalline nickel sulfate-6-water [ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ]. (See Fig 6.) **(E)**

$$\% \text{H}_2\text{O} = \frac{\sum A_r(\text{H}_2\text{O}) \times 100}{A_r(\text{NiSO}_4 \cdot 6\text{H}_2\text{O})} = \frac{6 \times 18.016 \times 100}{262.846} = \mathbf{41.12\%}$$

Thus  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  contains 41.12% water by mass.

Attempt Set 5 # 12.

**EXAMPLE 9** The percentage composition of zinc oxide can be found from experimental data. In an experimental investigation a 7.29 g sample of zinc oxide was dissolved in a nitric acid solution and the zinc extracted from it by electrolysis. This produced 5.84 g of zinc metal. Using this data determine the **percentage composition** of **zinc** and **oxygen** in zinc oxide. **(E)**

$$\% \text{Zn} = \frac{m(\text{Zn}) \times 100}{m[\text{zinc oxide}]} = \frac{5.84 \times 100}{7.29} = \mathbf{80.1\%}$$

Since the zinc oxide sample has a mass of 7.29 g and contained 5.84 g of zinc.

$$\begin{aligned} m(\text{oxygen}) &= m(\text{compound}) - m(\text{zinc}) \\ &= 7.29 - 5.84 \\ &= 1.45 \text{ g} \end{aligned}$$

Since the compound contains Zn and O only then the total mass of the zinc oxide (7.29 g) gives the mass of Zn + mass of O.

$$\% \text{O} = \frac{m(\text{O}) \times 100}{m[\text{zinc oxide}]} = \frac{1.45 \times 100}{7.29} = \mathbf{19.9\%}$$

Since the zinc oxide sample has a mass of 7.29 g and contains 1.45 g of oxygen.

Thus experimentally, zinc oxide contains 80.1% Zn and 19.9% O by mass.

Alternatively, as the compound contains Zn and O only then the percentage of O may be found using  $\% \text{O} = 100 - \% \text{Zn}$ .

Complete Set 5.



**FIGURE 6** Blue-green crystals of hydrated nickel(II) sulfate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

## Set 5 Chemical formulas

1. Give the chemical **symbol** and **formula** (where this is different to the symbol) for the following elements.

- |               |             |            |           |             |
|---------------|-------------|------------|-----------|-------------|
| a. zinc       | c. hydrogen | e. carbon  | g. sodium | i. nitrogen |
| b. phosphorus | d. iron     | f. calcium | h. oxygen | j. chlorine |

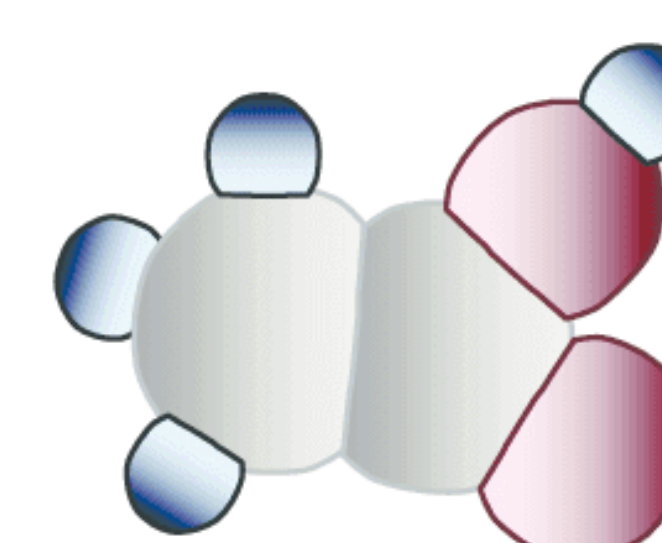
2. Give the **molecular formula** for each of the compounds listed. (See rules and common names p28-29.)

- |                         |                         |                        |
|-------------------------|-------------------------|------------------------|
| a. water                | g. hydrogen peroxide    | m. ammonia             |
| b. hydrogen sulfide     | h. carbon dioxide       | n. carbon monoxide     |
| c. sulfuric acid        | i. sulfurous acid       | o. nitric acid         |
| d. phosphoric acid      | j. acetic acid          | p. nitrous acid        |
| e. sulfur dioxide       | k. nitrogen trichloride | q. sulfur trioxide     |
| f. dinitrogen tetroxide | l. nitrogen monoxide    | r. dinitrogen monoxide |

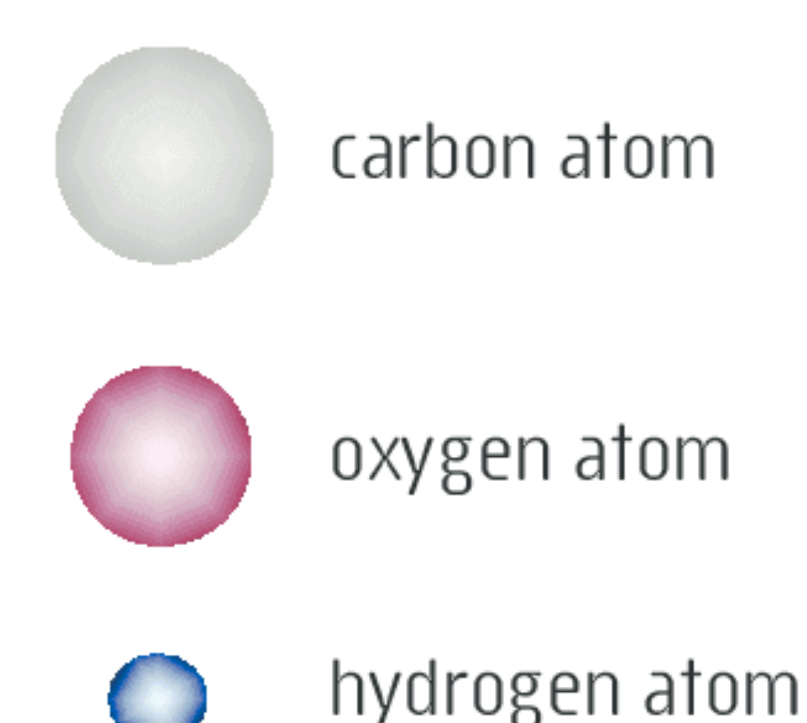
3. Give the **number** of **each type of atom** in one molecule of each compound. (See Fig 7.)

- |                                     |  |   |
|-------------------------------------|--|---|
| a. carbon dioxide ( $\text{CO}_2$ ) | c. hydrogen sulfide ( $\text{H}_2\text{S}$ )       | e. hydrogen sulfate ( $\text{H}_2\text{SO}_4$ ) |
| b. ammonia ( $\text{NH}_3$ )        | d. propane ( $\text{CH}_3\text{CH}_2\text{CH}_3$ ) | f. ethanoic acid ( $\text{CH}_3\text{COOH}$ )   |

4. The **polyatomic ions** hydroxide and ammonium have the respective formulas,  $\text{OH}^-$  and  $\text{NH}_4^+$ . **Describe** the composition of each of these ions and use this to **explain** why they have a net charge.



**FIGURE 7** Ethanoic acid (acetic acid) is the active ingredient in vinegar. Its molecules consist of a cluster of 8 atoms. The space filling model shows how these atoms are arranged in a single molecule of ethanoic acid  $\text{CH}_3\text{COOH}$ .





5. Examine these ionic formulas and give the formula for the individual **ions** present and the **ratio** of these ions. See page 247 for the formula and name of common ions.
- |                      |  |                                       |  |                                   |
|----------------------|--|---------------------------------------|--|-----------------------------------|
| a. LiCl              | c. MgO   | e. Al <sub>2</sub> S <sub>3</sub>     | g. FeO   | i. Fe <sub>2</sub> O <sub>3</sub> |
| b. KMnO <sub>4</sub> | d. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | f. Zn(HSO <sub>4</sub> ) <sub>2</sub> | h. Cr <sub>2</sub> (SO <sub>3</sub> ) <sub>3</sub> | j. Au(CN) <sub>3</sub>            |
6. Write the **ionic formula** for each of the following compounds.
- |                      |                      |                               |
|----------------------|----------------------|-------------------------------|
| a. zinc chloride     | g. sodium sulfide    | m. calcium oxide              |
| b. copper(I) bromide | h. iron(III) oxide   | n. silver sulfate             |
| c. calcium sulfate   | i. silver chromate   | o. barium hydroxide           |
| d. sodium nitrite    | j. iron(II) nitrate  | p. potassium hydroxide        |
| e. ammonium sulfate  | k. sodium dichromate | q. copper(II) hydrogensulfate |
| f. aluminium sulfate | l. zinc phosphate    | r. potassium permanganate     |
7. The presence of **water of crystallisation** allows many ionic compounds to be crystalline and brightly coloured. Use the following description of several of these compounds to write their **hydrated formula**. **(E)**
- Blue copper(II) sulfate crystals contain five molecules of water for every formula unit of copper(II) sulfate.
  - Iron(III) chloride is a yellow solid with six molecules of water for every formula unit of iron(III) chloride.
  - Green hydrated iron(II) chloride crystals contain two molecules of water for every formula unit of iron(II) chloride.
  - White crystalline zinc nitrate has two molecules of water for every formula unit of zinc nitrate.
  - Chromium(III) sulfate has two crystalline forms, each of which has a different colour. The green form has five molecules of water for every formula unit of chromium(III) sulfate while the violet form has fifteen molecules of water for every formula unit of chromium(III) sulfate.
8. Write the **empirical formula** for each of the following substances. **(E)**
- The household bleach and antiseptic hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).
  - Ozone (O<sub>3</sub>) the substance found in the upper atmosphere and responsible for absorbing harmful ultra violet light.
  - Lactic acid (CH<sub>3</sub>CH(OH)COOH or simply C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) an acid involved in many biochemical processes.
  - Arginine (C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>) an amino acid essential to living things.
9. Examine the elements present in the following compounds and so **classify** them as **ionic**, **molecular** or **covalent network** compounds. Use the general rules outlined on p28-29 and note the exceptions outlined.
- |                       |   |   |                                       |
|-----------------------|---|---|---------------------------------------|
| a. SO <sub>2</sub>    | f. H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | k. CO <sub>2</sub>                                  | p. Fe(HSO <sub>3</sub> ) <sub>2</sub> |
| b. K <sub>2</sub> S   | g. CH <sub>4</sub>                              | l. BaC <sub>2</sub> O <sub>4</sub>                  | q. CH <sub>3</sub> COOH               |
| c. NaHSO <sub>4</sub> | h. HCl  | m. CaSO <sub>4</sub>                                | r. SiC                                |
| d. SiO <sub>2</sub>   | i. ZnSO <sub>3</sub>                            | n. NO <sub>2</sub>                                  |                                       |
| e. NH <sub>4</sub> Cl | j. H <sub>2</sub> SO <sub>3</sub>               | o. AgCH <sub>3</sub> COO (See border note at left.) |                                       |
10. Calculate the **percentage composition of each element** in the following compounds.
- |  |                                |
|--|--------------------------------|
| a. methane (CH <sub>4</sub> )                          | c. ammonium sulfate            |
| b. barium nitrate [Ba(NO <sub>3</sub> ) <sub>2</sub> ] | d. copper(II) chloride-2-water |
11. Three compounds often used as sources of **nitrogen** in garden fertilisers are ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>], ammonium nitrate [NH<sub>4</sub>NO<sub>3</sub>] and urea [(NH<sub>2</sub>)<sub>2</sub>CO]. Which of these compounds is the most efficient in providing the greatest **mass** of **nitrogen** for a given mass of fertiliser? Explain. [Hint: Consider the %N in each of the fertilisers.]

The formula for the ionic salts of organic acids like ethanoic acid (CH<sub>3</sub>COOH) can be written with the positive metal ion at the end or the start of the formula, eg:

silver ethanoate:

**AgCH<sub>3</sub>COO or CH<sub>3</sub>COOAg**

sodium ethanoate:

**NaCH<sub>3</sub>COO or CH<sub>3</sub>COONa**

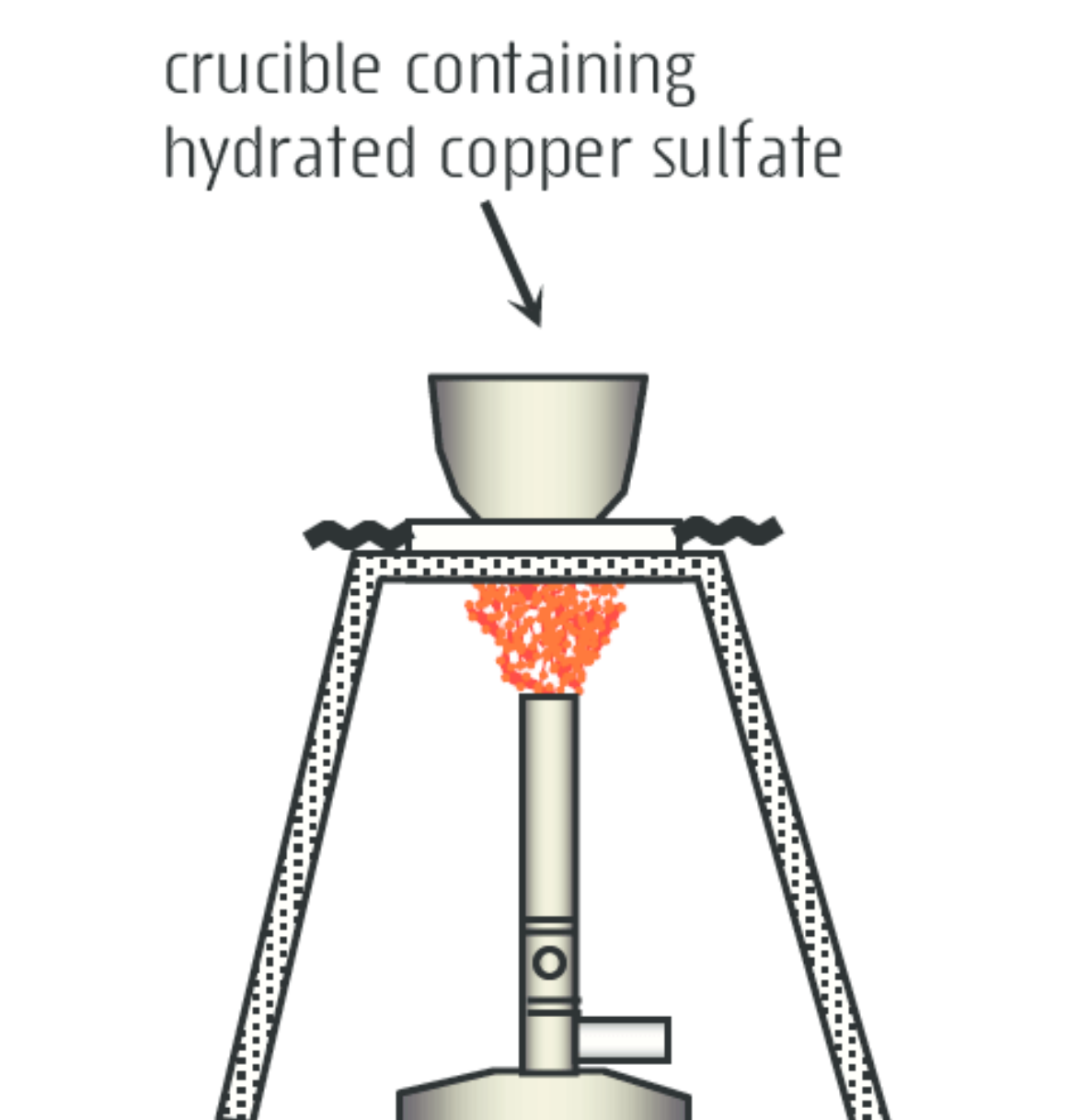


12. Determine the **percentage composition of water** in each of the hydrated compounds. (E)

- cobalt ethanoate-6-water  $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}]$
- magnesium chromate-6-water

13. The water of crystallisation present in **hydrated** copper sulfate is quite easily driven off by heating it to around  $110^\circ\text{C}$ . By contrast, copper sulfate itself is quite stable and does not decompose unless heated to above  $650^\circ\text{C}$ . In an experiment to find the **percentage of water** in a hydrated copper sulfate sample a student carefully weighed a 4.77 g sample of the hydrated copper sulfate. She added this to a crucible and gently heated the sample to around  $200^\circ\text{C}$  for ten minutes. (See Fig 8.) After allowing the sample to cool she re-weighed the crucible and its contents finding it had reduced in weight by 1.67 g.

- Account** for the weight loss of 1.67 g.
- Determine the **percentage of water** in the sample of hydrated copper sulfate. (E)
- This experimental data shows hydrated copper sulfate contains 35.0% water. The accepted theoretical value is 36.1% water. What is the **error** in this experimental result? Express the error as a % of the theoretical value.



**FIGURE 8** If the crucible of hydrated copper sulfate is strongly heated it will lose mass as the water of crystallisation is driven off.

14. Gavin needed to determine by investigation the percentage composition of **silver oxide**. While researching the properties of silver oxide he discovered this compound is quite unstable. When heated to above  $230^\circ\text{C}$  it decomposes forming **oxygen gas** and solid **silver**. With this in mind he carefully weighed a clean empty crucible then added a sample of silver oxide to it. The crucible was re-weighed with the silver oxide sample and then strongly heated to around  $500^\circ\text{C}$  for five minutes. After cooling, the crucible and its contents were re-weighed. His experiment produced the following results.

mass of the empty crucible ..... 22.84 g  
mass of the crucible plus silver oxide ..... 37.76 g  
mass of the crucible plus contents after heating ..... 36.69 g

- Determine the mass of **silver oxide** used in the experiment.
- Account** for the loss of mass when silver oxide is heated?
- From the experimental data determine the mass of **silver** and **oxygen** in the sample.
- What is the **experimental** percentage composition of **silver** in the silver oxide sample? (E)
- Determine the **theoretical** percentage composition of **silver** in silver oxide, ie from the known chemical formula  $\text{Ag}_2\text{O}$ ?
- This experimental data shows silver oxide contains 92.83% silver. What is the **error** in this procedure for determining the percentage of silver in silver oxide? Express the error as a % of the theoretical value.

15. A student investigation into the **percentage composition** of **magnesium oxide** involved burning a carefully weighed strip of magnesium ribbon to produce the oxide. The reaction was carried out in a covered crucible so that the resulting magnesium oxide could be captured and weighed. The student recorded the following data.

mass of the empty crucible ..... 25.59 g  
mass of the crucible plus magnesium ..... 26.09 g  
mass of the crucible plus magnesium oxide ..... 26.36 g

- Explain why the increase in mass of the crucible during this reaction does not contradict the **law of conservation of mass**.
- Use the student's experimental data to determine the **percentage of magnesium** in magnesium oxide? (E)
- The chemical formula of magnesium oxide is known to be  $\text{MgO}$ . Using this formula, determine the **theoretical** percentage of magnesium in magnesium oxide.
- The student's experimental data shows magnesium oxide contains 65% magnesium. What is the **error** in this procedure for determining the percentage of magnesium in magnesium oxide? Express the error as a % of the theoretical value.



# CHAPTER 5 | INVESTIGATING IN CHEMISTRY

FIGURE 1 Norm's fiendish napping fish



**Observation:** Norm has noticed his goldfish have a very predictable napping behaviour. They are lazy early in the morning then very active later the same day.

**Question:** What is causing my goldfish to change their activity? Is the water temperature affecting their activity?

**Dependent variable:** This is the variable of interest. In this case it is the goldfish activity. This is the variable Norm will observe during his investigation.

**Independent variable:** This is the factor Norm thinks is affecting the goldfish activity. In this case it is the water temperature. This is the variable Norm will change during his investigation.

**Hypothesis:** This states how Norm thinks the dependent variable is affected by the independent variable. His hypothesis must be a testable statement, eg 'The activity of my goldfish increases as the water temperature increases.'

**Controlled variables:** These are other variables that are kept constant as Norm thinks they may influence the results. Light intensity, noise levels and feeding times are some examples.

**Can Norm find the answer?**

He will need to design and conduct an investigation to find out!

In this investigation Norm must be mindful of the **ethical issues** of experimenting with live specimens, the gold fish.

## 5.1 Designing an investigation

The purpose of an investigation is to find the answer to a question by using the **scientific method**. To do this the question must be stated in the form of a testable **hypothesis** that clearly identifies two variables; the **dependent** and **independent**, as well as the expected relationship between these. (See Fig 1 and Example 1.)

**EXAMPLE 1** Zoe added some hydrochloric acid solution to powdered sodium carbonate and found the reaction happened rapidly producing a colourless gas. Riley requested similar equipment from the laboratory technician and repeated the same experiment. He found his reaction still produced a colourless gas but very slowly. He couldn't work out why his reaction was so much slower than Zoe's. Consider this situation and determine the question facing Riley. Suggest a hypothesis which could help answer Riley's question.

**Question:** Clearly Riley is uncertain why his reaction was so slow. Something is affecting the reaction speed (reaction rate) so Riley's question might be, '**What's affecting the speed (rate) of my reaction?**'

A hypothesis should frame the reaction rate as the dependent variable. A number of variables might be affecting the reaction rate, eg temperature, concentration, particle size or some other factor. One of these or some other variable would be framed as the independent variable that affects rate.

**Hypothesis 1** 'The rate of reaction between hydrochloric acid and sodium carbonate increases as the temperature of the reacting mixture increases.'

This hypothesis identifies rate as the dependent variable and temperature as the independent variable causing the change in reaction rate.

**Hypothesis 2** 'The rate of reaction between hydrochloric acid and sodium carbonate depends upon the particle size of the sodium carbonate.'

Here the hypothesis identifies particle size as being the independent variable that causes the change in reaction rate.

**Hypothesis 3** 'The rate of reaction between hydrochloric acid and sodium carbonate is directly proportional to the concentration of acid.'

In this hypothesis concentration is the independent variable. It clearly states the expected relationship between concentration and rate of reaction.

An investigation is then designed so that it can provide data (observations) that will support or refute the hypothesis, thus helping to answer the original question. The following steps can be used as a guide when designing your own chemistry investigation.

- **Question:** Clarify the question you want to investigate. What are you trying to find the answer to?
- **Hypothesis:** From your question formulate a hypothesis. This identifies the dependent and independent variables. It states how the dependent variable is affected by the independent variable.
- **Controlled variables:** Identify any other variables that could affect the result. Decide how you will keep these variables constant during your investigation.
- **Method:** Decide how you will change the independent variable while keeping the controlled variables constant. What observations need to be made? These observations either directly record the values of the dependent and independent variables or they allow their values to be calculated.
- **Design:** Determine your procedure and the equipment and materials required.
- **Research ethics:** Consider possible ethical issues arising from your intended investigation.
- **Risk assessment:** Conduct a risk assessment. You will need to consider the potential chemical hazards associated with the materials and equipment you are using by referring to relevant SDSs. Use appropriate safety procedures or modify your method.
- **Perform:** Carry out your investigation, collect and record data.
- **Data analysis:** Present your data in tabular or graphical form so that the relationship between the dependent and independent variable is clear. You may need to process your data to obtain values for the dependent and independent variables.
- **Conclusion:** With reference to the data or processed data make a conclusion regarding the validity of the hypothesis. In doing so, keep in mind the reliability of your data.
- **Reflect:** You should consider weaknesses in the investigation and how these might be avoided. Does your investigation present new questions? Reflecting may lead to new or improved investigations.
- **Report:** A written report informs others and enables them to evaluate your findings.

Attempt Set 6 # 1.



## 5.2 Assessing the risk

Making a **risk assessment** of your intended investigation is an important process that requires a careful consideration of the potential hazards. As part of the process you need to assess the possible hazards posed by each of the chemical substances involved in your investigation, reactants as well as products. This is done by referring to **Safety Data Sheets** (SDSs, previously Material Safety Data Sheets) specific to each of the substances involved. SDSs are available in all school laboratories and can also be found online. The **equipment** you are planning to use can also present safety issues. In this regard you must find out about the standard **handling procedures** for that equipment and any hazards associated with its use.

Having determined the potential hazards presented by the substances and equipment involved in your investigation you are in a position to assess the overall **level of risk** posed by your investigation. Typically this can be assessed as being **low**, **medium**, **high** or **extreme**. If the risk is considered low, then with the usual teacher supervision you would proceed with your investigation. A moderate risk will require **control measures** to be put in place. This may require the use of specific safety equipment or changes to your reagents or procedure that reduce the assessed risk to a low level. Investigations that pose high or extreme risk will need to be reconsidered.

Complete Set 6.

### Set 6 Investigating

- 1 A group of chemistry students proposed several hypotheses that they might investigate. Read these and answer the questions that follow.

**Hypothesis 1** 'The solubility of salt in water changes when the water temperature changes.'

**Hypothesis 2** 'When **dry ice** (Fig 2) is used to inflate a balloon the final volume of the balloon is directly proportional to the mass of dry ice placed into the balloon.'

**Hypothesis 3** 'When zinc dissolves in hydrochloric acid the volume of hydrogen gas produced increases in direct proportion to the mass of zinc used.'

**Hypothesis 4** 'The chemical reaction of any metal element with sulfuric acid always produces hydrogen gas.'

- For each of these determine the **dependent** and **independent** variable.
  - According to Hypothesis 4, what should be produced when iron nails are added to a sulfuric acid solution?
  - According to Hypothesis 2, what should happen to the inflated volume of a balloon when the mass of dry ice added to it is doubled?
  - One of these hypotheses does not clearly indicate how the dependent variable changes when the independent variable is altered. Rewrite this hypothesis so that it does clearly indicate what change to expect in the dependent variable.
- 2 The students who wrote the hypotheses in Question 1 decided to proceed with an investigation for Hypothesis 3, ie 'When zinc dissolves in hydrochloric acid the **volume** of **hydrogen** gas produced increases **in direct proportion** to the **mass of zinc** used.'
- Answer the following regarding their planned investigation.
- What chemical substances will be involved in their investigation? Refer to the **SDSs** for these substances and decide if they pose any **hazards** and if so what **control measures** could be put in place to minimise the risk.
  - What **data** should the students record in order to test their hypothesis?
  - The students decided to present their data graphically. How would their graph appear if it was to support their hypothesis? **Sketch** the appearance of the **graph** and label the axis and units. No scale is needed.



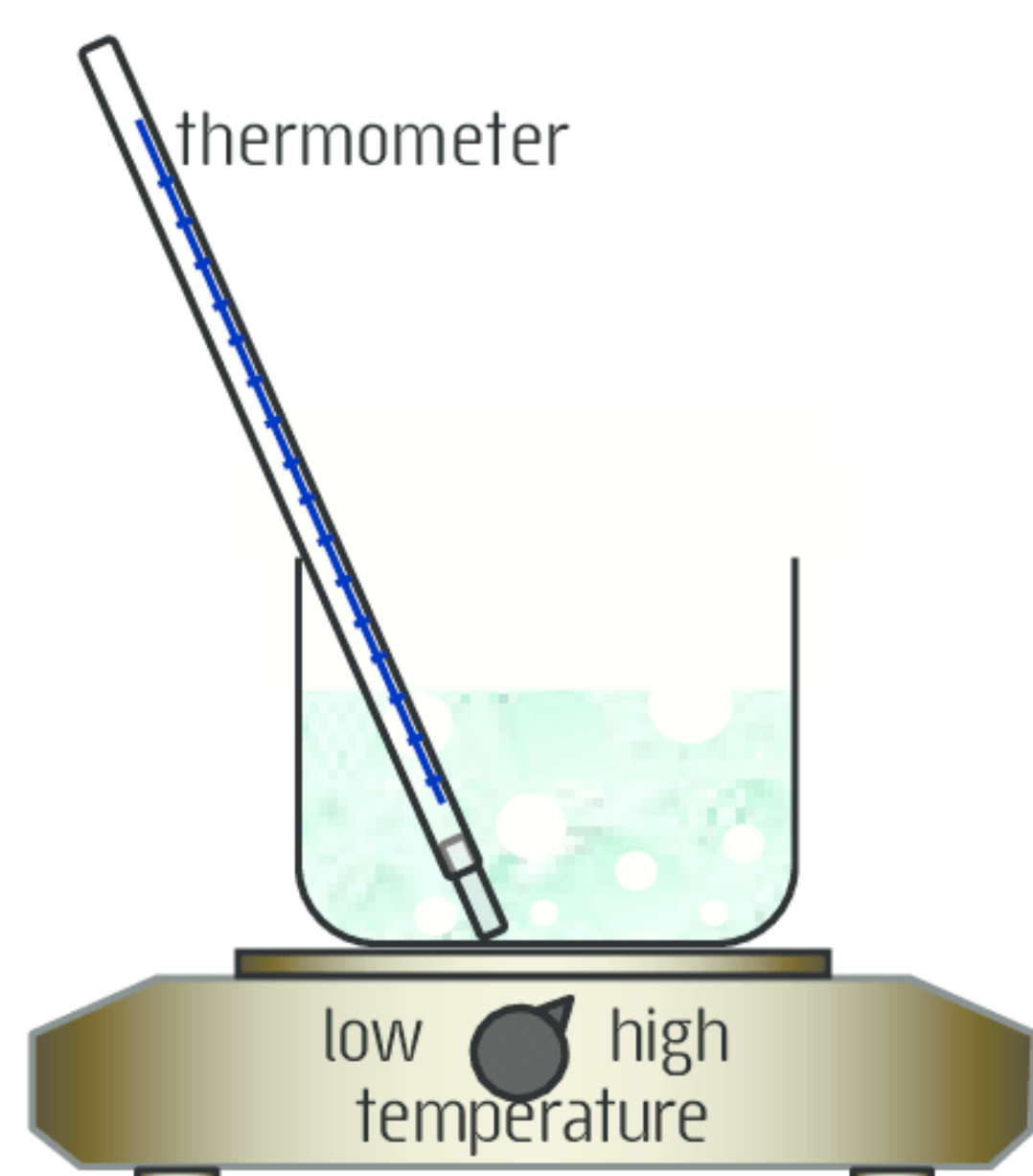
**FIGURE 2** **Dry ice** is the common name for solid carbon dioxide. It is a peculiar substance as it **sublimes** (at  $-78\text{ }^{\circ}\text{C}$ ) when changing phase. This means it converts directly from a solid to a gas without producing a liquid phase. So dry ice remains dry as it 'melts'. This can make it a handy coolant for food and beverages.

**Care** should be exercised when handling dry ice as its low temperature (less than  $-78\text{ }^{\circ}\text{C}$ ) means it will cause skin burns similar to touching a very hot object.

If using dry ice in a confined space provide adequate **ventilation**. Although  $\text{CO}_2(\text{g})$  is not toxic, if large volumes are formed then room air may be replaced with  $\text{CO}_2(\text{g})$  leading to asphyxiation due to lack of oxygen.



**FIGURE 3** Measuring the temperature of a boiling liquid gives its boiling point.



**Note:** Solute concentration can be found using:

$$\text{concentration} = \frac{\text{mass of solute}}{\text{volume of solution}}$$

The **rate of formation** of a substance in a chemical reaction can be calculated using:

$$\text{rate} = \frac{\text{amount produced}}{\text{time taken}}$$

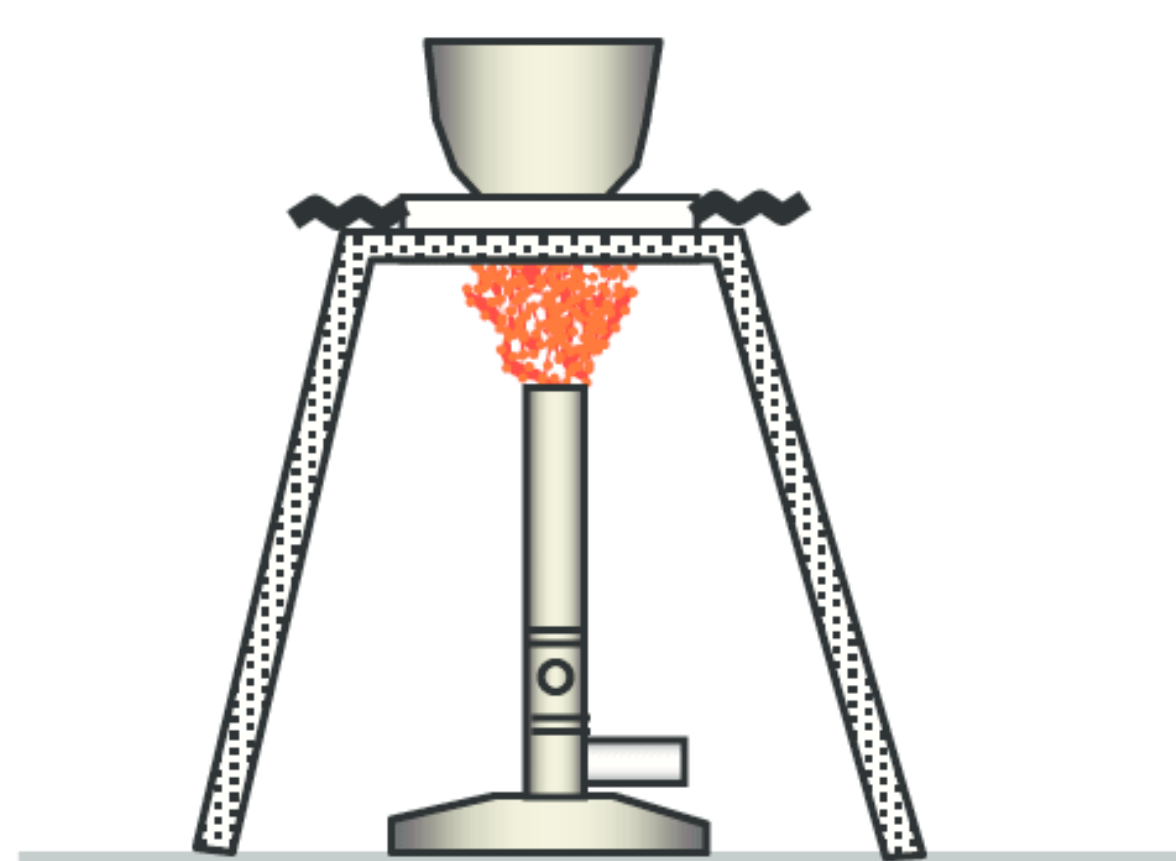
**Rate** can be expressed in a variety of units, for example:

**moles** per second..... $\text{mol s}^{-1}$

**grams** per second ..... $\text{g s}^{-1}$

**millilitres** per second.. $\text{mL s}^{-1}$

crucible originally contains  $\text{NaHCO}_3(\text{s})$



**FIGURE 4** As the crucible with  $\text{NaHCO}_3(\text{s})$  is strongly heated its contents decompose leaving behind only  $\text{Na}_2\text{CO}_3(\text{s})$ . The other products,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  escape from the crucible.

- 3 Darshan and Ben learnt in their chemistry class that when substances like salt or sugar dissolve in water they cause the boiling point of the resulting solution to be higher than that of the original pure water. The increase in boiling point is known as the **boiling point elevation**. They wondered if a clear relationship might exist between the solute concentration (see border note) and the size of the boiling point elevation. To investigate their ideas further they formulated a hypothesis that could be tested and might provide the answer to their question. (See Fig 3.)
  - a. What should they choose as the **dependent** variable in their hypothesis?
  - b. What should they choose as the **independent** variable in their hypothesis? This is the variable that will be altered in the investigation.
  - c. Write a suitable **hypothesis** for the question they are seeking to answer.
  - d. What are some of the **controlled variables** they should keep constant?
  - e. Briefly **describe a method** they could use in conducting an investigation that would provide data for the dependent and independent variables.
  - f. What are some of the **hazards** and **safety measures** that might be considered in this investigation. You may assume the group chose salt ( $\text{NaCl}$ ) as its solute.
  
- 4 Natalie and Jayzii conducted some chemical tests adding strips of magnesium metal to various hydrochloric acid solutions. The reaction as you would expect produces considerable bubbling and fizzing as the gas hydrogen is formed. They were puzzled however, by the rate of reaction, ie its speed, (see border note) which varied from moderate to very fast. They decided to investigate to find out what was affecting the rate of formation of hydrogen gas.
  - a. What is the **dependent variable** in their planned investigation?
  - b. Suggest four possible **independent variables** that they might investigate. These are the variables that they think might be affecting the rate of formation of hydrogen gas.
  - c. Consider your answer to (a) and (b) above and write an **hypothesis** for their investigation.
  - d. In the light of your suggested hypothesis what other variables should be **kept constant** in your investigation? These are any other factors, other than the independent variable you think might affect the rate of formation of hydrogen gas or any of their measurements.
  - e. In this investigation Natalie and Jayzii will need to know the rate of formation of hydrogen gas. What two measurements will they need to make in order to calculate this? (See border note.)
  - f. Suggest how they could make the necessary measurements that would allow them to calculate the rate of formation of hydrogen gas.
  
- 5 Two students investigated the hypothesis, '**When sodium hydrogen carbonate is heated it decomposes such that the molar amount of sodium carbonate produced is half the molar amount of sodium hydrogen carbonate that was decomposed.**' They conducted several experiments with different masses of  $\text{NaHCO}_3(\text{s})$  and measured the mass of  $\text{Na}_2\text{CO}_3(\text{s})$  that was produced. Their apparatus is shown in Fig 4. The results they obtained for each experiment included:
  - the mass of the empty crucible
  - the mass of the crucible with  $\text{NaHCO}_3(\text{s})$  before heating
  - the mass of the crucible with the reaction product  $\text{Na}_2\text{CO}_3(\text{s})$  after heating.
  - a. What are the **independent** and **dependent** variables in their investigation?
  - b. How should they **process** their data in order to obtain information about the dependent and independent variables?
  - c. **Construct a table** that would be suitable for recording their data. Include headings for any processed data that will need to be calculated and tabulated.
  - d. What should they graph in order to see if their hypothesis is valid?
  - e. How would their graph look if it did support their hypothesis?



- 6 A student wanting to investigate combustion reactions decided to explore the operation of a Bunsen burner. (See Fig 5.) He was quite sure that the temperature of a Bunsen flame was affected by the amount of air that mixed with the fuel as it travelled up the barrel of the Bunsen. He hypothesised, **'The temperature of a Bunsen flame increases in direct proportion to the area of the air hole opening at the base of the Bunsen.'**

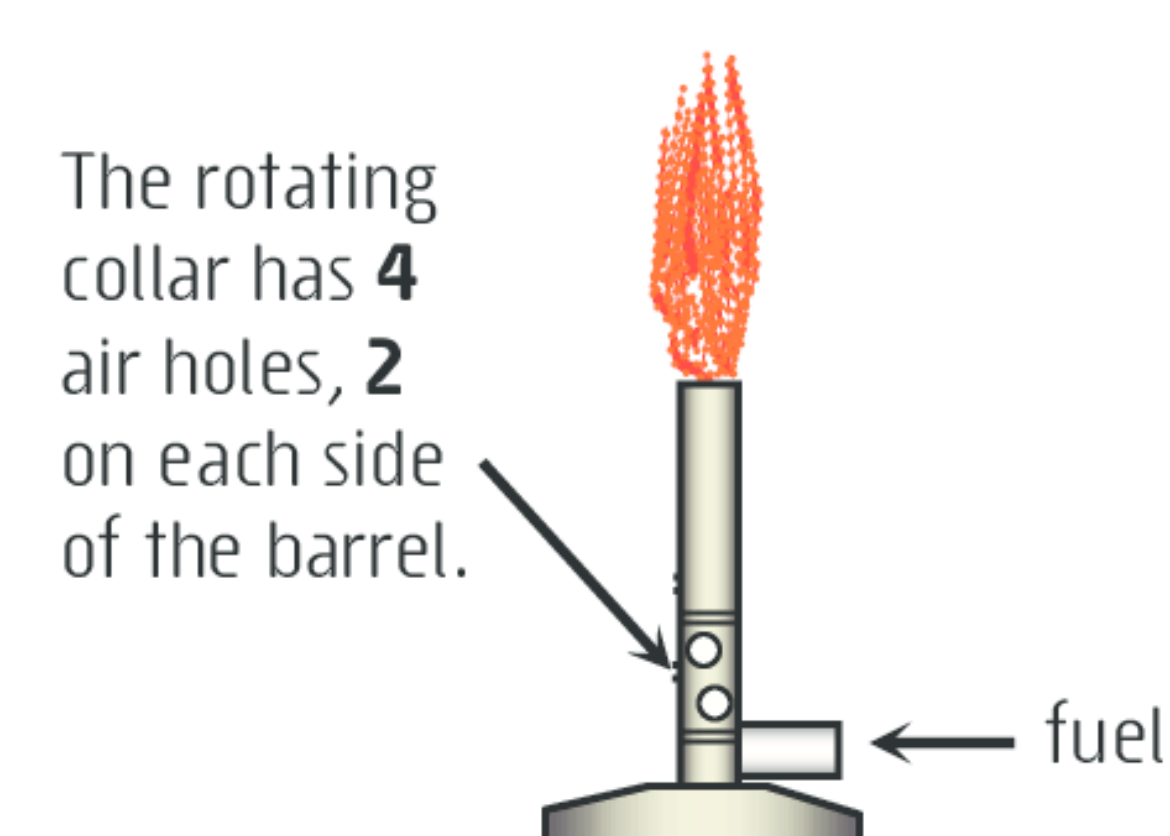
To test this hypothesis he made several aluminium foil covers with fixed diameter circular openings. These fit over the fully open Bunsen air holes so that the opening size can be controlled and measured. With the four Bunsen air holes fully open the smallest diameter foil covers were then taped over the air holes. The gas was turned on and the flame ignited. A high temperature thermistor placed in the Bunsen flame gave its temperature. The procedure was repeated using progressively larger diameter openings for the Bunsen air holes. The following data was collected.

Diameter of each Bunsen air hole opening (mm)	Total opening area of four Bunsen air holes (mm <sup>2</sup> )	Flame temperature (°C)
0 (fully closed air hole)		650
1.0		670
1.5		690
3.0		800
4.5		1000
6.0		1200
7.5 (fully open air hole)		1300

- What are the **independent** and **dependent variables** in this investigation?
- What are four other variables that the student should be careful to keep constant during the investigation?
- Process this data** in order to determine the values of the independent variable. This particular Bunsen has four identical air holes. Assume the air hole openings are circular.
- Graph this data and use it to draw a **conclusion** regarding the hypothesis.

- 7 Mitch had learnt in his chemistry class that pure water is a very poor conductor of electricity but when common table salt (NaCl) dissolved in it the solution formed would be quite a good conductor. He wondered if the amount of salt dissolved or indeed the type of salt used might have an effect on the degree of conductivity.

- Clearly identify the **dependent variable** and the two possible **independent variables** referred to by Mitch.
- Write two **hypotheses** that relate to Mitch's question.
- Choose one of your two hypotheses and **describe a method** you could use for an investigation into your hypothesis. You should indicate what apparatus you will need, the technique used and any measurements you will take. You should make specific reference to any controlled variables and the method used to keep these constant.
- Briefly outline how you would **process or present your data** in order to determine the validity of your hypothesis.



**FIGURE 5** Heat produced from a Bunsen burner comes from the combustion of the fuel natural gas (essentially methane, CH<sub>4</sub>). On this Bunsen a rotating collar surrounding the four air holes can be adjusted to vary the amount of air mixing with the fuel.



**FIGURE 6** According to the Australian mint, an Australian \$1 coin has a nominal mass of **9.00 g**.



**EXAMPLE 2** A student exercise involved measuring the mass of the same **\$1** coin. According to the Australian Mint, this has a nominal mass of **9.00 g**. Different groups of students made measurements using different balances. Their results are shown below. Comment on the **precision** and **accuracy** of their results.

Group	Mass (g)	Average
1	8.97, 9.02, 9.01, 8.97	<b>8.99 g</b>
2	8.67, 8.65, 8.65, 8.67	<b>8.66 g</b>
3	8.75, 7.98, 9.55, 8.81	<b>8.77 g</b>

**ANSWER:**  
**Group 1** results are **precise**, ie agree closely and **accurate**, ie close to the Mint's own accepted value of 9.00 g.  
**Group 2** measurements are **inaccurate** (not close to the accepted value) but **precise** (values agree closely).  
**Group 3** results are **inaccurate** and **imprecise**.

Attempt Set 7 # 1.



**FIGURE 7** The last digit of a digital display has some uncertainty, you will sometimes see the value of this digit fluctuate. The measurement shown here is written as 20.50 g rather than 20.5 g. Recording the zero better reflects the precision offered by the instrument.

5.3 Errors in numerical measurements

Investigations in chemistry always involve making and recording observations. Sometimes these are **qualitative**, ie they involve a written description such as the colour of a precipitate or the odour of a gas. Other observations involve a **numeric** measurement such as the mass of a reagent or the temperature of a reaction. These are **quantitative** observations. While quantitative measurements may appear more convincing and authoritative than qualitative ones it is very important to realise that numeric measurements **always** contain some degree of **error**, sometimes referred to as **uncertainty**.

**Accuracy** and **precision** are two different aspects of the error (uncertainty) in a measured value. (See Fig 6 and Example 2.) The closer a measured value is to the true or actual value, the more accurate it is. In Example 2, the measurements from Group 1 are quite accurate while those of Group 2 and 3 are inaccurate (assuming the coins mass is 9.00 g). Precision can be seen in a **set** of measurements that agree very closely, ie the measurements are spread over a **narrow range** of values. In Example 2, the measurements from Group 1 and 2 are equally precise (small range) but those of Group 3 are imprecise, ie there is a wide range of values. It is possible for a set of measurements to be precise (small range) but inaccurate, (not close to the accepted value) eg as seen in the measurements from Group 2.

The degree of precision and accuracy in a measurement depends upon the presence of two types of error, **random error** and **systematic error**. A systematic error may cause results to be **consistently lower** or **consistently higher** than the actual value. In Example 2, Group 2 results contain a systematic error. This could happen, for example, if the balance is in error giving consistently low values, ie it may need to be **recalibrated** or the students have forgotten to zero the balance or due to some consistent error with their technique.

Random errors, however, cause inconsistent results, ie some high and some low results. Random errors could be due to limitations in the balance (see 5.4), vibrations caused by people moving near or leaning on the bench or drafts near the balance or other environmental effects.

In a well designed and conducted investigation it may be possible to eliminate systematic error by using **correct technique** and **properly calibrated instruments**. However **random error** can be reduced but **never eliminated**. Even the accurate and precise results of Group 1 contain some random error, ie some values are a little high and some are a little low.

The effect of **random error** can be minimised by taking many measurements and **averaging** the result. This works, as in a large set of measurements for the same quantity there will be some randomly high results and some equally low results. Averaging tends to cancel these out leaving a more reliable answer. Occasionally a set of data contains a single result that is significantly different to the others or to the average, this is called an **anomaly** or **outlier**. The **outlier** should be eliminated from the averaging process. Outliers become most obvious when the data is graphed as these data points lie far from the line of best fit.

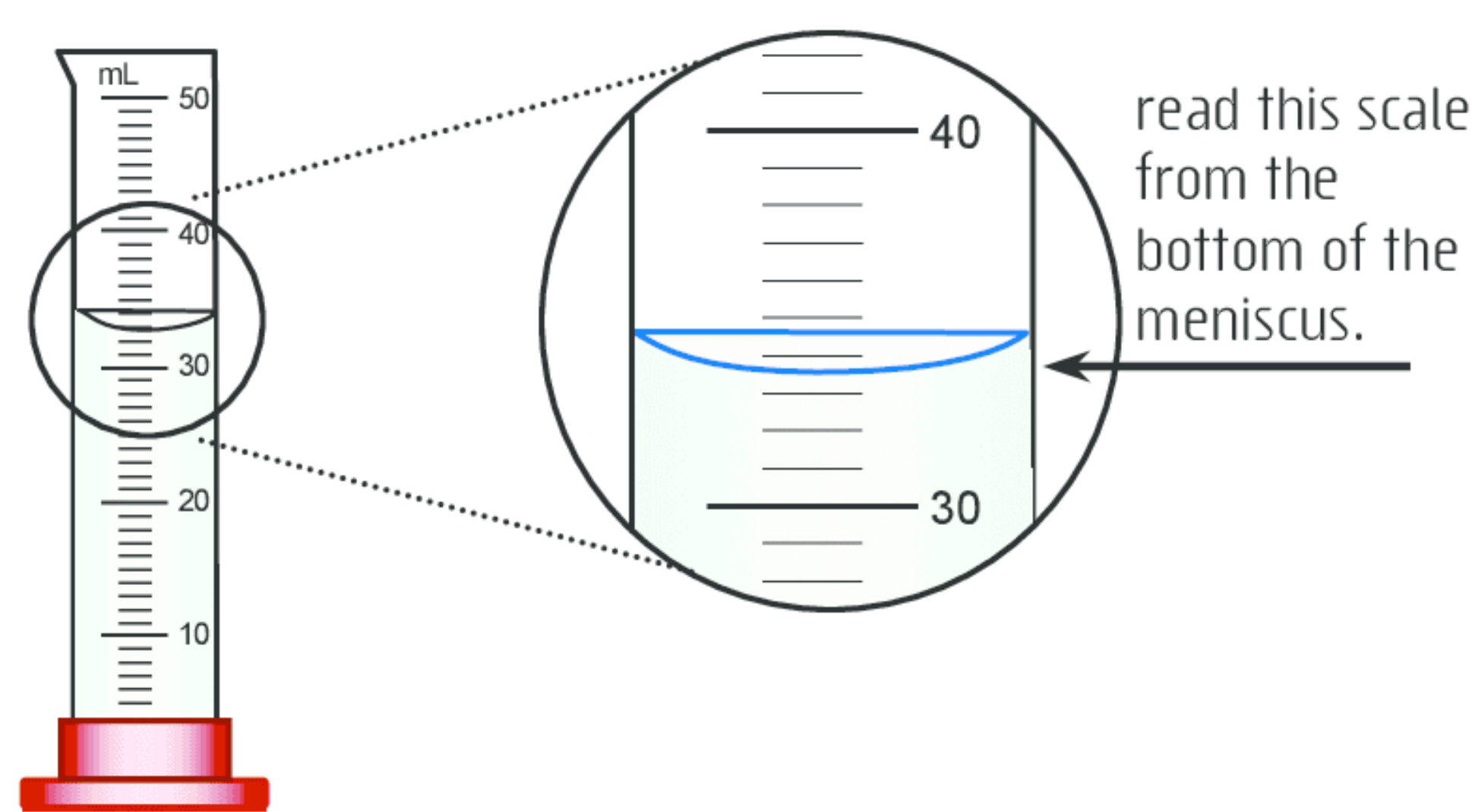
5.4 Making and recording measurements

The uncertainty (error) in a measurement depends upon the **instrument** itself, the **procedure** used and **skill** of the experimenter as well as **environmental** conditions under which the measurements are made (eg temperature, drafts or random vibrations). While it is possible to minimise some of these effects, a **limiting factor** is the precision offered by the instrument itself, ie the results can be no more precise than the instrument will allow.

When recording a measurement it is important to show the **precision offered by the instrument** used to make that measurement. To do this, all digits that are known with certainty are written, as well as a final digit which has some uncertainty. When recording a measurement from a **digital display** it is important to record all digits even if these are zeros at the end of a number. (See Fig 7.) Doing this correctly reflects the precision offered by the particular instrument used. When taking a reading from an instrument that has a **scale**, it is appropriate to read the scale to within **at least half the smallest scale division**. (See Fig 8.) If the scale divisions are large enough, you may reasonably estimate up to a tenth of one division but **no more than this**.



**FIGURE 8** The smallest divisions on this scale are 1 mL. It is reasonable to read it to within 0.5 mL, ie half the smallest division. As the divisions are quite large you may choose to measure to within 0.1 mL, ie 1/10<sup>th</sup> the smallest division. Thus, at best the volume in this measuring cylinder could be recorded as 33.7 mL or 33.8 mL. The last digit is known to have some uncertainty. It is **not** appropriate to record 33.75 mL as this indicates a higher precision than is available from this scale.



Every digit in a measurement, including the final uncertain one is a **significant figure**. The more significant figures there are in a measurement, the greater the precision. (See Example 3.) Table 1 shows the typical precision offered by some measuring cylinders.

Sometimes the inherent random error present in the measurements from an instrument are expressed as a **plus or minus**,  $\pm$  amount. This indicates the actual measured amount could be higher or lower than the recorded value by the  $\pm$  amount. (See Table 1.) For instruments with a scale the random error is usually  $\pm$  half the smallest scale division, for a digital display instrument it is  $\pm$  half the value of the last digit displayed. As well as quoting the random error, all measuring cylinders also quote a **temperature**, usually 20 °C, at which the measurements should be made. If the measuring temperature varies significantly from this then a systematic error will be introduced into the measurements. Random errors are minimised by using the most precise instrument that is practical for the task. (See Fig 9.)

**TABLE 1** Random error and recording measurements for a variety of measuring cylinders

Measuring cylinder	Smallest scale division	Random error as $\pm$	Measurement examples		
			Using significant figures only	Including $\pm$ random error	
10 mL	0.1 mL	$\pm 0.05$ mL	3.45 mL	3.45 mL $\pm 0.05$ mL	(ie 3.40–3.50 mL)
			7.80 mL	7.80 mL $\pm 0.05$ mL	(ie 7.75–7.85 mL)
50 mL	1 mL	$\pm 0.5$ mL	15.5 mL	15.5 mL $\pm 0.5$ mL	(ie 15.0–16.0 mL)
			42.5 mL	42.5 mL $\pm 0.5$ mL	(ie 42.0–43.0 mL)
250 mL	2 mL	$\pm 1$ mL	153 mL	153 mL $\pm 1$ mL	(ie 152–154 mL)
			227 mL	227 mL $\pm 1$ mL	(ie 226–228 mL)

**EXAMPLE 3** A student used three different digital mass balances to measure the mass of the same zinc granule. The values she recorded were 20.670 g, 20.7 g and 21 g. Comment on the **precision** and  $\pm$  **random error** in each of the balances used.

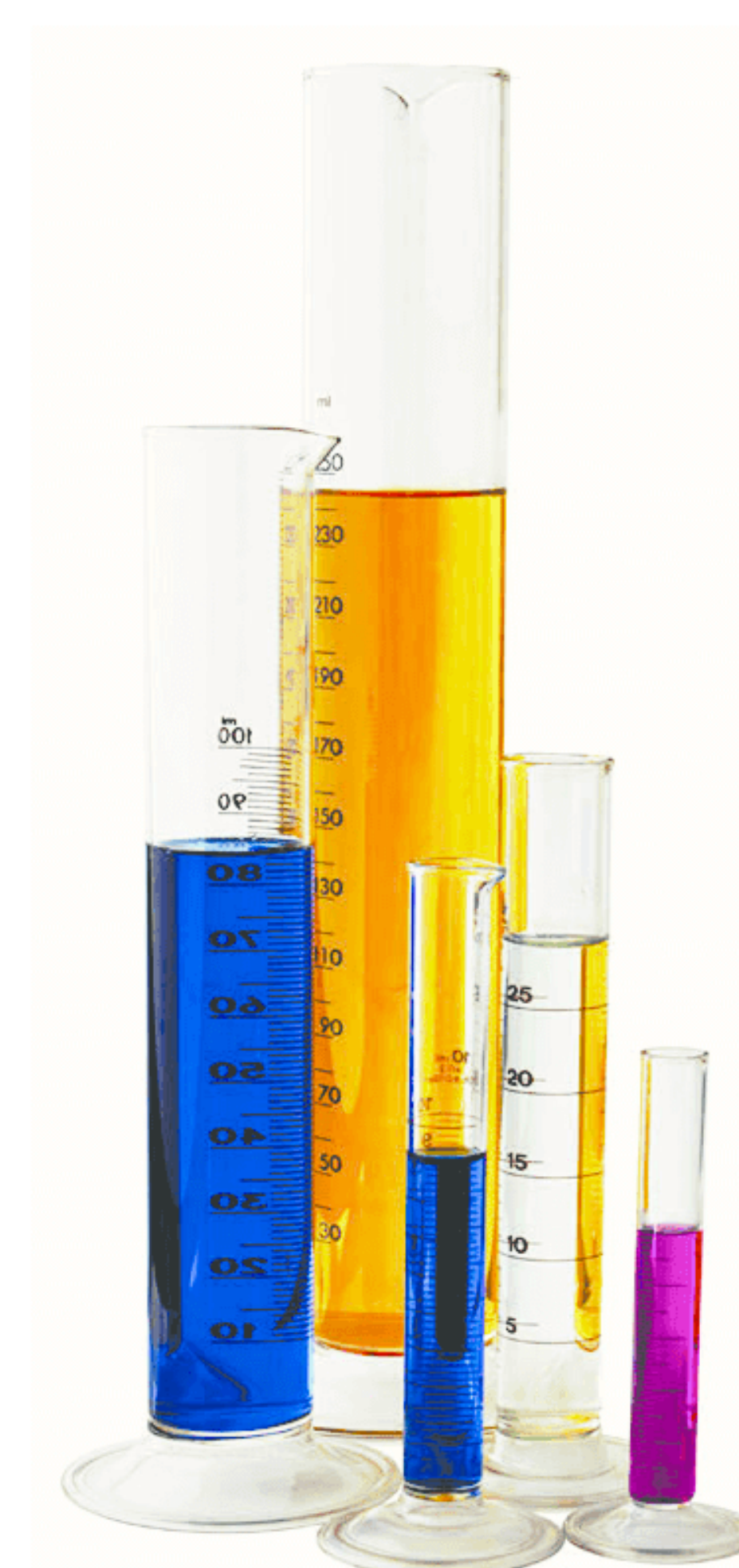
#### Measurement Comment

<b>20.670 g</b>	The recorded mass has five significant figures and so is the most precise measurement. The balance used is capable of measuring to one thousandth of a gram and has a random error of $\pm 0.0005$ g, ie half the value of the last displayed digit.
<b>20.7 g</b>	The recorded mass has three significant figures. This balance is capable of measuring to one tenth of a gram with a random error of $\pm 0.05$ g.
<b>21 g</b>	The recorded mass has two significant figures and is the least precise result. The balance can read to 1 g and has a random error of $\pm 0.5$ g.

## 5.5 Processing data and significant figures

When processing data from an investigation it is important to be aware of the number of significant figures in the measurements being processed. The following rules are used to count the number of significant figures (SF) in a measurement:

- ① All **non-zero** digits are significant, eg 7.92 (three SF). (**See border note at right.**)
- ② Zeros **between** two significant digits are significant, eg 60.3 (three SF), 9.0002 (five SF).
- ③ Zeros **before** the first non-zero digit are not significant, eg 0.35 (two SF), 0.009217 (four SF).
- ④ Zeros at the **end** of a number **and after** the decimal point are significant, eg 3.500 (four SF), 0.0710 (three SF).
- ⑤ Zeros at the **end** of a number and **before** the decimal point are not significant unless otherwise indicated, eg 3500 (two SF). If these zeros are significant then scientific notation can be used to show this, eg  $3.500 \times 10^4$  (four SF),  $3.50 \times 10^4$  (three SF) or  $3.5 \times 10^4$  (two SF).



**FIGURE 9** Scale division size and hence the random error varies with the size of a measuring cylinder. Typically, larger cylinders have larger scale divisions and hence larger random errors.

To minimise random errors in experimental work, choose the most precise instrument that is practical for the task. When measuring volumes of 10 mL or less use a 10 mL measuring cylinder, not a 50 mL or 250 mL cylinder as these have a greater inherent random error. Only use larger cylinders as appropriate, eg for measuring 30 mL, a 50 mL measuring cylinder may be suitable but not a 10 mL or 250 mL measuring cylinder.

Notice the reference temperature, **20 °C** and random error,  $\pm 0.5$  mL (half the 1 mL graduations) shown on this 50 mL cylinder.



Attempt Set 7 # 2 and 3.

#### Zeros!

The **non-zero** digits in a measurement are **always** significant but zeros **may** be significant.

**Key:** **significant zero's**..... 0  
**not significant zero's** ..... 0

- 100819.504..... ②
- 0.181954..... ③
- 0.00181954..... ③
- 181954.0..... ④
- 181954.000..... ④
- 1819540..... ⑤
- 181954000..... ⑤
- 181954.0..... ④
- 181954000.0..... ② and ④



**Exact numbers** are those which contain no uncertainty. Some examples include the number of protons in an oxygen nucleus is exactly 8, the coefficients of a balanced equation or the subscripts in a formula.

Attempt Set 7 # 4, 5 and 6.

**Important note to students:**  
The Current SCASA year 12 Examination design brief for use in 2016 refers to the use of significant figures in the following way. 'Numerical answers should be expressed to the **appropriate number of significant figures** and include units where applicable.' Students would be advised to check the current requirements regarding numeric answers and significant figures closer to the time of their examination.

Attempt Set 7 # 7.

Complete Set 7.

EXAMPLE 4 How many significant figures are present in each of the following volume measurements?		
7.08 x 10 <sup>3</sup> mL	three significant figures	see rule ① and ②
7.800 x 10 <sup>3</sup> mL	four significant figures	see rule ① and ④
7.0800 x 10 <sup>3</sup> mL	five significant figures	see rule ①, ② and ④
0.758 mL	three significant figures	see rule ① and ③
0.0708 mL	three significant figures	see rule ①, ② and ③
780 mL	two significant figures	see rule ① and ⑤

Data collected in an investigation often needs to be processed in order to calculate the value of some variable of interest. When this is done, the calculated result **must not** be more precise than the measured data used to calculate it. For a calculation that requires **multiplication** or **division**, the answer is given with as many significant figures as the measurement with the **least number** of significant figures.

EXAMPLE 5 Evaluate the following and give the answer to the correct number of significant figures.		
a. 1.498 g ÷ 6.2 x 10 <sup>-1</sup> L = 2.416129 g L <sup>-1</sup> = <b>2.4 g L<sup>-1</sup></b> (2SF)	This calculation involves division so the answer only has as many SF as the number with the least SF. As 6.2 x 10 <sup>-1</sup> L has the least SF (two) so the answer is rounded to two significant figures even though 1.498 g has four SF.	
b. $\frac{1.04 \text{ g} \times 7.000}{12.01 \text{ g mol}^{-1}}$ = 0.6061615 = <b>0.606 mol</b> (3SF)	This calculation involves multiplication and division so the answer only has as many SF as the number with the least SF. As 1.04 g has the least SF (three) so the answer is rounded to three significant figures even though 7.000 and 12.01 both have four SF.	

Sometimes a calculation will require **addition** or **subtraction** of data values. In this case, the answer is quoted with as many **decimal places** as the measurement with the least number of decimal places. When counting decimal places, the measurements must be expressed with the **same powers of ten**. See Example 6.

EXAMPLE 6 Evaluate the following and quote the answer to the correct number of decimal places (DP).		
a. 1.49 x 10 <sup>2</sup> g + 6.2 g = 149 g + 6.2 g = 155.2 = <b>155 g</b> (0 DP)	This calculation involves addition so the answer only has as many DP as the number with the least DP. As the measurement 1.49 x 10 <sup>2</sup> g has the least decimal places (nil) when written to the same powers of ten as 6.2, ie 1.49 x 10 <sup>2</sup> g becomes 149 g so the answer has nil decimal places.	
b. 7.5530 x 10 <sup>3</sup> L - 6.790 L = 7553.0 L - 6.790 L = 7546.21 L = <b>7546.2 L</b> (1 DP)	This calculation involves subtraction so the answer only has as many DP as the number with the least DP. Using the same powers of ten, the numbers are 7553.0 and 6.790. Thus 7553.0 has the least decimal places (one, when expressed with the same powers of ten) so the answer is rounded to one decimal place.	



## Set 7 Measurement errors and significant figures

1. A group of chemistry students conducted an investigation into the density of distilled water at 20 °C. To do this they needed to know the mass and volume of a sample of water to calculate its density using, **density = mass ÷ volume**. (See border note.) Their research had shown the density of water at 20 °C should be **1.00 g mL<sup>-1</sup>**.

Their procedure involved measuring 25.0 mL of water with a 50 mL measuring cylinder then pouring this into a preweighed 100 mL beaker. They reweighed the beaker + water and used this data to calculate the density of water. The measurements were repeated several times, drying and reweighing the beaker each time. See the table below.

Trial	Volume of water (mL)	Mass of empty beaker (g)	Mass of beaker + water (g)	Mass of water (g)	Density of water (g mL <sup>-1</sup> )
1	25.0	45.8	70.1		
2	25.0	45.8	70.0		
3	25.0	45.8	70.2		
4	25.0	45.8	67.9		
5	25.0	45.8	69.9		
6	25.0	45.8	70.1		

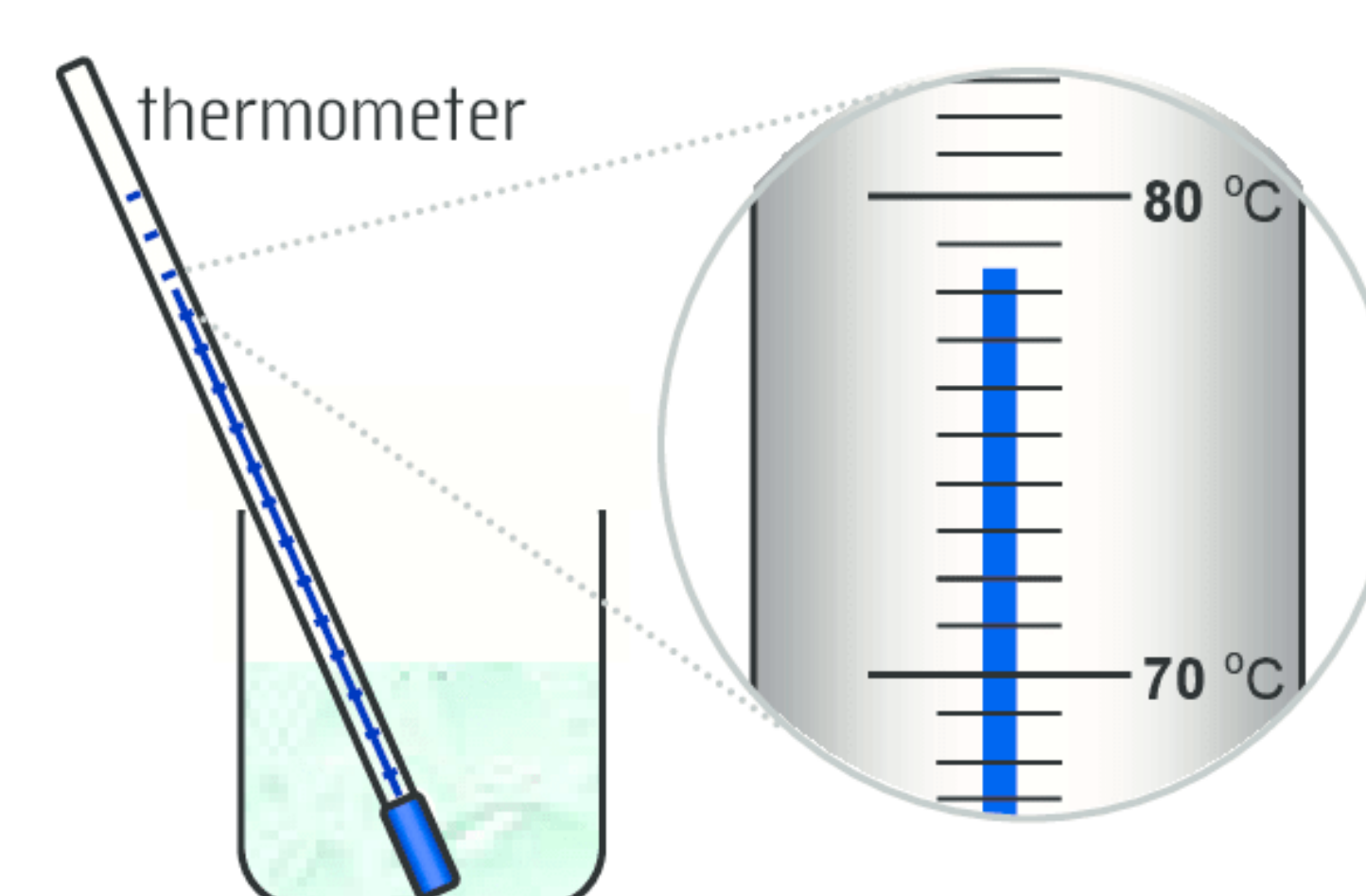
- a. Complete the table and determine the **density** of water for each trial.
  - b. With the exception of Trial 4, would you describe the measurements for the mass of the **beaker + water** as **precise** or **accurate**, both or neither? **Explain**.
  - c. The density of water at 20 °C is 1.00 g mL<sup>-1</sup> and so a 25.0 mL sample of water would be expected to have a mass of 25.0 g. With this in mind, refer to the students' results and use these to show your understanding of **outlier**, **random error** and **systematic error**.
  - d. When the students determined their density for water they used an **average** of all the results with the exception of Trial 4. Why does averaging the results give a more reliable answer and why were they justified in eliminating Trial 4? In your answer you should refer to **outliers** as well as **random** and **systematic** errors.
  - e. All school laboratories have **standard masses**, such as 10.00 g, 50.00 g and so on, that can be used for checking the **calibration** of a mass balance. **Describe** how the students could use these to check the calibration of their balance.
  - f. Apart from Trial 4, all of their results are a little low. This suggests a **systematic error** is causing the problem. Describe how their **technique** for measuring volume could be a source of this systematic error.
  - g. **Suggest** two possible causes of the rather large random error in Trial 4.
2. A student investigation involved **measuring** the **temperature** of some boiling water in a beaker as it slowly cooled to room temperature over a 10 minute period. The diagram at right (Fig 10) shows the appearance of the apparatus.
    - a. Students in the same group recorded the temperature shown in Fig 10 as **78 °C**, **78.5 °C**, **78.50 °C** and **79 °C**. Which of these is the most appropriate way to record the temperature shown? **Explain**.
    - b. In one group, the student responsible for measuring temperature, had a habit of **removing** the thermometer from the water (for ease of reading) before reading the temperature. What effect if any would this have on the temperature measurements and what sort of error is it?
    - c. How would the **size** of this error in part (b) change as the cooling water reached room temperature?
    - d. On graphing their results for the cooling water it became obvious that one of the temperature measurements did not fit the cooling trend. This data point was a long way off the line of best fit. What **type** of error was this and how should they deal with it?

The **density** of a material **compares** its **mass** to its **volume**. Essentially it describes how heavy a material is for its size. For this reason substances like gold that are very dense (19.3 g mL<sup>-1</sup>) feel heavy while substances like air that have a low density (0.00127 g mL<sup>-1</sup>) feel light. (When comparing same size samples.)

Density is calculated as follows:

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

**FIGURE 10** Monitoring the temperature of some hot water as it cools. An enlarged section of the thermometer's temperature scale is shown.





**FIGURE 11** The digital display for the mass balance in Question 3.



3. During a laboratory assessment a student was given the task of experimentally determining the amount of **water of crystallisation** present in some oxalic acid crystals. The crystals have a known formula of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , which means they should contain **14.3%** by mass  $\text{H}_2\text{O}$ . To measure this value the student weighed a sample of the crystals, ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) into a preweighed crucible. The crucible and crystals were heated for three minutes to expel the water of crystallisation thus forming anhydrous oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ). After cooling, the crucible and its remaining contents were reweighed. The student's results are shown here.

mass of empty crucible.....21.05 g  
 mass of crucible +  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .....24.10 g  
 mass of crucible +  $\text{H}_2\text{C}_2\text{O}_4$  (ie after heating) .....23.80

- a. Fig 11 shows how the crystals are weighed after heating. It is not appropriate to record this mass as 23.8 g. What should be recorded? **Explain.**
- b. According to the student's results, the oxalic acid crystals contain only 9.83% water. This is much lower than the expected 14.3% and was a result of insufficient heating, ie the crystals hadn't lost all of their water of crystallisation. What **type** of error is this? **Explain.**
- c. The student decides to **repeat** the investigation several times using the **same technique** as described above. He intends to **average** the repeat values in the hope of getting a final result closer to what is expected. Would this produce a result closer to the expected value of 14.3%? **Explain.**
- d. Before weighing the crucible it must be allowed to cool down inside a **desiccator**. What is a desiccator and why shouldn't hot objects be weighed on an electronic balance? (Apart from possibly causing damage to the balance.)

4. How many **significant figures** are shown in each of the following measurements?

- |                          |            |                          |                             |
|--------------------------|------------|--------------------------|-----------------------------|
| a. 57.81 mL              | d. 400 kPa | g. $6.6 \times 10^3$ kPa | j. $0.4^\circ\text{C}$      |
| b. 10.1 Pa               | e. 6250 L  | h. 1000.0 Pa             | k. 0.0032 g                 |
| c. $4.04 \times 10^4$ mg | f. 1000 g  | i. 0.09000 kg            | l. $1.00110 \times 10^6$ Pa |

When **rounding** a number, if the leftmost digit to be deleted is:

- **greater than 5** then increase the final remaining digit by 1.
- **less than 5** then the final remaining digit is unchanged.
- **equal to 5** then increase the final remaining digit by 1.

eg: The following are rounded to 2 SF.

6.54 becomes 6.5  
 6.55 becomes 6.6  
 6.56 becomes 6.6

**Scientific notation** is a convenient way of expressing large or small numbers. It expresses the number as a product of a number between one and ten and a power of ten, eg:

Avogadro's number  $6.02 \times 10^{23}$   
 mass of a proton  $1.67 \times 10^{-24}$  g  
 thickness of a page  $2.1 \times 10^{-5}$  m

5. **Round** the following numbers to the number of significant figures (SF) indicated. (See border note.)

- |                   |                                  |                                    |
|-------------------|----------------------------------|------------------------------------|
| a. 0.7875 (3 SF)  | d. 4.043549 (5 SF)               | g. 361.2 (1 SF)                    |
| b. 257814 (3 SF)  | e. 10.65 (2 SF)                  | h. $2.00031 \times 10^{-4}$ (4 SF) |
| c. 0.01252 (3 SF) | f. $6.250557 \times 10^6$ (5 SF) | i. $6.650 \times 10^3$ (2 SF)      |

6. Convert the following measurements to the units indicated. Express answers in **scientific notation** and with the **appropriate** number of **significant figures** (See appendix p248 relating common units.)

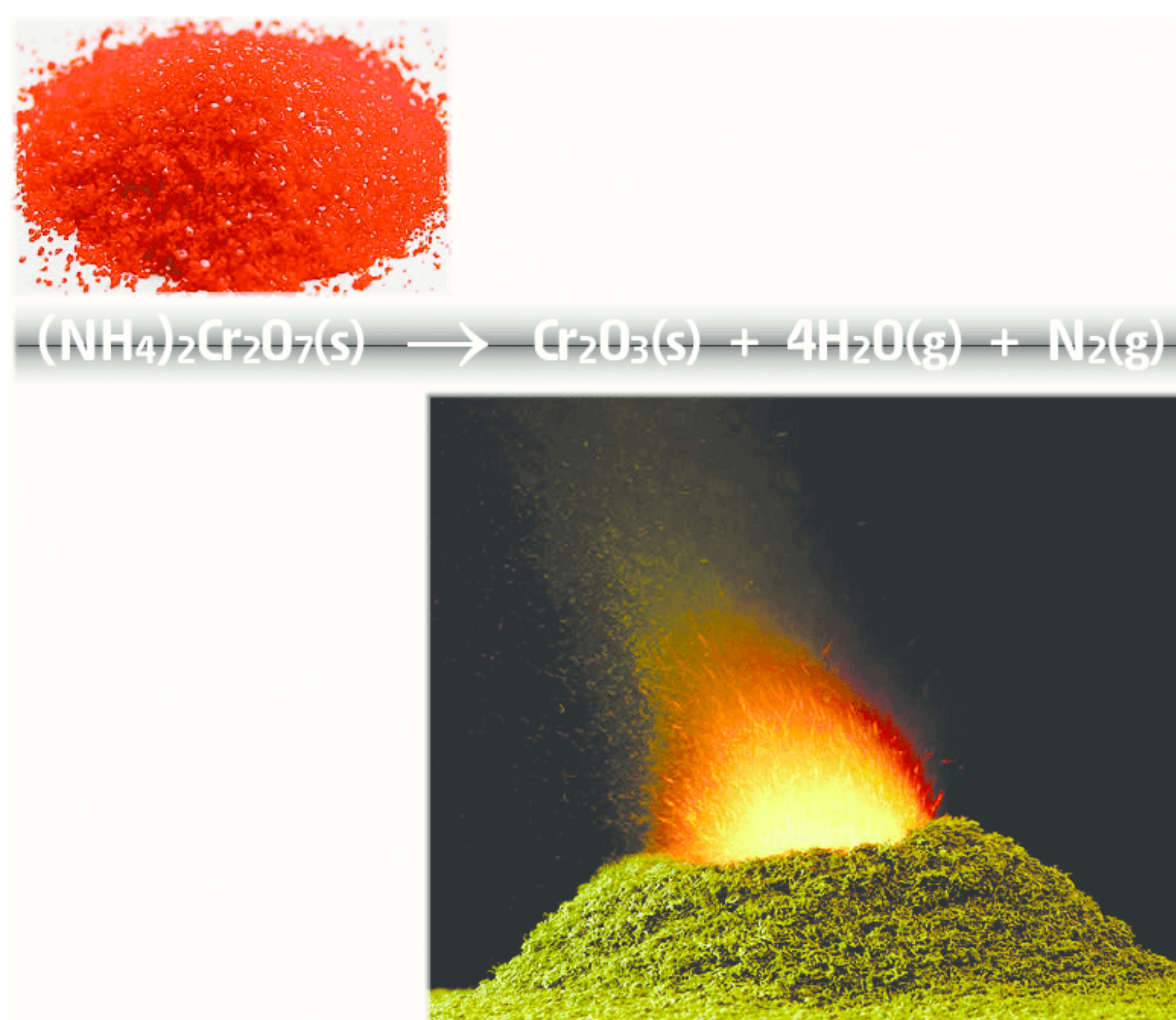
- |                               |                     |                               |
|-------------------------------|---------------------|-------------------------------|
| a. 6.59 kL to L               | e. 78631 Pa to kPa  | i. 7.25 tonne to kg           |
| b. 4.990 L to mL              | f. 14.99 mg to g    | j. 3.4 tonne to g             |
| c. $3.72 \times 10^6$ mL to L | g. 2.266 MPa to kPa | k. $356.9^\circ\text{C}$ to K |
| d. 989.27 MPa to Pa           | h. 7.62 atm to kPa  | l. 775 K to $^\circ\text{C}$  |



7. A student needs to process her **experimental data** as shown in the following examples. Evaluate these and express your answer to the correct number of **significant figures**.
- $265.3 \times 0.16$
  - $$\frac{3.8265}{0.07250}$$
  - $$\frac{1.350 \times 10^3 \times 350}{0.59962}$$
  - $$\frac{9.379 \times 10^2 \times 3.50}{0.59962 \times 17.008}$$
8. **Some experimental measurements are processed as shown here. Evaluate** these and round your answer to the correct number of significant figures.
- $3.042 + 192.1$
  - $0.08193 + 0.0032$
  - $1.731 \times 10^2 + 3.296 \times 10^3$
  - $192.1 - 3.042$
  - $8.192 \times 10^5 - 7.791 \times 10^4$
9. **Process** the following experimental data and round your answer to the correct number of significant figures. Take care as these calculations involve both addition and multiplication. (Note: Complete the addition or subtraction first, evaluate the number of significant figures in the result and then complete the calculation.)
- $$\frac{4.64 \times 10^3 + 14.592}{0.3766 \times 6.312}$$
  - $$\frac{7.332 \times 10^4 - 21}{9.728 \times 3.4741}$$
10. A student investigating the effect of the surface area of zinc granules on its reaction rate with hydrochloric acid counts out exactly 12 zinc granules. What is the **total surface area** of the twelve zinc granules if the average zinc granule is estimated to have a surface area of:
- $1 \times 10^2 \text{ mm}^2$
  - $1.0 \times 10^2 \text{ mm}^2$
11. You are designing an investigation that requires you to carefully measure out 5.0 mL of a hydrochloric acid solution and 95 mL of distilled water. You have at your disposal several measuring cylinders: 10 mL, 50 mL, 100 mL and 250 mL. What measuring cylinder(s) would you use? **Justify** your choice in terms of **minimising error**.
12. A student's investigation requires him to find the average mass of a single drop of water. To do this he uses a pipette to add **exactly** 20 drops of water to a beaker. He finds the beaker's mass increased by 1.059 g as a result of the added water. What value can he **reasonably quote** for the average mass of a single drop of water?
13. In order to dilute some sulfuric acid, Michelle measured **35 mL** of distilled water using a **250 mL** measuring cylinder. Then using a **10 mL** measuring cylinder (a more precise instrument) she added **6.55** mL of concentrated sulfuric acid to the same conical flask. As part of her data processing Michelle needed to add these volumes.
- What value can Michelle **reasonably quote** for the combined volume of distilled water and sulfuric acid? Assume the two volumes are additive.
  - What can Michelle do to obtain a **more precise** final result?



# CHAPTER 6 | CHEMICAL EQUATIONS



**FIGURE 1** The decomposition of **ammonium dichromate**,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (orange-red crystals, top left) is a spectacular exothermic chemical reaction producing plumes of dark green chromium(III) oxide (bottom right), large amounts of water vapour, nitrogen gas and considerable heat.

## 6.1 Chemical change

During a **chemical reaction** substances known as **reactants** disappear over time to be replaced by chemically different substances known as **products**. When this happens the total **mass** and number of each type of **atom** present is unchanged but the way in which the various atoms are bonded does change.

A chemical change is summarised using a **chemical equation**. It shows the chemical formula of the reactants and products and has an arrow,  $\rightarrow$  pointing towards the products. A plus sign (+) separates each substance in the equation.

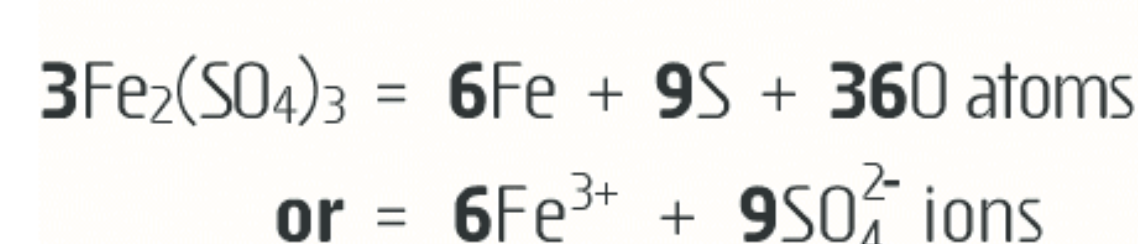
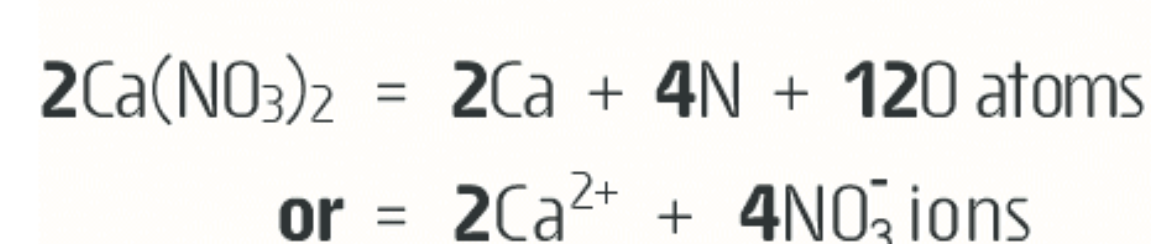
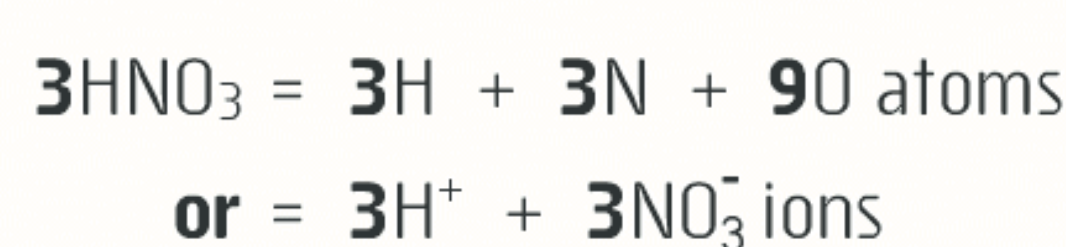
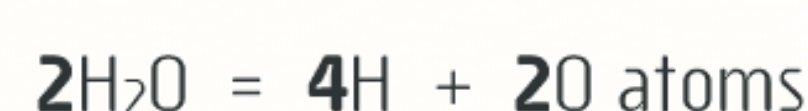
Sometimes reactions cannot go to completion. This happens when the reaction products are able to recombine to reform the original reactants. This situation is shown using a double arrow,  $\rightleftharpoons$ . The double arrow signifies a **reversible reaction** meaning both forward and reverse reactions are occurring.

Attempt Set 8 # 1.

## 6.2 Balancing chemical equations

In a balanced chemical equation numbers called **coefficients** are written in front of each formula. (See border note.) Coefficients are used to ensure there are equal numbers of atoms of each element on both the reactant and product side of the equation, ie ensuring conservation of mass.

**Coefficients** written in front of a formula apply to each atom or ion in that formula.



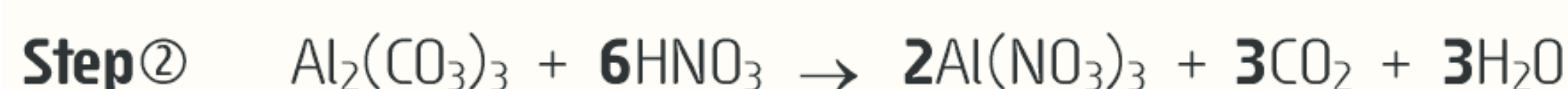
To write a balanced chemical equation:

- ① Write the formula of reactants (separated by a + sign) followed by an arrow with the formula of products (separated by a + sign) to the right of the arrow.
- ② Place coefficients in front of formulas as needed so that there are equal numbers of each type of atom on either side of the equation. (See border note.) Priority is to first balance any atoms that appear in only one formula on each side of the equation.
- ③ Write subscripts (s), (l), (g) or (aq) to show the physical state of each substance.

**EXAMPLE 1** A student dropped a solid piece of aluminium carbonate into a beaker of nitric acid solution. The solid fizzed and dissolved producing an aluminium nitrate solution, liquid water and carbon dioxide gas. Write a **balanced chemical equation** for this reaction.



The reactants are aluminium carbonate,  $\text{Al}_2(\text{CO}_3)_3$  and nitric acid,  $\text{HNO}_3$ . These substances are written first followed by an arrow pointing to the products aluminium nitrate  $[\text{Al}(\text{NO}_3)_3]$ , carbon dioxide  $[\text{CO}_2]$  and water  $[\text{H}_2\text{O}]$ . Ensure all **formulas** are correct.



**Al** is balanced first  $[2\text{Al}(\text{NO}_3)_3]$  as it appears in only two formulas. **N** is balanced next as it is now fixed at **6N** on the product side  $[2\text{Al}(\text{NO}_3)_3]$  and also appears in two formulas only,  $\therefore$  write **6HNO<sub>3</sub>**. H is now fixed at **6H** on the reactant side  $[6\text{HNO}_3]$  and only appears in two formulas so it is balanced next. **C** can now be balanced. At this point **O** is balanced. Notice **O** appears in all five formulas and hence this is the most difficult element to balance. It should be left till last to be balanced.



Add the subscript **(s)**, **(l)**, **(g)** or **(aq)** as appropriate for each substance.

Attempt Set 8 # 2, 3, and 4.

## 6.3 Net ionic equations

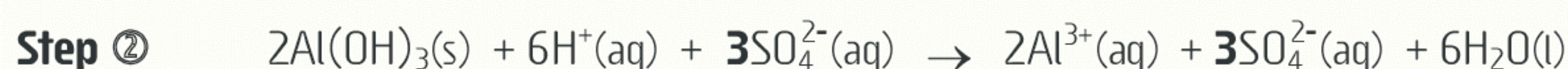
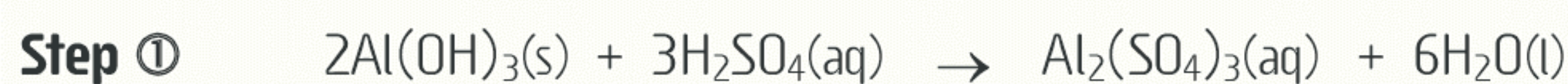
Chemical reactions that happen in aqueous solution (where some substances are dissolved in water) are often better understood as a **net ionic equation**. In these equations any dissolved substances that are mainly present as ions are shown as ions in the equation. Ions which are present in solution but do not take part in the chemical change are called **spectator ions**. These ions are not included in the net ionic equation.



When writing a **net ionic equation**:

- ① First write the balanced chemical equation, including phases, ie (s), (l), (g) or (aq).
- ② Do not change the formulas of any solids (s), liquids (l) or gases (g).
- ③ Rewrite in ion form the formula of any dissolved ionic compound or dissolved strong acid. (See border note at right.)
- ④ Remove any spectator ions. To do this, reduce by an equal amount the number of any ion that appears unchanged on both sides of the equation until it is either gone from the equation or appears on only one side of the equation.

**EXAMPLE 2** Write a **net ionic equation** for the reaction between solid aluminium hydroxide and sulfuric acid solution to form aluminium sulfate solution and water.

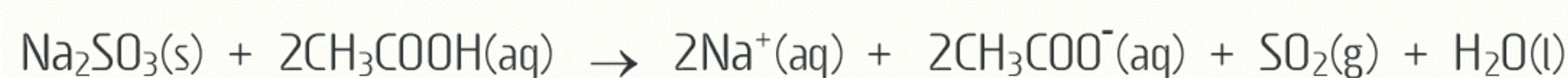
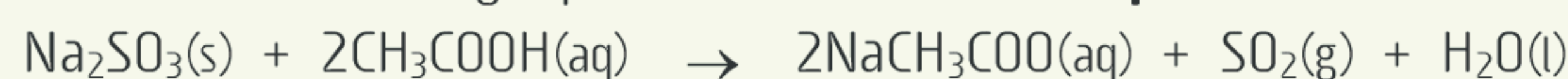


As  $\text{H}_2\text{SO}_4(\text{aq})$  is a strong acid and is dissolved in water, ie **(aq)**, then  $3\text{H}_2\text{SO}_4$  is written as  **$6\text{H}^+ + 3\text{SO}_4^{2-}$** . The product  $\text{Al}_2(\text{SO}_4)_3$  is ionic and dissolved in water so it is written as  **$2\text{Al}^{3+} + 3\text{SO}_4^{2-}$** . All other substances are solids, liquids or gases, therefore their formulas are left as they are.



The equation contained spectator ions ( $\text{SO}_4^{2-}$ ) so  **$3\text{SO}_4^{2-}(\text{aq})$**  ions were removed from each side of the equation to give the net ionic equation.

**EXAMPLE 3** Convert the following equation into a **net ionic equation**.



$\text{Na}_2\text{SO}_3(\text{s})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$  are in solid, liquid and gas phase respectively so their formulas are left as they are. Although  $\text{CH}_3\text{COOH}(\text{aq})$  is dissolved it is neither ionic nor a strong acid and so its formula is left as is. The product  $2\text{NaCH}_3\text{COO}(\text{aq})$  is dissolved and ionic so its formula is rewritten as  **$2\text{Na}^+ + 2\text{CH}_3\text{COO}^-$** . This equation does not contain spectator ions and so is left as it is.

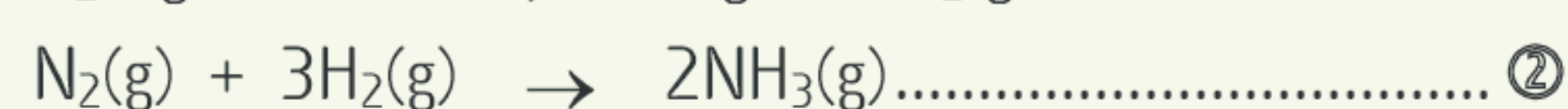
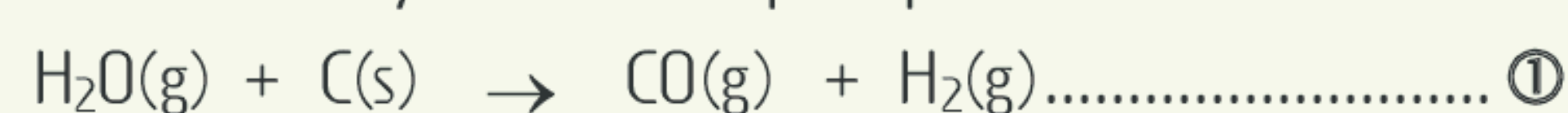
Attempt Set 8 # 5, 6 and 7.

## 6.4 Sequential reactions (E)

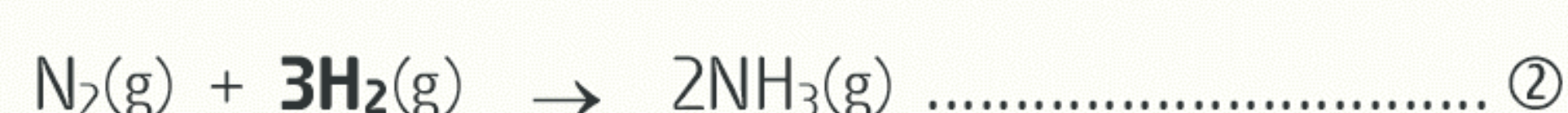
In a series of **sequential reactions**, the product of an initial reaction goes on to become a reactant for a subsequent reaction. Many natural and industrial processes involve sequential reactions. (See Fig 2.) The equations for several sequential reactions can be added to produce one overall equation. When adding sequential equations:

- ① Identify the product in the first equation that becomes a reactant in the second equation. This is the **linking reagent**.
- ② Multiply the coefficients of each equation by an appropriate factor so that the quantity (ie coefficient) of the **linking reagent** found in step① is the same in both equations.
- ③ All the reactants from both equations are written as the reactants of a single equation. Similarly all the products of both equations added to the product's side of the equation.
- ④ If a reagent appears on both sides of the equation it is reduced by an equal amount until it is either gone from the equation or appears on only one side of the equation.

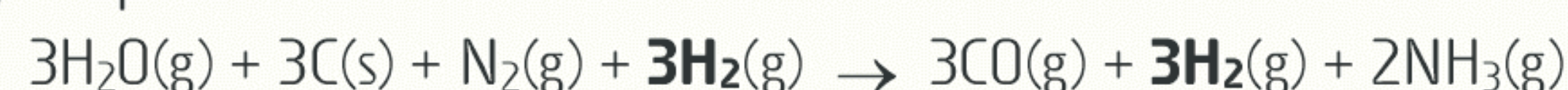
**EXAMPLE 4** Ammonia is a most important substance used in the manufacture of fertilisers and explosives. It can be manufactured by the two step sequence shown here. **Add these two equations.**



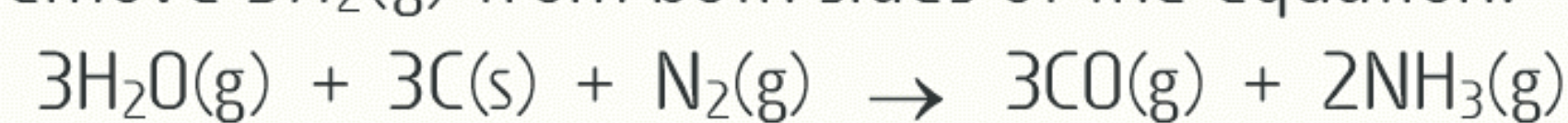
$\text{H}_2$  is the linking reagent as it is the product of the first reaction that becomes a reactant of the second reaction. Thus equalise the quantity of  $\text{H}_2(\text{g})$  in both equations. To do this multiply the coefficients of equation ① by three and leave equation ② as is.



Add both to give a single equation.

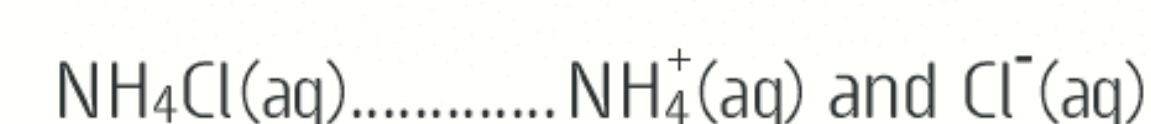
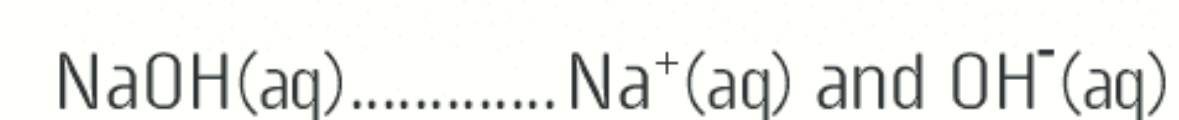


Simplify the result, ie remove  $3\text{H}_2(\text{g})$  from both sides of the equation.

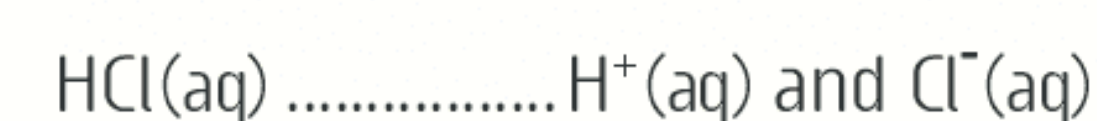


**Ionic substances** include any compounds that contain a combination of metal elements (or  $\text{NH}_4^+$ ) and non-metal elements.

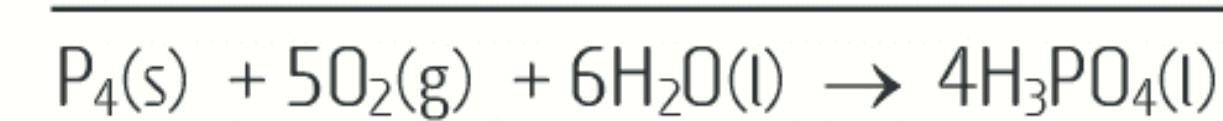
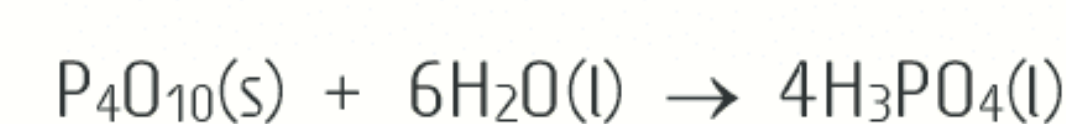
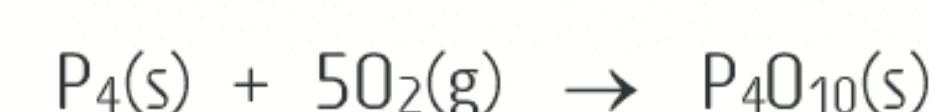
When dissolved in water these are best represented as independent ions. Eg:



When dissolved in water **strong acids** are also best represented as independent ions. Eg:



**FIGURE 2** Many natural and industrial processes involve sequential reactions. The manufacture of **phosphoric acid** by the 'electric furnace method' is one example. It involves burning phosphorus ( $\text{P}_4$ ) in air ( $\text{O}_2$ ) to form phosphorus(V) oxide ( $\text{P}_4\text{O}_{10}$ ). Adding water to  $\text{P}_4\text{O}_{10}$  produces phosphoric acid. The two sequential reactions and the overall reaction for this process are shown here.



Phosphoric acid is ranked amongst the top ten industrial chemicals to be manufactured worldwide. Its major use is in the manufacture of phosphate fertiliser. Polyphosphates derived from phosphoric acid are used in detergents to aid in water softening.

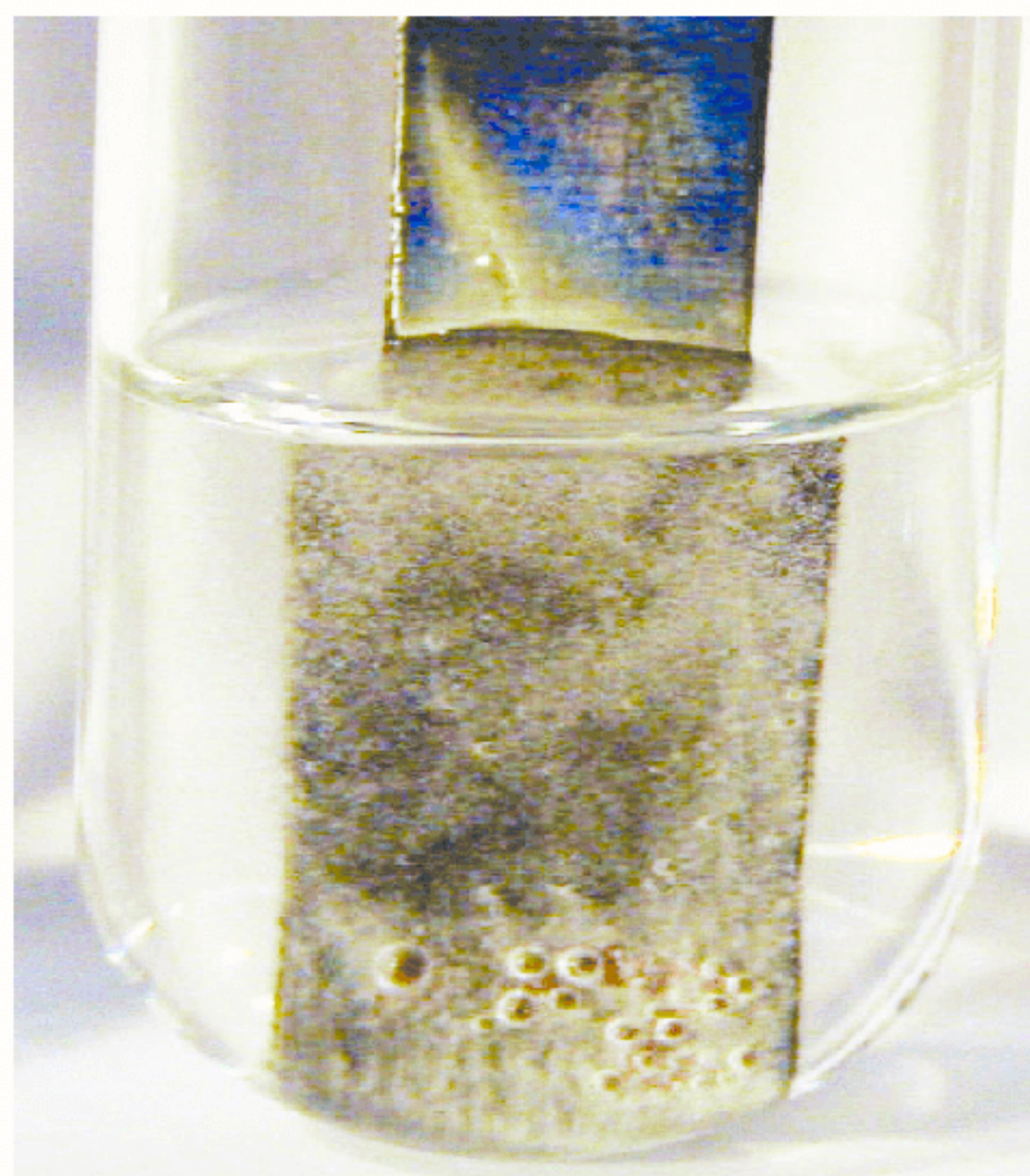
Around the home phosphoric acid may be found as an ingredient in rust removers. Low concentrations are found in cola style **soft drinks**, for its tangy effect. Phosphates manufactured from phosphoric acid are also found in products like baking powder.

Complete Set 8.



## Set 8 Writing chemical equations

**FIGURE 3** A zinc strip [Zn(s)] reacting with a dilute hydrochloric acid solution [HCl(aq)]. Notice the formation of hydrogen gas bubbles [H<sub>2</sub>(g)] on the surface of the zinc strip.



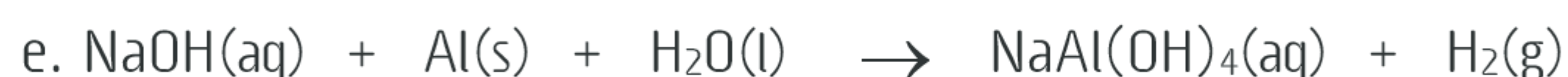
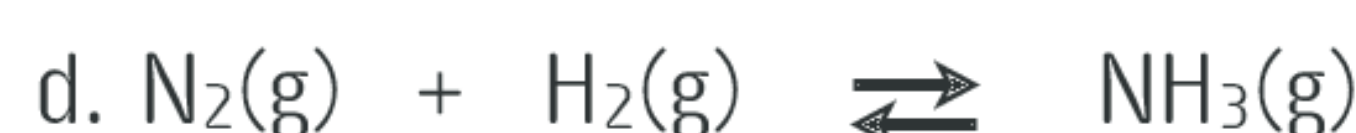
Remember a double arrow,  $\rightleftharpoons$  signifies a **reversible reaction**. Thus both forward and reverse reactions are occurring.

1. Consider the balanced equation shown here for the reaction occurring in Fig 3.



- Name** the reactants and products of this reaction.
- In this reaction what substances are consumed and what substances are formed?
- In this reaction, one atom of Zn is consumed and one atom of Zn is produced, thus the atoms of Zn are conserved. Is this true for all atoms in all reactions? **Explain**.
- A student performed an investigation into this reaction. He found the consumption of 6.48 g of reactants (Zn and HCl) resulted in the formation of 7.32 g of ZnCl<sub>2</sub> and 2.55 g of H<sub>2</sub>. Clearly the student has made a significant error. **Explain**.

2. Use appropriate coefficients to **balance the following** partially written chemical equations.



3. **Rewrite** these word equations as **balanced chemical equations**. Be sure to use correct formula and show the phase of each substance.

- solid copper(II) carbonate + nitric acid solution gives copper(II) nitrate solution + carbon dioxide gas + water liquid
- sulfuric acid solution + copper(II) hydroxide suspension gives copper sulfate solution + water liquid
- solid aluminium oxide + nitric acid solution gives aluminium nitrate solution + water liquid
- granulated zinc + hydrochloric acid solution gives zinc chloride solution + hydrogen gas
- sulfur dioxide gas + potassium hydroxide solution gives potassium sulfite solution + water (**This is a reversible reaction.**)
- ammonium chloride solution + solid calcium hydroxide gives ammonia gas + calcium chloride solution + water (**This is a reversible reaction.**)



**FIGURE 4** Soft drinks owe their fizz to carbon dioxide gas. CO<sub>2</sub>(g) is injected into soft drink under pressure. When this is done most of the CO<sub>2</sub>(g) dissolves in the drink forming CO<sub>2</sub>(aq). A portion of the dissolved CO<sub>2</sub>(aq) then reacts with water producing the unstable compound carbonic acid, H<sub>2</sub>CO<sub>3</sub>(aq). All of these reactions are reversible.



then



Releasing the cap on a soft drink bottle causes the unstable H<sub>2</sub>CO<sub>3</sub>(aq) to decompose thus reforming CO<sub>2</sub>(aq) then CO<sub>2</sub>(g). The CO<sub>2</sub>(g) appears as bubbles throughout the drink. A similar effect happens if the drink is shaken.

4. Some chemical changes involving everyday substances are described below. Use the information given to write a **chemical equation** for each of these reactions. The formula and phase of the different substances involved are given here.

sodium carbonate	Na <sub>2</sub> CO <sub>3</sub> (s)	carbonic acid	H <sub>2</sub> CO <sub>3</sub> (aq)
sodium sulfate	Na <sub>2</sub> SO <sub>4</sub> (s)	carbon dioxide	CO <sub>2</sub> (g)
rust	Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O(s)	ethanoic acid	CH <sub>3</sub> COOH(aq)
sodium hydrogencarbonate	NaHCO <sub>3</sub> (s)	sodium ethanoate	NaCH <sub>3</sub> COO(aq)
sodium hydrogensulfate	NaHSO <sub>4</sub> (aq)	iron	Fe(s)
citric acid	H <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> (s)	oxygen gas	O <sub>2</sub> (g)
sodium citrate	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> (aq)	water	H <sub>2</sub> O(l)

- Baking soda** and vinegar are two common kitchen products. The active compounds in each of these are **sodium hydrogencarbonate** and **ethanoic acid** respectively. When baking soda and vinegar are mixed a fizzing reaction occurs. The reaction produces **sodium ethanoate**, **water** and **carbon dioxide**.
- Aerated soft drinks like lemonade and cola contain carbonic acid. (See Fig 4.) This gives the beverage its fizz. One way of adding carbonic acid to a beverage is to dissolve carbon dioxide gas under pressure in it. The dissolved **carbon dioxide** gas then reacts with **water** in the drink to produce **carbonic acid**. (**This is a reversible reaction.**)
- Antacid tablets like Alka-Seltzer can be taken to relieve the symptoms of indigestion. The two active compounds in an antacid tablet are solid **sodium hydrogencarbonate** and solid **citric acid**. When dissolved in water these two compounds react forming **sodium citrate** solution, **water** and **carbon dioxide** gas.

*Continued next page.*



- d. Ordinary steel wool as used around the home will be seen to go rusty after some use. The reaction involves **iron** from the steel wool reacting with **water** and **oxygen** gas to form the red-brown substance known as **rust**.
- e. One swimming pool chemical used to adjust pH contains the active compound **sodium hydrogensulfate**. When added to water it reacts with any excess base like **sodium carbonate**, to produce **water**, **carbon dioxide** and **sodium sulfate**. By doing this the pool water pH is lowered. (**This is a reversible reaction.**)
5. Use coefficients where necessary to **balance** the following ionic equations. (See border note.)
- $\text{Fe}^{3+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Fe}_2(\text{CO}_3)_3(\text{s})$
  - $\text{Ca}^{2+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$
  - $\text{Al}(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + \text{H}_2(\text{g})$
  - $\text{SO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{SO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
6. **Rewrite** the following balanced chemical equations in **net ionic** form. (See border note.)
- $\text{Al}_2(\text{CO}_3)_3(\text{s}) + 6\text{HNO}_3(\text{aq}) \rightarrow 2\text{Al}(\text{NO}_3)_3(\text{aq}) + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
  - $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{KOH}(\text{aq}) \rightarrow \text{K}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
  - $\text{MgO}(\text{s}) + 2\text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{Mg}(\text{CH}_3\text{COO})_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $\text{Co}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CoCl}_2(\text{aq}) + \text{H}_2(\text{g})$
  - $\text{CO}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $3\text{NH}_3(\text{g}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow (\text{NH}_4)_3\text{PO}_4(\text{aq})$
  - $3\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Pb}_3(\text{PO}_4)_2(\text{s}) + 6\text{NaNO}_3(\text{aq})$
  - $2\text{AgNO}_3(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Ag}_2\text{SO}_4(\text{s}) + 2\text{HNO}_3(\text{aq})$
7. **Convert** the following word equations to balanced **net ionic equations**.
- solid calcium carbonate + nitric acid solution  $\rightarrow$  calcium nitrate solution + carbon dioxide gas + water liquid
  - hydrochloric acid solution + aluminium hydroxide suspension  $\rightarrow$  aluminium chloride solution + water liquid
  - solid magnesium oxide + nitric acid solution  $\rightarrow$  magnesium nitrate solution + water liquid
  - calcium granules + sulfuric acid solution  $\rightarrow$  calcium sulfate solid + hydrogen gas
  - carbon dioxide gas + sodium hydroxide solution  $\rightarrow$  sodium carbonate solution + water
  - barium chloride solution + sodium sulfate solution  $\rightarrow$  barium sulfate solid + sodium chloride solution
8. Consider the following chemical situations, each of which involves two or more sequential reactions. Rewrite these sequential reactions as a single balanced equation. (**E**)
- The **extraction of iron** in a blast furnace involves many sequential reactions. The two reactions shown happen in a region of the furnace where temperatures range between 700 °C to 1200 °C.  
 $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$  (In this reaction C and CO<sub>2</sub> react to form CO.)  
 $\text{CO}(\text{g}) + \text{FeO}(\text{s}) \rightarrow \text{Fe}(\text{l}) + \text{CO}_2(\text{g})$  (Here, CO reduces FeO to Fe.)
  - Ozone** (O<sub>3</sub>) an **allotrope** of oxygen (see border note) is present in low concentrations in the upper atmosphere (the stratosphere). Its presence is vital to life on earth as it protects us by absorbing harmful UV rays present in sunlight. Two reactions involved in its formation are shown here.  
 $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$  (This reaction absorbs UV energy.)  
 $\text{O}_2(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_3(\text{g})$  (O<sub>3</sub> goes on to absorb UV in other reactions.)
  - The destruction of ozone by **chlorofluorocarbons** (CFCs) was first recognised during the mid-1970s. Peak production of CFCs occurred in 1977 and since then their use has decreased to the point where their use is now largely prohibited. These reactions show one way that CFCs can destroy ozone.  
 $\text{CFCl}_3(\text{g}) \rightarrow \text{CFCl}_2(\text{g}) + \text{Cl}(\text{g})$  (CFC decomposes in the upper atmosphere.)  
 $\text{Cl}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{ClO}(\text{g}) + \text{O}_2(\text{g})$  (Cl atoms destroy ozone, O<sub>3</sub>.)  
 $\text{ClO}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{Cl}(\text{g}) + \text{O}_2(\text{g})$  (ClO depletes O needed for O<sub>3</sub> formation as well as producing more Cl that goes on to destroy more O<sub>3</sub>.)

**Note:** All equations must be **balanced for charge**. This means the same total charge appears on either side of the equation. When checking charge the ion coefficient must be considered, eg

Na<sup>+</sup> ..... has a charge of +1  
 2Zn<sup>2+</sup> ..... has a charge of +4  
 SO<sub>4</sub><sup>2-</sup> ..... has a charge of -2  
 3PO<sub>4</sub><sup>3-</sup> ..... has a charge of -9

**Note:** Only **dissolved substances**, ie those with the **(aq)** subscript, may be written in ion form. To be written in ion form the dissolved substance must be **ionic**, eg NaOH, CaCl<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or a **strong acid**, eg H<sub>2</sub>SO<sub>4</sub>, HCl or HNO<sub>3</sub>.



# CHAPTER 7 | ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

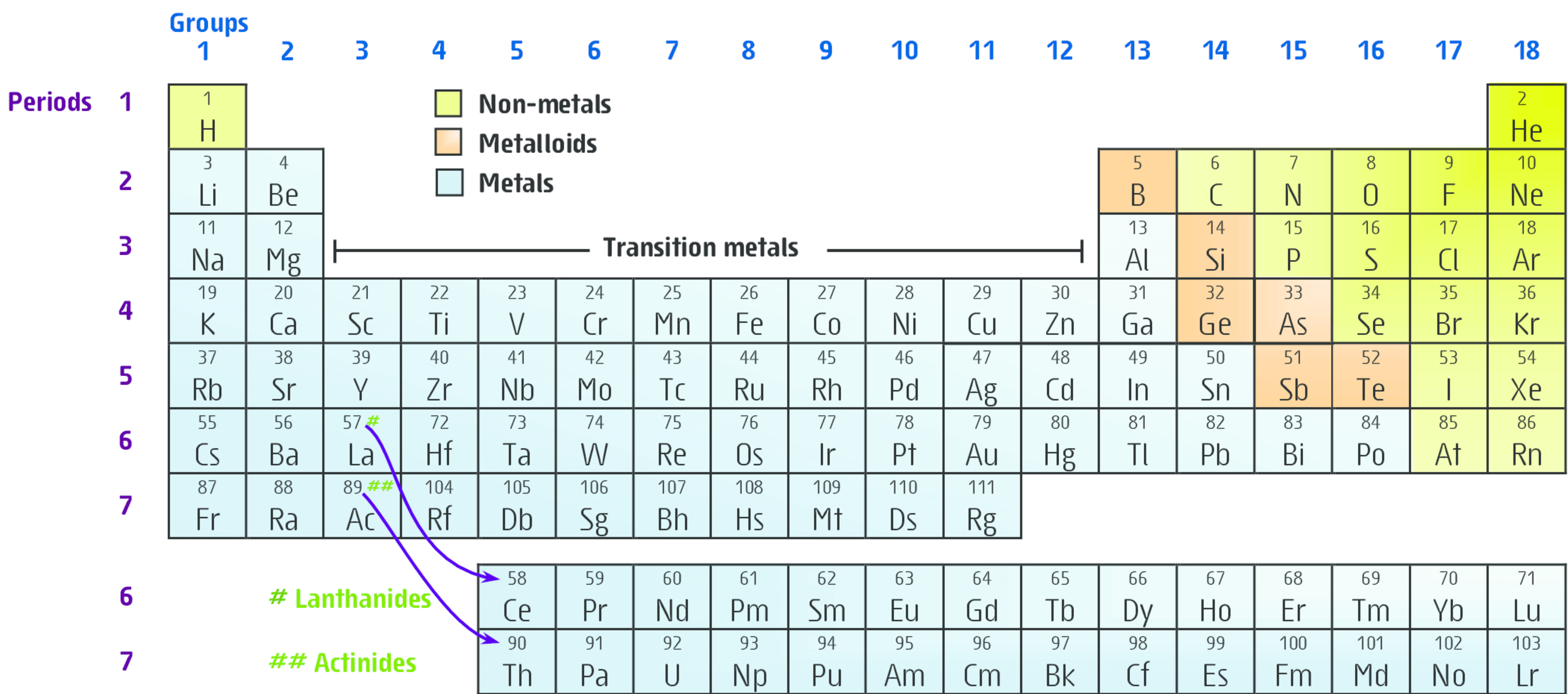
The first recorded attempts to relate elemental properties using a periodic table occurred during the nineteenth century. The most notable of these early attempts was achieved by **Dmitri Mendeleev** in 1869. His form of the periodic table is accepted as the precursor to the modern version. It sequenced elements according to increasing molar mass (atomic number was unknown at the time). Using his periodic table Mendeleev was able to quite accurately predict the existence and properties of the then unknown elements gallium, scandium and germanium.

## 7.1 The periodic table and chemical periodicity

It has long been recognised that the physical and chemical properties of the elements show gradual changes with atomic number. Furthermore it is clearly evident that these changes in properties are **periodic**. This means that at certain intervals of atomic number (2, 8, 8, 18, 18 and so on) there occur elements of very similar chemical and physical properties. Thus the element of atomic number 3 (Li) is much like the elements of atomic numbers 11, 19, 37 and 55 (Na, K, Rb and Cs respectively).

The **periodic table** (see Fig 1) is an arrangement of the known elements, organised in a way that highlights the periodic nature of their repeating properties. This is achieved by arranging elements into rows in order of increasing atomic number (left to right) and vertically in columns according to similar chemical properties. Horizontal rows of elements are called **periods** while vertical arrangements are known as **groups**. Organised this way the periodic table becomes an excellent guide to the probable properties of an element and even the types of compounds it might form.

FIGURE 1 The periodic table showing atomic number of the elements, their groups and periods.



**Metal** elements like Cu, Fe, Al, Ni and so on show a number of common physical properties. All metals are:

- good conductors of electricity
- good conductors of heat
- malleable and ductile
- shiny (when scratched)
- solids at room temperature (excepting mercury).

**Non-metal** elements however, are characterised by poor electrical and heat conductivity. Most are gases at room temperature while those that are solids are brittle.

## 7.2 Periodic trends: An introduction (E)

The organisation of the periodic table is such that from left to right across any period, the elements show a gradual change from **metallic** to **non-metallic** properties. From top to bottom down any group, the **physical** and **chemical** properties tend to remain similar though increasing in **metallic nature**. This is especially evident in groups 14, 15 and 16 where elements range from non-metallic at the top of each group (C, N and O) to metallic at the bottom of each group (Pb, Bi and Po). (See Fig 1.)

Some groups of elements are given special names due to their very strong similarities.

- **Halogens:** Group 17. These are all quite reactive non-metal elements. They produce ionic compounds with metals where the halogens form -1 ions, eg NaF, CaCl<sub>2</sub>, and AlBr<sub>3</sub>.
- **Noble gases:** Group 18. These non-metal gases all have very low chemical reactivity. There are only a handful of examples where noble gases form compounds.
- **Alkali metals:** Group 1. All are soft low melting point metals that react vigorously with water and acids to produce hydrogen gas. Alkali metal compounds are all ionic with the elements always forming +1 ions, eg LiCl, Na<sub>2</sub>S, and K<sub>3</sub>PO<sub>4</sub>.
- **Alkali earth metals:** Group 2. All are metals that react strongly with acids producing hydrogen gas. They also react with water (except Be) producing a metal hydroxide and hydrogen gas. Their compounds are ionic (except Be) with the metals always forming +2 ions, eg MgCl<sub>2</sub>, CaS and Sr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

Attempt Set 9 # 1, 2, 3, 4 and 5.



7.3 Quantum mechanical model of electron arrangement

The periodic table shows us that the chemical and physical properties of the elements repeat periodically with certain increments in atomic number (2, 8, 8, 18, 18, 32 and so on). The **quantum mechanical model** (as first proposed by Bohr) can help to explain this repeating chemical behaviour by relating an element’s chemical and physical properties to the number of electrons it has (remember,  $N(e) = N(p) = \text{atomic number}$ ) and the way they are arranged within the electron cloud. It states that electrons occur in **shells** (also known as **levels**) of increasing energy and distance from the nucleus. These shells are numbered 1, 2, 3, 4.... and so on with higher numbered shells generally being further from the nucleus and having a higher energy. The model specifies the maximum number of electrons that can fit into any shell is given by  $2n^2$  where n is the shell number. (See Fig 2.)

7.4 Electron configuration

The **electron configuration** of an atom or ion shows the shells (1, 2, 3, 4 ...) containing electrons and the number of electrons in each of these shells. The order in which electrons fill the available shells follows a general pattern where electrons fill the lowest numbered shells (lowest energy) first. It is sufficient for our purposes to know the filling order for the **first 20 electrons** in any atom is: 2 electrons will fill the 1<sup>st</sup> shell, then 8 electrons fill the 2<sup>nd</sup> shell, then a further 8 electrons fill the 3<sup>rd</sup> shell and finally 2 electrons fill the 4<sup>th</sup> shell.

It may be interesting to note however, for atoms with more than 20 electrons the 3<sup>rd</sup> shell recommences filling to its ultimate capacity of 18 electrons and only then does the 4<sup>th</sup> shell fill to 8 electrons and the 5<sup>th</sup> shell to 2 electrons. A similar filling pattern can be seen for the remaining shells. (See Table 1.)

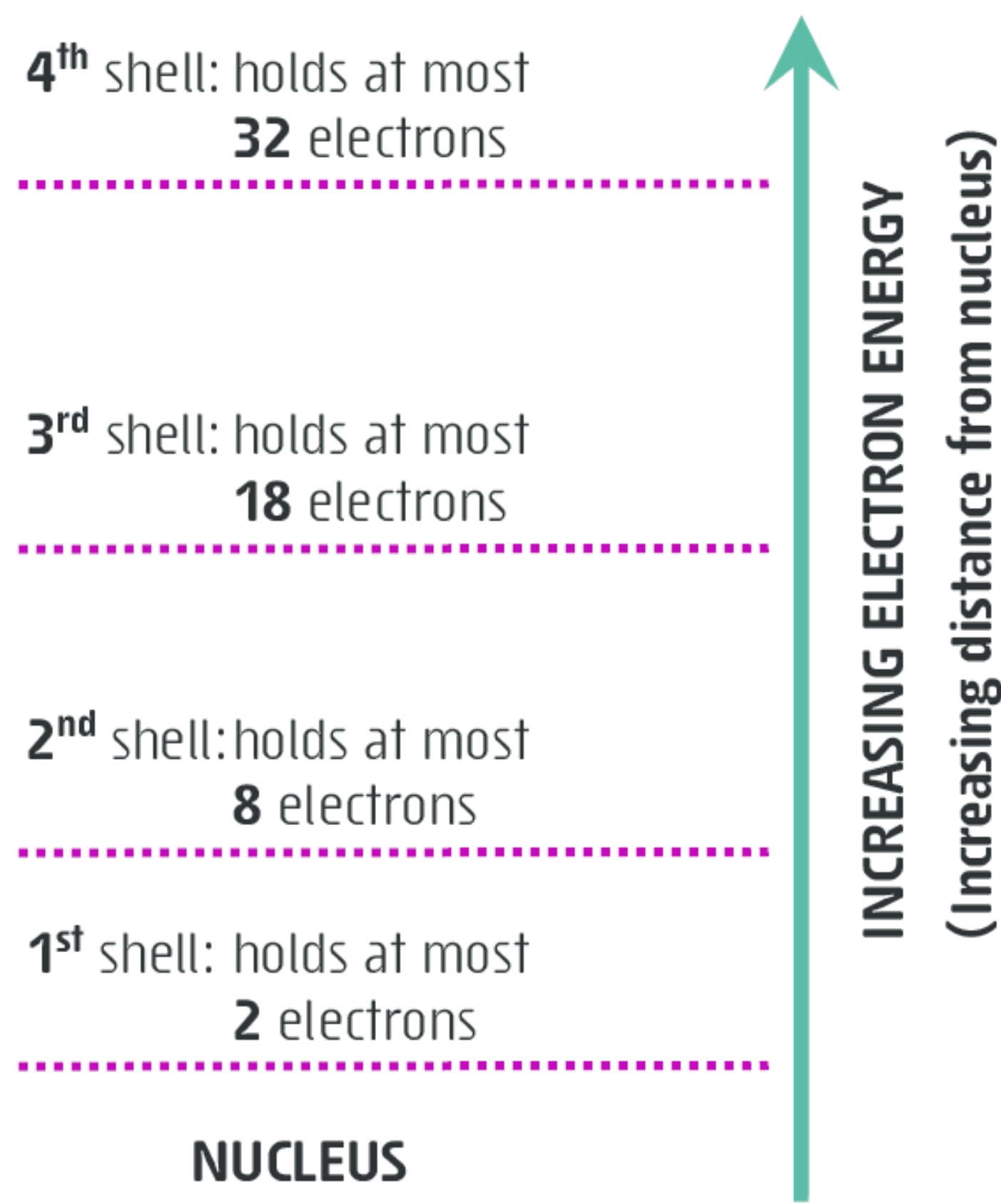
TABLE 1 Electron filling order for elements with up to fifty six electrons

Number of electrons in the atom	Shell number and maximum occupancy with arrows showing filling sequence					
	1 <sup>st</sup> shell	2 <sup>nd</sup> shell	3 <sup>rd</sup> shell	4 <sup>th</sup> shell	5 <sup>th</sup> shell	6 <sup>th</sup> shell
up to 20 electrons	2 then	→ 8 then	→ 8 then	→ 2 then		
21 to 38 electrons			→ 18 then	→ 8 then	→ 2 then	
39 to 56 electrons			→ 18 then	→ 8 then	→ 2	

TABLE 2 Electron configuration of some of the first fifty elements

Element	Atomic number	Number of electrons	Electron configuration	Number of valence electrons (see border note)
helium	2	2	2	2
lithium	3	3	2, 1	1
carbon	6	6	2, 4	4
fluorine	9	9	2, 7	7
neon	10	10	2, 8	8
sodium	11	11	2, 8, 1	1
magnesium	12	12	2, 8, 2	2
aluminium	13	13	2, 8, 3	3
phosphorous	15	15	2, 8, 5	5
argon	18	18	2, 8, 8	8
calcium	20	20	2, 8, 8, 2	2
selenium	34	34	2, 8, 18, 6	6
bromine	35	35	2, 8, 18, 7	7
krypton	36	36	2, 8, 18, 8	8
strontium	38	38	2, 8, 18, 8, 2	2
tin	50	50	2, 8, 18, 18, 4	4

FIGURE 2 Each **shell** (energy level) can hold progressively more electrons than the previous shell. The energy of an electron increases with its distance from the nucleus. Generally electrons fill the lowest energy shells first (close to the nucleus). There are, however, a few interruptions to this filling pattern. (See Table 1.) The third shell and upwards show a tendency to partly fill while higher shells begin filling in preference.



**Valence electrons** are those electrons occurring in the outermost shell that normally contains electrons. These are the electrons that determine the chemical and physical properties of an element. Not surprisingly elements with the same number of valence electrons are found to have very similar properties. This explains the pattern of repeating elemental properties seen in the periodic table.



7.5 Valence electrons and Lewis structures

**Valence electrons** are those electrons in the outermost shell (highest numbered shell) of an atom that normally contains electrons. The **Lewis structure** for an atom (Fig 3) or ion (Fig 4) shows one dot for each of its valence electrons. Electrons in shells below the valence shell are known as **core electrons**. Core electrons are not involved in chemical bonding and these are not shown in the **Lewis structure**.

**FIGURE 3** These **Lewis structures** show an atom's **valence electrons**. Each dot represents one valence electron. Individual atom's normally have a maximum of eight valence electrons.

Attempt Set 9 # 6.



7.6 Electron configuration and ion formation

Atoms form ions by gaining or losing electrons. Positive ions have fewer electrons while negative ions have more electrons than the original neutral atom. This means the electron configurations of an atom and its ion must be different. Usually the ion will have an electron configuration like that of the **nearest noble gas**.

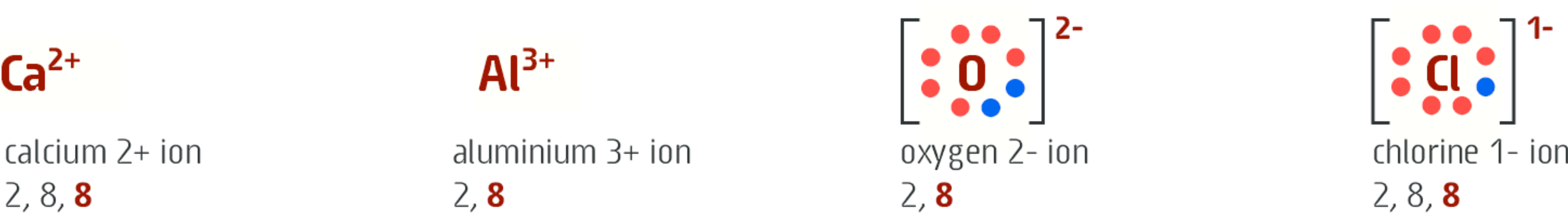
Noble gas electron configurations have **8 valence electrons** in the outer shell (except He which has 2 valence electrons). These noble gas elements rarely change their electron configuration while other elements readily gain or lose sufficient electrons to form ions with noble gas electron configurations (known as the **octet rule**). This behaviour indicates '**the electron configurations of noble gases are uniquely stable**'.

**TABLE 3** Electron configurations of selected ions

Ion	Atomic number	Number of electrons in an atom of the element	Number of electrons in the ion	Electron configuration of the ion	Matching noble gas
Li <sup>+</sup>	3	3	2 (lost 1e)	2	helium
O <sup>2-</sup>	8	8	10 (gained 2e)	2, 8	neon
F <sup>-</sup>	9	9	10 (gained 1e)	2, 8	neon
Al <sup>3+</sup>	13	13	10 (lost 3e)	2, 8	neon
S <sup>2-</sup>	16	16	18 (gained 2e)	2, 8, 8	argon
Cl <sup>-</sup>	17	17	18 (gained 1e)	2, 8, 8	argon
Ca <sup>2+</sup>	20	20	18 (lost 2e)	2, 8, 8	argon
Br <sup>-</sup>	35	35	36 (gained 1e)	2, 8, 18, 8	krypton

**FIGURE 4** The **Lewis structure** of an **ion** shows the electrons present in its outermost shell that **normally** contains electrons, ie its valence shell. For this reason **metal ions** usually have no dots. **Non-metal ions** typically have 8 dots (an octet) and are bracketed to show these electrons are not shared.

Complete Set 9.



You will notice all of the ions shown in Fig 4 have **eight electrons**, called an octet, in the outermost shell of their **electron configuration**. This is unlike their parent elements shown in Fig 3. The tendency of atoms to gain, lose or share electrons until they have eight electrons in their outermost shell is known as the **octet rule**.



## Set 9 Electronic structure and the periodic table

- Using a periodic table find the **group** and **period** number for the following elements.
  - carbon
  - calcium
  - the element of atomic number 31
  - the element having 53 protons in its nucleus

- Name or give the symbols for all the elements that match the following description:
  - elements that would have similar chemical properties to chlorine
  - the halogen from the fourth period
  - the fifth period element with similar chemical properties to magnesium
  - the transition metals from the fourth period.

- The following passage describes the organisation of elements into the periodic table. Complete the passage by selecting the correct terms from the ones listed.

The periodic table is an organiser of the properties of the (a) \_\_\_\_\_. The elements are organised into horizontal rows called (b) \_\_\_\_\_ according to increasing (c) \_\_\_\_\_ and vertically into (d) \_\_\_\_\_ according to similar (e) \_\_\_\_\_. Across any period the physical properties of the elements show a major change from (f) \_\_\_\_\_ properties on the left side of the table to (g) \_\_\_\_\_ properties on the right side. In a similar way the (h) \_\_\_\_\_ properties also vary greatly across any period of the periodic table. Within any group of the periodic table the chemical and physical properties of the elements tend to be (i) \_\_\_\_\_ showing only some gradual increase in metallic properties down any group.

The periodic table shows that the properties of the elements repeat at specific intervals of (j) \_\_\_\_\_. Thus the properties of the elements of atomic numbers 2, 10, 18, 36, 54 and 86 turn out to be very similar. This group of similar elements is known as the (k) \_\_\_\_\_. This example shows the chemical and physical properties of the elements repeat at intervals in atomic number of 8 then (l) \_\_\_\_\_ then (m) \_\_\_\_\_ then 18 then (n) \_\_\_\_\_. This pattern of repeating properties occurs for all elements, for example lithium, atomic number 3 will be very similar to elements of atomic numbers 11, 19, 37, 55 and 87. This group of similar elements is known as the (o) \_\_\_\_\_. Similarly the elements of atomic numbers 4, 12, 20, 38, 56 and 88, known as the (p) \_\_\_\_\_, will have very similar properties.

- Use the periodic table to determine if the following pairs of elements are most likely to have similar or different chemical properties. In a few words **justify** your answer.
  - N and P
  - Ar and He
  - C and O
  - oxygen and selenium
  - potassium and bromine
  - magnesium and sulfur
- From each of the following pairs of elements choose the one the most likely to be a good conductor of electricity and heat. **(E)**
  - Be and Ca
  - B and Tl
  - Sc and Ge
  - selenium and titanium

- Give the **electron configuration** and **Lewis structure** for the following atoms.
  - Na
  - S
  - Ca
  - P
  - Cl
  - Ga

- Give the **electron configuration** and **Lewis structure** for the following ions.
  - $\text{Na}^+$
  - $\text{S}^{2-}$
  - $\text{Mg}^{2+}$
  - $\text{Ca}^{2+}$
  - $\text{Cl}^-$
  - $\text{O}^{2-}$

- The species  $\text{Na}^+$ ,  $\text{O}^{2-}$  and Ne are said to be isoelectronic. **Suggest** a meaning for the term **isoelectronic**. You will need to compare their electron configurations.

Remember the number of protons in an atom of an element is given by its **atomic number**. For a neutral atom this also gives the number of electrons.

32  
metallic  
alkali metals  
atomic number  
periods  
18  
elements  
properties  
non-metallic  
atomic number  
groups  
8  
chemical  
similar  
noble gases  
alkali earths



**FIGURE 5** The most abundant **isotopes** of carbon occurring on Earth are  $^{12}\text{C}$  (98.9%) and  $^{13}\text{C}$  (1.1%). The isotope  $^{14}\text{C}$  is extremely rare, and constitutes <0.01% of naturally occurring carbon in atmospheric  $\text{CO}_2$ .

$^{14}\text{C}$  is formed in the upper atmosphere by the interaction of cosmic rays on  $^{14}\text{N}$  atoms. However,  $^{14}\text{C}$  is radioactive and slowly decays back to  $^{14}\text{N}$ . It takes about 5730 years for half of a  $^{14}\text{C}$  sample to decay.

**Carbon dating** uses this principle to date the age of once living things. These isotopes appear chemically identical and so living things absorb them both, either from the atmosphere, as  $\text{CO}_2$ , or from the food they eat. When the tissue dies the amount of  $^{12}\text{C}$  remains constant, but  $^{14}\text{C}$  decays. Measuring the ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$  in a sample indicates how long ago the tissue died.



Here a sample is being removed from bone for carbon dating using **accelerator mass spectrometry** (AMS). The bone is part of a human femur that is thought to be from the medieval period.

Carbon dating using AMS requires only a very small sample of material, minimising the damage to a specimen.

Photographed at Oxford Radiocarbon Accelerator Unit, University of Oxford, UK.

9. **Compare** the electron configurations for the three isotopes, **carbon-12**, **carbon-13** and **carbon-14**. (See Fig 5.) What does this imply about the **chemical properties** of these three isotopes of carbon and of other isotopes in general?

10. The electron configuration of an element is related to its position in the periodic table.  
a. Using a periodic table find the group and period of the following elements.

Element	Electron configuration	Number of valence electrons	Periodic table	
			Group	Period
Li	2, 1	1		
Sr	2, 8, 18, 8, 2	2		
Cl	2, 8, 7	7		
Se	2, 8, 18, 6	6		
Al	2, 8, 3	3		

- b. Having completed the table from Question 10a, examine the data for any relationship between electron configuration, valence electrons and periodic table position. Now write your ideas as a statement about the following:
- i. What is the relationship between an element's **number** of valence electrons and its **electron configuration**?
  - ii. How does an element's **number of valence electrons** compare to its periodic table **group number** for groups 1 and 2, for groups 13 to 18 inclusive?
  - iii. What is the relationship between an element's **period number** and its **electron configuration**?

11. Apply the patterns you found in Question 10 to complete this table. You should **not** need to refer to a periodic table to complete this question but you **will** need to have checked your answer to Question 10.

Periodic table		Number of valence electrons	Valence shell number	Electron configuration of a neutral atom
group	period			
				2, 8, 6
	2	3		
	3	5		
14	3			
1	4			
17	4			

12. There is a clear relationship between the electron configuration of the noble gases and the electron configuration of most monatomic ions. The following questions explore this relationship for the ions of some elements from the main groups 1 and 2 and 13-18 of the periodic table.

Element	Electron configuration	Ion	Ion electron configuration	Nearest noble gas	Noble gas electron configuration
K	2, 8, 8, 1	$\text{K}^+$	2, 8, 8	Ar	2, 8, 8
Mg		$\text{Mg}^{2+}$			
S		$\text{S}^{2-}$			
F		$\text{F}^-$			
N		$\text{N}^{3-}$			
Sr		$\text{Sr}^{2+}$			

- a. **Complete** this table showing the electron configuration for each of the atoms and ions as well as the identity and electron configuration of the nearest noble gas.
- b. How does the electron configuration of each element compare with that of its ion?
- c. How do the electron configurations of the monatomic ions compare with those of their **nearest noble gas**?
- d. **Suggest** why the noble gas elements do not normally form ions.
- e. Is this relationship between the electron configuration of monatomic ions and noble gases true for **all** monatomic ions? Hint: Look at the ions of transition metals like Zn and Cu.

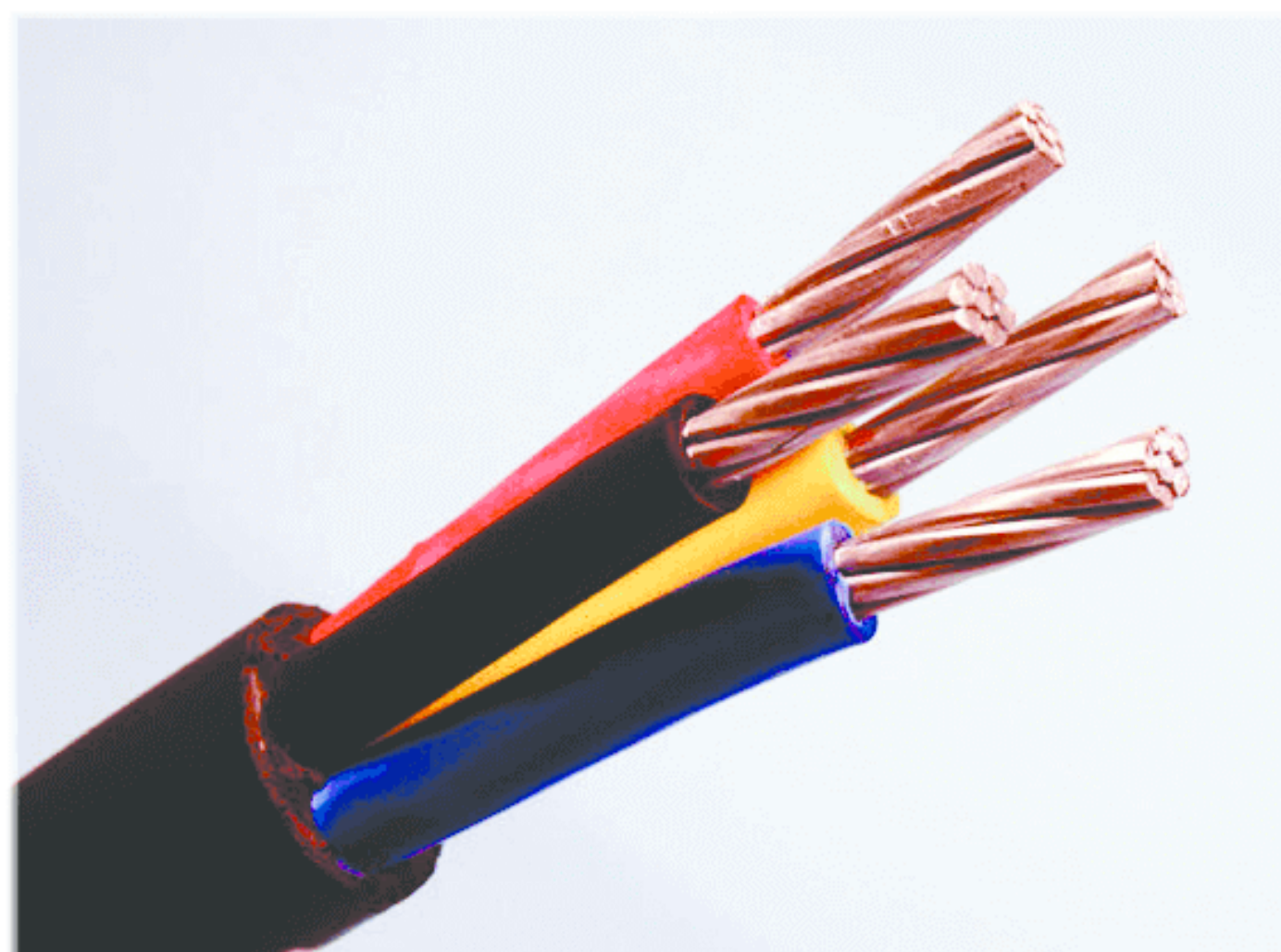


# CHAPTER 8 | CHEMICAL BONDING



**FIGURE 1** Malleable and ductile substances are those that dent or stretch when a force is applied and can be drawn into wires. By contrast, a brittle substance will crack and shatter under the same conditions.

For a substance to be malleable its particles must be able to move past one another without breaking the bonds between them. In a brittle substance the bonds between the particles break if the particles move in relation to one another.



**FIGURE 2** This electric power cable consists of four copper wires coated with a plastic material. The copper conducts the electric current while the plastic coating is an insulator that is non-conducting.

For a material to be an **electrical conductor** the charged particles within it, **electrons** or **ions**, must be able to move, ie be **mobile**. When a voltage is applied to such a material the charged particles will move and so conduct a current. In metals it is the flow of **freely mobile electrons**, that constitutes the electric current. (See Fig 5.)



**FIGURE 3** The shiny lustre of this stainless steel kettle is typical of all polished metal surfaces. Stainless steel is a good choice of material for this use as it has a high **heat conductivity** (typical of all metals) as well as a high resistance to corrosion.

## 8.1 Classes of substance

**Physical properties** of substances include features like melting point, malleability and ability to conduct heat or electricity. (See Fig 1, 2, and 3.) Patterns in these properties suggest four distinct classes of substance can be identified. Each class of substance displays its own characteristic combination of these physical properties. An understanding of the bonding and structure of these substances gives a basis for explaining their physical properties.

**TABLE 1** Four classes of substance

Physical property	Metallic	Ionic	Covalent molecular	Covalent network
Electrical conductivity in the solid state	conductors	non-conductors	non-conductors	non-conductors*
Electrical conductivity in the molten state	conductors	conductors	non-conductors	
Electrical conductivity when dissolved in water		conductors	non-conductors*	
Malleable and ductile or hard and brittle	malleable and ductile	hard and brittle	soft	hard and brittle*
Melting point	moderate to high*	high	low	very high
Examples	copper (Cu), Gold (Au), aluminium (Al), iron (Fe), titanium (Ti)	magnesium iodide (MgI <sub>2</sub> ), zinc sulfate (ZnSO <sub>4</sub> ), sodium chloride (NaCl)	carbon dioxide (CO <sub>2</sub> ), water (H <sub>2</sub> O), oxygen (O <sub>2</sub> ), sugar (C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	silicon (Si), silicon dioxide (ie quartz, SiO <sub>2</sub> ), diamond and graphite (C)

\*Within each class of substance there are important examples that have **distinctly different** physical properties, for example:

- Covalent molecular acids (like HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>) are quite good electrical conductors when dissolved in water.
- Graphite, a covalent network substance conducts electricity and is brittle though soft.
- The metal mercury has a low melting point (-39 °C) making it a liquid at room temperature.

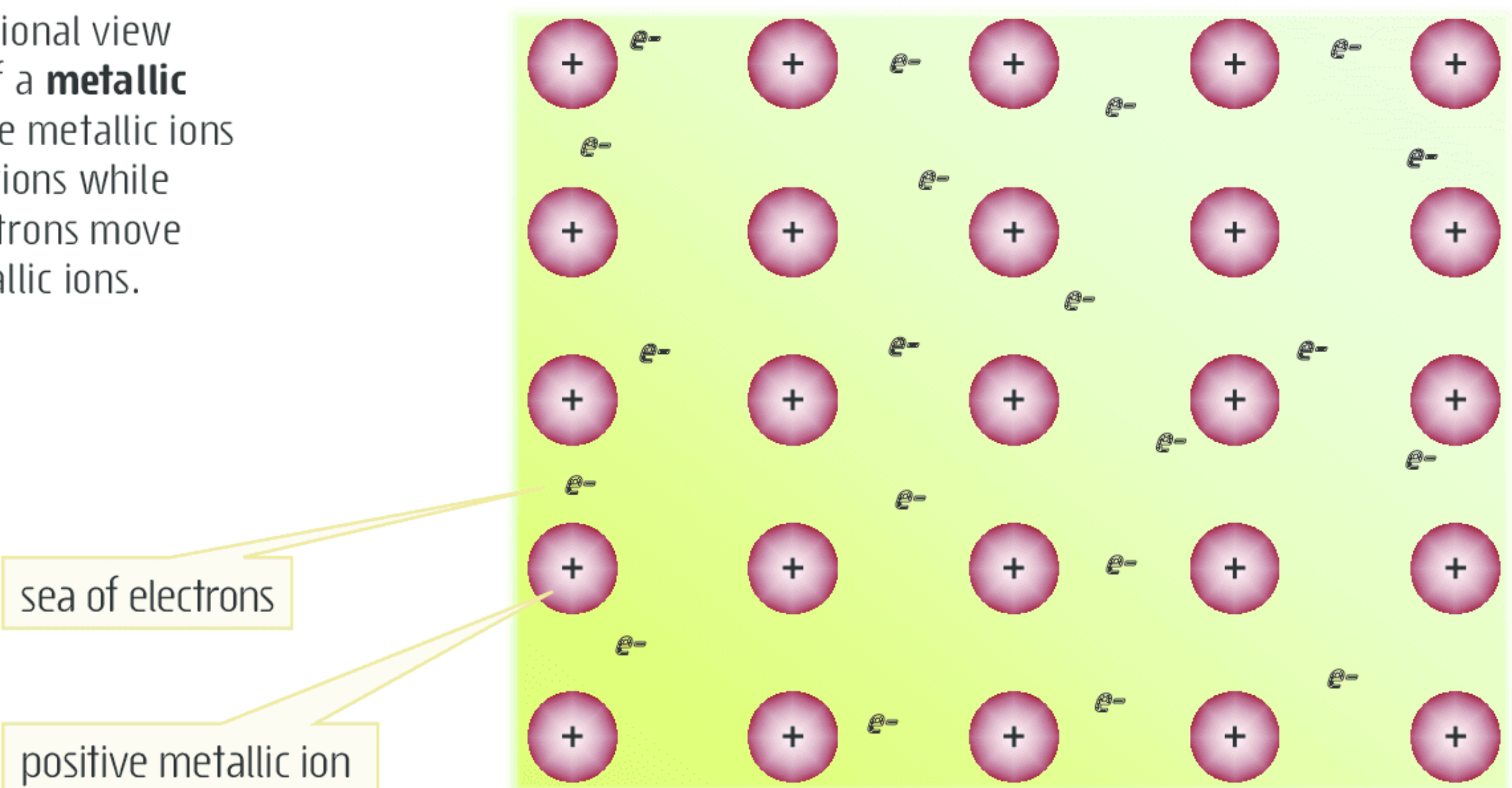
## 8.2 Metallic substances

Of the first 100 elements, 18 are **non-metals**, 6 are **metalloids** while the remaining 76 are **metals**. (See periodic table p48.) In metallic substances, atoms achieve a noble gas electron configuration by releasing their valence electrons, thus forming positive metal ions and free electrons. The positive metal ions occupy fixed positions within a three dimensional lattice. Valence electrons released from the metal atoms are free to move at random amongst the lattice of metal ions. For this reason the electrons are said to be **delocalised** and described as a **mobile sea of electrons**. (See Fig 4.)

**Bonding** within the metallic lattice is due to strong electrostatic attraction between the stationary metal ions (+ charge) and the mobile sea of electrons (- charge). Metallic bonds are said to be **non-directional** as they occur equally in all directions between all metal ions and the sea of electrons.

Attempt Set 10 # 1 and 2.

**FIGURE 4** A two dimensional view showing the structure of a **metallic lattice**. Within the lattice metallic ions vibrate about fixed positions while delocalised valence electrons move freely amongst the metallic ions.



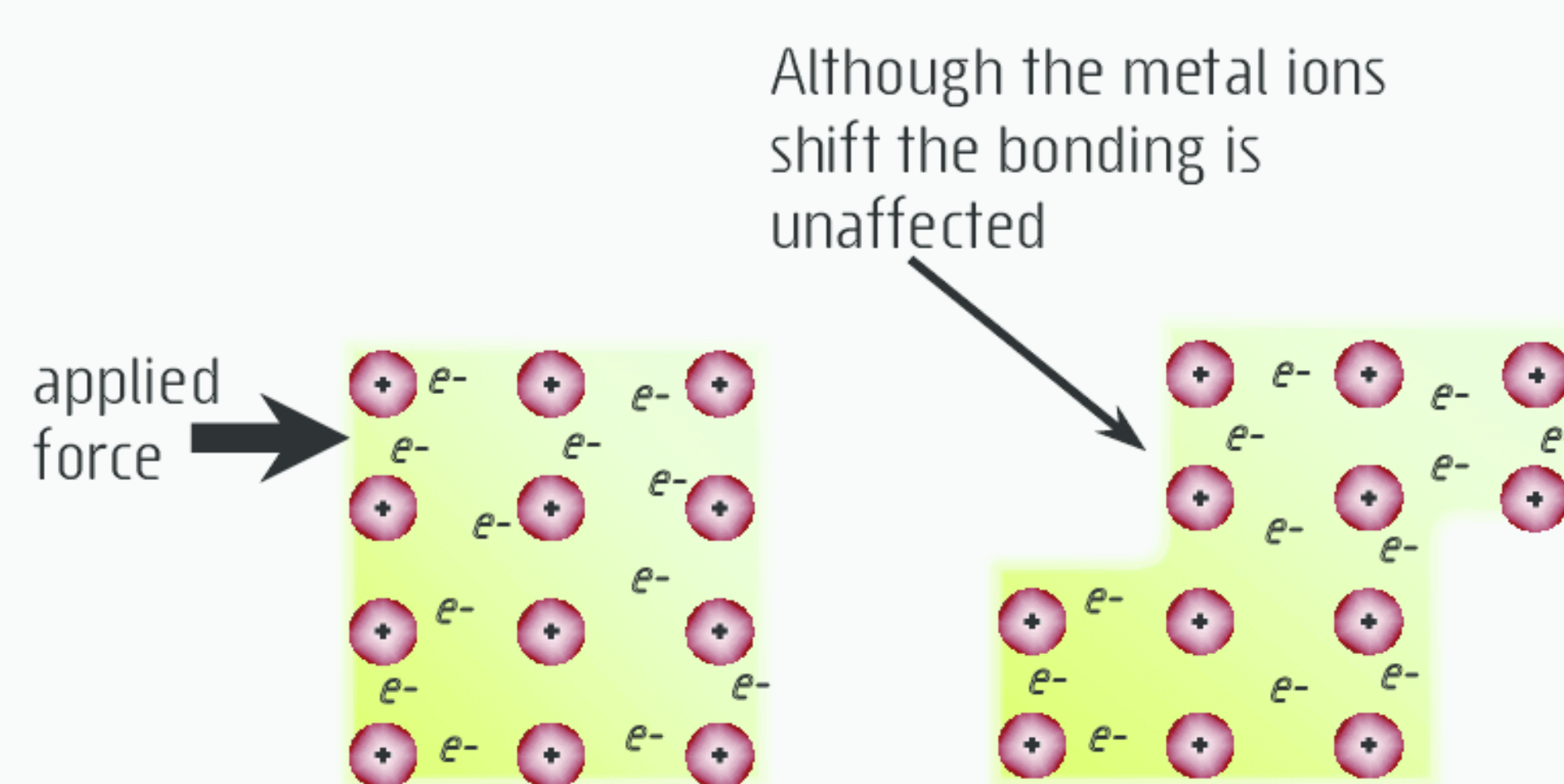


**TABLE 2** Understanding metallic properties

**Good conductors of electricity:** Valence electrons that form the sea of electrons are mobile, ie they can move freely throughout the metallic lattice. If a voltage is applied to a metal, electrons from the mobile sea of electrons move towards the positive terminal of the power supply. Positive metal ions remain stationary in their fixed positions. It is the ability of these valence electrons to move and thus to conduct charge that allows metals to be good conductors of electricity. (See Fig 5.)

**Good conductors of heat:** Electrons within the sea of electrons are mobile and so can carry heat energy (as kinetic energy) throughout the metal lattice. The vibration of metallic ions also contributes to the flow of heat through the metal lattice.

**Malleable and ductile:** Bonding between metal ions and the sea of electrons is non-directional. This means individual metal atoms can move in relation to each other without breaking the bonds between them and the sea of electrons. This allows a metal to change shape, ie be dented, bent or stretched without breaking.



**Solid at room temperature:** Strong attractive forces between the metal ions and sea of electrons hold the metallic lattice together. As a consequence a moderate to high temperature is needed to disrupt the lattice and allow the metal to melt. The metal mercury (MP=-39 °C) is an exception as it is a liquid at room temperature.

Complete Set 10.

## Set 10 Metallic substances

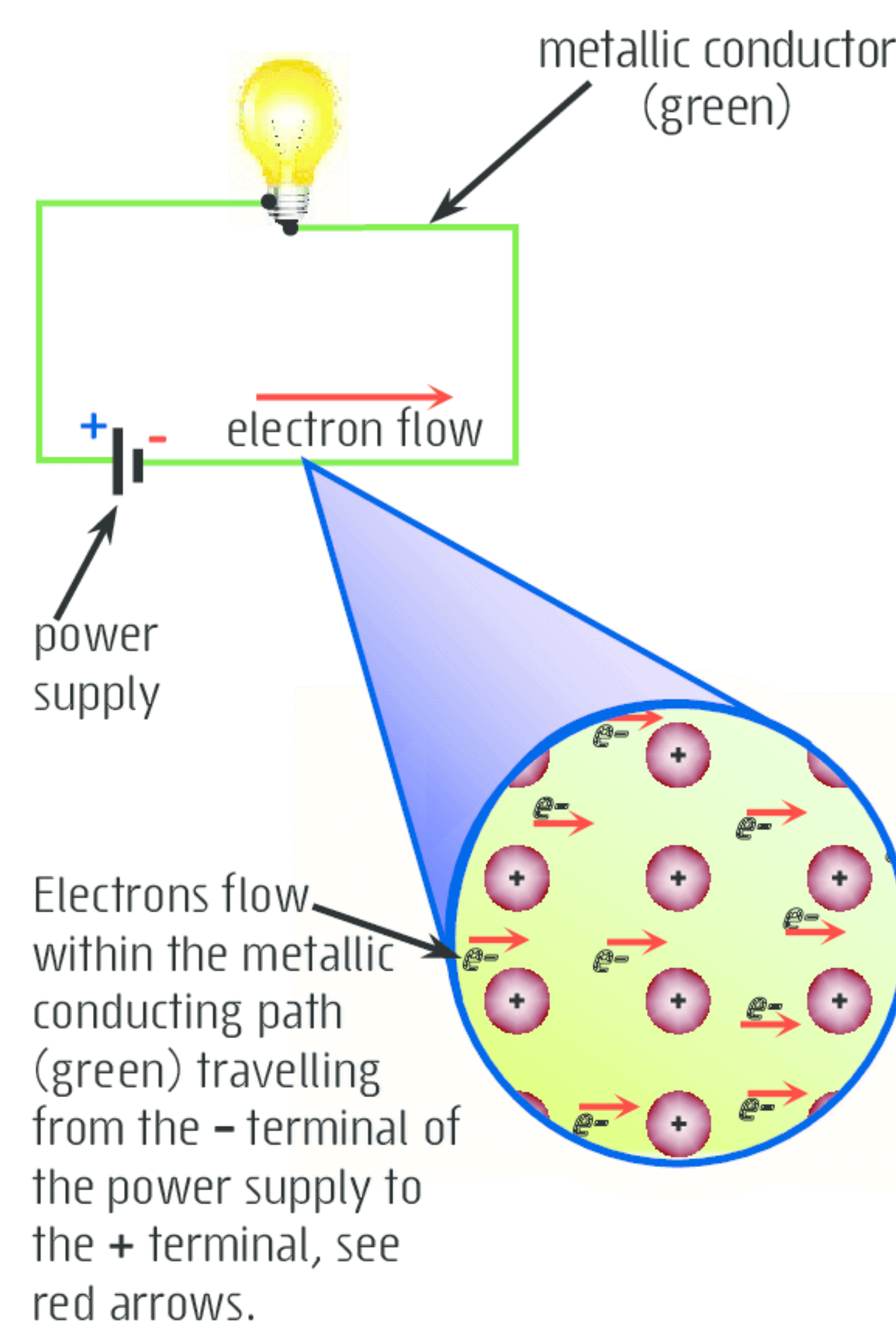
- The following passage describes the formation and structure of a metal. Use the list of terms to correctly complete the passage.

In the formation of the metallic structure, metal atoms lose their (a) \_\_\_\_\_ electrons and form positive (b) \_\_\_\_\_ ions and free (c) \_\_\_\_\_. The resulting metal ions occupy (d) \_\_\_\_\_ positions forming a regular three dimensional (e) \_\_\_\_\_. Valence electrons released by the metal atoms (f) \_\_\_\_\_ amongst the positive metal ions. These free moving electrons are sometimes referred to as a (g) \_\_\_\_\_.

The stability of the metallic structure comes from the strong (h) \_\_\_\_\_ attraction between the (i) \_\_\_\_\_ metal ions and the sea of electrons. This electrostatic bond, known as the (j) \_\_\_\_\_ bond acts in all directions between the positive metal ions and the sea of electrons and so is referred to as a (k) \_\_\_\_\_ bond.

- Both aluminium and sodium form a metallic structure. **Compare** the **metallic structure** of these elements. How are they similar? How are they different? (Hint: Consider the ion charges and the number of mobile electrons per ion.)
- Use your knowledge of metallic bonding to account for the following typical physical properties of metals.
  - Metals are known to be good conductors of electricity.
  - Metallic elements are both malleable and ductile.
  - Metals are good conductors of heat.
- The **melting point** of a solid depends upon the strength of attraction (bonding) between its particles (atoms, ions or molecules). The stronger this is, the higher its melting point will be. Using a text reference or the internet find the melting points of the first three elements of the third period **Na**, **Mg** and **Al**. What **trend** is evident in the melting point of these metals and hence what can be inferred about the strength of the metallic bond for the metallic elements of the third period?

**FIGURE 5** Electrical **conductivity** in metals.



electrostatic  
metal  
valence  
positive  
non-directional  
electrons  
sea of electrons  
fixed  
lattice  
metallic  
move freely



The larger the **heat conductivity value** shown in the table the better the metal is able to conduct heat.

Similarly the higher the **electrical conductivity value** the better the metal is able to conduct electricity.

5. The **electron-sea model** (Fig 4) accounts for the conductivity of metals in terms of the metal valence electrons that form the sea of mobile electrons. These mobile electrons readily conduct heat and electrical energy through the metallic structure. With this in mind Harry suggested to his teacher that, “**The conductivity of metals should increase as the number of valence electrons increase.**” Do the following conductivity data from **Set A** (consecutive elements from period 3) and/or **Set B** (consecutive elements from period 4) support Harry’s hypothesis? Explain. Hint: Complete the table to show the number of valence electrons for each of the elements and look for any pattern between valence electron number and conductivity. (See border note.)

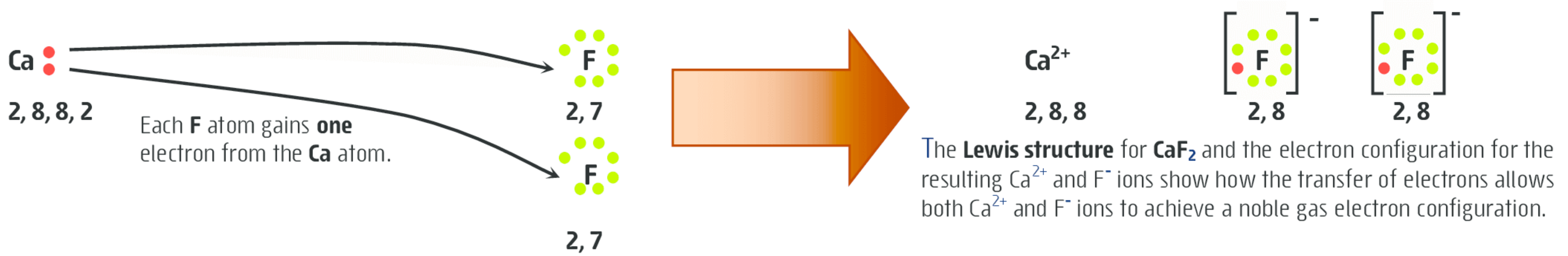
Set	Element	Number of valence electrons	Heat conductivity $\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$	Electrical conductivity $\Omega^{-1} \text{m}^{-1}$
A	sodium		141	21
	magnesium		156	23
	aluminium		237	38
B	potassium		102	14
	calcium		200	29
	scandium	3 valence electrons	15.8	1.8
	titanium	4 valence electrons	22	2.3
	vanadium	5 valence electrons	30	5

### 8.3 Ionic compounds

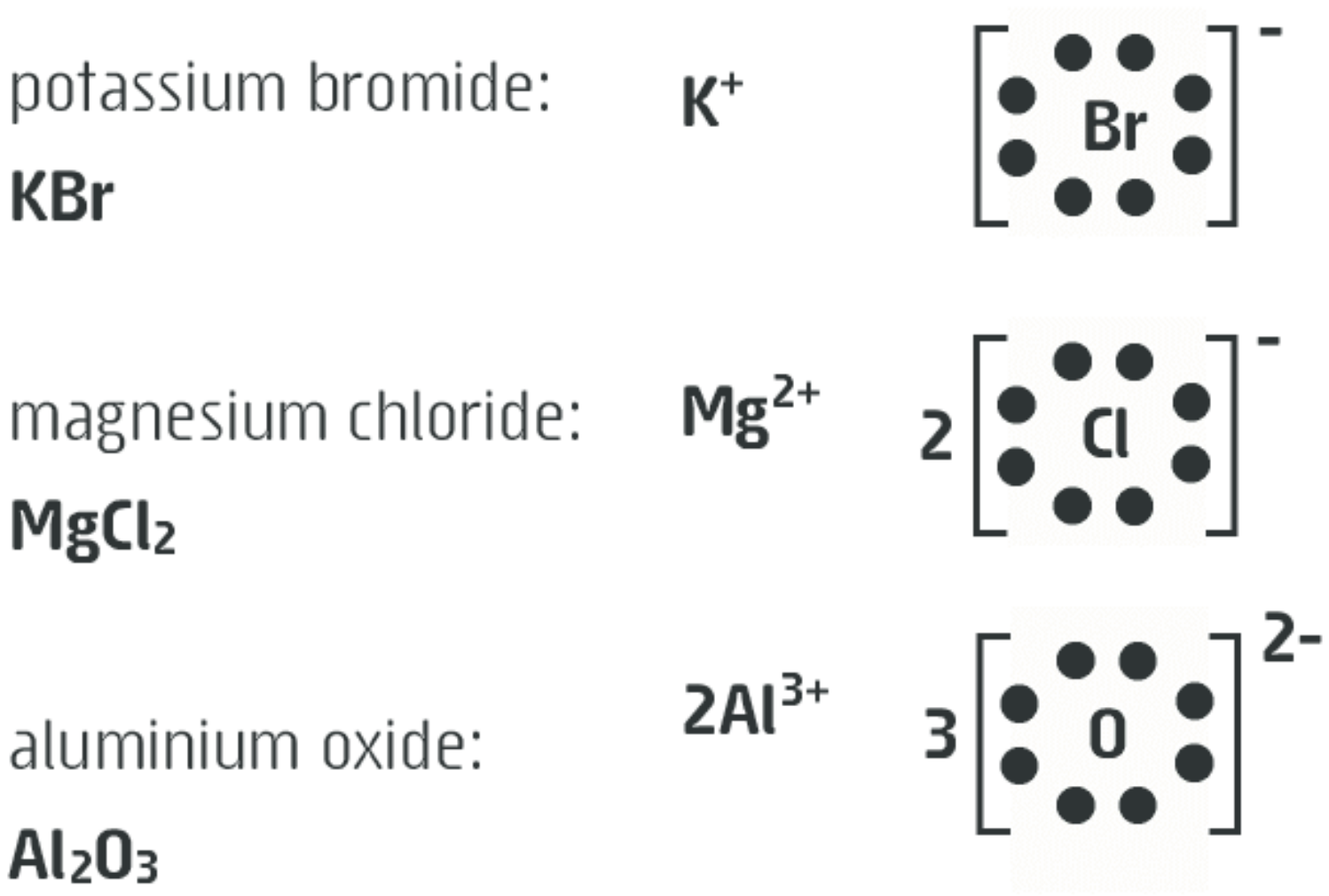
Of the first 100 elements only 18 are **non-metals**. Of these 6 are noble gases and one, astatine, is extremely rare, leaving 11 non-metal elements to form the many ionic compounds found on Earth.

Ionic compounds form from a combination of **metallic** elements (or  $\text{NH}_4^+$  ions) with **non-metallic** elements, eg NaCl, CaO,  $\text{MgSO}_4$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{NH}_4\text{Cl}$  and so on. The metal element in these compounds loses all of its valence electrons to form a positive ion with a noble gas electron configuration. The lost electrons are transferred to the non-metal element that forms a negative ion also with a noble gas electron configuration. Figures 6 and 7 use **Lewis structures** (p50) to show this.

**FIGURE 6** Electron configurations and Lewis structures are used here to show the transfer of electrons in the formation of the ionic compound  $\text{CaF}_2$



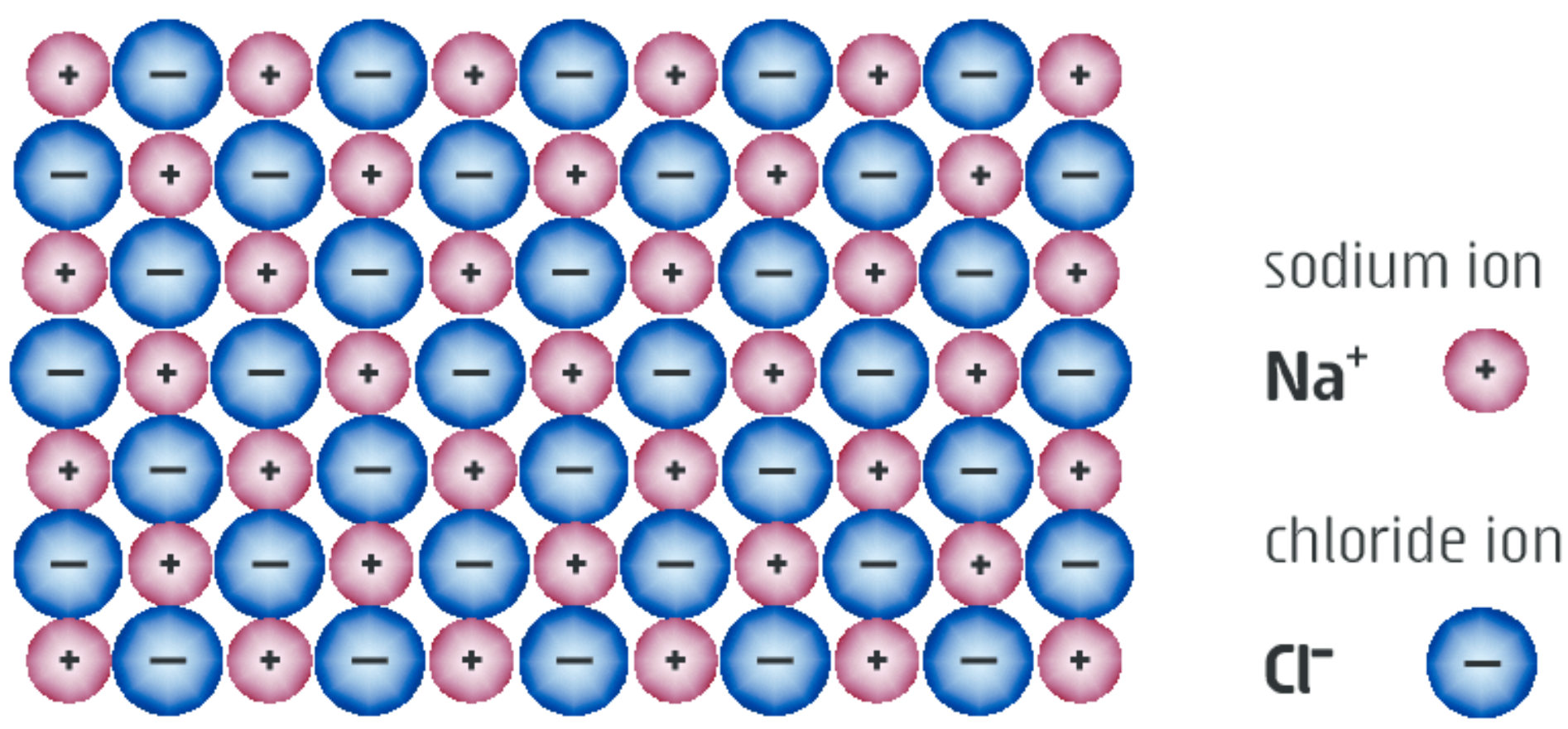
**FIGURE 7** Lewis structures for some ionic compounds. Square brackets around the negative ions are a reminder that their valence electrons are exclusively associated with the ion. These valence electrons are **not** shared with the neighbouring ion.



Attempt Set 11 # 1, 2, 3 and 4.

The resulting positive and negative ions arrange into a three dimensional **ionic lattice**. (See Fig 8.) Bonding in the ionic lattice is due to **strong electrostatic attraction** between neighbouring **positive** and **negative** ions. Any given positive ion is attracted simultaneously to all surrounding negative ions and vice versa. Although repulsive forces between like charged ions will also occur these forces are much weaker as the like charged ions are further apart in the lattice (diagonally arranged) than the adjacent unlike charged ions. Electrostatic forces reduce considerably as the distance between ions increases.

**FIGURE 8** This two dimensional diagram is a representation of the sodium chloride (NaCl) ionic lattice. It shows the typical structure of an ionic lattice. Note the **unlike** charged ions are **closer** together than like charged ions. This ensures attractive forces within the lattice are greater than repulsive forces. Hence the ionic lattice is a stable and strongly bonded structure.





**TABLE 3** Understanding the properties of ionic compounds

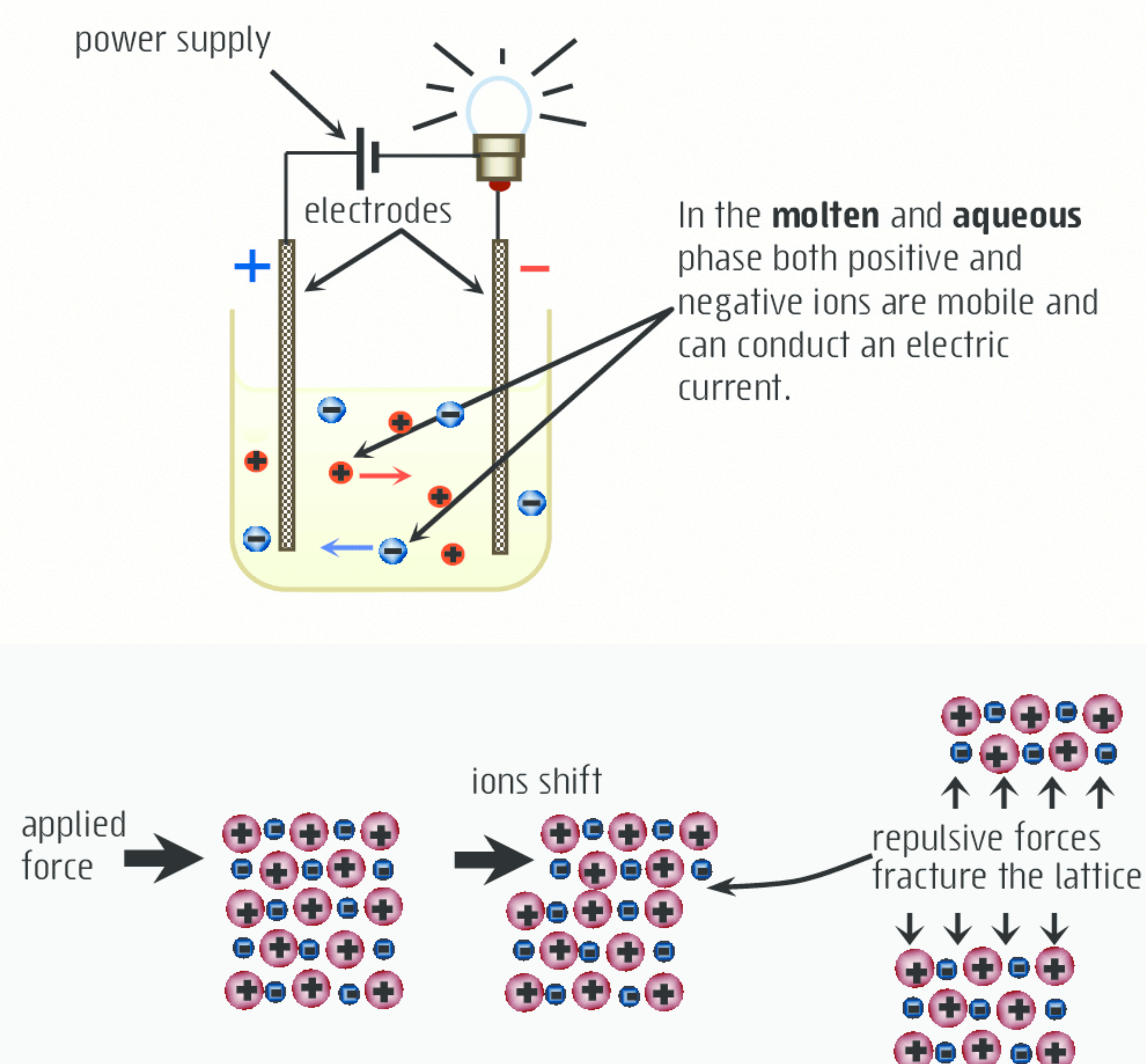
**Poor conductors of electricity in the solid phase:** In an ionic **solid** the ions are tightly held in fixed positions within the lattice, thus they are unable to move and carry charge. Electrons within the ionic lattice are also tightly held by individual ions and hence also unable to move and carry charge through the ionic solid. An **absence** of **mobile** charged particles means ionic solids are non-conductors of electricity.

**Good conductors of electricity when molten:** In the **molten phase**, ions are mobile and free to move and carry charge throughout the ionic liquid. Both positive and negative ions carry charge. Positive ions move towards the negative electrode while negative ions move towards the positive electrode.

**Good conductors of electricity when in aqueous solution:** In an **aqueous solution** individual ions from the ionic solid are mobile and free to move independently of one another. Their mobility and charge enable them to conduct an electric current through the ionic solution. Both positive and negative ions are involved in conducting the current. The current consists of positive ions moving toward the negative electrode and negative ions moving toward the positive electrode.

**Hard and brittle:** If a large force is applied to the ionic lattice it will cause layers of ions to move. When this happens, like charged ions will be forced to align alongside one another, ie no longer diagonally aligned. This means **like** charges will be **closer** together than unlike charges. Consequently **repulsive forces** will exceed attractive forces and the lattice will break apart rather than simply dent or bend.

**High melting and boiling points:** Ionic bonds are strong electrostatic attractive forces between ions. These strong attractive forces extend throughout the ionic lattice keeping individual ions in fixed positions. Thus a high temperature, ie high particle kinetic energy, is needed to disrupt (melt) the ionic lattice.



Complete Set 11.

## Set 11 Ionic compounds

- The following passage describes the formation and structure of an ionic compound. Use the list of terms to correctly complete the passage.

Ionic compounds form when (a) \_\_\_\_\_ elements, ie elements from the left hand side of the periodic table, combine with (b) \_\_\_\_\_ elements. The metal atoms form (c) \_\_\_\_\_ ions by (d) \_\_\_\_\_ their valence electrons while the non-metal atoms (e) \_\_\_\_\_ these electrons forming (f) \_\_\_\_\_ ions. In this process both metal and non-metal atoms form ions with a (g) \_\_\_\_\_ electron configuration.

The resulting ions arrange themselves into a (h) \_\_\_\_\_ lattice of alternating positive and negative ions. In this lattice structure (i) \_\_\_\_\_ charged ions are close together while (j) \_\_\_\_\_ charged ions are always further apart. This arrangement allows the overall (k) \_\_\_\_\_ forces between unlike charges to exceed the (l) \_\_\_\_\_ forces between like charges. This ensures the (m) \_\_\_\_\_ of the ionic lattice structure and the strength of the ionic bond.

- Describe** the formation of the ionic solid calcium sulfide (CaS) from separate neutral atoms of calcium (Ca) and sulfur (S). Consider the following:

- electron transfer
- formation of the ionic bond
- structure of the ionic lattice.

- Draw **Lewis structures** that show the arrangement of valence electrons in each of the following compounds.

a. NaF      b. K<sub>2</sub>S      c. CaO      d. AlCl<sub>3</sub>      e. Al<sub>2</sub>S<sub>3</sub>      f. MgBr<sub>2</sub>

attractive  
three dimensional  
negative  
non-metal  
gain  
like  
metal  
losing  
positive  
stability  
noble gas  
unlike  
repulsive



- Use the example of the ionic solid calcium oxide to describe the meaning of the following statement:  
**'Within an ionic solid there are two types of electrostatic force. The combined effect of these forces produces the ionic bond.'**
- All ionic substances are known to be brittle. **Describe** this property and **show** with the aid of a diagram how the structure of these substances gives rise to their brittle nature.
- Ping and Sindhu wanted to explore the **electrical conductivity** of an ionic compound in its different phases. They chose to test  $\text{AgNO}_3(\text{s})$ ,  $\text{AgNO}_3(\text{l})$  and  $\text{AgNO}_3(\text{aq})$ .
  - Compare** the structure and composition of  $\text{AgNO}_3(\text{s})$ ,  $\text{AgNO}_3(\text{l})$  and  $\text{AgNO}_3(\text{aq})$ .
  - Sketch** an apparatus that Ping and Sindhu could use to perform their tests.
  - What **safety precautions** should Ping and Sindhu consider?
  - What conductivity results would you **predict** for each of their experiments?
  - Account** for your predictions in (d).

## 8.4 Covalent bonding

**Noble gas** elements show very little chemical reactivity. This behaviour is attributed to their unique electron configurations. Most atoms tend to achieve a noble gas electron configuration by bonding to other elements. In doing this each atom achieves an octet in its valence level. This is generally known as the **octet rule**. Hydrogen is an exception as when it bonds it achieves two valence electrons, like the noble gas He.

A **covalent bond** occurs whenever **non-metal** elements bond to other **non-metal** elements. These elements are found on the upper right hand side of the periodic table and typically have many valence electrons. In a covalent bond, valence electrons are shared between the bonded atoms so that each atom achieves a noble gas electron configuration. (See Fig 9 and 10.)

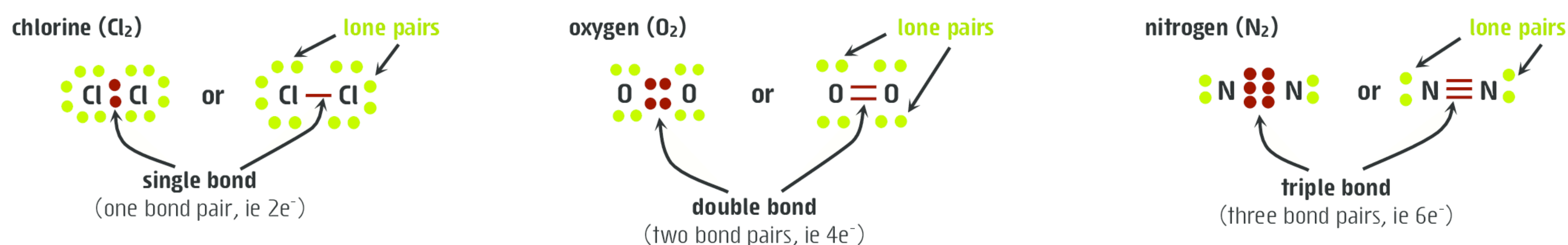
**FIGURE 9 Lewis structures** showing the formation of a covalent bond in a  $\text{F}_2$  molecule



One **valence electron** is provided by each F atom in forming the covalent bond. The resulting **Lewis structure** of the  $\text{F}_2$  molecule and the electron configuration of each F atom shows that by sharing electrons both F atoms achieve an **octet** in their valence level. For this to happen the two F atoms must remain in close proximity to one another, i.e. **bonded**.

Covalent bonds are **directional**, unlike ionic and metallic bonds. A single covalent bond is aligned along an axis through the two atoms that share electrons. The bonding electrons are localised along this axis and between the two bonded atoms. The covalent bond arises from the mutual attraction of two atomic nuclei (+ charge) for the same localised shared pair of valence electrons (- charge).

Types of covalent bond include **single** bonds, **double** bonds and **triple** bonds. A single covalent bond occurs when two atoms share two valence electrons. It can be represented by a single dash — or a pair of dots ••. A double covalent bond involves two atoms sharing four valence electrons. It is represented by a pair of dashes == or two pairs of dots ••. A triple covalent bond is formed when two atoms share six valence electrons. It is represented by three dashes ≡ or three pairs of dots •••. (See Fig 10.)



**FIGURE 10** Pairs of atoms form covalent bond(s) by sharing 2, 4 or 6 electrons. Lewis structures can be used to show this. Shared pairs of valence electrons are placed between bonded atoms and are known as **bond pairs**. Unshared (non bonding) pairs of valence electrons are known as **lone pairs**.

Attempt Set 12 # 1.

Covalent bonds as described here can occur in two **very different** types of substance, **covalent molecular** substances and **covalent network** substances.



## 8.5 Covalent molecular substances

Examples include most non-metal elements, eg chlorine ( $\text{Cl}_2$ ), oxygen ( $\text{O}_2$ ), nitrogen ( $\text{N}_2$ ) (Fig 10) and most compounds formed from a combination of non-metal elements only, eg  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HBr}$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

In these covalent molecular substances, small groups of atoms become covalently bonded to one another forming many small **clusters of atoms**, known as **molecules**. One drop of water for example, would contain around  $1.5 \times 10^{21}$   $\text{H}_2\text{O}$  molecules. The strong covalent bonds within the molecules are referred to as **intramolecular forces**. Various **weak forces** of attraction such as **van der Waals** forces allow some degree of **weak** attraction between molecules. (See Fig 11.) These weak forces between molecules are known as **intermolecular forces**.

**TABLE 4** Understanding the properties of covalent molecular substances

**Non-conductors of electricity in either solid, liquid or aqueous phase (\*See exceptions below.):** The electrons in a covalent molecular substance are localised within each atom's electron cloud or as shared electrons within covalent bonds. None of these electrons are free to move independently. Also these substances **do not** contain ions. The absence of any freely mobile charged particles explains why covalent molecular substances are non-conductors of electricity.

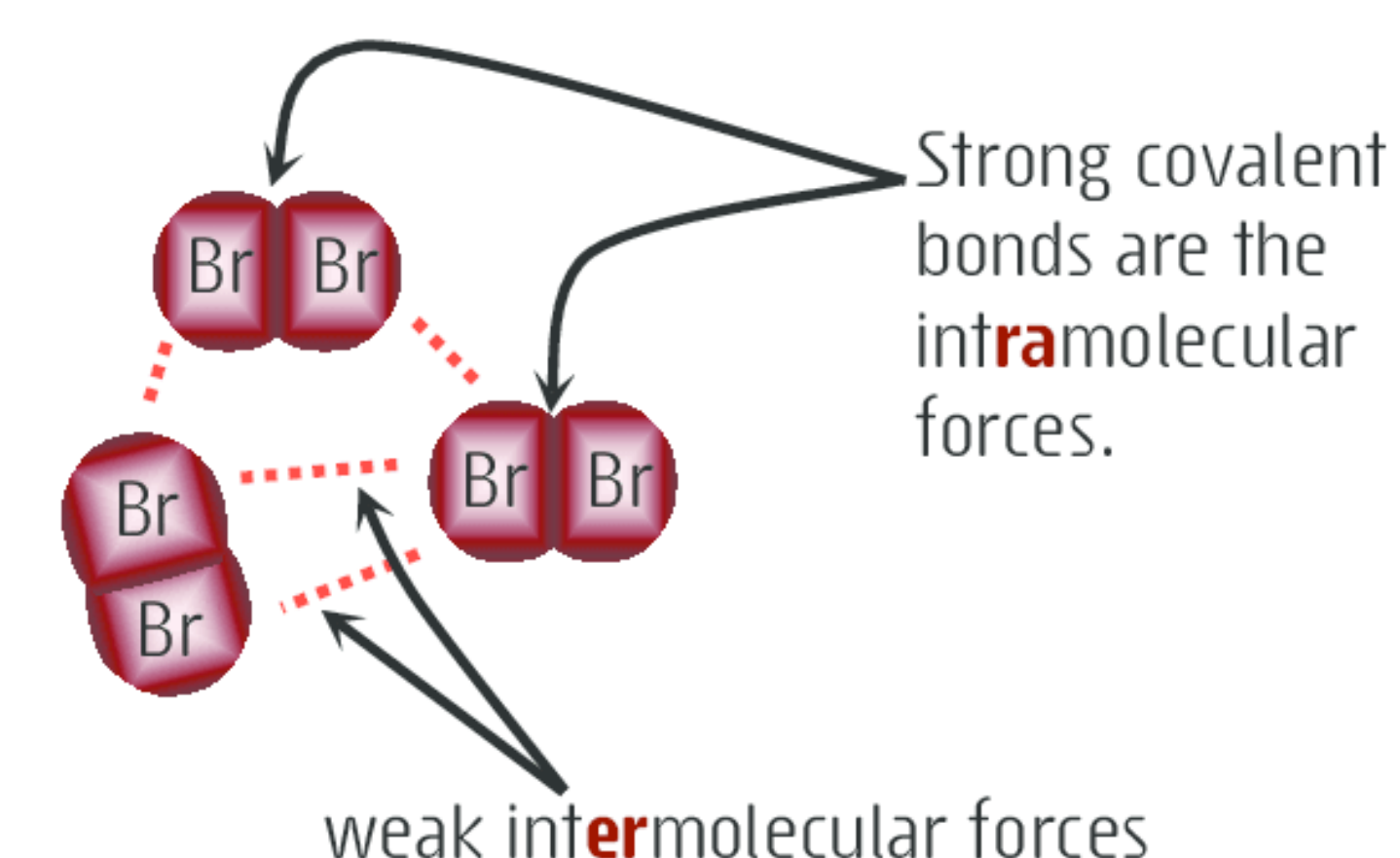
**\*Some are good conductors of electricity when in aqueous solution:** Covalent molecular substances which are acidic or basic, eg  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  react with water (ionise) producing free mobile ions. (See p138-9.) The resulting ions are able to move freely throughout the solution carrying charge and hence conducting an electric current.

**Soft and weak:** Strong covalent bonds (intramolecular forces) only form between the atoms **within** molecules. Only **weak** intermolecular forces of attraction occur between neighbouring molecules. (See Fig 11.) Consequently molecules are easily separated from one other and hence these substances are weak and soft.

**Low to moderate melting and boiling points:** When a molecular substance melts or boils, only the **weak** intermolecular forces (forces between molecules) need to be broken or overcome. Thus the weakly bonded lattice of molecules in the solid phase is easily disrupted by heat energy to form a liquid or gas. It must be understood that the strong covalent bonds occurring between atoms within the molecule (intramolecular forces) are unaffected when a substance melts or boils. (See Fig 11.)

**FIGURE 11** Two distinct types of bonding are present in a molecular substance. **Covalent bonds** are the strong **intramolecular forces** that keep atoms clustered together within the molecule. (See bromine,  $\text{Br}_2$  below.)

Much weaker **intermolecular forces** (also known as **van der Waals** forces) keep molecules bonded to one another. These are the forces that are easily overcome when a molecular liquid **boils** or **evaporates**. The covalent bonds between pairs of bromine atoms are **not affected** by physical changes like **melting**, **evaporating** or **boiling**.



## 8.6 Lewis structures for molecular species

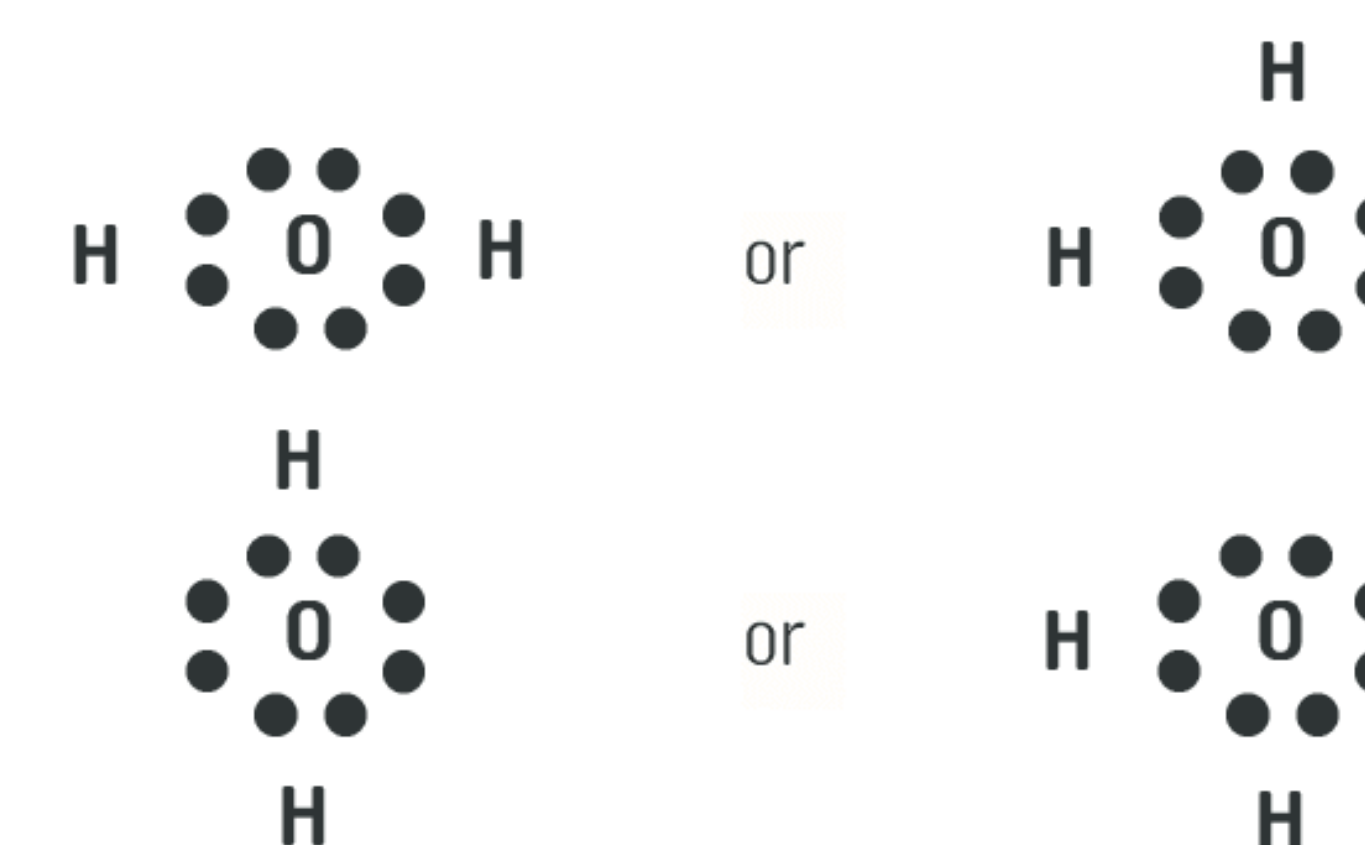
A **Lewis structure** is used to show the arrangement of valence electrons and thus the bonding within a molecule.

To draw a **Lewis structure** for a molecular substance:

- ① Draw a skeleton structure by allocating a single bond (two electrons) between each atom and its neighbour. If a central atom is needed, this cannot be hydrogen and is rarely oxygen. Otherwise the priority for the central atom is usually the element from the lowest periodic table group number. If possible, hydrogen is usually found attached to oxygen.
- ② Calculate the number of valence electrons still to be allocated. This is the total number available to the molecule, less those already allocated to single bonds in step ①.
- ③ The remaining electrons are allocated as lone pairs (not shared between atoms) so that each atom achieves an octet (not hydrogen, which has two electrons in total). If there are too few electrons to achieve this, reassign some lone pairs of electrons to form multiple bonds.

Attempt Set 12 # 2, 3 and 4.

**Caution!** It must be noted that Lewis structures are not intended to show the **actual shape** of a molecule. Molecular shape can be found from the Lewis structure by applying **VSEPR** theory. (See p126.) For this reason any of these Lewis structures are acceptable for a **bent** molecule like water.



**EXAMPLE 1** Draw Lewis structures for the covalent molecular compounds  $\text{NF}_3$ ,  $\text{HCN}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{CO}_3$ .

$\begin{array}{c} \text{F} - \text{N} - \text{F} \\   \\ \text{F} \end{array}$ <p><math>\text{NF}_3</math> has a total of 26 valence electrons (7 from each F atom and 5 from N). The skeleton structure uses 6 valence electrons so 20 more need to be allocated. Use lone pairs only.</p>	$\text{H} - \text{C} - \text{N}$ <p><math>\text{HCN}</math> has 10 valence electrons in total (1 from H, 4 from C and 5 from N). The skeleton structure uses 4 valence electrons so 6 more electrons need to be allocated. Multiple bonds are needed.</p> $\begin{array}{c} \text{H} - \text{C} \equiv \text{N} : \\ \text{or} \\ \text{H} : \text{C} :: \text{N} : \end{array}$ <p>Using a triple bond, instead of two more lone pairs ensures both C and N achieve an octet with the available valence electrons.</p>	$\begin{array}{c} \text{H} - \text{O} - \text{N} - \text{O} \\   \\ \text{O} \end{array}$ <p><math>\text{HNO}_3</math> has 24 valence electrons in total (1 from H, 6 from each O and 5 from N). The skeleton structure uses 8 valence electrons so 16 more need to be allocated. Multiple bonds are needed.</p>	$\begin{array}{c} \text{O} \\    \\ \text{H} - \text{O} - \text{C} - \text{O} - \text{H} \end{array}$ <p><math>\text{H}_2\text{CO}_3</math> has 24 valence electrons in total (1 from each H, 6 from each O and 4 from C). The skeleton structure uses 10 valence electrons so 14 more need to be allocated. Use multiple bonds.</p> <p>A double bond is used as this enables all C and O atoms to achieve an octet with the available valence electrons.</p>
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Complete Set 12.



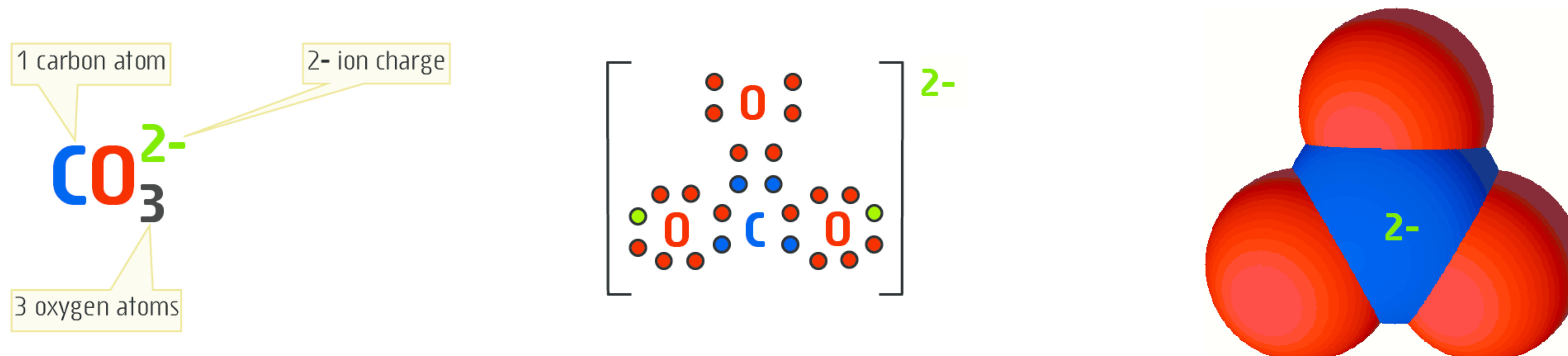
**Note:** Sections identified in this text with an **(E)** may be considered an extension to the Chemistry Course Units 1 and 2. These cover content considered desirable for developing a good understanding of the Chemistry Course Units 1 or 2 or they lead into content covered later in Chemistry Course Units 3 or 4. Their inclusion is for the convenience of teachers and students.

## 8.7 Covalent bonding in polyatomic ions (E see border note)

Many ionic compounds contain one or more polyatomic ions. While these ions form part of an ionic compound, the atoms within the polyatomic ion are covalently bonded to each other. It must be stressed, that since a polyatomic ion has a net positive or negative charge it is not a molecule nor a compound in its own right but instead can only exist along with an oppositely charged ion within an ionic compound. The arrangement of valence electrons in a polyatomic ion can be shown using a Lewis structure. The diagram is drawn using the same procedure as for a molecular substance. (See Example 1 and 2.) Remember, the number of valence electrons within an ion must be adjusted to reflect its charge. (See Fig 12.)

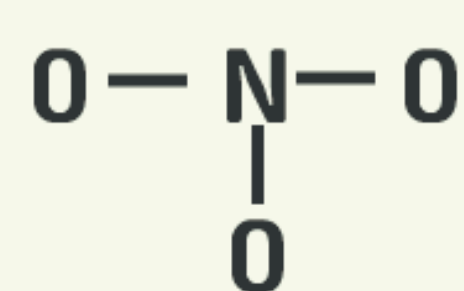
**FIGURE 12 Polyatomic ions** like carbonate,  $\text{CO}_3^{2-}$ , nitrate,  $\text{NO}_3^-$  and so on consist of a cluster of **covalently bonded** atoms that has a net positive or negative charge. For this reason a polyatomic ion is not a molecule or compound in its own right but instead can only exist along with an oppositely charged ion such as in an ionic compound.

**Negatively charged** polyatomic ions have gained an amount of electrons equal to their charge. The carbonate ion,  $\text{CO}_3^{2-}$  for example has a total of 24 valence shell electrons, 6 from each O atom, shown in **red** (ie 18) plus 4 from the carbon atom (**in blue**) and an extra two (**in green**) that give it its **2-** charge. This can be seen in the Lewis structure for the carbonate ion drawn here.

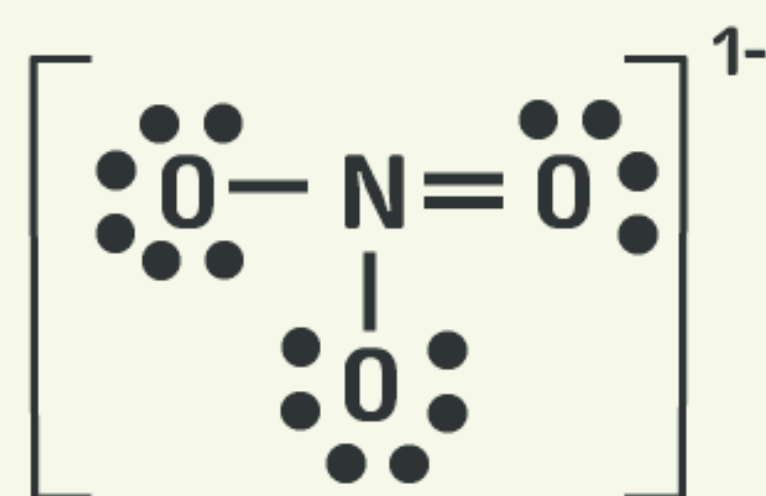


For a **positive ion**, reduce the number of valence electrons by an amount equal to its charge. Thus an ammonium ion,  $\text{NH}_4^+$  has **8** valence electrons in total, **5** from the **N** atom, **1** from each **H** atom and **one less** because of its **1+** charge. Remember, the square brackets around the ion are a reminder that their valence electrons are exclusively associated with the ion. These valence electrons are not shared with other ions.

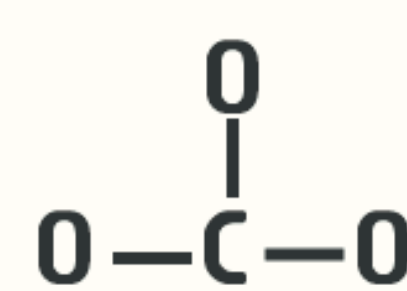
### EXAMPLE 2 Draw Lewis structures for the nitrate ion ( $\text{NO}_3^-$ ) and the carbonate ion ( $\text{CO}_3^{2-}$ ). (E)



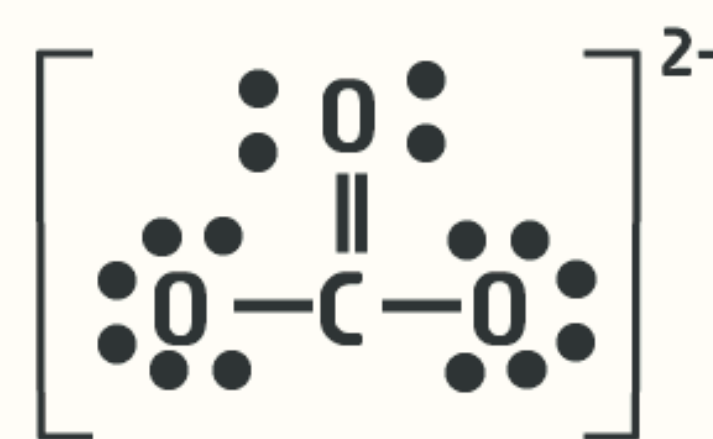
$\text{NO}_3^-$  has 24 valence electrons in total, 6 from each O, 5 from N and 1 extra for the 1- charge. The skeleton structure uses 6 valence electrons so 18 more electrons need to be allocated. Multiple bonds are needed for each atom to achieve an octet.



Using a double bond instead of another lone pair ensures all N and O atoms achieve an octet with the available valence electrons.



$\text{CO}_3^{2-}$  has 24 valence electrons in total, 6 from each O, 4 from C and 2 extra for the 2- charge. The skeleton structure uses 6 valence electrons so 18 more electrons need to be allocated. Multiple bonds are needed for each atom to achieve an octet.



A double bond is used to enable all C and O atoms to achieve an octet with the available valence electrons.



## Set 12 Molecular substances

1. Use the list of terms to correctly complete the passage about covalent bonds.

Atoms form covalent bonds when (a) \_\_\_\_\_ elements combine with other non-metal elements. The atoms share a pair of valence (b) \_\_\_\_\_ forming what is called a single (c) \_\_\_\_\_ bond. The bond is due to the mutual attraction of two atomic nuclei (+) for the same pair of (d) \_\_\_\_\_ electrons (-). Each of the bonded atoms contributes one electron to the shared pair. In this way each atom (e) \_\_\_\_\_ one valence electron by (f) \_\_\_\_\_ one valence electron [share one gain one]. Atoms continue this process until they achieve a (g) \_\_\_\_\_ electron configuration. This means the atoms will then have an (h) \_\_\_\_\_ in their valence level.

A pair of atoms can also form a (i) \_\_\_\_\_ covalent bond by sharing four valence electrons or a triple covalent bond by sharing (j) \_\_\_\_\_ valence electrons.

noble gas  
six  
non-metal  
sharing  
valence  
double  
electrons  
octet  
gains  
covalent

2. Use the list of terms to correctly complete the passage describing the formation and structure of a covalent molecular substance.

Covalent bonding can produce two distinctly different types of substance known as (a) \_\_\_\_\_ and covalent network. Covalent molecular substances consist of atoms covalently bonded to form small (b) \_\_\_\_\_ or groups of atoms. These clusters of covalently bonded atoms are known as (c) \_\_\_\_\_. There may be two, three, four and so on atoms in each molecule.

Intramolecular forces refer to the strong (d) \_\_\_\_\_ bonding within the molecule. Intermolecular forces also occur (e) \_\_\_\_\_ molecules. These are known to be very weak forces. These weak intermolecular forces are generally referred to as (f) \_\_\_\_\_ forces. When a covalent molecular substance changes phase from solid to liquid to gas, it is the weak (g) \_\_\_\_\_ known as van der Waals forces that are overcome. The much stronger (h) \_\_\_\_\_ between the atoms forming the molecule are (i) \_\_\_\_\_.

van der Waals  
covalent bonds  
molecules  
covalent molecular  
unaffected  
between  
intermolecular forces  
covalent  
clusters

3. Predict the **electrical conductivity** of sucrose (common sugar) in each of the phases,  $C_{12}H_{22}O_{11}(s)$ ,  $C_{12}H_{22}O_{11}(l)$  and  $C_{12}H_{22}O_{11}(aq)$ . Use your knowledge of chemical bonding to **justify** your predictions.

4. Covalent molecular substances typically have low melting and boiling points. This occurs despite covalent bonding being a very strong form of chemical bond. **Account** for this observation. Your answer should clearly refer to **intermolecular forces** and **intramolecular forces**.

5. Draw **Lewis structures** for the following molecular substances.

a. $F_2$	e. $NH_3$	i. $PH_3$	m. $SO_2$	q. $H_2SO_4$	u. $HClO_2$
b. $H_2$	f. $H_2S$	j. $CF_4$	n. $SO_3$	r. $H_2SO_3$	v. $HClO_3$
c. $O_2$	g. $HCl$	k. $PBr_3$	o. $CS_2$	s. $H_2CO_3$	w. $HClO_4$
d. $N_2$	h. $CH_4$	l. $CO_2$	p. $HNO_3$	t. $HClO$	

6. Using the example of **ammonia**,  $NH_3$  **compare** the meanings of the following terms. A **labelled sketch** and **Lewis structure** would be an essential part of your answer.

- **bond pair** and **lone pair**
- **atom** and **molecule**
- **intermolecular forces** and **intramolecular forces**

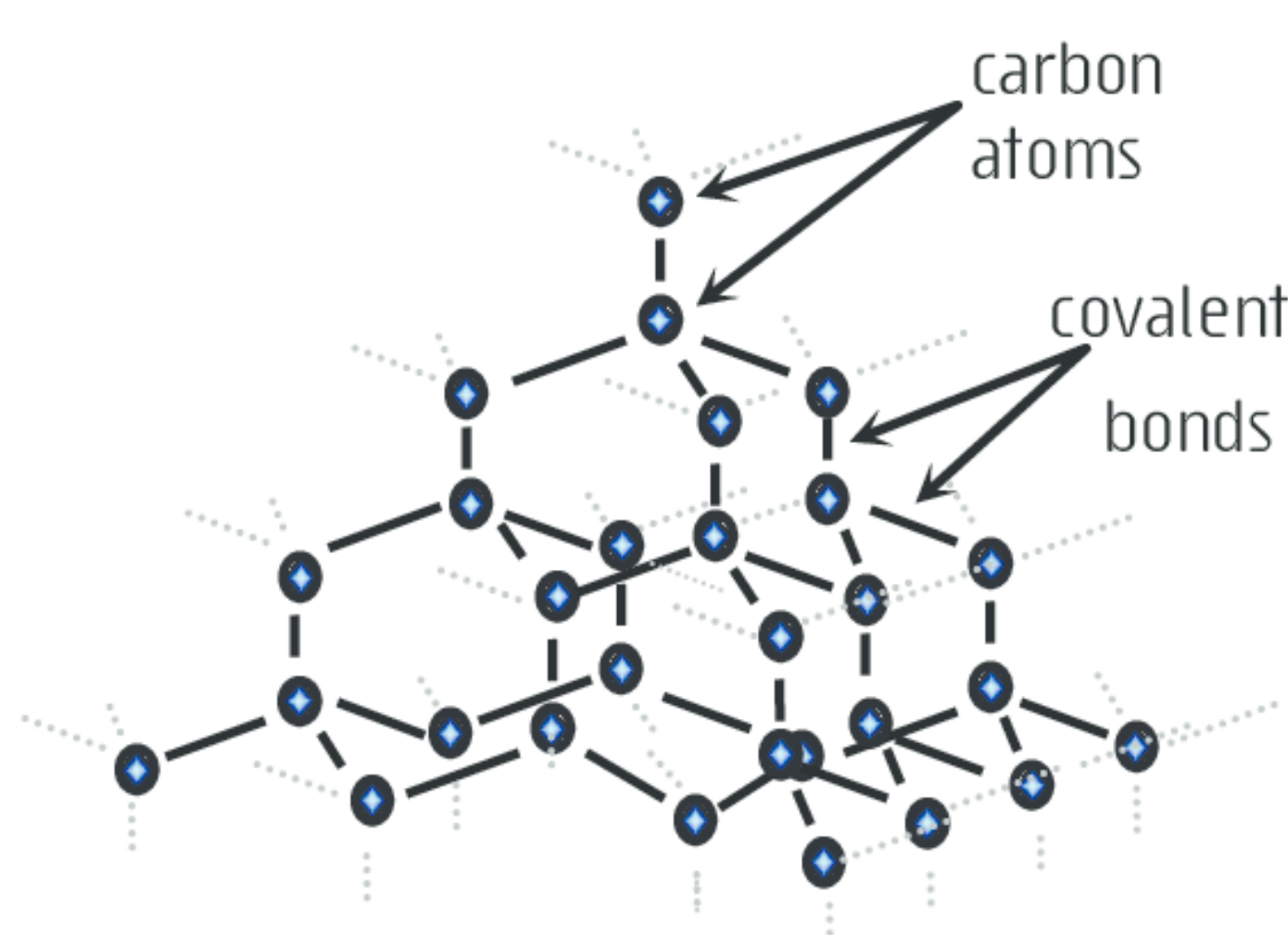
7. Molecular substances like hydrogen chloride ( $HCl$ ), sulfuric acid ( $H_2SO_4$ ) and nitric acid ( $HNO_3$ ) are poor conductors of electricity in the solid, liquid and gas phase. In this way they are similar to all other covalent molecular substances. When dissolved in water however, they form highly conducting solutions. This behaviour is unlike most covalent molecular substances. **Account** for the unusual behaviour of these substances. (You may need to research the **ionisation** process, see 16.2 and 16.3 p138-139)





**FIGURE 13** Diamond and graphite (black lumps) both consist of **pure carbon**. Their vastly different properties are caused by the different arrangement of covalently bonded carbon atoms. **Different forms of the same element** like these are known as **allotropes**.

**FIGURE 14** The covalent network structure of **diamond** (below) has each carbon atom covalently bonded to four neighbouring atoms. This strongly bonded three dimensional structure explains the high melting point and hardness of diamond. Diamond's melting point is in excess of 3550 °C. This extremely high temperature is needed to break all of the strong covalent bonds between neighbouring carbon atoms in the diamond structure.



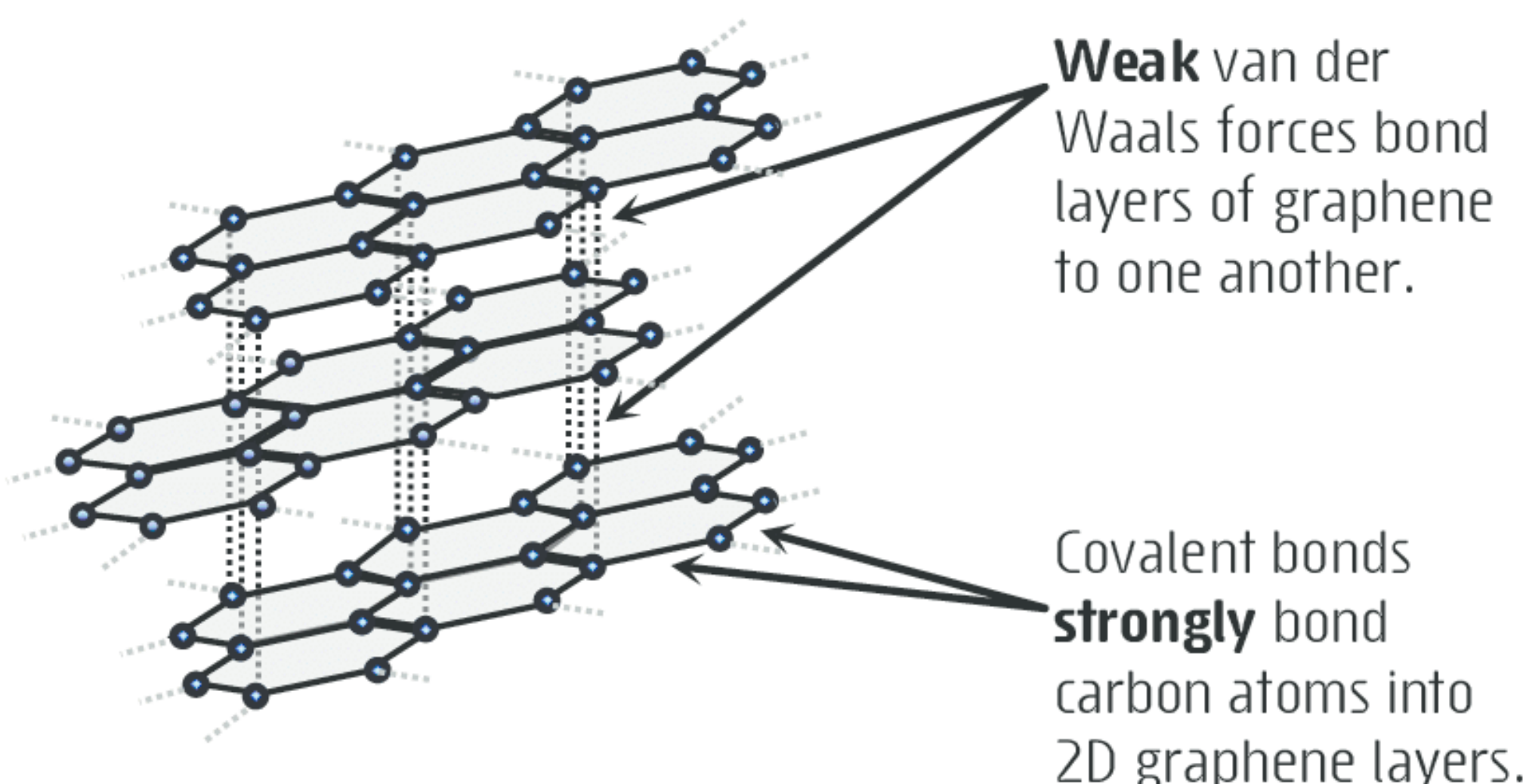
## 8.8 Covalent network substances and carbon allotropes

Common substances that form covalent network structures include **boron** (B), **carbon** (graphite and diamond, Fig 13), **silicon** (Si), **silicon dioxide** (SiO<sub>2</sub>, Fig 16) and **silicon carbide** (SiC). Atoms in these substances form covalent bonds with multiple neighbouring atoms resulting in a **continuous array of covalently bonded atoms**. (See Fig 14, 15 and 16.) This covalent network structure is unlike that of a covalent molecular material as the strong covalent bonding extends continuously throughout the substance. Remember, in a covalent molecular substance the strong covalent bonds only occur between the few atoms within a molecule while weak intermolecular forces occur between molecules. This different structure gives covalent network substances properties that contrast strongly with those of covalent molecular materials.

**Diamond** and **graphite**, two **allotropes** of carbon (Fig 13), highlight the typical properties of covalent network substances while showing the dramatic effect of structure in altering these properties. In diamond each carbon atom is bonded to **four** neighbouring carbon atoms in a **three dimensional** arrangement called a tetrahedron, a shape similar to a tripod. (See Fig 14) This three dimensional array of covalently bonded atoms produces a hard, brittle, non-conducting, high melting point and boiling point substance that is typical of most covalent network substances.

In **graphite** (Fig 15) however, each carbon atom is covalently bonded to three neighbouring atoms to form flat **two dimensional** sheets, called **graphene**, of interlocking hexagonal rings of carbon atoms. Graphite consists of multiple graphene sheets stacked one on top of the other with only **weak bonds**, van der Waals forces, acting between the graphene layers. In this structure one valence electron from each carbon atom remains **delocalised** and is able to move freely between the graphene layers. As a consequence of this different structure, graphite is soft and a good conductor of electricity unlike diamond which is very hard and non-conducting.

**Figure 15** The unusual covalent network structure of **graphite** (at right) has strong covalent bonding within two dimensional layers of carbon atoms. Only weak van der Waals forces occur between these layers with some valence electrons free to move throughout the structure. As a result graphite is soft, has a high melting point and will conduct an electric current.



**TABLE 5** Understanding the properties of covalent network substances

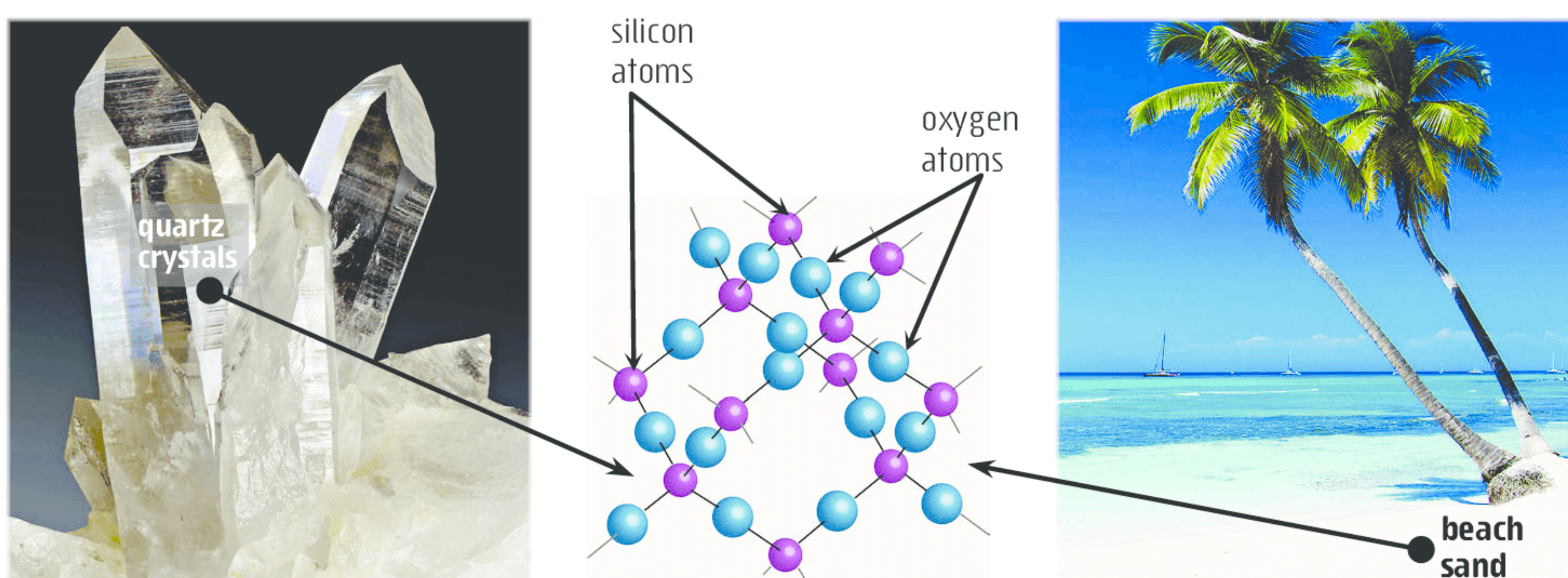
**Non-conductors of heat or electricity:** Electrons in these substances are held in fixed positions within the atom's shells, lone pairs or covalent bonds. As the electrons are not free to move independently they are unable to conduct electricity or heat through the substance. **Graphite**, an allotrope of carbon is a notable exception where some valence electrons are delocalised (not located in a specific lone pair or bond pair) and so are free to move throughout the structure. Consequently graphite is a good conductor of electricity.

**Very hard and brittle:** Strong covalent bonds occur between all atoms within a covalent network structure. (See Fig 14 and 16.) This continuous array of strongly bonded atoms is difficult to disrupt and so these substances are characteristically hard and brittle. **Graphite** is a notable exception where its atoms are covalently bonded into rings of six carbon atoms. These rings interlock to form strongly bonded, flat, two dimensional layers. (See Fig 15.) As only weak bonding forces occur between these layers they are able to slip over one another with ease. This causes graphite to be a soft material.

**Very high melting and boiling points:** Strong covalent bonds occur between all atoms within the structure. A very high temperature (high particle kinetic energy) is needed to disrupt this continuous array of strongly bonded atoms.

**FIGURE 16** **Quartz** is one of the more common compounds found in the Earth's crust. It is a crystalline form of **silica** (SiO<sub>2</sub>) where each silicon atom is covalently bonded to **four** neighbouring oxygen atoms while each oxygen atom is covalently bonded to **two** neighbouring silicon atoms. This produces a covalent network structure similar to that of diamond. As with diamond quartz is very hard, brittle and has a high melting point.

**Weathering** of rocks that are rich in quartz, eg granite, results in the formation of small quartz particles called **sand**. Erosion accumulates these fragmented quartz particles to form sand dunes and coastal beaches.

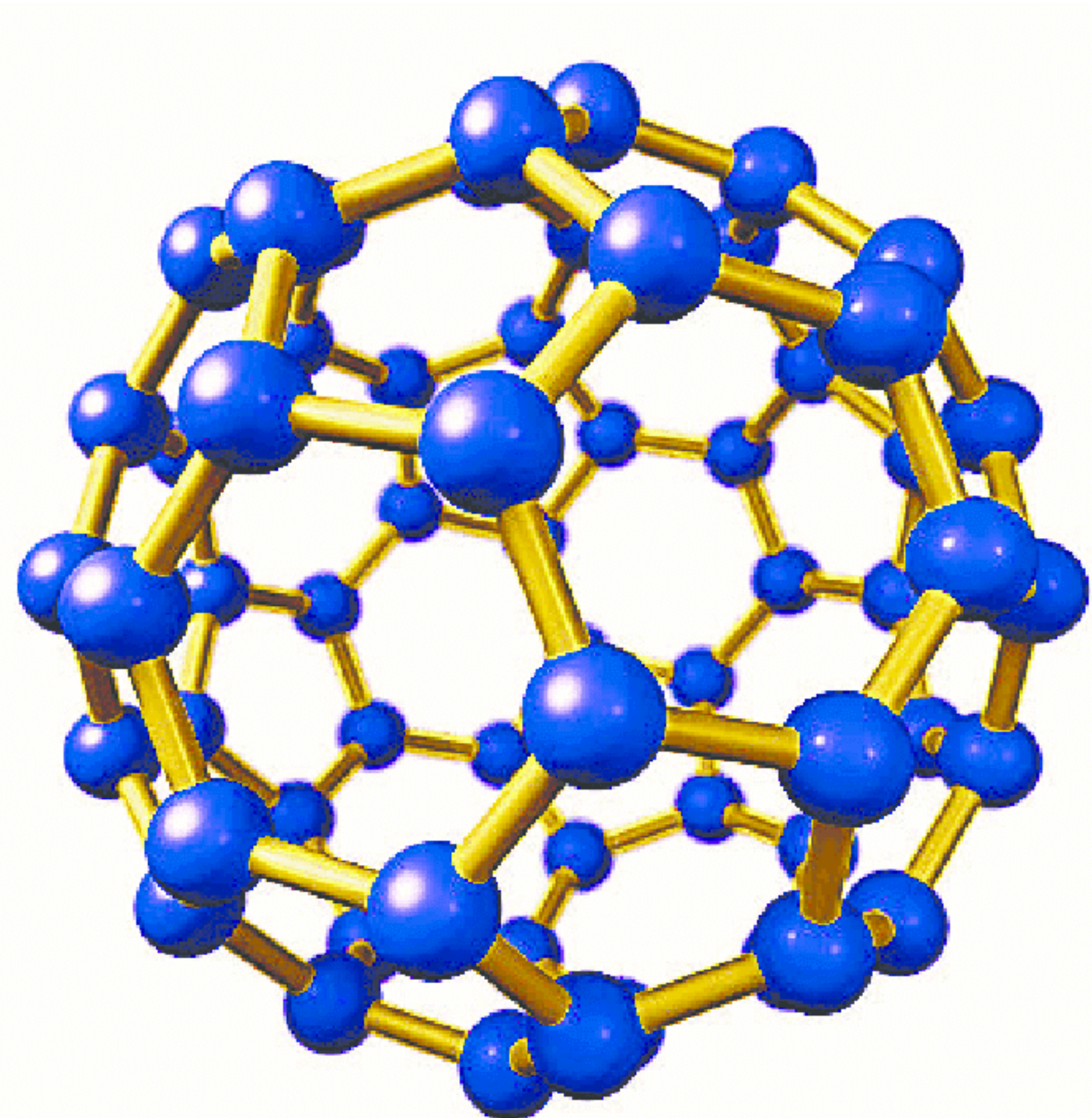


Attempt Set 13 # 1, 2, 3 and 4.



## 8.9 Fullerenes: Newly discovered allotropes of carbon

**Fullerenes** are a recently discovered allotropic form of carbon. The molecule known as a buckminsterfullerene,  $C_{60}$ , or commonly referred to as a 'buckyball' was the first of these to be discovered in 1985. The molecule consists of 60 carbon atoms covalently bonded into a cage structure consisting of 12 pentagons and 20 hexagons and resembling a soccer ball shape. (See Fig 17.) Similar cage structures have been identified with 70, 80 and more carbon atoms.  $C_{60}$  and other fullerenes occur naturally in small concentrations in soot.



**FIGURE 17** The 1985 discovery of  $C_{60}$  was the result of a **collaborative effort** between Harold W. Kroto from the University of Sussex, Richard E. Smalley and Robert F. Curl of Rice University in Houston along with several of their undergraduate students.

**Kroto** was attempting to verify the existence of certain long chain carbon structures that he and other radio astronomers had previously identified as existing in interstellar space. Kroto hypothesized these chains were created in the carbon rich atmosphere of red giant stars. To replicate these conditions and test his hypothesis Kroto needed the help of Smalley who had invented a piece of equipment called a '**supersonic cluster beam apparatus**'.

The apparatus used pulsed laser beams to vaporise a small sample of graphite. The resulting vapour was cooled and the condensed powder analysed using **mass spectrometry**. (See p9.) This revealed the presence of the long chain carbon structures Kroto had hypothesised would form. Interestingly, the mass spectrum also showed an abundance of a previously unknown substance whose mass corresponded to a **cluster of 60 carbon atoms**.

The structure they proposed for  $C_{60}$  is shown at left. They named their structure **buckminsterfullerene** after the philosopher and architect, R. Buckminster Fuller (1895-1983), who had designed similar looking geodesic domes. Its resemblance to a soccer ball has given it the nickname '**buckyball**'. In 1996 **Kroto**, **Smalley** and **Curl** were awarded the **Nobel Prize in Chemistry** for their discovery of fullerenes.

While the carbon atoms within  $C_{60}$  are strongly bonded to one another by covalent bonding there is very little attraction between neighbouring  $C_{60}$  molecules (van der Waals forces only). As a result the black or brownish solid is a soft powdery material. It sublimes at 800 K, and in its pure form is a semiconductor.

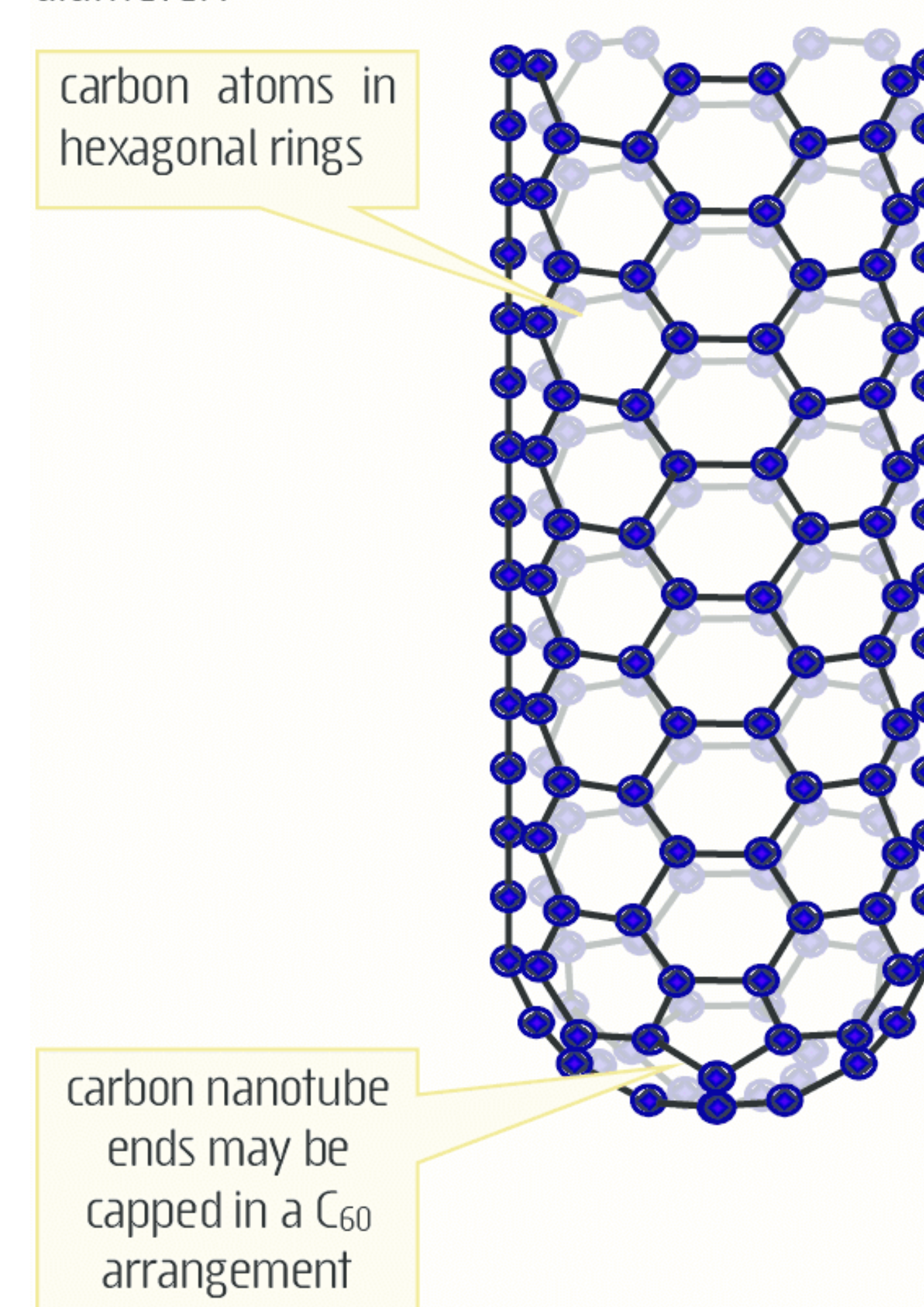
Another more recently discovered group of fullerenes are the tube structures known as **carbon nanotubes (CNTs)**. (See Fig 18 and 19.) These were discovered in 1991 by Iijima Sumio of NEC Corporation in Tsukuba, Japan. CNTs can be **visualised** as a **graphene** sheet, ie a single layer of graphite, rolled into a cylinder shape. (See Fig 15 and 23.) Along the length of the cylinder, carbon atoms are covalently bonded into interlocking hexagonal arrangements. The ends of a CNT may be open or capped off with a hemispherical arrangement of carbon atoms bonded into interlocking pentagon and hexagon arrangements as in  $C_{60}$ . Carbon nanotubes typically have a diameter of around **1 nanometre** ( $1 \times 10^{-9}$  m) or more and lengths of up to several micrometres. Their length, however, is potentially unlimited and depends on the conditions of manufacture. Nanotubes can also be produced with **multiple walls** where two or three concentric CNTs of increasing diameter fit within one another. (See Fig 19.) These are referred to as multi walled nanotubes (**MWNTs**).

Every atom in a single carbon nanotube (CNT) is bonded to its neighbouring atoms by strong covalent bonds. This gives an individual CNT great strength and flexibility. Although individual CNTs are very tiny, when compared to a steel sample of the same dimensions, they are much stronger and lighter with a **tensile strength** of around 100 times that of steel and a **density** around a quarter. The potential of creating super strong lightweight structures using CNTs has captured the imaginations of engineers and researchers worldwide.

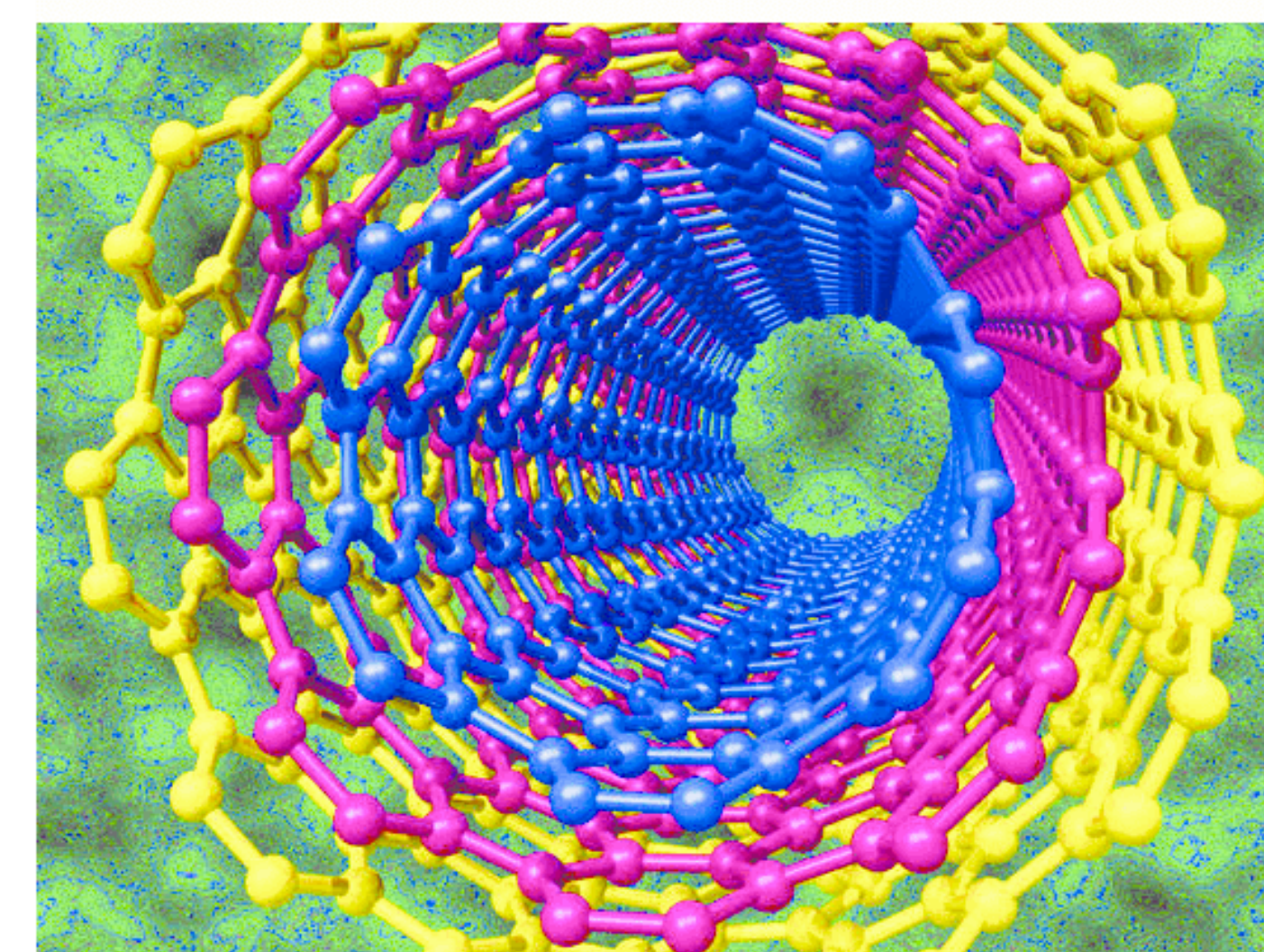
CNTs also have unusual **electrical properties**. Depending upon their diameter and symmetry they can be semiconductors or excellent conductors. Individual CNTs are capable of carrying current densities 1000 times greater than metals like copper or silver. CNTs can also conduct current down the tube length producing almost no heating effect, a major advantage over other conductors. These properties suggest a wide range of potential uses from globe filaments and efficient power transmission to electronic semiconductor devices such as transistors, diodes and computing applications.

Fullerenes have generated great interest due to their unique mechanical, optical and electrical properties. The extremely large **surface area** of these structures and their ability to act as molecular containers as well as their potential to bond to surfaces and allow other structures to bond to their surface suggest a variety of applications may be possible. The study and potential application of fullerenes and other similar structures has evolved into a whole new field of scientific endeavour known as **nanotechnology**. (See p65-6.)

**FIGURE 18** Nanotubes are so called because their diameter is of the order of a nanometre. A nanometre is a billionth of a metre, ie  **$1 \times 10^{-9}$  m**. A single carbon atom has a diameter of around 0.15 nm and the largest atoms are less than 0.5 nm in diameter.



**FIGURE 19** The 3D representation above is of a **multi walled carbon nanotube** open at both ends.



Complete Set 13.



## Set 13 Covalent network substances and carbon allotropes

carbon  
structure  
germanium  
weak  
high  
every atom  
molecular  
covalently  
silicon  
molecules  
vast array



**FIGURE 20** Diamond and graphite (pencil 'lead') both consist of **pure carbon**. Their vastly different properties are caused by the different arrangement of covalently bonded carbon atoms. (See Fig 14 and 15 p62.)

Find out more! Try an internet search for **cubic BN** or **hexagonal BN**.

- The following passage describes the bonding and structure of covalent network substances. Use the list of terms to complete the passage.

Within a covalent network material atoms are (a) \_\_\_\_\_ bonded to one another forming a single vast array that involves (b) \_\_\_\_\_ within the sample. The ability to form such vast arrays of covalently bonded atoms relies on the (c) \_\_\_\_\_ bonding capacity of group 14 elements like (d) \_\_\_\_\_, (e) \_\_\_\_\_ and (f) \_\_\_\_\_. Other elements like boron and nitrogen can also form covalent network substances.

The nature of the covalent bonds within a covalent network substance is the same as those in a covalent (g) \_\_\_\_\_ substance. The vast difference in properties between covalent molecular and covalent network substances is caused by a difference in (h) \_\_\_\_\_. Covalent molecular substances have a structure where small numbers of atoms covalently bond to one another forming clusters of tightly bonded atoms known as (i) \_\_\_\_\_. Only (j) \_\_\_\_\_ van der Waals forces exist between the molecules. By comparison, in a covalent network substance every atom in the sample is covalently bonded to its neighbouring atoms to form one single (k) \_\_\_\_\_ of covalently bonded atoms.

- Carbon dioxide** ( $\text{CO}_2$ ) is a gaseous substance present in low concentrations in the Earth's atmosphere ( $\approx 0.04\%$  by volume). The substance **silicon dioxide** ( $\text{SiO}_2$ ) is present in vast quantities in the Earth's crust. It is commonly known as quartz or sand. Despite their similar looking formula these substances are quite different. **Compare** the structure and bonding of carbon dioxide ( $\text{CO}_2$ ) with that of silicon dioxide ( $\text{SiO}_2$ ). Thus **account** for the different phase of carbon dioxide and silicon dioxide.

- Diamond** and **graphite** (see Fig 20) are two **allotropes** of carbon which both form a covalent network structure. These substances have extremely high melting points. Diamond is a non-conductor of electricity and the hardest known naturally occurring material. Graphite however, is soft and a reasonable electrical conductor. **Compare** and **contrast** these allotropes. Consider the following:

- What are allotropes?
- Compare the bonding and structure of these two allotropes.
- Relate their different physical properties of hardness and electrical conductivity to their particular structure.

- The compound **boron nitride**, **BN** occurs in two different allotropes. Both forms have a covalent network structure. **Cubic BN** has a structure much like diamond while **hexagonal BN** has a structure much like that of graphite.

- What physical properties would you expect for hexagonal BN?
- Draw a section of a single layer of the hexagonal BN. Clearly indicate the boron and nitrogen atoms as well as the covalent bonds.
- Although hexagonal BN has many properties in common with graphite it does not conduct electricity. What can you conclude regarding the valence electrons in hexagonal BN?
- Which of the allotropes would be most suited to use on the tips of cutting tools like a saw blade or machining tool for cutting metal? Justify your choice.

- The group of substances called **fullerenes** are recently discovered **allotropes** of carbon. The following questions relate to these allotropes.

- Scientific research is often described as a **collaborative** or **team** effort with major discoveries often being **unexpected**. In a few lines use the discovery of  $\text{C}_{60}$  to **elaborate** on these points.
- Briefly describe the **structure** of a  $\text{C}_{60}$  molecule.
- Materials like  $\text{C}_{60}$  are sometimes referred to as **nanoparticles**. What does the prefix '**nano**' mean and how is this related to the particles of  $\text{C}_{60}$ ?
- Would you expect a solid sample of  $\text{C}_{60}$  to be **soft** or **hard**? Justify your answer with reference to its **structure** and **bonding**?



6. **Carbon nanotubes** (CNTs) are also fullerenes. These too are a fairly recent discovery. Answer the following questions regarding CNTs.
- CNTs are described as being like rolled up sheets of **graphene**. What is graphene and why doesn't it have a formula like  $C_{60}$  does? Include a 2D sketch of a section of graphene and label the atoms, bonds and ring structures that are present.
  - One application of CNTs involves adding them to plastics to produce **composite** materials with greater **strength**. What property of CNTs give plastics this extra strength and in terms of bonding and structure why should a CNT have this property?
  - What are some other **properties** of CNTs?

## 8.10 Nanotechnology

**Nanoparticles** are particles with at least one dimension in the **1-100 nanometre** range. (1 nanometre = 1 nm =  $1 \times 10^{-9}$  metres.) Nanotechnology involves the study of nanoparticles and structures as well as their manufacture and potential use. Nanoparticles often have properties that differ greatly from those of the bulk material of which they are made. Many of these unique properties are due to **quantum effects** that result from their small particle size.

Zinc oxide and titanium oxide for example are white opaque solids that give excellent UV protection. In their **macro particle** form (fine particles but larger than nanoparticles) they are the active ingredient in some sunscreens and cosmetics. A disadvantage of these products is the visible white opaque layer they leave on the skin. (See Fig 21.) A new alternative uses ZnO and  $TiO_2$  in the form of nanoparticles. In this particle size range an interesting quantum effect occurs as ZnO and  $TiO_2$  become **invisible** while still protecting against UV exposure.

Various optical effects like these are commonly shown by nanosized particles. The varied colours seen in the solutions in Fig 22 are due to the presence of different size nanoparticles of cadmium selenide, CdSe. These particles, known as **quantum dots**, are finding application as biological tracers due to their stability and bright and varied colours. Quantum dots also exhibit unique electrical properties that may find application in the future technology of quantum computing.



**FIGURE 22** The unique colours produced by these solutions/colloids is due to the presence of nanosized particles called quantum dots. The colour is produced when ultra violet light ('black light') is shone onto the sample. This is an example of a **quantum effect** because the bulk material (CdSe) from which the dots are made is neither soluble in water nor exhibits this range of colours.

The actual colour or wavelength of light produced varies with the dot size. The smaller the dot, the closer its colour is to the blue/violet end of the spectrum and the larger the dot, the closer to the red end. Quantum dots are traditionally 2-10 nanometres in size and made from various metal sulfides or selenides like ZnS, ZnSe, CdSe and so on.

Carbon nanotubes, CNTs also exhibit electrical properties quite different to the material from which they are composed. Graphite for example, a conductor of electricity, is composed of stacks of **graphene** sheets loosely bonded together. (See Fig 15.) When these graphene sheets are in the form of a CNT structure (Fig 23) they show quite different patterns of conductivity to graphite. Depending upon their dimensions and symmetry, CNTs can be excellent conductors of electricity or semiconductors. Their wide range of electrical properties and excellent thermal conductivity indicate the potential for using CNTs to create nano-sized transistors and diodes.

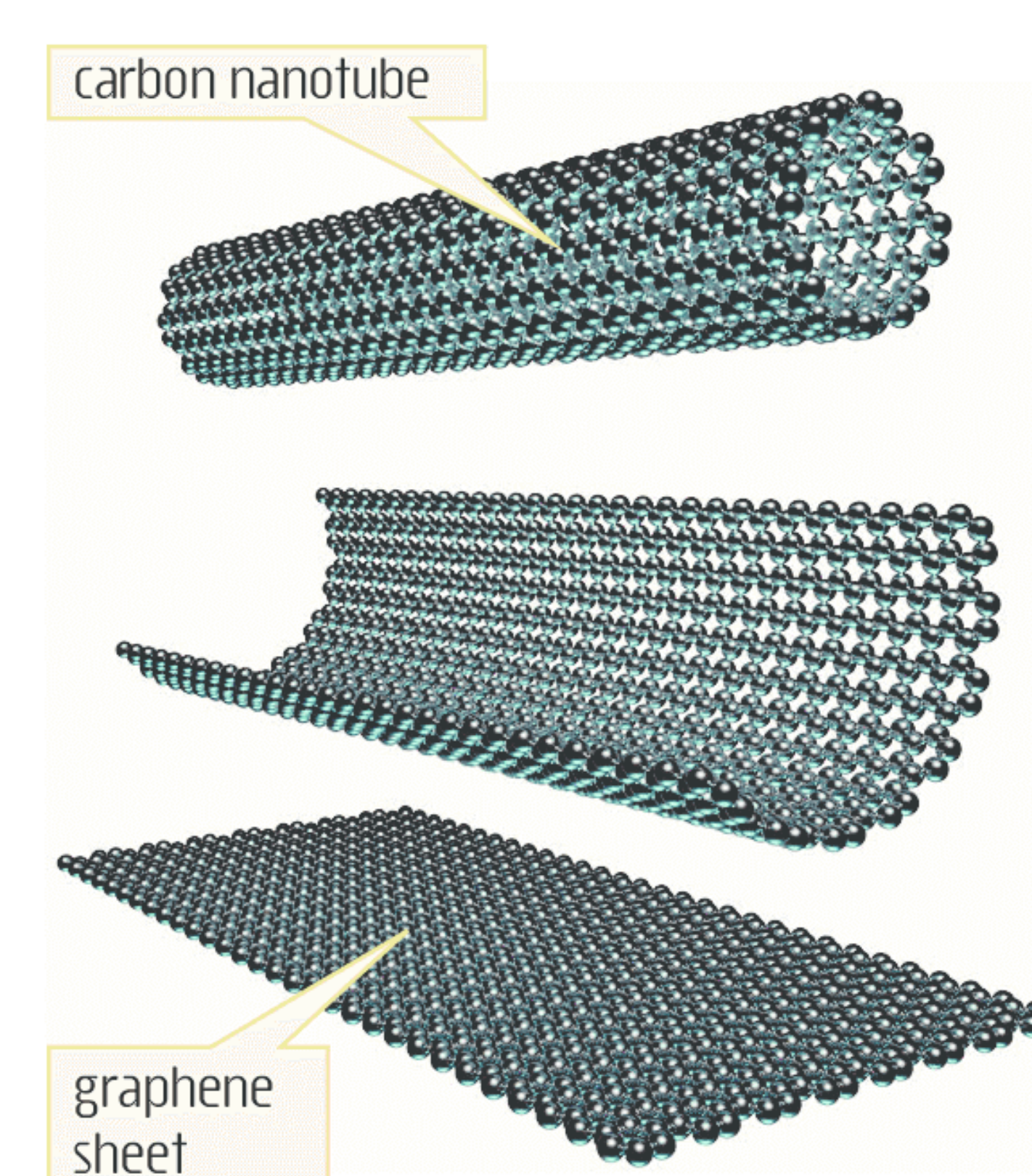
Stanford University's School of Engineering recently reported in the science journal, 'Nature' (September 2013) the first **computer** made entirely of carbon nanotubes. While this particular computer is described as basic, consisting of 178 transistors, it was able to count and sort numbers as well as run its own operating system. Importantly, its development demonstrates proof of concept for the use of CNTs in this way and will likely encourage further research in this field. CNTs have potential advantages in this area as they can potentially be manufactured into thinner layers than silicon and are much more efficient at carrying currents. CNTs could result in computers that are smaller, faster, more energy efficient and run cooler than silicon based computers.

**FIGURE 21** Many cosmetics and sunscreens rely on the UV protection of **opaque** ZnO and  $TiO_2$ . Preparations like these leave a white opaque film on the skin as seen below.



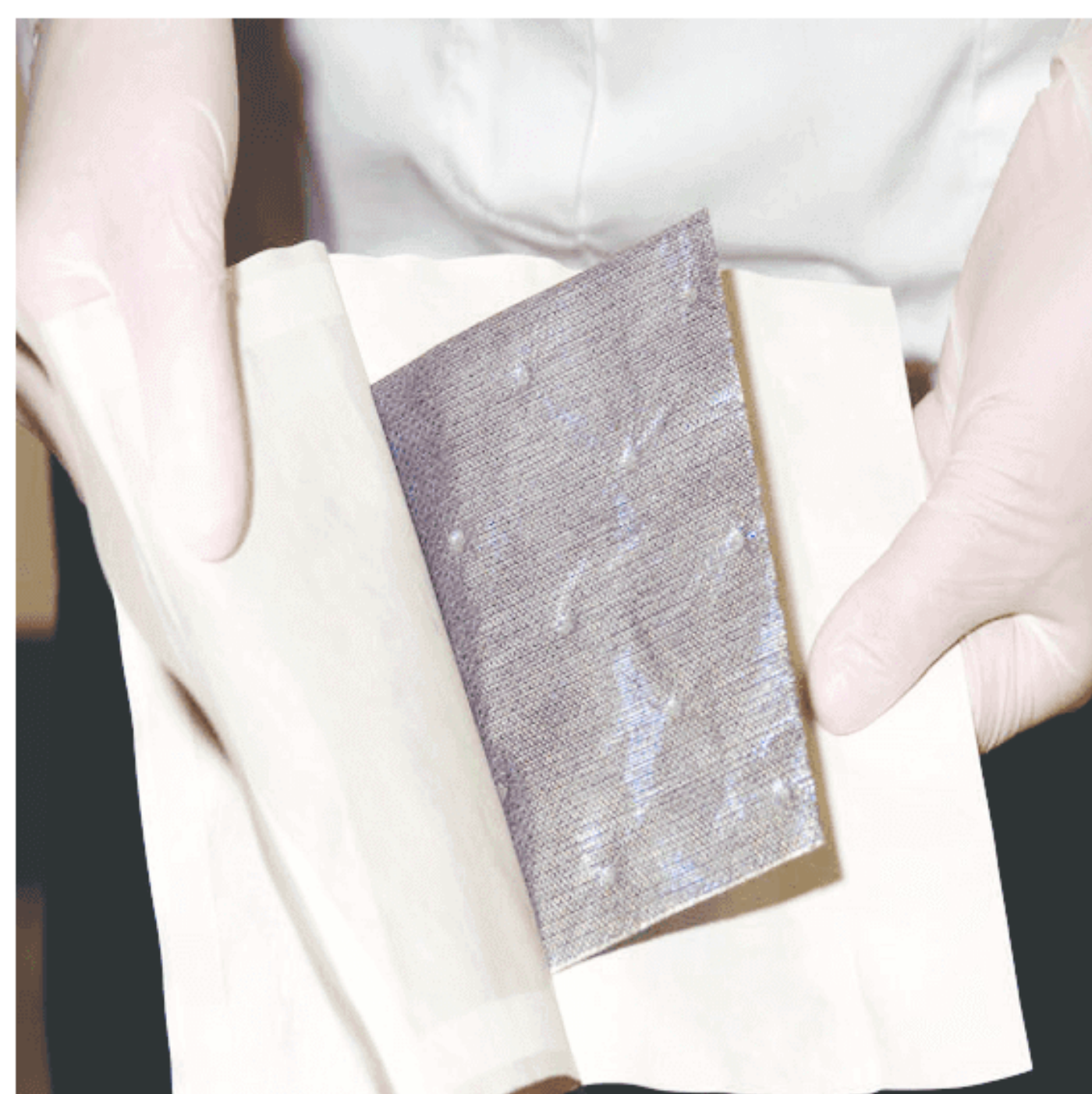
Similar preparations using ZnO and  $TiO_2$  in the nanoparticle form are **invisible** but still afford the same UV protection. This change in opacity is a **quantum effect** that depends on particle size.

**FIGURE 23** Carbon nanotubes (CNTs) can be **visualised** as rolled sheets of graphene. CNTs have unique electrical properties that vary depending upon the tube diameter and symmetry.

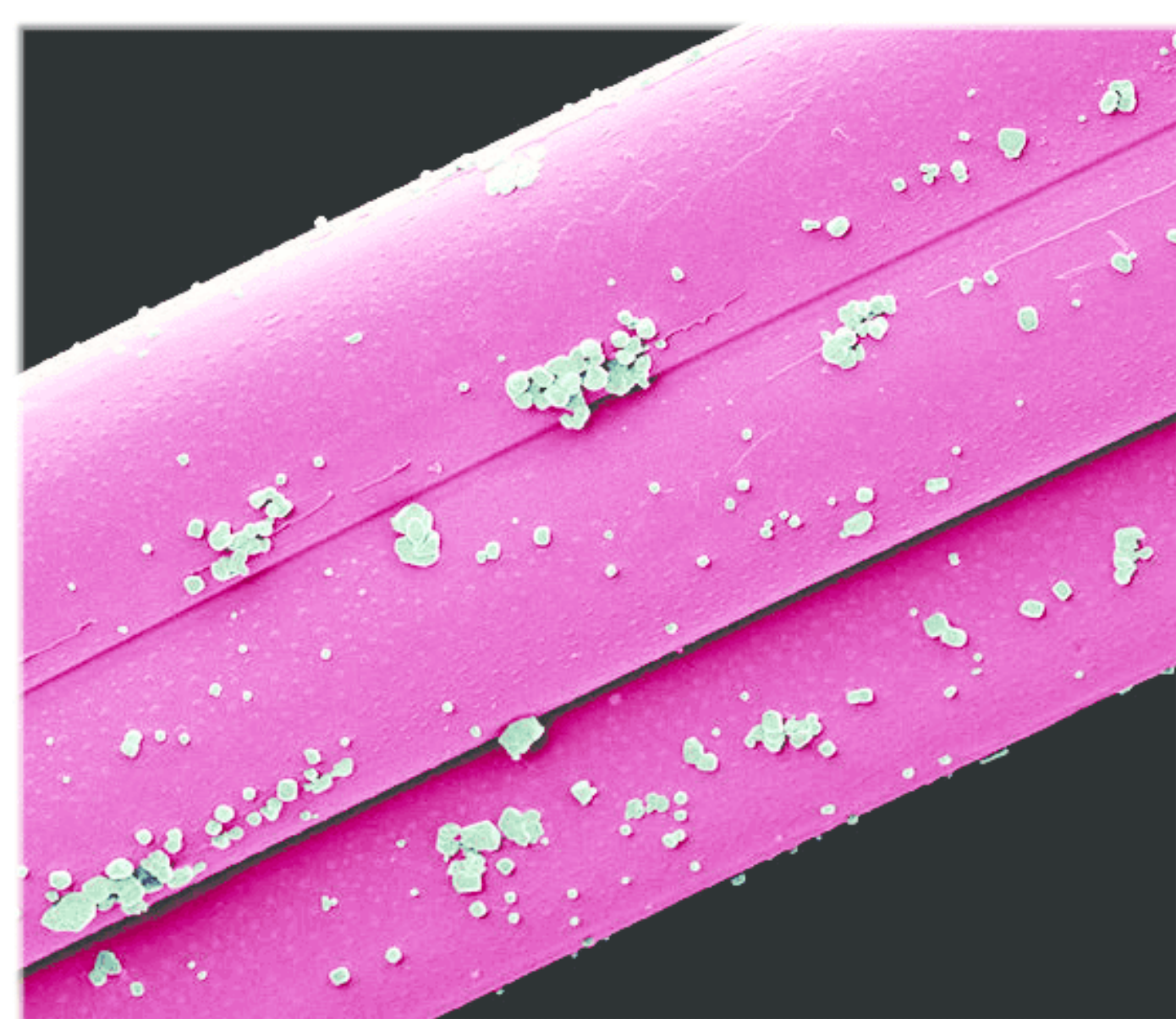




**FIGURE 24** The 'Acticoat 7' wound dressing shown here is impregnated with **nanosize** particles of **silver**. The silver particles have an **antimicrobial** effect, helping to prevent some bacterial and fungal infections. This dressing is designed to be used on wounds like leg ulcers, pressure sores and other chronic (long-term) wounds.



The coloured scanning electron micrograph (SEM) of fibres from an Aquacel-Ag wound dressing showing the **nanosize** particles of **silver**.



**FIGURE 25** Researchers are exploring the use of a **nanocomposite** material consisting of **epoxy resin** and **carbon nanotubes**, previously used in sports equipment, to manufacture wind turbine blades. Blades made this way are approximately 50 percent lighter than comparable glass fibre blades and much stronger. This allows for longer blades resulting in significantly increased power output and the ability of the wind turbines to operate in lighter wind speed.



**FIGURE 26** The Lockheed Martin F-35 is said to be the first mass produced aircraft to include structural nanocomposites, namely carbon nanotube reinforced epoxy.



Image courtesy of Lockheed Martin.

The long known **antibacterial** and **antifungal** effects of **silver** is due to the release of silver ions from the silver surface. However, when used in **nanoparticle** form the vastly increased **surface area** greatly enhances this antibacterial effectiveness. For this reason nanosilver has found wide application in medical products such as surgical bandages (Fig 24), instruments and masks and now in many other consumer items such as socks, children's toys, eating utensils and refrigerators, as well as cosmetics and personal care products. There is however, a growing concern that such widespread and unregulated use of nanoparticles could present unknown environmental or health risks. The extent to which these silver nanoparticles can over time be released into the aquatic environment, for example, by washing clothing impregnated with nanoparticles, is unknown, as is their possible effects. For this reason some groups such as the 'Friends of the Earth' have called for a moratorium on the use of silver nanoparticles in commercial products.

A new and very exciting area of **nanodevice** research is occurring in the medical field of detection, diagnosis and treatment of disease, especially cancer. These technologies are in various stages of discovery and development. Nanoparticle structures called **dendrimers** for example, are being designed as molecular carriers. Each dendrimer is capable of carrying several molecules, one that recognizes cancer cells, another that is a therapeutic agent able to kill cancer cells, a third molecule on the dendrimer recognizes when the cancer cell dies and yet another is able to signal the cancer cell's death. The aim is to use the nanosize dendrimer as a carrier that can deliver its therapeutic package specifically to individual cancer cells, kill the cell and then report back to a detector on its effectiveness. These devices would greatly reduce any side effects of the therapeutic drugs on otherwise healthy tissue while seeking out cancer tissue at a cellular level.

It is anticipated **therapeutic nanodevices** like the dendrimers described above and other diagnostic, detection and therapeutic devices like **quantum dots**, **nanoshells** and **nanopores** may be available for clinical use within the next 5 to 15 years.

## 8.11 Nanocomposites

Although the science of nanotechnology is new, nanoparticles and their use is not. **Carbon black** for example (essentially **soot**) is an **amorphous** form of carbon consisting of particles from a few nanometres in size to several hundred nanometres in size. Hence much of this form of carbon is in the nanoparticle range. Carbon black has long been used as an **additive** in **rubber** tyre manufacture. The rubber of most automotive tyres contains around 25% carbon black and its presence in tyre rubber greatly improves resistance to wear and abrasion. Adding higher percentages of carbon black will increase the electrical conductivity of the tyre rubber and help prevent the build-up of static electricity on the tyre surface. This is particularly important for fuel truck tyres where sparks due to static discharge could be catastrophic.

Materials like tyre rubber are known as **nanocomposites** and are made by adding nanosized particles of one material to a matrix of a bulk material such as a metal, polymer or ceramic (eg concrete). The resulting nanocomposite can have enhanced or modified properties such as improved mechanical strength, electrical and thermal conductivity, catalytic and optical properties. Modern nanocomposite applications involve the addition of manufactured **nanotubes** or **graphene** to **plastics** like polypropylene, polystyrene, polycarbonate and epoxy resins. (See Fig 25 and 26.) The nanotubes may make up as little as 1-5% by volume of the nanocomposite but their presence may increase stiffness by 50% and mechanical strength by 20%. The nanoparticles work by literally slowing down or preventing crack formation through the polymer due to their own high tensile strength.

The potential for nanocomposites is far greater than simply improving mechanical strength or wear characteristics. Researchers are looking at a great variety of ways to use the unique properties of nanoparticles to produce novel nanocomposite materials. The improvement of **lithium ion batteries**, used in portable electronics and electric cars, for example is limited by the nature of the graphite present in both the anode and cathode. Graphite electrodes are brittle and have limited electrical conductivity. An important limitation is the rate of diffusion of lithium ions through the porous graphite matrix of the **electrodes**. A variety of nanocomposites are being researched as replacements for the graphite based electrodes used in lithium ion batteries. Some options include carbon nanotubes, graphene sheets and nanocomposites such as two dimensional nanosheets of molybdenum sulfide coated with one dimensional multiwall carbon nanotubes.



Recently a **carbon-silicon nanocomposite** material has been shown to be an effective replacement for these graphite electrodes. A silicon based anode like this has the advantage of having a much greater energy storage capacity,  $\approx 10$  times that of carbon. However, silicon is problematic as it undergoes significant expansion and contraction during the charge discharge cycle. This can lead to the electrode crumbling and failing to operate. Using the carbon-silicon nanocomposite material seems to avoid this problem while maintaining the higher energy storage capacity of silicon and good conductivity of lithium ions through the structure.

## 8.12 Imaging and manipulating nanoparticles

**Optical microscopes** rely on magnifying an image produced by **visible light** that is transmitted through or reflected from an object. However, because of diffraction effects this only works if the object being viewed is larger than the wavelength of light being used to view it. As the wavelength of visible light ranges from 400 nm for red light to 750 nm for violet light it is not possible to directly observe atoms (size  $< 0.5$  nm) or nanoparticles (size 1–100 nm) with optical microscopes. Other non-optical methods must be used to view such small objects.

The first of these to be devised was the **transmission electron microscope (TEM)** which appeared in the middle of last century. It relies on the wave properties of an electron beam to generate an image of a sample. The much smaller electron wavelengths, typically 100,000 times smaller than visible light photons, means it is possible to resolve much smaller objects with an electron beam than with a light beam. TEMs generate an image by passing the electron beam through a specially prepared, extremely thin sample. The transmitted beam is magnified and viewed on a fluorescent screen or digitally converted to an optical image. A newer type of TEM is the **high resolution transmission electron microscope (HRTEM)**, using this it is possible to achieve image resolution of around 0.2 nm.

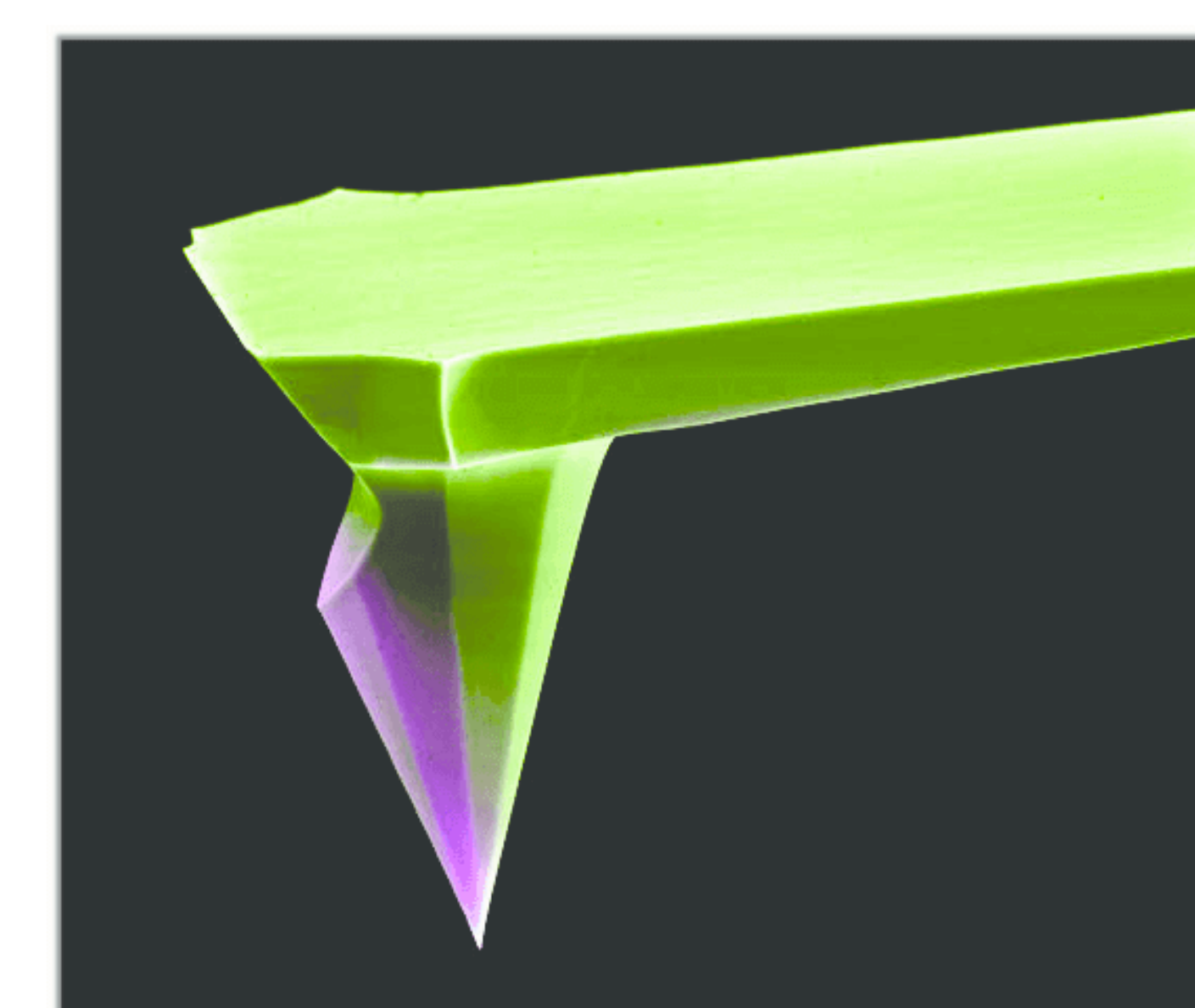
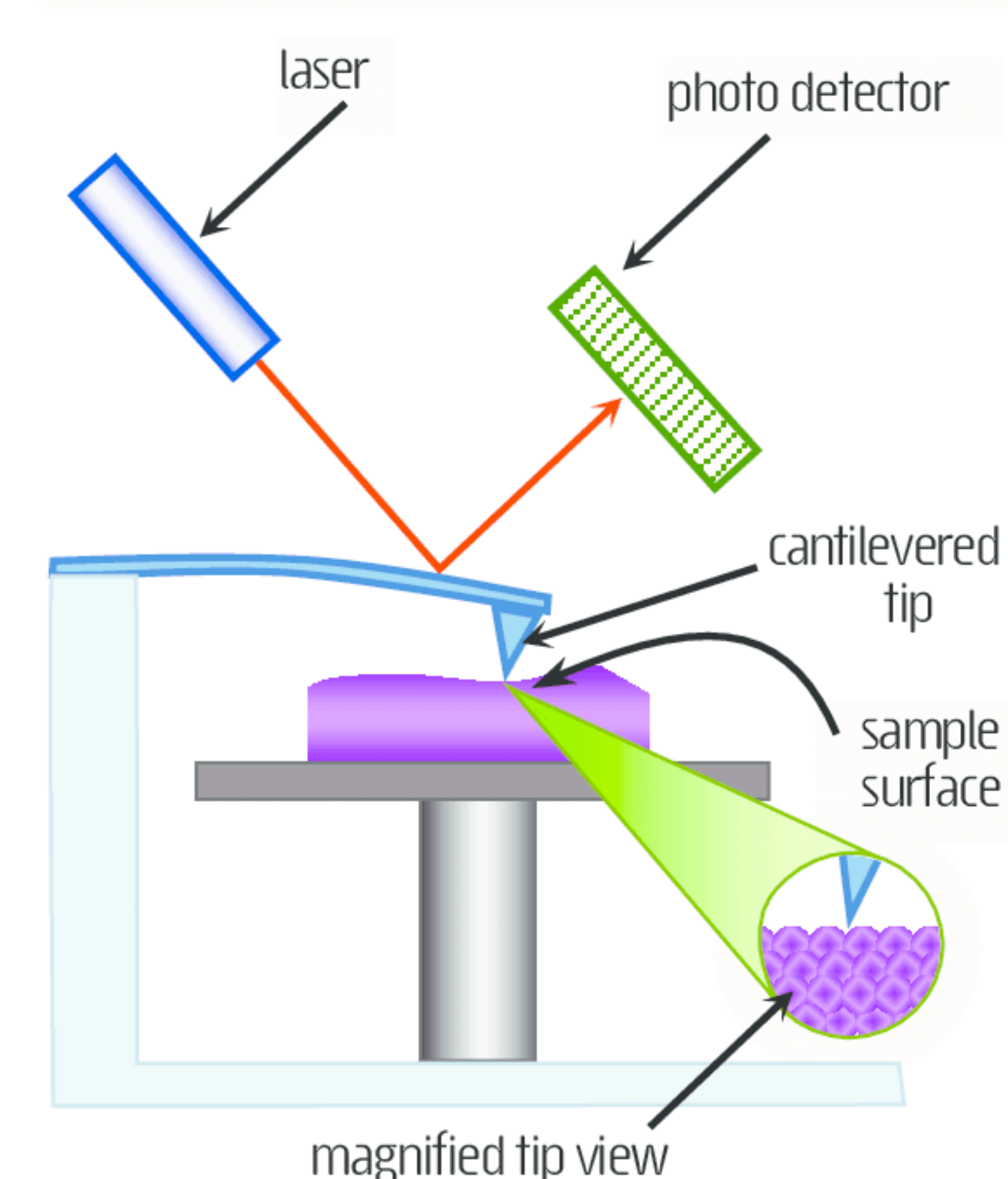
A variation of the TEM is the **scanning electron microscope (SEM)**. This uses a narrow beam of electrons to scan across the surface of a specimen. The resulting signals reveal information about the sample surface including texture, chemical composition and structure. Data obtained this way is used to create a computer generated image of the surface.

A newer approach to ‘viewing’ surface structures at the nanolevel involves the **scanning tunnelling electron microscope (STEM or STM, Fig 27.)** It is said that the development of the STM in 1981, with its ability to ‘see’ individual atoms, was a crucial turning point in the development of modern nanotechnology. The STM uses a completely different approach to produce an image by literally ‘feeling’ the surface features of a sample. To do this it uses an **ultra fine needle** (Fig 28), only two or three atoms across at its tip, that is moved back and forth across a surface at a distance of around 1 nm. A tiny voltage applied between the needle tip and the scanning surface produces a current by a process known as **tunnelling**. This tunnelling current is very sensitive to the gap distance so a feedback process is used to adjust the tip height (gap) to maintain a constant current. The resulting vertical motion of the tip gives a contour map of the surface. By scanning back and forth a 3D image of the surface structure at the atomic level can be produced. (See Fig 16 p18 and Fig 29 p68.) STM resolution is better than 0.1 nm horizontally and 0.01 nm vertically.

The foremost device currently used to study and manipulate materials at the nanoscale is the **atomic force microscope (AFM)**. (See Fig 27.) This also uses a scanning needle tip to investigate a surface. Instead of detecting a current it operates by measuring the force between the cantilevered tip and the surface being scanned. The size of the force is strongly dependent on the gap distance between the tip and the surface.

The AFM has the advantage of actually being **able to pick up individual atoms** or nanoparticles on a surface and deposit them in a desired location. This gives the possibility of engineering complex nanostructures atom by atom or the ability to arrange previously constructed nanoparticles. The tip of the AFM is made of a very hard material like silicon or silicon nitride. The AFM also has the advantage of being able to be used on a greater range of surfaces.

**FIGURE 27** The **scanning tunnelling electron microscope (STM)** was the precursor for the **atomic force microscope (AFM)**. The AFM develops a 3D image of a surface by measuring the force between a cantilevered tip and the surface. The size of this force varies with the gap width between the tip and the surface. A laser and a photodiode detector array measure the movement of the tip as the force between the tip and surface change. The vertical tip motion is translated into a contour line of the surface features. By scanning back and forth a 3D contour map of the whole surface can be produced. This essentially maps the electron cloud density at the surface and reveals the position of atoms on the surface.



**FIGURE 28** A coloured scanning electron micrograph, **SEM** image of a cantilever and tip (magnified by 1000 times), as used in the atomic force microscope, AFM.

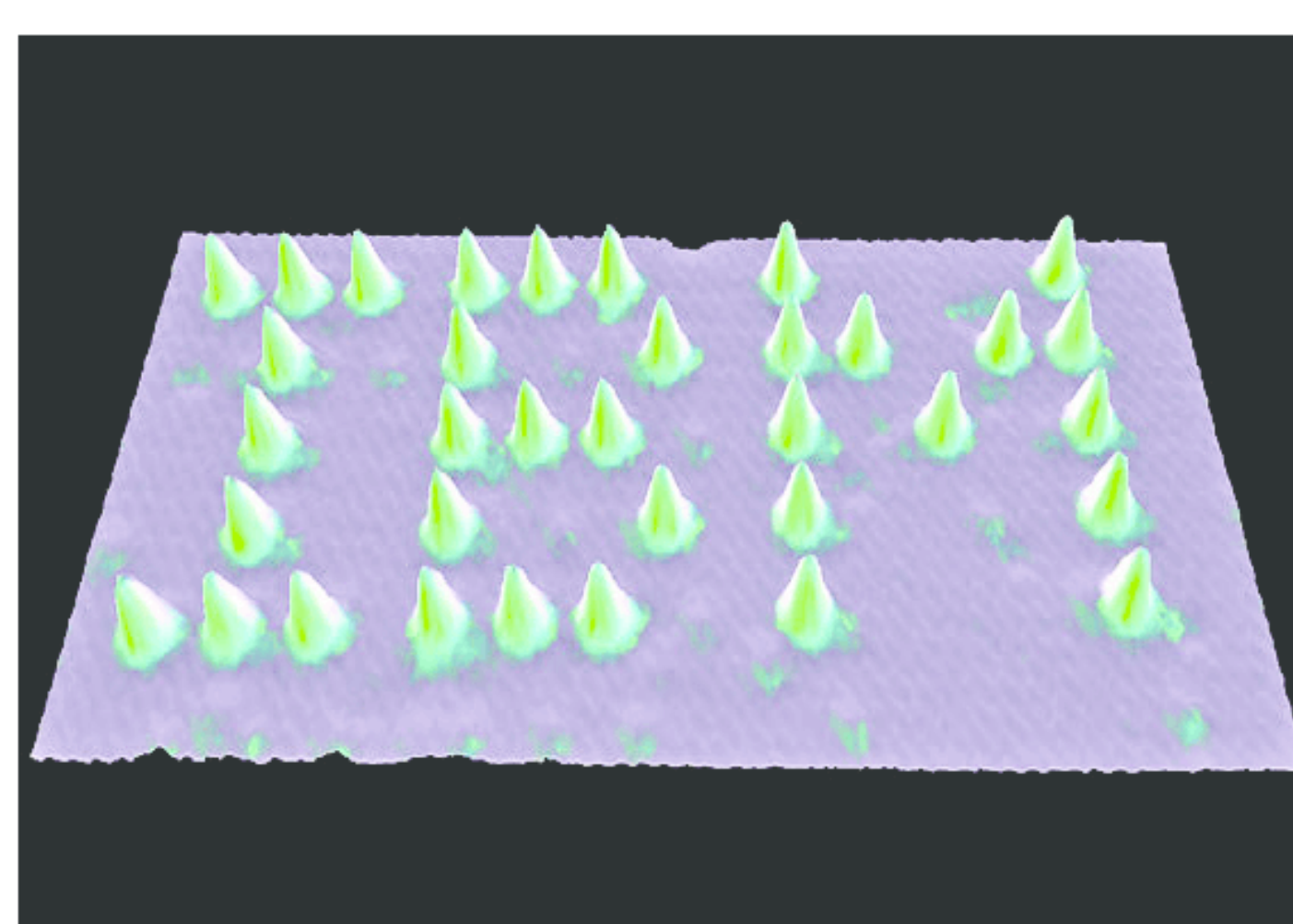
The AFM tip has the advantage of being able to pick up individual atoms or nanoparticles on a surface and deposit them in a desired location. This gives the ability to engineer complex nanostructures atom by atom or the ability to arrange previously constructed nanoparticles.



## 8.13 Manufacturing nanoparticles

A variety of **chemical** and **physical** means can be used to create nanoparticles. Nanosized particles of metal oxides like  $\text{TiO}_2$  and  $\text{ZnO}$ , as used in sunscreens, are produced by a physical technique involving **grinding** of the bulk material in a ball mill until particles of the desired size are achieved. **Electric arc discharge** is a common technique used to produce carbon nanotubes (CNTs). This involves passing a large DC electric current between two graphite electrodes, an anode and a cathode, in an inert atmosphere. This method is similar to the method used by Iijima Sumio in 1991 when he discovered the presence of needle like structures (CNTs) in the soot that formed at the graphite cathode.

**Laser ablation** is another important method for producing high quality CNTs. This process is similar to the method Smalley, Curl and Kroto used in their original discovery of  $\text{C}_{60}$ . In this technique, high powered laser pulses are used to vaporise a graphite target in an inert atmosphere. The vaporised carbon atoms reassemble in the form of CNTs on a water cooled collector surface. A small amount ( $\approx 1\%$ ) of a metal catalyst such as Ni/Co may be incorporated in the graphite target to enhance the process. The laser ablation method has also been used to create single walled CNTs covered with quantum dot lead sulphide particles. These have application as photoconductive devices (devices whose electrical conductivity increases with exposure to light) in electronic systems.



**FIGURE 29** IBM Fellow Don Eigler became the first person in history to move and control an individual atom. On November 11 1989, Eigler and his team used a custom-built **scanning tunnelling microscope** (STM) to spell out the letters IBM with 35 xenon atoms. This unprecedented ability to manipulate individual atoms is said to have signalled a quantum leap forward in nanoscience experimentation and heralded in the age of nanotechnology. Image courtesy of IBM.

Many other techniques exist for producing nanoparticles including **solution evaporation**, **chemical vapour deposition**, **microbial synthesis** and **chemical precipitation** from solution. Perhaps the ultimate goal of manufacture is to construct nanoparticles one atom at a time by shifting them into position using something like an atomic force microscope. This technique for constructing nanostructures was first demonstrated on November 11 1989 by Don Eigler and colleagues at IBM. (See Fig 29.) The researchers positioned 35 xenon atoms on a copper surface to spell out the company logo IBM. Although this technique is well understood, at present there is no example of using it for commercial production of nanostructures.

## 8.14 Safety of nanomaterials

While a great deal is known about the environmental, health and safety issues of the bulk materials used in nanotechnology, eg C, Ag, Au,  $\text{ZnO}$ , CdSe and so on, very little is known about the risks associated with their use in nanoparticle form. As discussed earlier, the properties of nanoparticles often differ markedly from those of the parent material due to quantum effects arising from their small particle size. For example, it can't be assumed that carbon nanotubes are safe simply because the bulk material carbon is safe.

Although at present there are no proven health or environmental risks associated with the use of nanoparticles it should not be assumed they pose no risk. There are examples of other materials that are now known to be extremely hazardous when inhaled in their particulate or micro fibrous form that are quite harmless as bulk materials. For example it is now generally accepted that workers exposed to brick dust or glass fibre particles should take precautions by wearing breathing masks even though the bulk materials are quite inert and harmless. It might be assumed the same risks could apply to workers exposed to airborne nanoparticles.

At present it is difficult to make an informed risk assessment on the public and environmental exposure to various nanomaterials. These materials and their applications are appearing quickly making it difficult for researchers, safety regulators or government legislators to keep up. Recently the Australian Government completed a four year study (NETS) which was intended to provide guidelines for the development of the nanotechnology industry in Australia. This is a worldwide issue and many other jurisdictions are considering legislation and industry regulation in this area.



# Set 14 Review: Bonding, structure and nanotechnology

- Classify the listed substances as **metallic**, **ionic**, **covalent molecular** or **covalent network**.
 

a. NaI

d. Al<sub>2</sub>O<sub>3</sub>

g. C

j. CaC<sub>2</sub>

m. Sc

p. CS<sub>2</sub>

b. Mg

e. SiO<sub>2</sub>

h. CH<sub>4</sub>

k. CH<sub>3</sub>OH

n. Si

q. HCl

c. SO<sub>2</sub>

f. CO<sub>2</sub>

i. H<sub>2</sub>SO<sub>4</sub>

l. TiO<sub>2</sub>

o. SiC

r. Sr
- Distinguish between the terms '**covalent bond**' and '**covalent molecular**'.
- The following list includes both molecular and ionic substances. Determine the type of bonding present and draw a **Lewis structure** for each substance.
 

a. calcium chloride (CaCl<sub>2</sub>)

e. phosphorous trifluoride (PF<sub>3</sub>)

b. chlorine gas (Cl<sub>2</sub>)

f. magnesium nitride Mg<sub>3</sub>N<sub>2</sub>

c. hydrogen cyanide (HCN)

g. formaldehyde (H<sub>2</sub>CO)

d. lithium oxide (Li<sub>2</sub>O)

h. hydrogen phosphate (H<sub>3</sub>PO<sub>4</sub>)
- Complete** the following table. Remember substances may exhibit more than one type of bonding. Use the most appropriate terms to describe the bonding, structure, phase and physical properties of the listed substances.

Substance	Bonding	Structure	Phase	Physical properties		
	covalent, ionic, metallic	covalent molecular, metallic, covalent network or ionic lattice	solution, solid, liquid or gas	Electrical conductivity yes/no/semi	Hard and brittle yes/no	Malleable and ductile yes/no
Zn(s)						
Zn(NO <sub>3</sub> ) <sub>2</sub> (s)						
Zn(NO <sub>3</sub> ) <sub>2</sub> (l)						
Zn(NO <sub>3</sub> ) <sub>2</sub> (aq)						
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)						
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (l)						
SiO <sub>2</sub> (s)						
C(graphite)(s)						
C(diamond)(s)						
C <sub>60</sub> (s)						

- Many ionic substances contain polyatomic ions. Such ions may contain **single**, **double** or **triple** covalent bonds. Draw Lewis structures for the following polyatomic ions. (See border note, you may need to refer to Fig 12 and Example 2 p60.) **(E)**

a. hydroxide OH<sup>-</sup>

c. cyanide CN<sup>-</sup>

e. nitrite NO<sub>2</sub><sup>-</sup>

b. carbonate CO<sub>3</sub><sup>2-</sup>

d. nitrate NO<sub>3</sub><sup>-</sup>

f. chlorate ClO<sub>3</sub><sup>-</sup>
- Remember!** When drawing the Lewis structure for a polyatomic ion like NH<sub>4</sub><sup>+</sup> or SO<sub>4</sub><sup>2-</sup>, **add** or **subtract** enough valence electrons to satisfy its charge. A negative ion will have extra valence electrons equal to its charge. A positive ion will have fewer valence electrons equal to its charge. (See 8.7 p60.)



6. **Choose** a material with physical properties suited to the following uses. Select from the listed substances. **Justify** your choice.
- aluminium oxide** ( $\text{Al}_2\text{O}_3$ )  
**graphite** (C)  
**candle wax**  
(assume to be  $\text{C}_{25}\text{H}_{52}$ )

**diamond** (C)  
**tungsten** (W)  
**woods metal**  
(a low MP alloy)

**copper** (Cu)  
**marble** (essentially  $\text{CaCO}_3$ )  
**carbon nanotubes (CNTs)**
- a. A material to be used on the surface of an electronic circuit board. It must be able to flex if the board bends and needs to conduct an electric current.
- b. A material to be used as a sliding electrical contact. It is preferred the material itself wears out rather than the contact over which it slides. Materials like this are used to make electric motor and generator brushes.
- c. A material to be used as the active ingredient in a relatively inexpensive cutting compound like that used in certain types of metal polish. The material needs to be in powder form and have good abrasive powers.
- d. An automatic fire sprinkler is activated by temperatures of around  $74\text{ }^\circ\text{C}$ . The heat causes a small plug of material to melt thus allowing water to flow to the sprinkler. The material must be strong enough to withstand normal water pressure.
- e. A reinforcing material that can be used with epoxy resins or other plastics to produce strong and lightweight composite materials.
7. **Predict** the **formula** and **bonding** for the compounds that form when the elements **A** and **B** chemically combine. All of these elements are from the **second** or **third period** of the periodic table only. The number of valence electrons for the elements is shown in column 1 and 2.

Number of valence electrons		Formula	Bonding covalent, ionic or metallic
Element A	Element B		
1	7		
1	5		
2	1		
3	6		
4	6		
6	7		
7	7		

8. **Carbon nanotubes** (CNTs) are a recently discovered (1991) allotrope of carbon. They can be represented by the formula  $\text{C}_x$ . This is unlike a molecule of buckminsterfullerene which has a defined formula,  $\text{C}_{60}$ . Also while CNTs may be only a few nanometres in diameter their length is of the order of micrometres and potentially much greater. Describe the **bonding** and **structure** of a CNT and account for the features described.
9. Common **window glass** and glass used to make optic fibres are essentially mixtures of the same materials. Common window glass or soda-lime glass is a mixture of  $\text{Na}_2\text{O}$  ( $\approx 13\%$ ),  $\text{CaO}$  ( $\approx 11\%$ ),  $\text{K}_2\text{O}$  ( $\approx 4\%$ ) and  $\text{SiO}_2$  ( $\approx 72\%$ ). The mixture is heated to form a solution which when cooled becomes a clear amorphous substance known as glass.
- a. The passage referred to glass as an **amorphous** substance. What does this say about the structure of glass? (Use a text book or internet search.)
- b. Why is glass referred to as a **mixture** and not a **compound**?
- c. What types of bonding are present within glass? **Justify** your answer.
- d. It is well known that glass is a strong but brittle substance. Can its properties be justified with reference to its chemical composition? **Explain**.



10. The **chiton** is a marine animal with a flat oval shape and eight segments to its body. (See Fig 30.) It attaches itself to rocks at the tidal zone. Along its central underside are two parallel rows of teeth (radula) which it uses to feed by scraping algae from rock surfaces over which it slowly moves. Research has shown that its teeth are capped with a layer of insoluble crystalline  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ .
- The passage referred to a **crystalline**  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  layer. What does the term crystalline tell us about the structure of the  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  layer?
  - The major component of the rocks onto which chitons attach themselves is silica ( $\text{SiO}_2$ ). How does the presence of  $\text{SiO}_2$  affect rock hardness? **Explain**.
  - Explain** why the presence of a crystalline  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  layer on chiton teeth can be an advantage to the chiton?
11. **Nanotechnology** involves the study of nanoparticles including their structure, properties, manufacture and potential use.
- Define** a nanoparticle and give two examples that do not involve carbon.
  - Nanoparticles often exhibit **quantum effects**. Describe what is meant by a quantum effect as applied to nanoparticles and give an example to support your answer.
12. Materials like fibreglass and carbon fibre reinforced plastics are common examples of **composite materials**. These have been used for many decades to produce strong, flexible and relatively lightweight structures as diverse as golf club shafts, aerospace components, buildings and automotive parts. A relatively new type of composite are **nanocomposites**.
- What** is a nanocomposite? Use an example to illustrate your answer.
  - Why** are nanocomposites potentially superior to fibreglass and carbon fibre plastics?
13. Nanotechnology researchers are developing a new range of products called **nanodevices**. A potential application in the field of medical diagnoses and treatment, involves the use of nanostructures called **dendrimers**. (See p66.) It is hoped these will provide a better way of administering cancer drugs to treat cancer patients. Briefly describe the structure of this nanodevice (see p66) and explain why it is called a nanodevice rather than a nanoparticle.
14. **Laser ablation** is one of the many techniques used to produce nanoparticles. Briefly **describe** how this process works. Name some of the other techniques used to produce nanoparticles.

**FIGURE 30** This top view of a chiton shows eight overlapping shell sections held in place with a girdle of softer tissue. Its **radula** are found in two parallel rows on its underside. Below is an image of a chiton commonly found in the waters around New Zealand.





# CHAPTER 9 | PERIODIC TRENDS

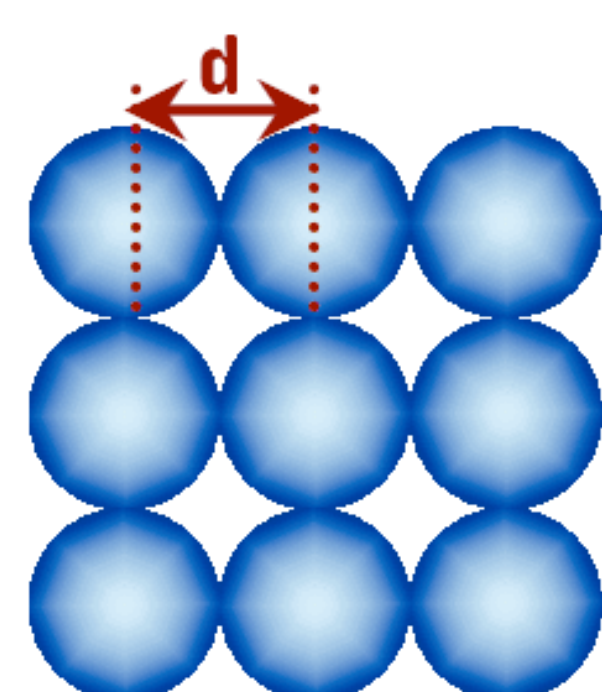
## 9.1 Chemical periodicity

As outlined in Chapter 7 the **physical** and **chemical properties** of the elements show gradual changes with atomic number. It is also evident that these changes in properties are **periodic**. This means that at certain intervals of atomic number (2, 8, 8, 18, 18 and so on) there occur elements of very similar chemical and physical properties. The electron configuration of the elements show a similar repeating pattern in their **valence shell electron structure**. In this chapter we explore in detail some of these properties and see how they are related to an element's position in the periodic table.

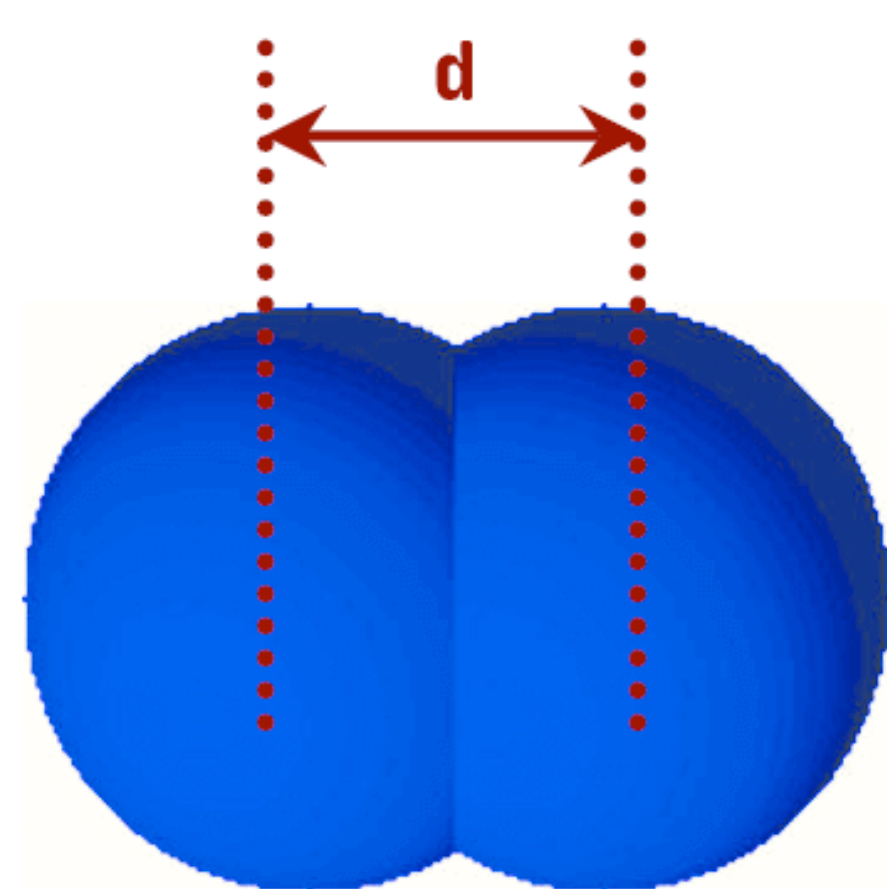
## 9.2 Periodic trends: Atomic radius

This graph of **atomic radius** against **atomic number** (Fig 2) shows there is a clear relationship between an atom's radius (Fig 1) and its position in the periodic table.

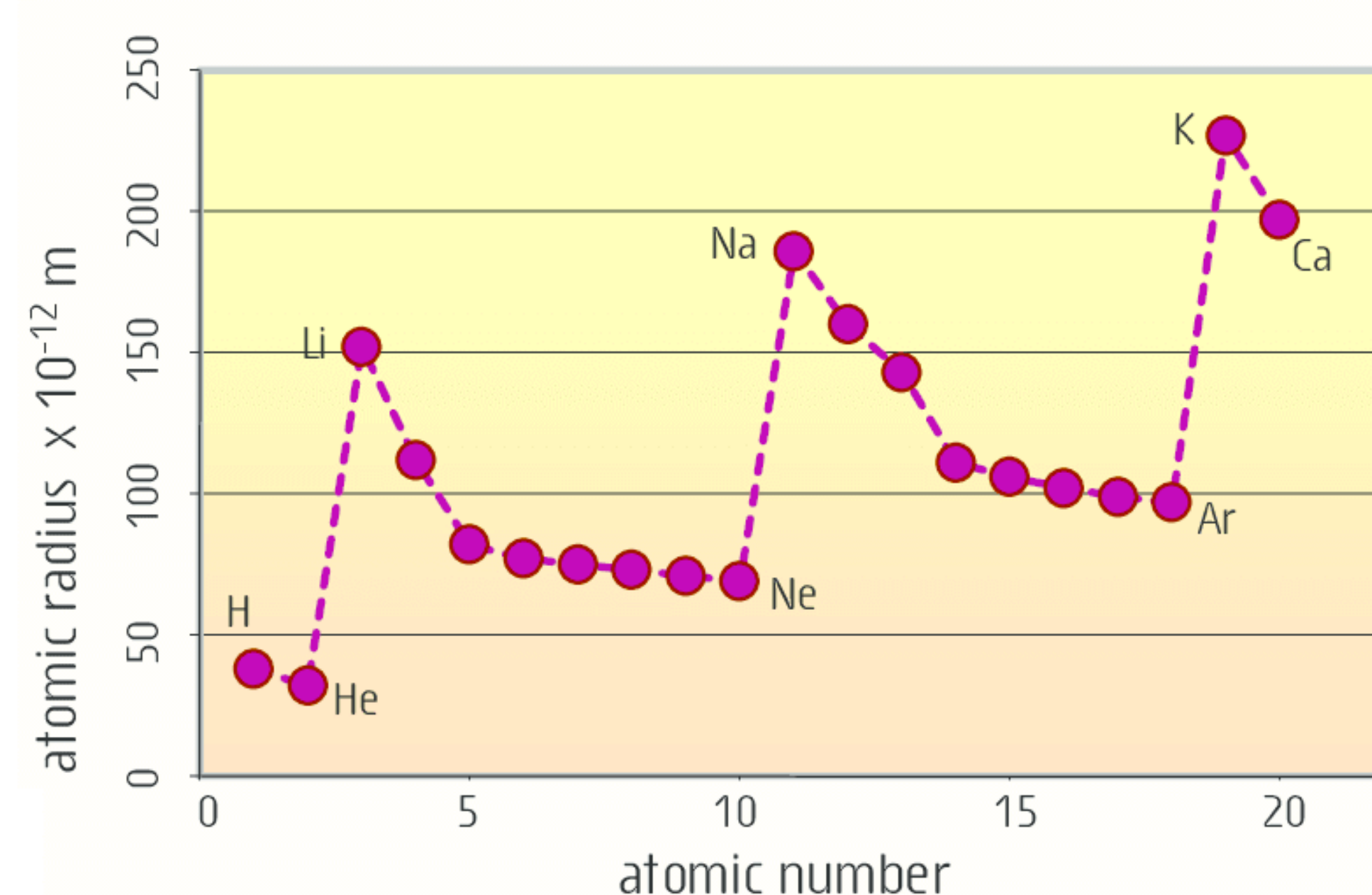
**FIGURE 1** The **atomic radius** of a **metal** atom is defined as being half the distance between the centres of two adjacent atoms in the metallic lattice, ie  $\frac{1}{2}d$ .



For **non-metal** atoms that form diatomic molecules (eg  $F_2$ ,  $H_2$ ) atomic radius is half the distance between the centres of two bonded atoms, ie  $\frac{1}{2}d$ .



Attempt Set 15 # 1 and 2.



**FIGURE 2** Graphing the **atomic radius** of the elements against their **atomic number** reveals two clear trends.

- Atomic radius of the elements increases down any group of the periodic table. As seen here with **Li**, **Na** and **K** and also **He**, **Ne** and **Ar**.
- The atomic radius of the elements decreases left to right across any period of the periodic table, eg **Li to Ne** and also **Na to Ar**.

The decrease in atomic radius that occurs for elements further to the right in any period (eg Li to He) might be unexpected but is primarily due to the atom's increasing **nuclear charge**. A higher nuclear charge (positive) increases the attraction of electrons (negative) bringing them, on average, closer to the nucleus thus resulting in a decrease in atomic radius. So despite the increasing number of protons, neutrons and electrons, atoms further to the right in a period show a decrease in size as measured by their atomic radius.

The trend of increasing atomic radius down any group of the periodic table (eg Li, Na, K) is due to the higher **shell number** of the outer electrons for elements lower in a group. This occurs as at the start of each new period electrons commence filling the next highest numbered shell. These higher numbered shells are on average further from the nucleus and so atoms further down a group will have a larger radius despite their larger nuclear charge.

## 9.3 Periodic trends: First ionisation energy

An element's **ionisation energy** is a measure of how strongly it holds onto its electrons. Importantly ionisation energy greatly affects an element's tendency to form positive or negative ions. This in turn has implications for the type of bonding the element will undergo with itself and with other elements. (See 9.6 and 9.7.)

Specifically the **first ionisation energy** ( $E_1$ ) of an element measures the minimum amount of energy needed to remove the single most loosely bound electron from an atom in the neutral gaseous state.



The graph in Figure 7 shows there is a periodic relationship between an element's first ionisation energy and its atomic number or position in the periodic table.







TABLE 1 Bonding capacity of the main group elements.

Main Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Usual ionic bonding charge	1+	2+	3+	4+ or 4-	3-	2-	1-	nil
Covalent bonding capacity	nil	nil	nil	4 bonds	3 bonds	2 bonds	1 bond	nil

When non-metal elements share electrons with other non-metal elements (called covalent bonding) they do so until they achieve an **octet** in their valence shell. For this reason a strong relationship exists between an element's **covalent bonding capacity** (the number of covalent bonds it forms) and its group number. This can be seen in the hydrides of the elements C (group 14), N(group 15), O (group 16) and F (group 17). (See Fig 5.)



FIGURE 5 The **covalent bonding capacity** for the elements from groups 14 to 17 are represented here by the elements **C**, **N**, **O** and **F**. As can be seen these elements have a covalent bonding capacity of 4, 3, 2, and 1 covalent bonds respectively. It must be noted this represents their usual number of covalent bonds. Elements can use their **lone pairs** to form extra covalent bonds. Also elements like oxygen may form fewer covalent bonds than expected by using **donor** bonds. These are bonds where an element accepts two electrons in a single bond without using any of its valence electrons.

Attempt Set 15 # 6.

**Metal** elements like Na, Ca, Cu, Fe, Al, Ni and so on show a number of common **physical properties**. All metals are:

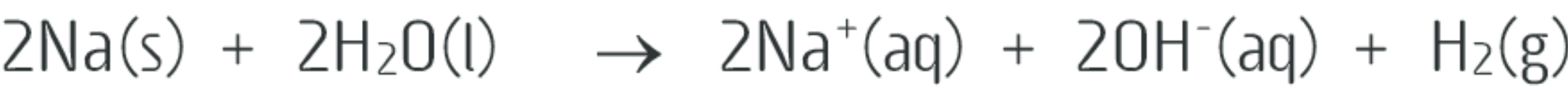
- good conductors of electricity
- good conductors of heat
- malleable and ductile
- shiny (when scratched)
- solids at room temperature (excepting mercury which is a liquid).

**Oxygen** reacts with most metal elements to produce a metal oxide containing the **O<sup>2-</sup>** ion. With the alkali metals the reactions are more complex. While **Li** does produce an oxide, Li<sub>2</sub>O, the other alkali metals; Na, K, Rb, Cs and Fr, produce either a peroxide (containing the peroxide ion, **O<sub>2</sub><sup>2-</sup>**, eg Na<sub>2</sub>O<sub>2</sub>) or a superoxide (containing the superoxide ion **O<sub>2</sub><sup>-</sup>** eg KO<sub>2</sub>). Sodium can also form an oxide, ie Na<sub>2</sub>O if the oxygen supply is limited.

## 9.6 Understanding metallic properties (E)

Metallic properties are typical for elements with **low ionisation energy**. A low ionisation energy is essential if atoms are to form the positive ions required for the metallic structure (see 8.2 p54-5) that gives metals their unique physical properties. (See border note.) Consequently metallic elements are only found on the **left side of the periodic table** where ionisation energies are low. This relationship is also seen in the groups of the periodic table where from top to bottom down any group, as the atom's ionisation energies decrease, so the element's metallic properties increase. This is especially evident in groups 14, 15 and 16 where elements range from non-metallic at the top of each group (C, N and O) to metallic at the bottom of each group (Pb, Bi and Po).

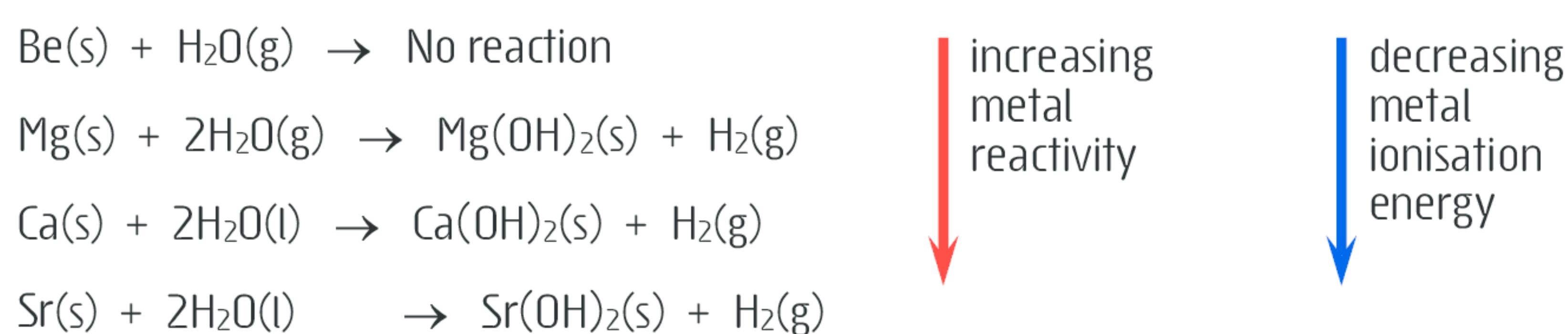
Metallic elements are typically **good reducing agents**, ie they tend to lose electrons and become oxidised, when reacting with substances like acids, oxygen and water. This property is also associated with their low ionisation energy. Remember, a low first ionisation energy means an atom's outer electron is easily lost. Group 1 elements for example have particularly low ionisation energies (Fig 3) and their reactions with acids, water, oxygen (see border note) and chlorine are all vigorous. The reactions shown here are representative of all the metallic elements from group 1 (Li, Na, K, Rb, Cs and Fr).



In each of these reactions the **group 1** metals form **ionic compounds** by losing their single valence electron to form a **1+ ion**.

While **group 2** metals show similar reactions they tend to be **less vigorous** than those of group 1. This can be attributed to their slightly higher ionisation energies. The impact of ionisation energy is also seen within group 2. As ionisation energy decreases down the group (Fig 3 p73) there is a corresponding increase in reactivity. For example, beryllium at the top of the group (highest ionisation energy) isn't oxidised by water, the next element magnesium is slowly oxidised by steam [H<sub>2</sub>O(g)] the remaining metals calcium, strontium and barium (lowest ionisation energies) are all readily oxidised by cold water [H<sub>2</sub>O(l)].





In each of these reactions the **group 2** metals form **ionic compounds** by losing their two valence electrons to form **2+ ions**.

Attempt Set 15 # 7.

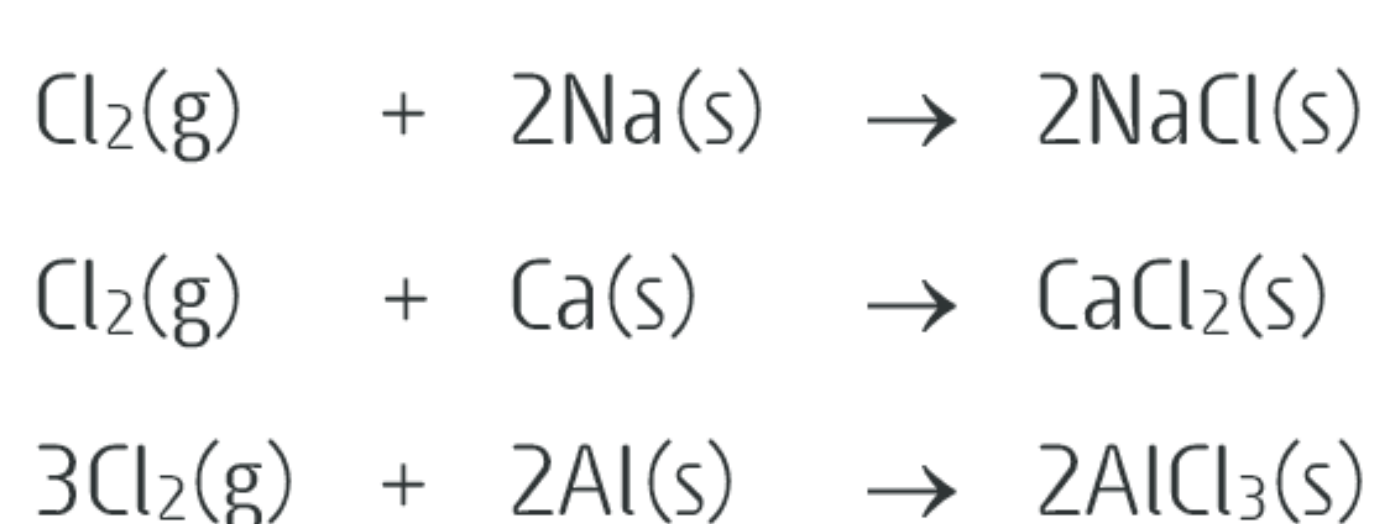
## 9.7 Understanding non-metal properties (E)

Left to right across each period of the periodic table the elements show **increasing ionisation energy**. As a result elements further to the right in a period become progressively less able to form positive ions and hence less able to form metallic structures. At some point in each period the tendency for elements to form metallic structures with the associated positive ions and sea of electrons (Fig 4 p54), is overcome by a tendency for elements to **share electrons** with one another by forming **covalent bonds**.

The group 14 elements of highest ionisation energy; **carbon (a non-metal)**, **silicon** (a metalloid) and **germanium** (a metalloid); achieve an octet in their valence shell by forming covalent bonds. Each atom shares all four of its valence electrons with neighbouring atoms to form four covalent bonds. As a result, they form **covalent network** structures with physical properties of high hardness and brittleness, high melting and boiling points and semi conducting or non electrical conductivity. (See 8.8 p62.)

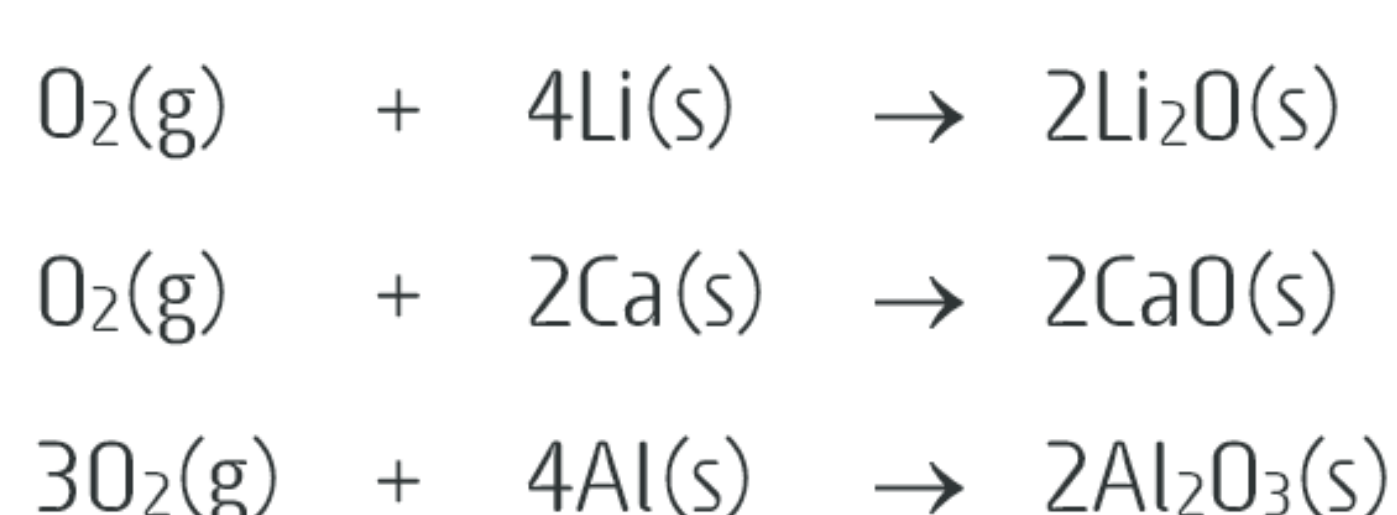
Elements in the upper right of the periodic table are characterised by having the **highest ionisation energies**, **highest electronegativity** and **most valence electrons**. Many of these non-metals need only a few covalent bonds to achieve a full valence shell. Group 17 elements for example all have seven valence electrons and thus form **diatomic molecules** with a single covalent bond (eg  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ ). The group 18 non-metal elements (the noble gases He, Ne, Ar, Kr, Xe) already have eight valence electrons and so do not normally bond to other atoms. These elements exist as monatomic gases. The molecular non-metal elements from group 15, 16 and 17 exist as gases or low melting point solids or liquids at room temperature, ie  $\text{N}_2\text{(g)}$ ,  $\text{P}_4\text{(s)}$ ,  $\text{O}_2\text{(g)}$ ,  $\text{S}_8\text{(s)}$ ,  $\text{Se}_8\text{(s)}$ ,  $\text{F}_2\text{(g)}$ ,  $\text{Cl}_2\text{(g)}$ ,  $\text{Br}_2\text{(l)}$  and  $\text{I}_2\text{(s)}$ . (See Fig 6.)

The **high ionisation energy** and **high electronegativity** of non-metal elements means in chemical reactions with metals they tend to be **reduced** (gain electrons). In doing so the non-metal atoms form negative ions with an octet in their valence level. (See ionic bonding 8.3 p56-7.) Group 17 elements for example have particularly high ionisation energies and electronegativities and their reactions with metals are typically rapid and release a lot of energy. The reactions shown here for chlorine are representative of the group 17 elements  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$ .



In each of these reactions, Cl atoms gain one electron forming a **1-** ion with eight electrons in their valence shell. While this is typical of other group 17 elements the **reactivity decreases** down the group (ie  $\text{F}_2$  is most reactive while  $\text{I}_2$  and  $\text{At}_2$  are the least reactive). This pattern is in line with the decreasing electronegativity (tendency to gain electrons) going down the group.

Group 16 elements like oxygen and sulfur have similar though less vigorous reactions with metals where they form **2-** ions with eight electrons in their valence shell.

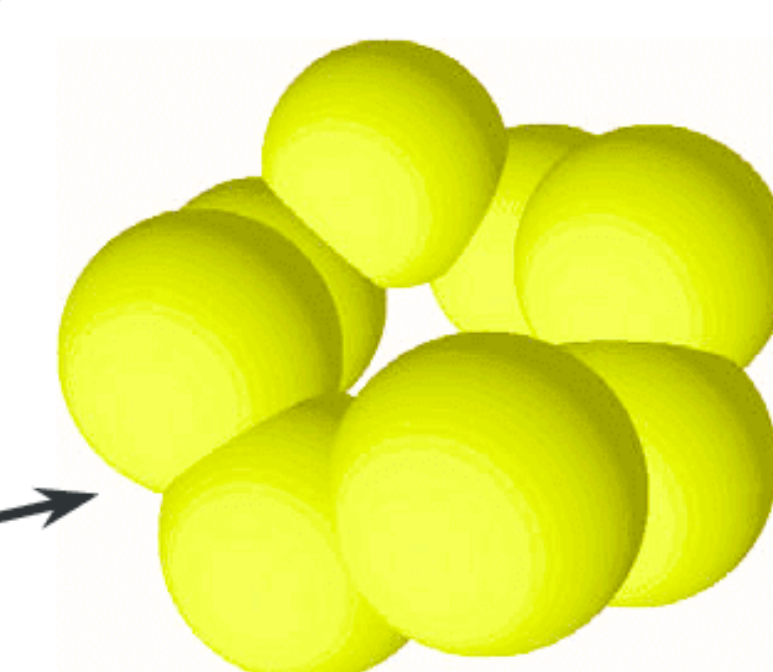


**Non-metal** elements are characterised by poor electrical and heat conductivity. Most are gases at room temperature while those that are solids are brittle.

**FIGURE 6** It must be noted that some of the non-metal elements exist in a variety of allotropic forms with different molecular structures other than those listed here. **Oxygen** for example normally occurs as  **$\text{O}_2$**  however, it also exists as **ozone,  $\text{O}_3$** . The yellow, solid form of sulfur commonly used in the laboratory is **rhombic** sulfur which consists of puckered  **$\text{S}_8$**  rings of sulfur atoms.



The rhombic sulfur crystals pictured here consist of **ring shaped  $\text{S}_8$**  molecules.



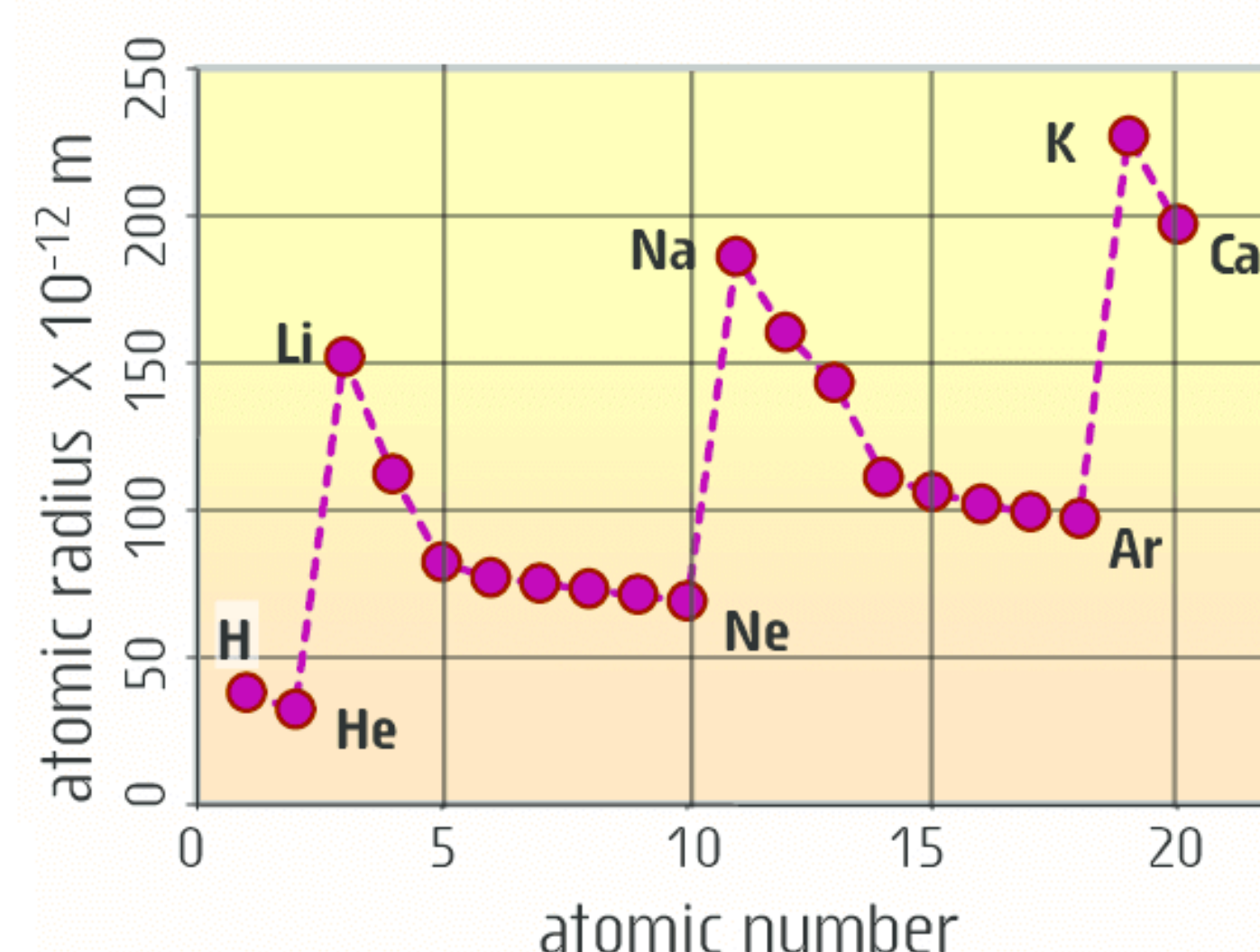
Heating rhombic sulfur above its melting point ( $113^\circ\text{C}$ ) causes it to change to a viscous red liquid. In this allotrope of sulfur the  $\text{S}_8$  rings have broken open and joined to one another to form long **chains** of sulfur atoms with no specific molecular formula.

Complete Set 15.



## Set 15 Periodic trends

**FIGURE 7** Graph of **atomic radius** against atomic number for the first twenty elements.



shielding  
gaseous phase  
most loosely  
physical  
increases  
atomic number  
periodic trend  
minimum  
further  
decreases  
nuclear charge  
positive  
 $\text{Na}^+(\text{g}) + \text{e}^-$

- Contrary to expectations, the size of an atom as measured by its **atomic radius**, does not simply increase as the number of subatomic particles in the atom (protons, neutrons and electrons) increases. Figure 7 shows that left to right in a period of the periodic table the atomic radius actually decreases as the atomic number increases.

- Use a **labelled sketch** to show what is meant by atomic radius of a metal element.
- Explain** how the data in Figure 7 supports the statement, "Left to right in a **period** of the periodic table the atomic radius decreases as the atomic number increases".
- Account** for the trend in atomic radius across a **period** of the periodic table.
- What** is the trend in atomic radius for the elements within a **group** of the periodic table? **Support** your answer with data from Figure 7.
- Account** for the trend in atomic radius within a **group** of the periodic table.

- Use your knowledge of **atomic radius** to answer the following.
  - Which element from the third period of the periodic table has the smallest atomic radius?
  - Rank the following elements in order of increasing atomic radius: Br, F and Cl.
  - Rank the following elements in order of increasing atomic radius: Br, Ca, Cu.

- Complete** the following passage by selecting the correct terms from the ones listed.

**Ionisation energy** is an atomic property that affects an element's chemical and (a) \_\_\_\_\_ properties. The first ionisation energy of an element is defined as the (b) \_\_\_\_\_ energy required to remove the (c) \_\_\_\_\_ bound electron from a neutral atom in the (d) \_\_\_\_\_.

The equation for the ionisation of a sodium atom and its first ionisation energy ( $E_1$ ) is represented here:



Importantly the lower an atom's first ionisation energy the more easily it can form (f) \_\_\_\_\_ ions.

When ionisation energy is plotted against atomic number a (g) \_\_\_\_\_ is evident where ionisation energy initially increases with increasing (h) \_\_\_\_\_ then suddenly decreases before resuming its steady increase. This pattern is clearly evident in the periodic table where ionisation energy generally (i) \_\_\_\_\_ from left to right in all periods and (j) \_\_\_\_\_ from top to bottom in all groups.

The increase in ionisation energy from left to right in a period is attributed to increasing (k) \_\_\_\_\_ that gives rise to stronger attraction between the nucleus and the electrons. Decreasing ionisation energy down a group occurs despite increasing nuclear charge. This happens as the outermost electrons for elements lower in a group occur in higher shells which are a significantly (l) \_\_\_\_\_ from the nucleus. Thus these electrons are more weakly attracted to the nucleus. As well as this, an increased (m) \_\_\_\_\_ effect by inner electrons (core electrons) also contributes to the decreasing ionisation energy down a group.

- The first ionisation energy of **magnesium**, **calcium** and **strontium** are given here.

First ionisation energy	Magnesium	Calcium	Strontium
	0.738 MJ mol <sup>-1</sup>	0.596 MJ mol <sup>-1</sup>	0.556 MJ mol <sup>-1</sup>

- Where** do these three elements occur in the **periodic table**?
- Account** for the **trend** in first ionisation energy of these elements. In your answer you should refer to atomic radius, nuclear charge and electron to nucleus attraction.
- Would you expect the first ionisation energy for sodium to be higher or lower than that of magnesium? **Explain**.



5. **Rank** the following elements in order of the property given. **State** your **reason** for the ranking with reference to the expected group or period trends generally shown in the periodic table.

Property	Reason for ranking
a. <b>Ionisation energy:</b> Mg, Ar, P lowest _____ highest	
b. <b>Ionisation energy:</b> Cl, F, Br lowest _____ highest	
c. <b>Atomic radius:</b> Ga, Ca, Br lowest _____ highest	
d. <b>Atomic radius:</b> I, F, Cl lowest _____ highest	
e. <b>Electronegativity:</b> N, O, C lowest _____ highest	
f. <b>Electronegativity:</b> O, Br, Mg lowest _____ highest	
g. <b>Number of valence electrons:</b> Ca, K, Ga lowest _____ highest	

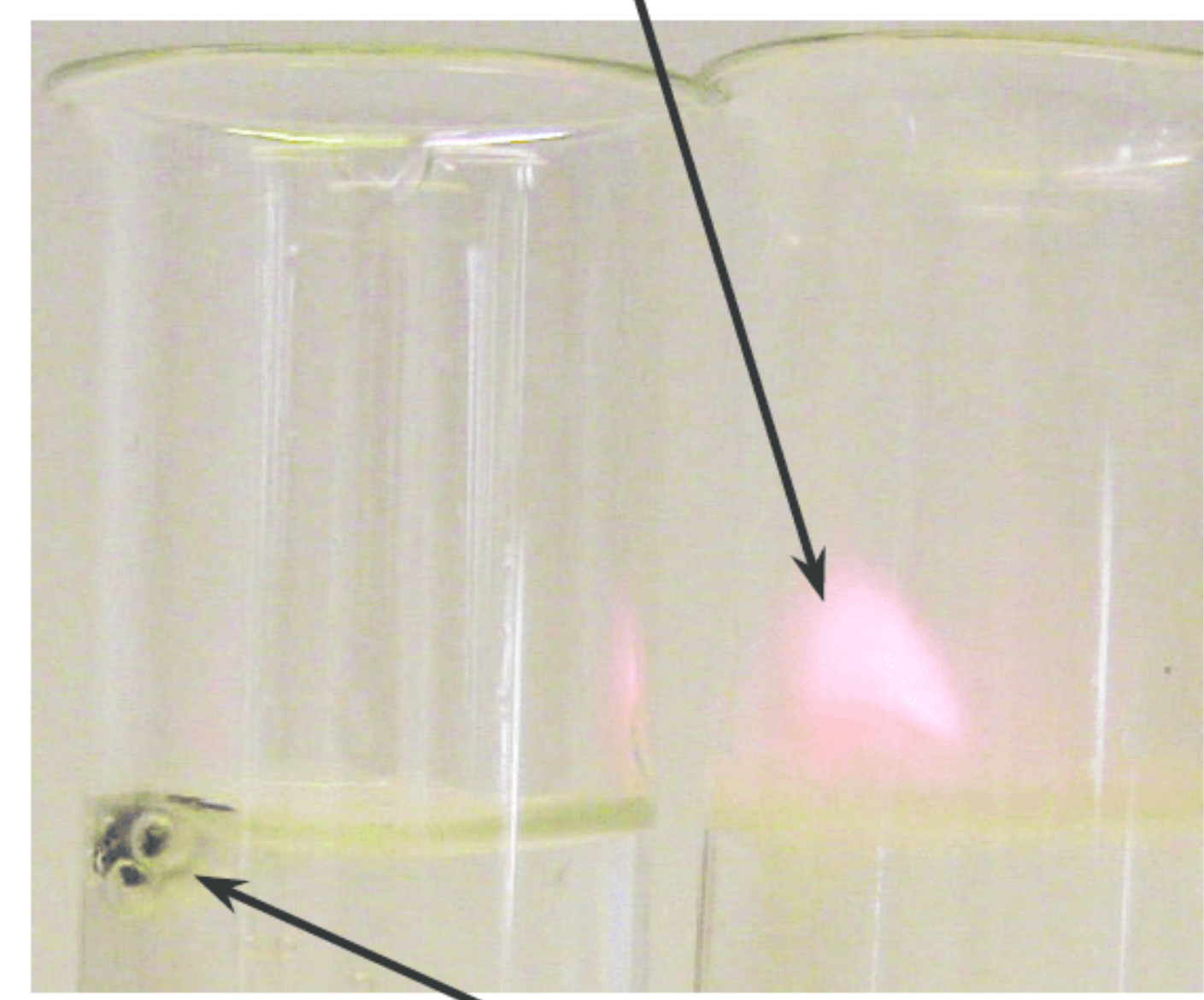
6. **Predict** the **formula** and type of **bonding** for the compounds that form when the elements **A** and **B** chemically combine. The periodic group number for the elements is shown in column 1 and 2. **State** the bonding type as **metallic**, **ionic** or **covalent**.

Periodic table group number		Formula	Bonding covalent, ionic or metallic
Element A	Element B		
<b>16</b> (non-metal)	<b>17</b>		
<b>13</b> (not boron)	<b>16</b> (non-metal)		
<b>14</b> (not Sn or Pb)	<b>14</b> (not Sn or Pb)		
<b>1</b> (not H)	<b>15</b> (non-metal)		
<b>13</b> (not boron)	<b>17</b>		
<b>2</b>	<b>16</b> (non-metal)		
<b>17</b>	<b>17</b>		

7. The elements in any group of the periodic table are said to increase in **metallic character** down the group. **(E)**
- State** the physical properties that are typical of metallic elements.
  - Name** two groups where this trend is most evident. Briefly **justify** your choice.
  - This group trend for metallic properties is said to be related to ionisation energy of the elements. What is the trend in ionisation energy within a group and how does this **account** for the increasing metallic nature of the elements in that group?
8. Consider the elements of the **third period** of the periodic table (elements Na to Ar). For this period describe the **relationship** between the element's **periodic group number** (ie 1, 2, 13, 14, 15, 16, 17 or 18) and its:
- covalent bonding capacity** with hydrogen
  - ionic bonding charge** (valence).



**FIGURE 8** The group 1 metal, **potassium**, (below right) reacts violently with water producing potassium hydroxide and hydrogen. Heat from this vigorous reaction ignites the hydrogen producing a characteristic bright pink flame.



The group 2 metal, **calcium**, (above left) has a similar though much less vigorous reaction with water.

9. Many metal elements react with water to produce an ionic metal hydroxide and hydrogen gas. In some cases the reaction is vigorous or almost violent, (Fig 8) while with other metals the reaction only happens with steam or not at all.
- Write **ionic equations** for the reaction of **potassium** and **calcium** with **water**.
  - Although all group 1 metal elements react strongly with water there is a trend in **reactivity** where elements lower in the group react most vigorously. For example, Li reacts moderately with water while potassium reacts vigorously (possibly exploding!) when added to water. Use your knowledge of ionisation energy of group 1 metals to **account** for their **reactivity** with water.
  - Typically group 2 metals react more slowly with water than group 1 metals. In particular beryllium (Be) shows no reaction with water, magnesium (Mg) reacts with steam only while the remaining metals all react with cold water.
    - Use your knowledge of ionisation energy to **account** for the differing **reactivity** of group 2 metals with water compared to group 1 metals.
    - In their reaction with water, group 1 metals form 1+ ions while group 2 metals form 2+ ions. Use your knowledge of periodic trends in valence electrons to **account** for this observation.
    - Use your knowledge of ionisation energy to **account** for the variation in **reactivity** of the different group 2 metals with water.

10. Refer to the properties of the elements **A**, **B**, **C** and **D** and then choose one that fits the descriptions given. If no element matches the description given write nil.

Element	First ionisation energy	Number of valence electrons	Electronegativity
<b>A</b>	Medium	4	2.6
<b>B</b>	Low	1	1.2
<b>C</b>	High	7	3.5
<b>D</b>	High	6	1.1

- an element most likely to form ions with a **1+** charge
  - the element most likely to form a **single covalent bond** with other non-metal elements
  - an element whose properties favour a **metallic** structure
  - the element most likely to form a **covalent network** structure
  - the element belonging to **group 18** of the periodic table
  - an element whose properties are **inconsistent** with known elements.
11. Consider the fluorides of the third period elements.
- NaF   MgF<sub>2</sub>   AlF<sub>3</sub>   SiF<sub>4</sub>   PF<sub>3</sub>   SF<sub>2</sub>   ClF**
- Classify the bonding in these fluorides as **ionic bonding** or **covalent bonding**? Justify your answer with reference to electronegativity and ionisation energy.
  - Account for the different **covalent bonding capacity** of Si, P, S and Cl.
  - Account for the different **ionic bonding capacity** of Na, Ca, and Al.



# CHAPTER 10 | INTRODUCING MOLES



**FIGURE 1** The Latin translation of **mole** is 'massive heap'. **Avogadro's number** is so large that this many grains of sand (of diameter  $\approx 0.5$  mm) could cover the surface of Australia to a depth of  $\approx 7$  m and have a mass of around 200 million million tonnes!

In quantitative chemistry the particular value of  **$6.022 \times 10^{23}$** , ie one **mole**, has a special significance.

A **single atom** of the isotope  $^{12}\text{C}$  (carbon-12) has a very small mass,  $1.99265 \times 10^{-23}$  g.

**Avogadro's number** however, is such that this number of  $^{12}\text{C}$  atoms (ie  $6.022 \times 10^{23}$  atoms of  $^{12}\text{C}$ ) has a mass of exactly 12 g. This mass is equal to the **relative atomic mass** of  $^{12}\text{C}$ , ie exactly **12**, expressed in grams.

In every case, **one mole** of atoms (ie  **$6.022 \times 10^{23}$**  atoms) of any isotope will have a mass equal to the isotope's relative atomic mass ( $A_r$ ) expressed in grams.

Using this concept allows Chemists to count atoms, molecules or ions by simply weighing a sample of the relevant substance.

Attempt Set 16 # 1.

Most substances consist of particles that contain two or more atoms or ions which combine to form a single **molecule** or **formula unit** of the substance. The formula of these substances shows the number of each atom or ion that makes up a single 'particle' of the substance.

A single particle of oxygen gas for example consists of a cluster (molecule) containing two oxygen atoms. This is shown by its formula  $\text{O}_2$ . Similarly a single particle (molecule) of water,  $\text{H}_2\text{O}$  consists of two hydrogen atoms and one oxygen atom.

A single **formula unit**, (a hypothetical particle) of the ionic substance  $\text{Al}_2(\text{SO}_4)_3$  consists of two  $\text{Al}^{3+}$  ions and three  $\text{SO}_4^{2-}$  ions.

Attempt Set 16 # 2.

## 10.1 The mole concept

When substances combine in a chemical reaction they do so at a particle level, combining in whole number particle ratios, ie one particle (atom, ion or molecule) of one substance may combine with one particle of another and so on. For this reason it is important that chemists are able to count particles of a substance. The **mole** (mol) is the standard chemical unit for describing the amount of a substance in numbers of particles. The mole is a number equal to  $6.02 \times 10^{23}$ , known as **Avogadro's number**. One mole of a substance contains  $6.02 \times 10^{23}$  particles (ie atoms, ions, molecules or formula units) of that substance. (See Fig 1.)

## 10.2 Molar mass of the elements

The mass of different atoms varies according to the number of subatomic particles (protons, neutrons and electrons) it contains. A carbon-12 atom for example has a mass of  $1.9926 \times 10^{-23}$  g while a sulfur-32 atom has a mass of  $5.3091 \times 10^{-23}$  g. For convenience the periodic table of the elements lists data for the **relative atomic mass** of the different elements. **Relative atomic mass** compares the mass of an element's atoms (taking into account its various isotopes and their abundance) to **one twelfth the mass of a carbon-12 atom** (which is  $\approx 1.660 \times 10^{-24}$  g). Thus sulfur has a relative atomic mass of 32.07 as its atoms are on average (allowing for its various isotopes and their abundance) 32.07 times the mass of one twelfth of a carbon-12 atom.

The **molar mass (M)** of an element is defined as the '**mass of one mole of its atoms**'. One mole of carbon-12 atoms is defined as having a mass of exactly 12.0 g. For all other elements the molar mass is equal to the element's relative atomic mass expressed in grams.

**EXAMPLE 1** Use a periodic table to find the **molar mass** of Na, S, Cl, Sn and Fe.

<b>M(Na)</b> = 22.99 g mol <sup>-1</sup>	Using a periodic table (see the inside back cover) look up the relative atomic mass for each element. This gives the molar mass of the element, ie the mass of $6.02 \times 10^{23}$ atoms of the element. Quote your answer in g mol <sup>-1</sup> .
<b>M(S)</b> = 32.07 g mol <sup>-1</sup>	
<b>M(Cl)</b> = 35.45 g mol <sup>-1</sup>	
<b>M(Sn)</b> = 118.7 g mol <sup>-1</sup>	
<b>M(Fe)</b> = 55.85 g mol <sup>-1</sup>	

Knowing the molar mass of an element provides a way of indirectly **counting** its **atoms** by **weighing** on a mass balance. Thus weighing 22.99 g of sodium is equivalent to counting out one mole or  $6.02 \times 10^{23}$  atoms of sodium. Similarly weighing 32.07 g of sulphur is equivalent to counting out one mole or  $6.02 \times 10^{23}$  atoms of sulfur.

## 10.3 Molar mass from chemical formula

Most substances consist of particles that are not single atoms. Instead their particles consist of combinations of several atoms or ions. (See border note.) The molar mass of these substances is found by adding together the molar masses of all the elements shown in the formula.

**EXAMPLE 2** Calculate the molar mass of oxygen gas ( $\text{O}_2$ ).

<b>M(O<sub>2</sub>)</b> = $2 \times \text{M(O)}$ = $2 \times 16.00$ = <b>32.00 g mol<sup>-1</sup></b>	Each particle (molecule) of $\text{O}_2$ consists of two O atoms. Adding the molar mass of these components gives the molar mass of $\text{O}_2$ .
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**EXAMPLE 3** Determine the molar mass of ethanoic acid ( $\text{CH}_3\text{COOH}$ ).

<b>M(CH<sub>3</sub>COOH)</b> = $2 \times \text{M(C)} + 4 \times \text{M(H)} + 2 \times \text{M(O)}$ = $2 \times 12.01 + 4 \times 1.008 + 2 \times 16.00$ = <b>60.05 g mol<sup>-1</sup></b>	Each particle (molecule) of $\text{CH}_3\text{COOH}$ has two C atoms, two O atoms and four H atoms. Adding the molar mass of these components gives the molar mass of $\text{CH}_3\text{COOH}$ .
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**EXAMPLE 4** What is the molar mass of calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ]?

<b>M[Ca(NO<sub>3</sub>)<sub>2</sub>]</b> = $\text{M(Ca)} + 2 \times \text{M(N)} + 6 \times \text{M(O)}$ = $40.08 + 2 \times 14.01 + 6 \times 16.00$ = <b>164.10 g mol<sup>-1</sup></b>	Each formula unit ('particle') of $\text{Ca}(\text{NO}_3)_2$ contains one Ca atom, two N atoms and six O atoms. The combined molar masses of these components gives the molar mass of $\text{Ca}(\text{NO}_3)_2$ .
--	--



## 10.4 Relating mass and moles

The mass and moles of a substance are related as shown below.

$$m = n \times M \quad \text{also expressed as} \quad n = \frac{m}{M} \quad \text{where: } n = \text{the moles of the substance in mol}$$

$$m = \text{the mass of the substance in g}$$

$$M = \text{the molar mass of the substance in g mol}^{-1}$$

**EXAMPLE 5** The compound ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$ , is an active ingredient in some garden fertilisers. Calculate the number of moles of  $(\text{NH}_4)_2\text{SO}_4$  contained in a 38.5 g sample of  $(\text{NH}_4)_2\text{SO}_4$ .

$$n[(\text{NH}_4)_2\text{SO}_4] = \frac{m}{M} = \frac{38.5}{132.15} = 0.291 \text{ mol}$$

Simply substitute the mass of the substance, 38.5 g and molar mass, 132.15 g mol<sup>-1</sup> to obtain the number of moles present.

Attempt Set 16 # 3 and 4.

## 10.5 Moles within moles

Ionic compounds consist of **formula units** (hypothetical particles) that are made up of two or more ions. Many of these compounds have a tendency to separate into their individual ions when they dissolve in water. By referring to a compound's formula it is possible to determine the number of moles of ions that are contained within a given number of moles of the compound. (See Example 6.) In a similar way the number of moles of each type of atom in a given number of moles of substance can also be found from its formula. (See Example 7.)

**EXAMPLE 6** How many moles of  $\text{Fe}^{3+}$  ions and  $\text{SO}_4^{2-}$  ions are contained in 1.8 moles of  $\text{Fe}_2(\text{SO}_4)_3$ ?

$$n(\text{Fe}^{3+} \text{ ions}) = 2 \times n[\text{Fe}_2(\text{SO}_4)_3]$$

$$= 2 \times 1.8$$

$$= 3.6 \text{ mol}$$

The subscript 2 alongside  $\text{Fe}^{3+}$  in the formula for iron(III) sulfate means there are two  $\text{Fe}^{3+}$  ions in each formula unit of  $\text{Fe}_2(\text{SO}_4)_3$ . Thus the moles of  $\text{Fe}^{3+}$  are twice the moles of  $\text{Fe}_2(\text{SO}_4)_3$  formula units.

$$n(\text{SO}_4^{2-} \text{ ions}) = 3 \times n[\text{Fe}_2(\text{SO}_4)_3]$$

$$= 3 \times 1.8$$

$$= 5.4 \text{ mol}$$

The subscript 3 alongside  $\text{SO}_4^{2-}$  in the formula for iron(III) sulfate means there are three  $\text{SO}_4^{2-}$  ions in each formula unit of  $\text{Fe}_2(\text{SO}_4)_3$ . Thus the moles of  $\text{SO}_4^{2-}$  are three times the moles of  $\text{Fe}_2(\text{SO}_4)_3$ .

**EXAMPLE 7** How many moles of N atoms and H atoms are contained in 3.2 moles of ammonia ( $\text{NH}_3$ )?

$$n(\text{N atoms}) = 1 \times n(\text{NH}_3)$$

$$= 1 \times 3.2$$

$$= 3.2 \text{ mol}$$

The subscript 1 (implied) alongside N in the formula for ammonia ( $\text{NH}_3$ ) means there is one N atom in each molecule of  $\text{NH}_3$ . Thus the moles of N atoms are equal to the moles of  $\text{NH}_3$  molecules.

$$n(\text{H atoms}) = 3 \times n(\text{NH}_3)$$

$$= 3 \times 3.2$$

$$= 9.6 \text{ mol}$$

The subscript 3 alongside H in the formula for ammonia ( $\text{NH}_3$ ) means there are three H atoms in each molecule of  $\text{NH}_3$ . Thus the moles of H are three times the moles of  $\text{NH}_3$  molecules.

## 10.6 Measuring gases

While the molar amount of a solid is readily found by measuring its mass this is not so easily achieved for a gas. The molar amount of a gas is most easily found by measuring its **volume**. The unit of volume used most frequently for this is the **litre (L)**.

$$1 \text{ L} = 1000 \text{ mL} \quad \text{also} \quad 1 \text{ L} = 1000 \text{ cm}^3 = 1 \text{ dm}^3 \quad \text{and} \quad 1000 \text{ L} = 1 \text{ m}^3$$

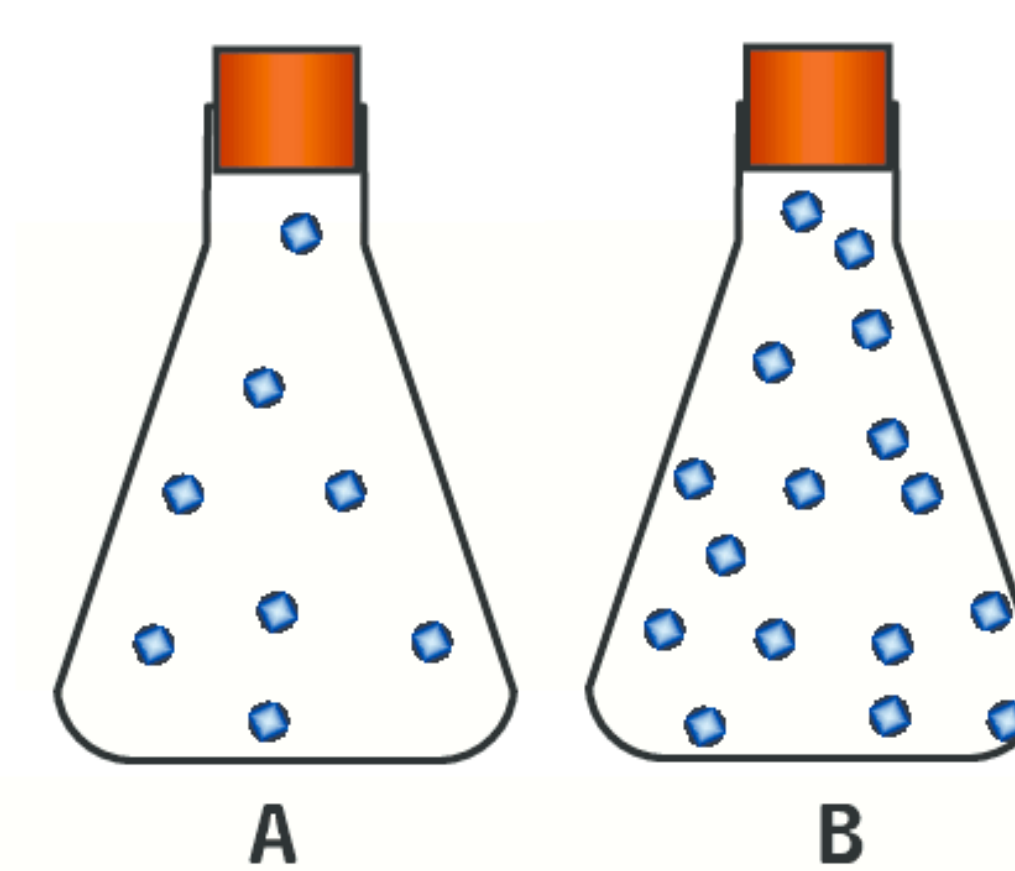
As well as volume the **temperature** and **pressure** of a gas also affect the moles present. More moles of gas will fit into a container when the temperature is low and the pressure high. (See Fig 2.) So when measuring the amount of gas by volume, its temperature and pressure must also be noted. The SI unit for measuring pressure is the **pascal (Pa)**. Average atmospheric pressure at sea level is quoted as being 101,325 Pa, ie 101.325 kPa. This is equivalent to one **standard atmosphere (atm)** of pressure. (Not to be confused with STP.)

$$\text{normal atmospheric pressure} = 1.000 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \times 10^5 \text{ Pa}$$

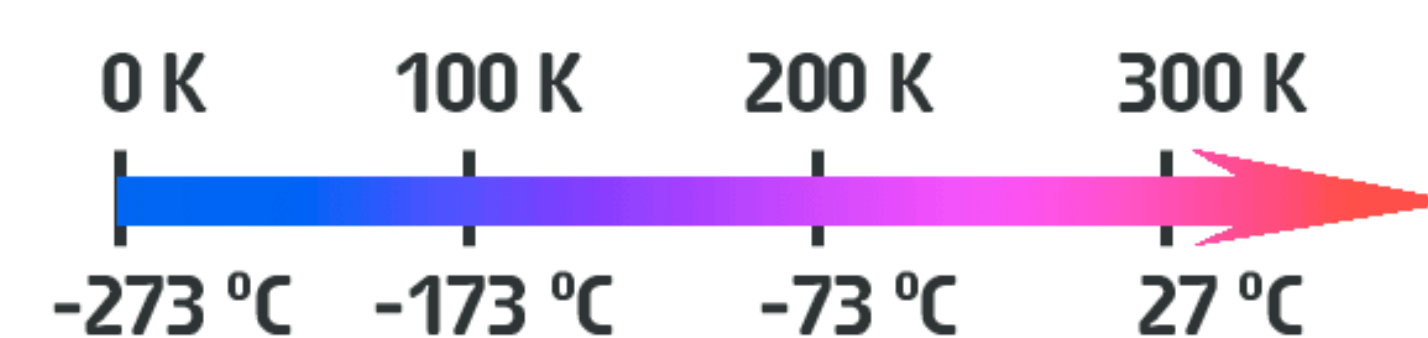
The SI unit of temperature is the **kelvin (K)** though it is often recorded in **celsius** ( $^{\circ}\text{C}$ ). (See Fig 3.) By definition, **absolute zero, 0 K** (or  $-273.15^{\circ}\text{C}$ ) is the lowest temperature that can be achieved. It is the temperature at which all **particles** of matter are **motionless**, ie have zero kinetic energy and an **ideal gas** would have zero volume.

$$\text{Temperature (kelvin)} = \text{Temperature (celsius)} + 273.15$$

Attempt Set 16 # 5.

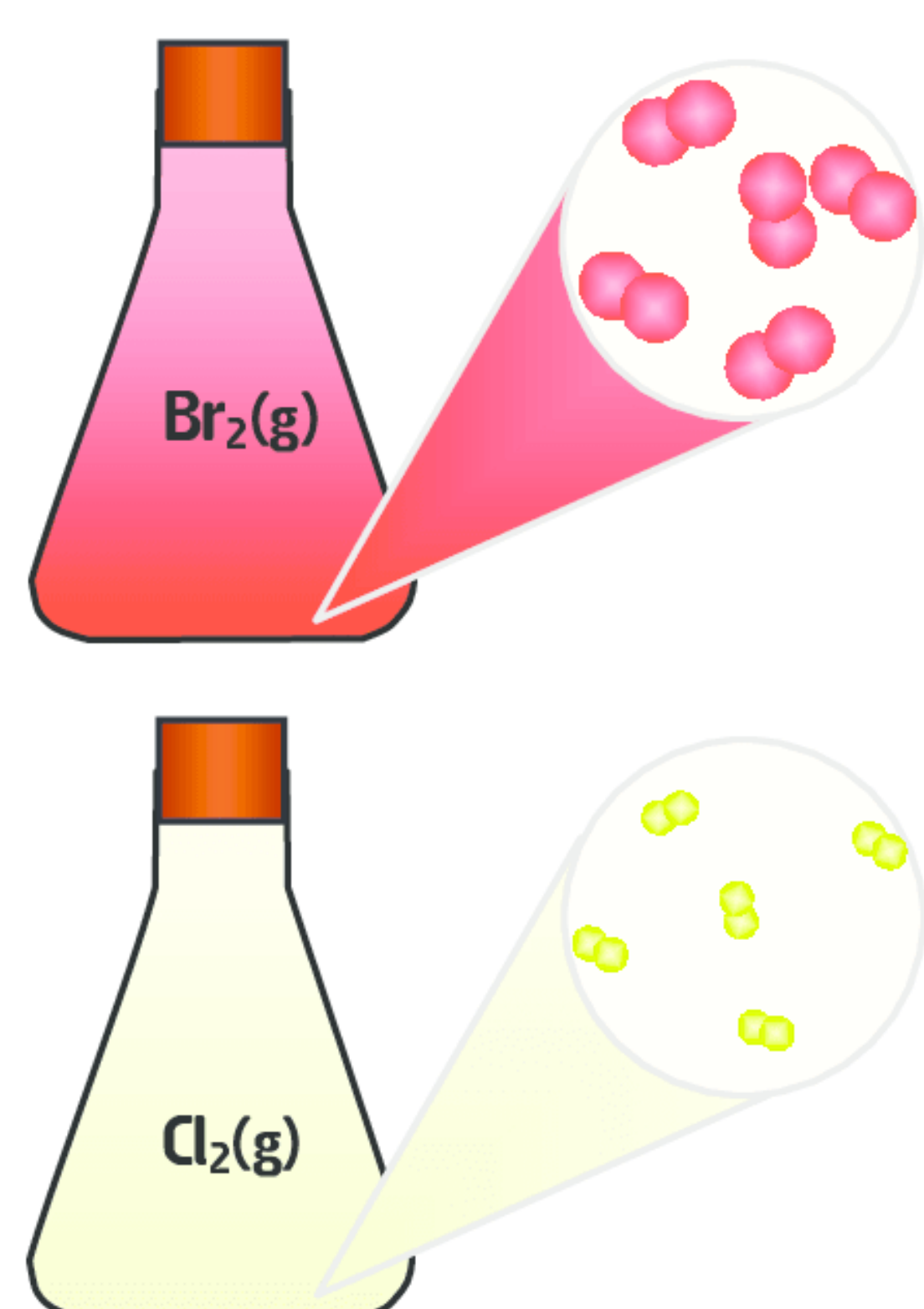


**FIGURE 2** The volume of gas on its own is not a reliable measure of the moles of gas present. Flasks **A** and **B** have the same volume but flask **B** contains twice as much gas as flask **A**. This can happen because the gas in flask **B** is at twice the pressure as that in flask **A**. Similarly the temperature of a gas can affect the moles of gas present in a given volume. (See p2-3.)



**FIGURE 3** Kelvin and Celsius temperature scales compared.





**FIGURE 4** These two **22.71 L** flasks contain the gases **bromine** and **chlorine** both at 100.0 kPa and 273 K (0 °C). Each flask contains exactly **1.00 mole of gas**. This occurs despite the obvious difference in the molecular size and molar mass of the two gases. Thus one mole of any gas irrespective of its chemical composition will have a **molar volume** of 22.71 L at STP conditions.

It must be noted that the molar volume of a gas will change for different conditions of temperature and pressure, eg at 50.0 kPa and 273.15 K molar volume will be 45.42 L.

#### Sodium carbonate decahydrate

(Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O) is a very useful household compound. Commercially known as **washing soda** it is used as a laundry water softening agent. It can also be used as a cleaning agent as it dissolves grease and oils. Gloves should be worn when handling washing soda as its solution is quite basic.

Commercially its main use is in glass making where it is a major ingredient along with sand (SiO<sub>2</sub>) and calcium carbonate (CaCO<sub>3</sub>).

**Oxalic acid** (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is an organic acid found naturally in many plants such as rhubarb, star fruit and parsley. While not toxic to people in small quantities it can cause health problems in larger doses as it readily combines with dissolved Ca<sup>2+</sup>, Mg<sup>2+</sup> and Fe<sup>2+</sup> ions present in the body to form insoluble precipitates.

Around the home it may be found as the active ingredient in some metal cleaners and rust removers.

**Ethanoic acid** (CH<sub>3</sub>COOH) is the active ingredient (≈ 5–18% by mass) in **vinegar**. It gives vinegar its characteristic pungent odour and sharp sour taste. Around the home it is used as a food acid, in preserving vegetables and other food products and for de-scaling basins and kettles by removing insoluble carbonate deposits.

One method for determining the molar amount of a gas is to measure its volume at some reference conditions of temperature and pressure. The commonly used conditions are those recommended by IUPAC and are known as **standard temperature and pressure, STP**. This refers to a pressure of **100.0 kPa** and a temperature of **273.15 K** (0 °C). One mole of gas measured at these conditions will occupy a volume of **22.71 L**, irrespective of what the gas is. This STP molar volume of a gas (see Fig 4) can be used to find the moles of gas from its STP volume as shown below.

$$n(\text{gas}) = \frac{V_{\text{stp}}}{22.71}$$

where: **n(gas)** = the moles of gas (mol)

**V<sub>stp</sub>** = the volume of gas in litres (L) at STP

**EXAMPLE 8** Excess hydrochloric acid was added to some zinc granules producing 4.39 L of hydrogen gas measured at STP (ie 100.0 kPa and 273 K). How many moles of hydrogen were formed?

$$n(\text{H}_2) = \frac{V_{\text{(stp)}}}{22.71} = \frac{4.39}{22.71} = 0.193 \text{ mol}$$

Since the gas volume is measured at STP then one mole of it will have a volume of 22.71 L.

Complete Set 16.

## Set 16 Relating moles, mass and gas volume

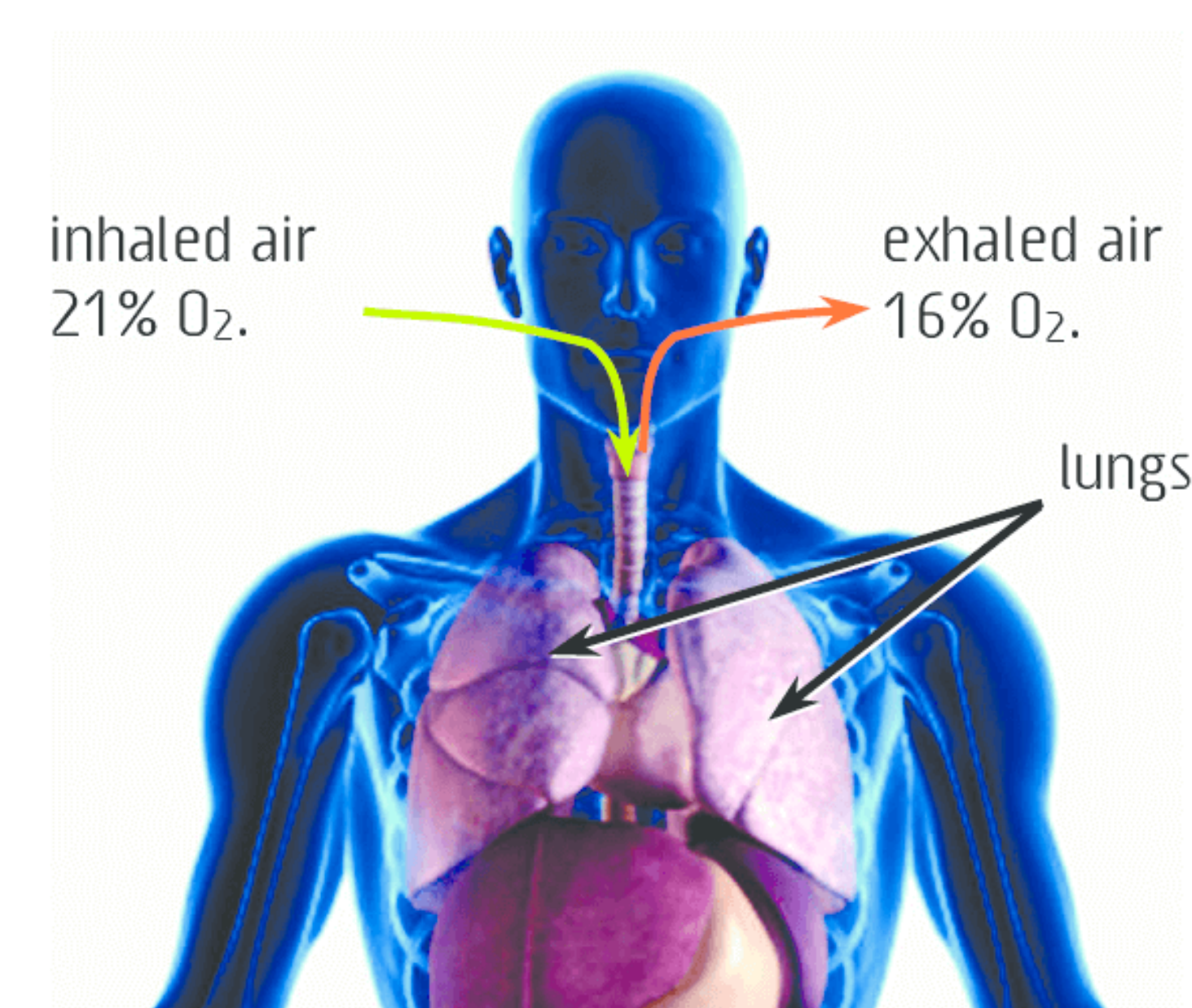
- Use a periodic table to find the **molar mass** of the following elements.
  - lithium (Li)
  - zinc (Zn)
  - oxygen atoms (O)
  - nitrogen atoms (N)
  - lead
  - iron
- Calculate the **molar mass** of the following substances.
  - oxygen gas (O<sub>2</sub>)
  - hydrogen gas (H<sub>2</sub>)
  - calcium chloride (CaCl<sub>2</sub>)
  - copper(II) sulfate (CuSO<sub>4</sub>)
  - ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]
  - chlorine gas
  - iron(III) oxide
  - copper(II) hydrogensulfate
  - aluminium sulfate
  - barium hydroxide
  - sodium carbonate-10-water (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O)**
  - copper(II) ethanoate-1-water
- Determine the **mass** in grams of each of the following.
  - 3.15 mol of magnesium bromide (MgBr<sub>2</sub>)
  - 1.74 × 10<sup>-3</sup> mol of iron(III) oxide (Fe<sub>2</sub>O<sub>3</sub>)
  - 0.395 mol of copper(II) hydrogensulfate [Cu(HSO<sub>4</sub>)<sub>2</sub>]
  - 1.25 × 10<sup>3</sup> mol of sodium carbonate-10-water (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O)
  - 7.38 × 10<sup>-2</sup> mol of sulfuric acid
  - 4.72 × 10<sup>2</sup> mol of **oxalic acid-2-water** (oxalic acid dihydrate, see border note)
- The mass of each substance is given in grams. Convert this to an equivalent amount in **moles**.
  - 250 gram of water (H<sub>2</sub>O), about the amount in a glass of water
  - 1.29 × 10<sup>-3</sup> gram of ammonium sulfate-2-water [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O]
  - 4.29 grams of **ethanoic acid** (see border note)
- Many substances consist of particles that are themselves a combination of smaller particles. In this way 3.0 mol of oxygen gas (O<sub>2</sub>) consists of 6.0 mol of oxygen (O) atoms. With this in mind and referring to Example 6 and 7 (from p81) answer the following questions.
  - How many moles of nitrogen (N) atoms and hydrogen (H) atoms are present in 4.50 mol of ammonia (NH<sub>3</sub>)?
  - Determine the number of moles of hydrogen atoms (H), sulfur atoms (S) and oxygen atoms (O) in 0.25 mol of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).
  - Find the moles of iron ions (Fe<sup>3+</sup>) and oxide ions (O<sup>2-</sup>) present in 1.7 mole of iron(III) oxide (Fe<sub>2</sub>O<sub>3</sub>).
  - How many moles of calcium ions (Ca<sup>2+</sup>) and phosphate ions (PO<sub>4</sub><sup>3-</sup>) are present in 0.28 moles of calcium phosphate [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]?



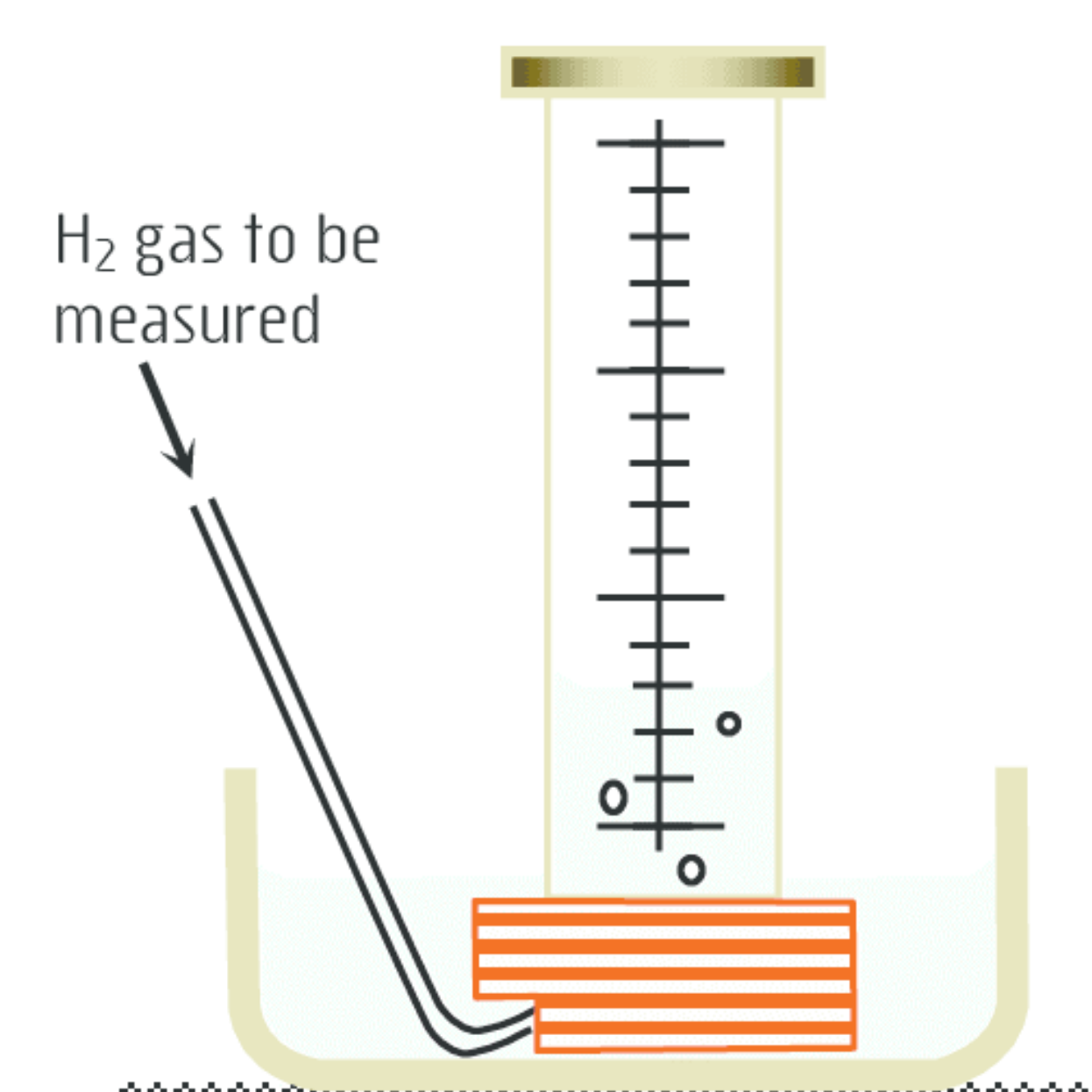
6. Determine the **molar amount** of each of the following gases. All volumes are measured at **STP**. (See border note.)
- 472.0 L of carbon dioxide gas ( $\text{CO}_2$ )
  - $3.50 \times 10^3$  L of hydrogen gas ( $\text{H}_2$ )
  - $1.700 \times 10^2$  mL of chlorine gas ( $\text{Cl}_2$ )
7. Determine the **volume** that would be occupied by the following gases at STP conditions.
- 2.50 moles of carbon dioxide gas ( $\text{CO}_2$ )
  - 0.550 moles of oxygen gas ( $\text{O}_2$ )
  - 8.32 gram of hydrogen gas ( $\text{H}_2$ ). Take care, the quantity given is in grams.
  - $6.50 \times 10^{-2}$  grams of ammonia gas ( $\text{NH}_3$ )
8. Oxygen is a most important gas for all living things. It plays an important role in the chemical reaction known as respiration. When breathing normally in a relaxed mode the average adult will inhale about 0.50 L of air per breath. (See Fig 5.) Remember only 21.0% by volume of the air we breathe is oxygen gas.
- Calculate the **mass** of oxygen ( $\text{O}_2$ ) that has been inhaled in this breath if the volume was measured at STP.
  - On average it is known that exhaled air contains around 16% by volume oxygen gas. With this in mind determine the **mass** of oxygen **absorbed** by the average person in a week? Assume an average breathing rate and volume of 14 breaths per minute at 0.50 L per breath. Assume STP conditions apply.
9. The complete combustion of a tank of petrol produced 219 kg of carbon dioxide gas.
- What **volume** of carbon dioxide is produced when measured at STP?
  - What **mass** of oxygen is used by a car in burning a tank of petrol? You may assume that for every 1.00 L of carbon dioxide produced, 1.00 L of oxygen is consumed.
10. An experiment to investigate the reaction of zinc with hydrochloric acid involved adding a measured mass of zinc to excess hydrochloric acid and measuring the amount of hydrogen gas produced. The gas was collected in an inverted measuring cylinder by the downward displacement of water. (See Fig 6.) The hydrogen gas collected had a volume of 163.5 mL when measured at 0 °C and 100.0 kPa. How many **moles** of hydrogen were produced in the experiment? (You may assume the collected gas is pure dry hydrogen.)
11. **Dry ice** (Fig 2 p35) is the common name used for solid carbon dioxide. Dry ice sublimates (converts directly from a solid to a gas) above -78 °C. A student wanted to use dry ice to inflate a large balloon to a volume of around 32 L (STP). The student did this by weighing approximately 55 g of solid dry ice, adding this to the balloon and tying it off. Will the balloon inflate as expected once all of the dry ice has sublimated? Use a calculation to support your answer.
12. A  $9.00 \times 10^2$  kg sample of **bauxite**, the ore from which aluminium is obtained, contains  $4.70 \times 10^3$  moles of hydrated alumina ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) along with other impurities. What is the maximum **mass** of Al that can be extracted from this ore sample?

**STP** (Standard temperature and pressure) refers to 100.0 kPa and 273.15 K (0 °C). When a gas volume is measured at these conditions it is possible to determine the molar amount of gas as every 22.71 L of gas corresponds to one mole of it.

**FIGURE 5** On average an adult will inhale about 0.50 L of air per breath. The inhaled air contains 21% by volume  $\text{O}_2(\text{g})$  while the exhaled air still contains around 16% by volume  $\text{O}_2(\text{g})$ .



**FIGURE 6** Hydrogen gas can be collected in a measuring cylinder by the **downward displacement of water** and its volume read from the measuring cylinder scale.



Any gas with a low solubility in water can be collected and measured this way. This includes gases such as oxygen ( $\text{O}_2$ ) and carbon dioxide ( $\text{CO}_2$ ). Gases like ammonia ( $\text{NH}_3$ ), hydrogen chloride ( $\text{HCl}$ ) and chlorine ( $\text{Cl}_2$ ) should not be collected this way as they are quite soluble in water.



# CHAPTER 11 | STOICHIOMETRY WITH MOLES, MASS AND GAS VOLUMES

**Stoichiometry** is a specialised science term. It comes from the Greek, 'stoikheion' which means element and 'metry' to measure. It is the study of the relationship between the amounts of each reagent in a chemical reaction.

The **coefficients** for the balanced equation give the '**molar recipe**' for the reaction. Thus in Example 1 the molar amount of  $\text{H}_2\text{O}$  produced can vary but it must always be **three times** ( $6/2$ ) the molar amount of  $\text{C}_2\text{H}_6$  used. The molar amount of  $\text{CO}_2$  produced however, is always **twice** ( $4/2$ ) the molar amount of  $\text{C}_2\text{H}_6$  used.

## 11.1 Quantities in chemical reactions

The **coefficients** in a balanced chemical equation give the **relative** number of molecules, formula units or moles of each substance in the reaction. The **actual amounts** of each substance is always in the same ratio as the coefficients. (See border note.)

**EXAMPLE 1** What information is given by the coefficients in the balanced equation for the combustion of ethane ( $\text{C}_2\text{H}_6$ )?

	$2\text{C}_2\text{H}_6(\text{g})$	$+ 7\text{O}_2(\text{g})$	$\rightarrow 4\text{CO}_2(\text{g})$	$+ 6\text{H}_2\text{O}(\text{g})$
Substances involved in the reaction	$\text{C}_2\text{H}_6(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
Relative number of <b>molecules</b>	2 molecules	7 molecules	4 molecules	6 molecules
Relative number of <b>moles</b>	2 moles	7 moles	4 moles	6 moles

## 11.2 Mole to mole calculations

The **molar amount** of any **two** substances used or produced in a reaction is in the same **ratio** as their **stoichiometric ratio**. This is the ratio of their **coefficients** in the balanced equation. Consider the general chemical equation shown here (at left).



Where: **a**, **b**, **c** and **d** are the **coefficients** of substances **A**, **B**, **C** and **D** and **n(A)**, **n(B)**, **n(C)** and **n(D)** are the **moles** of substances **A**, **B**, **C** and **D**

In general:  $\frac{\text{moles of A in the reaction}}{\text{moles of B in the reaction}} = \frac{\text{coefficient of A in the reaction}}{\text{coefficient of B in the reaction}}$  ie  $\frac{n(A)}{n(B)} = \frac{a}{b}$

thus for **A**,  $n(A) = \frac{a}{b} \times n(B)$  or  $n(A) = \frac{a}{c} \times n(C)$  or  $n(A) = \frac{a}{d} \times n(D)$

The stoichiometric relationship is often written as:

$$n(\text{unknown}) = \frac{\text{coefficient(unknown)}}{\text{coefficient(known)}} \times n(\text{known})$$

This form of the stoichiometric relationship allows the molar amount of an unknown to be readily found from the known molar amount of another substance present in the reaction.

Attempt Set 17 # 1, 2 and 3.

**EXAMPLE 2** Determine the molar amount of oxygen ( $\text{O}_2$ ) used and carbon dioxide ( $\text{CO}_2$ ) produced when 0.795 mole of ethane ( $\text{C}_2\text{H}_6$ ) is burnt in air.



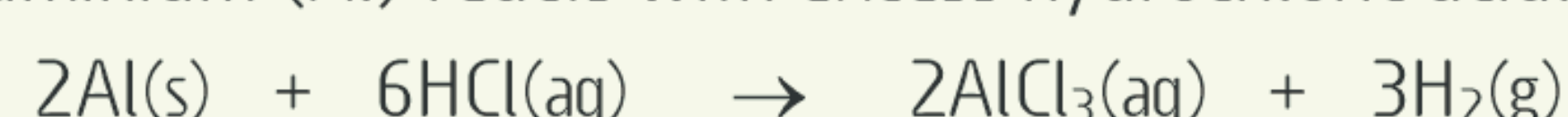
$n(\text{O}_2) = \frac{7}{2} \times n(\text{C}_2\text{H}_6) = \frac{7}{2} \times 0.795 = \mathbf{2.78 \text{ mol}}$  The coefficient of  $\text{O}_2$  is **seven**, while that of  $\text{C}_2\text{H}_6$  is **two**, thus the molar amount of  $\text{O}_2$  in the reaction is **3.5 times** ( $7/2$ ) the molar amount of  $\text{C}_2\text{H}_6$ .

$n(\text{CO}_2) = \frac{4}{2} \times n(\text{C}_2\text{H}_6) = \frac{4}{2} \times 0.795 = \mathbf{1.59 \text{ mol}}$  The coefficient of  $\text{CO}_2$  is **four**, while that of  $\text{C}_2\text{H}_6$  is **two**, thus the molar amount of  $\text{CO}_2$  is **twice** ( $4/2$ ) the molar amount of  $\text{C}_2\text{H}_6$ .

## 11.3 Calculations involving mass and moles

If the mass of any one substance involved in a reaction is known, then by converting this to an equivalent amount in moles ( $n = m/M$ ), the molar amounts of all the other substances involved in the reaction can be found. The relationship  $m = nM$  can be used to find the mass of a substance once the molar amount of it is found.

**EXAMPLE 3** Determine the moles of hydrochloric acid ( $\text{HCl}$ ) used and hydrogen ( $\text{H}_2$ ) produced when 6.08 g of aluminium ( $\text{Al}$ ) reacts with excess hydrochloric acid. (See Fig 1.)

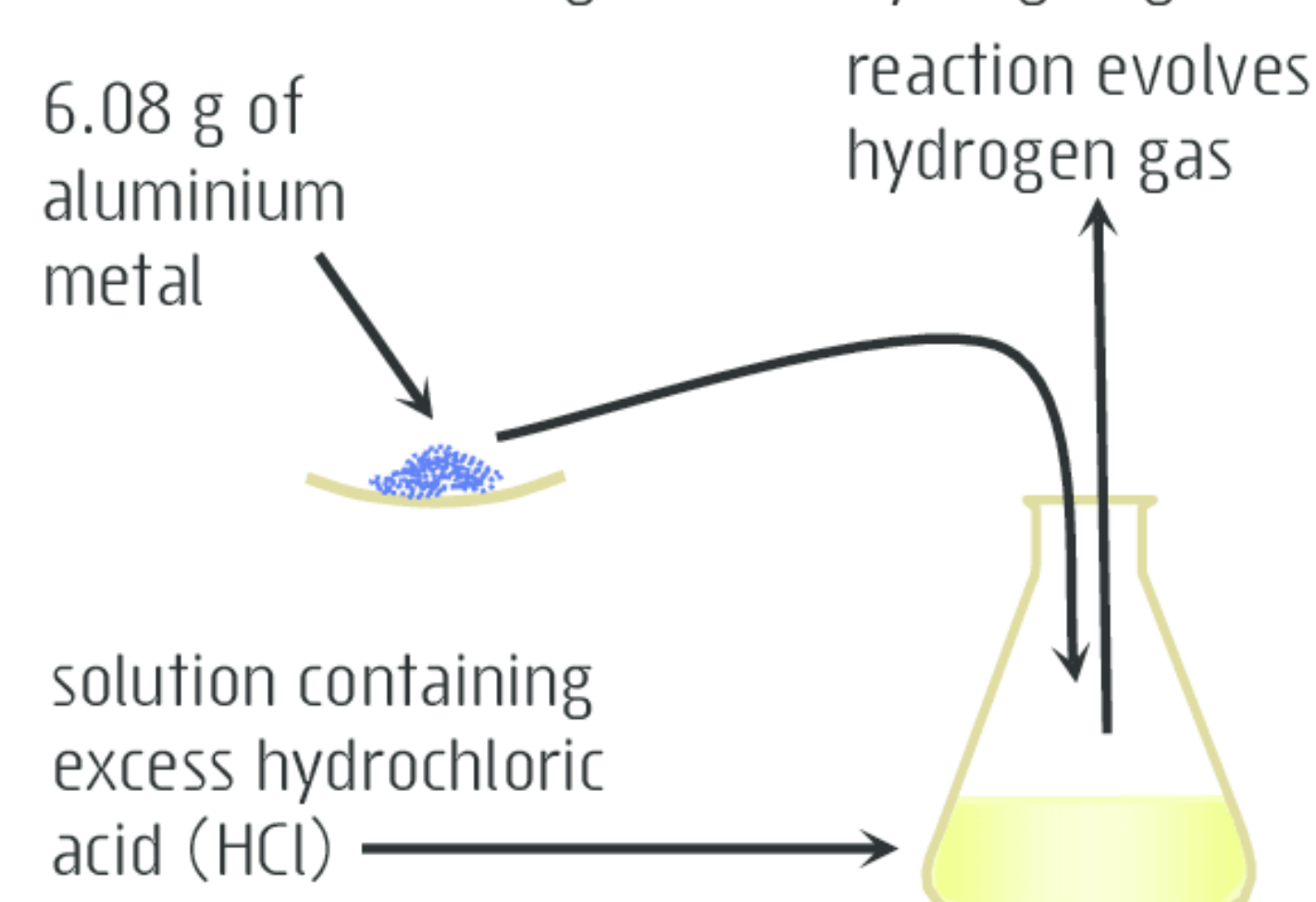


$n(\text{Al}) = \frac{m}{M} = \frac{6.08}{26.98} = \mathbf{0.225 \text{ mol}}$  Find the moles of Al from the given mass.

$n(\text{HCl}) = \frac{6}{2} \times n(\text{Al}) = \frac{6}{2} \times 0.225 = \mathbf{0.676 \text{ mol}}$  The coefficient of  $\text{HCl}$  is **six**, while that of  $\text{Al}$  is **two**, thus the molar amount of  $\text{HCl}$  in the reaction is **three times** ( $6/2$ ) that of  $\text{Al}$ .

$n(\text{H}_2) = \frac{3}{2} \times n(\text{Al}) = \frac{3}{2} \times 0.225 = \mathbf{0.338 \text{ mol}}$  The coefficient of  $\text{H}_2$  is **three**, while that of  $\text{Al}$  is **two**, thus the molar amount of  $\text{H}_2$  is **one and a half times** ( $3/2$ ) the molar amount of  $\text{Al}$ .

**FIGURE 1** Excess hydrochloric acid and aluminium reacting to form hydrogen gas.



Attempt Set 17 # 4 and 5.



**EXAMPLE 4** What mass of aluminium chloride ( $\text{AlCl}_3$ ) is formed if  $1.22 \times 10^{-2}$  g of hydrochloric acid ( $\text{HCl}$ ) reacts with excess aluminium ( $\text{Al}$ )?



$$n(\text{HCl}) = \frac{m}{M} = \frac{1.22 \times 10^{-2}}{36.458} = 3.35 \times 10^{-4} \text{ mol}$$

Find the moles of  $\text{HCl}$  from the given mass.

$$n(\text{AlCl}_3) = \frac{2}{6} n(\text{HCl}) = \frac{2}{6} \times 3.35 \times 10^{-4} = 1.12 \times 10^{-4} \text{ mol}$$

The coefficient of  $\text{AlCl}_3$  is **two**, while that of  $\text{HCl}$  is **six**, thus the molar amount of  $\text{AlCl}_3$  is **one third** ( $2/6$ ) that of  $\text{HCl}$ .

$$m(\text{AlCl}_3) = n \times M = 1.12 \times 10^{-4} \times 133.33 = 1.49 \times 10^{-2} \text{ g}$$

Convert the moles of  $\text{AlCl}_3$  to an equivalent mass.

Complete Set 17.

## Set 17 Stoichiometry with mass and moles

- The explosive **trinitrotoluene** (TNT or  $\text{C}_7\text{H}_5\text{O}_6\text{N}_3$ , see Fig 2) reacts with oxygen according to the equation shown below. Refer to this equation to complete the partially written mole equations.



$$\text{a. } n(\text{CO}_2) = \frac{28}{?} \times n(\text{C}_7\text{H}_5\text{O}_6\text{N}_3)$$

$$\text{c. } n(\text{H}_2\text{O}) = \frac{?}{?} \times n(\text{O}_2)$$

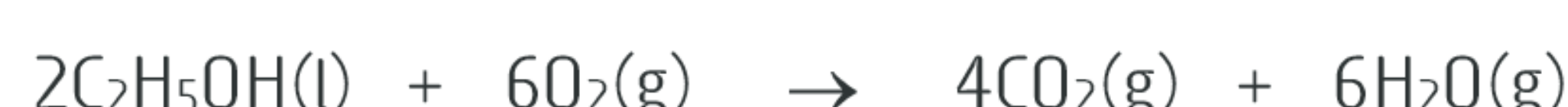
$$\text{b. } n(\text{O}_2) = \frac{?}{4} \times n(\text{C}_7\text{H}_5\text{O}_6\text{N}_3)$$

$$\text{d. } n(\text{CO}_2) = \frac{?}{?} \times n(\text{N}_2)$$

- A 9.63 mol sample of aluminium is dissolved in excess sulfuric acid. Determine the **moles of sulfuric acid** consumed and the **moles of aluminium sulfate** produced.



- A small **spirit burner** of the type used in camping, contains 200 mL of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), which is equivalent to 3.41 moles of it. Find the **moles of oxygen** used during its complete combustion.



- Propane is commonly used for **gas barbeques**. A particular cylinder contains 4.5 kg of propane. If the gas is pure propane ( $\text{C}_3\text{H}_8$ ), determine the **molar amounts** of **carbon dioxide** and **water** produced from its complete combustion.



- Hydrofluoric acid** (see border note) cannot be stored in glass containers as it has the ability to dissolve the silicate compounds of which glass is composed. The following equation shows how hydrofluoric acid dissolves sodium silicate ( $\text{Na}_2\text{SiO}_3$ ).

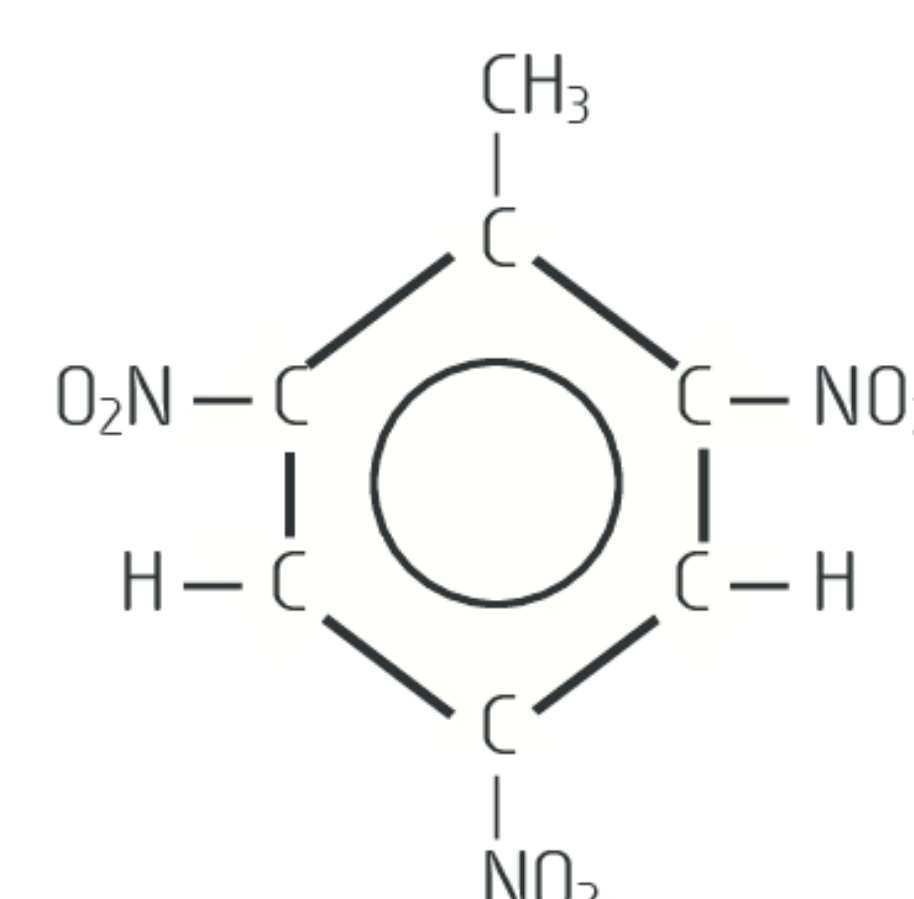


- How many **moles of sodium silicate** can be dissolved by 3.72 g of  $\text{HF}$ ?
- How many **moles of sodium fluoride** are formed when 16.77 g of  $\text{Na}_2\text{SiO}_3$  dissolves by the action of excess  $\text{HF}$ ?
- Determine the number of **moles of  $\text{H}_2\text{SiF}_6$**  formed when 82.59 g of  $\text{HF}$  reacts with excess sodium silicate.

- Hydrogen gas is produced in the laboratory by reacting zinc with hydrochloric acid.



- What **mass of zinc** is needed to produce  $9.25 \times 10^{-2}$  g of hydrogen gas?
- What **mass of zinc chloride** in **mg** is formed when  $7.00 \times 10^{-3}$  g of zinc is used?



**FIGURE 2** A single molecule of **TNT** (**trinitrotoluene**) consists of three nitro groups ( $\text{NO}_2$ ) and one methyl group ( $\text{CH}_3$ ) attached to a flat hexagonal ring of six carbon atoms. TNT was first prepared in 1863 by the German chemist Joseph Wilbrand. Today TNT is a widely used explosive. It has the advantage over other explosives that it is quite insensitive to rough handling, reducing the risk of unexpected explosions.

The large volume of gas produced from its detonation (see equation) contributes to its explosive effect.



**Hydrogen fluoride's** ( $\text{HF}$ ) ability to readily dissolve silicates allows it to be used for such things as etching glass and dissolving mineral samples for chemical analysis. It should only be used with appropriate safety equipment as it is dangerously corrosive and poisonous.

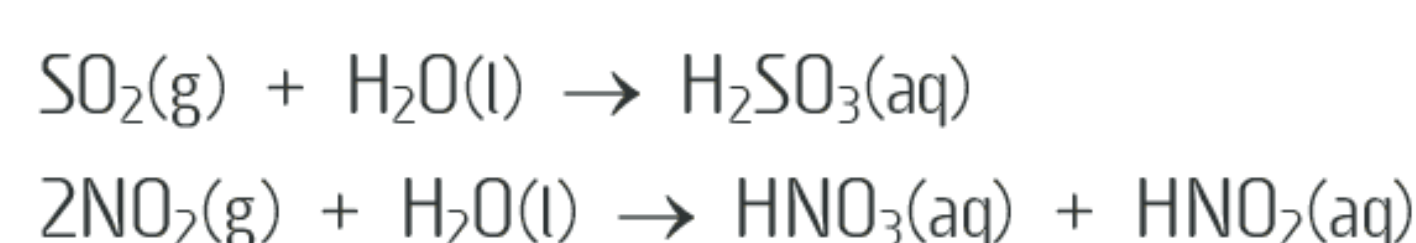
Hydrogen fluoride is readily absorbed through skin contact and can interfere with the nervous system, cause deep tissue burns and dissolve bone. Its effects are not always immediate so medical treatment should be sought urgently upon exposure. This can help minimise injury.





**FIGURE 3** The Tower of the Winds clocktower can be found in Athens. It is dated at around 50 BC. Acid rain can damage limestone buildings like this as well as being harmful to plants and aquatic organisms.

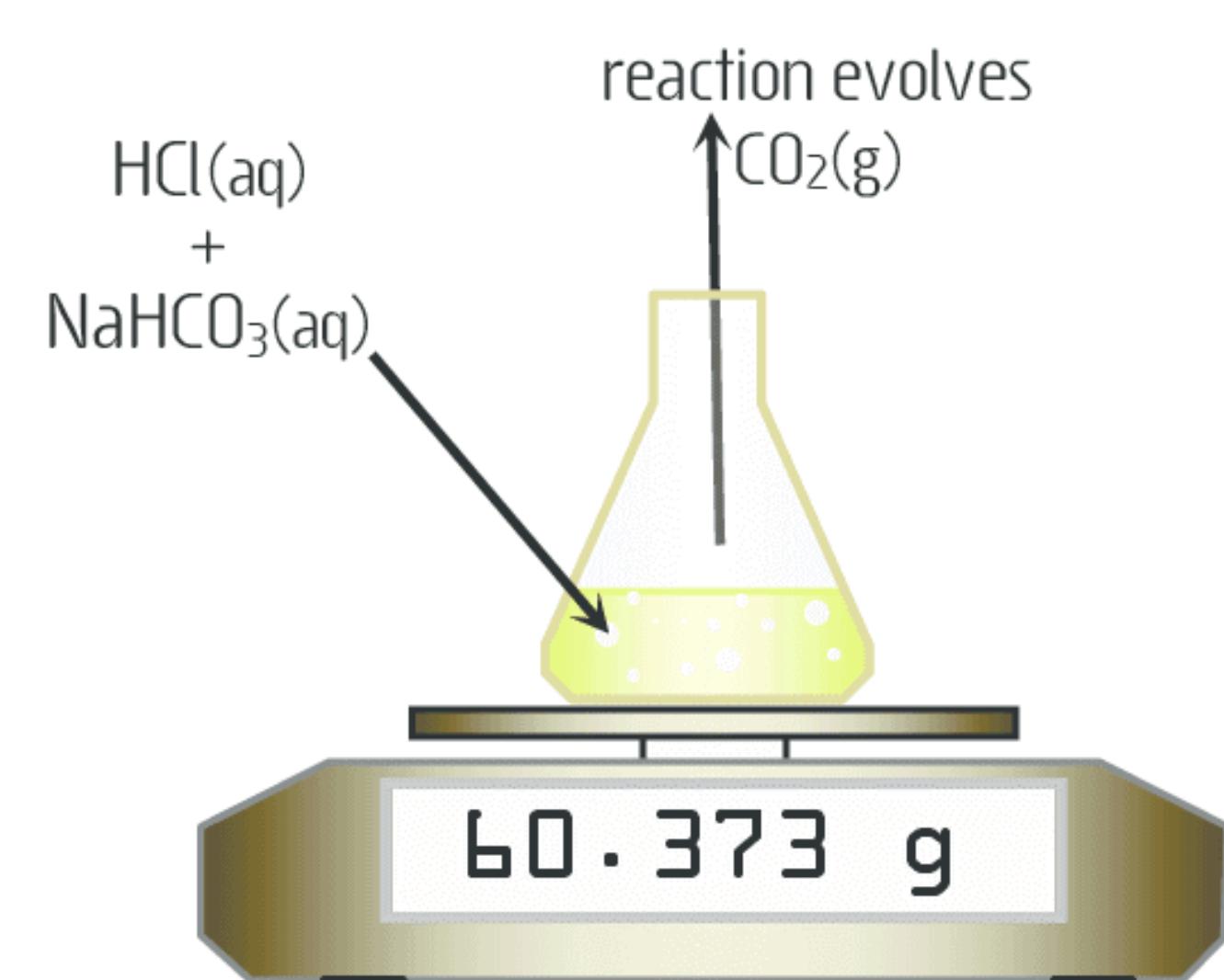
Acidic rain is produced when atmospheric pollutants like sulfur oxides and nitrogen oxides dissolve in rain water, eg:



These gases occur naturally in the atmosphere as a result of volcanoes, lightning and biological processes. In recent years however, their concentrations have increased as a result of emissions from motor vehicles, coal power generation and mineral processing.

**%Purity:** To find the percentage purity of a compound in a mixture:

$$\% \text{purity} = \frac{m(\text{compound in mixture}) \times 100}{m(\text{mixture})}$$



**FIGURE 3** Carbon dioxide has a very low solubility in warm acid solutions like the reaction mixture involved in this experiment. So as the gas  $\text{CO}_2$  is formed it escapes from the reaction mixture. The loss of mass in the reaction mixture can be assumed to be equal to the mass of  $\text{CO}_2$  produced.

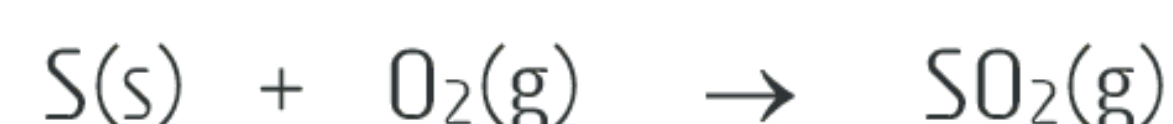
**Systematic error** can occur in this procedure if vigorous fizzing leads to spattering and the resulting loss of solution from the flask. This will cause the weight loss to be consistently greater than it should be.

Are your answers sometimes just a little bit off those quoted in the back of the book?

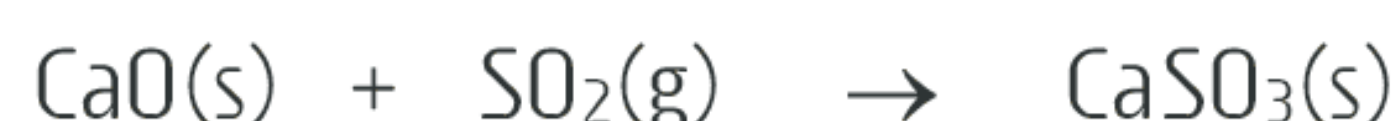


When performing a multi-step calculation always carry the full number into later parts of the calculation. Only round off to the appropriate number of significant figures at the end of your calculation.

7. The gas sulfur dioxide is a major atmospheric pollutant which gives rise to **acid rain**. (See Fig 3.) Fuels such as coal, petrol and diesel often contain impurities in the form of sulfur or its compounds. It has been estimated the combustion of such fuels results in the formation of about 29.5 million tonnes of sulfur dioxide annually. Assume the sulfur dioxide is formed according to the equation below and answer the questions that follow.



- How many **moles of sulfur** are contained in these fuels?
- In coal fired power stations the polluting sulphur dioxide gas can be removed by passing the smoke stack exhaust gases through a spray of slurried lime ( $\text{CaO}$ ) inside a 'wet scrubber'. (See Fig 4 p155.) The following reaction occurs.



Assume 75% of the sulphur dioxide produced annually comes from coal fired power stations and determine the **mass of lime** required to remove the resulting  $\text{SO}_2(\text{g})$ .

- Lime is typically produced by heating calcium carbonate (from marine shells or limestone) in a hot kiln. Write an equation for this reaction and use this to **justify** the statement, "lime production is a major greenhouse gas contributor"

8. An experiment to determine the % composition of  **$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$**  in a brand of **washing soda** involved decomposing a 3.312 g sample of it according to the reaction shown. This resulted in the formation of 0.4959 g of carbon dioxide.



- From the mass of carbon dioxide formed, find the **mass of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$**  present in the 3.312 g sample of washing soda.
- Determine the **% purity** of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  in the washing soda. See the border note at left for help on calculating the % purity of a substance. **(E)**

9. The **purity** of a sodium hydrogen carbonate sample can be found by experiment. In such an exercise Matthew added a carefully weighed sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) sample to a conical flask containing a concentrated hydrochloric acid solution. The recorded data is shown here. (See Fig 3.)



mass of impure $\text{NaHCO}_3$ .....	4.362 g
mass of flask + $\text{HCl}(\text{aq})$ solution .....	57.982 g
mass of flask + $\text{HCl}(\text{aq})$ solution + impure $\text{NaHCO}_3$ after reaction .....	60.373 g

- Determine the **mass of  $\text{CO}_2(\text{g})$**  that was formed. You may assume the weight loss of the flask and its contents is entirely due to evolution of  $\text{CO}_2(\text{g})$ . (See Fig 3.)
- Use your answer from (a) to find the **mass of sodium hydrogen carbonate** ( $\text{NaHCO}_3$ ) actually present in the impure measured sample.
- What is the **% purity** of  $\text{NaHCO}_3$  in the sodium hydrogen carbonate sample? **(E)**
- If the experiment is not conducted carefully, the weight loss in the reaction mixture will exceed the mass of carbon dioxide that is produced. **Explain** how this could happen and how it could be avoided.
- What type of **error** is this, systematic or random? Briefly **justify** your answer.

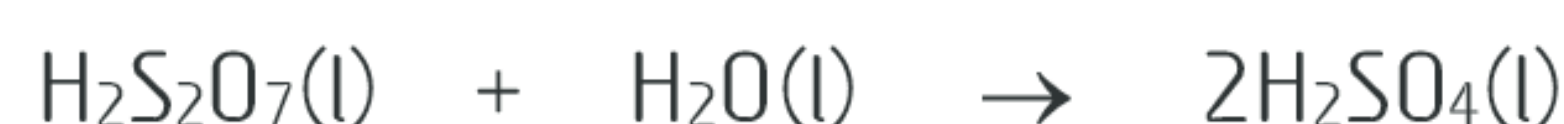
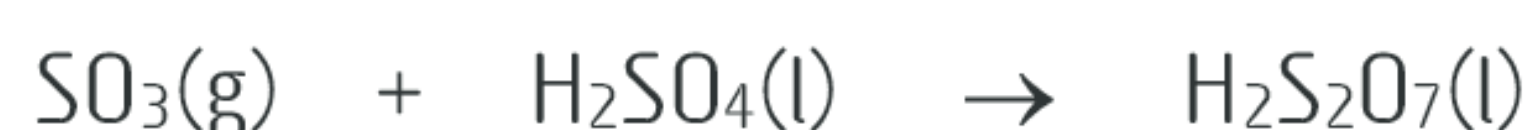
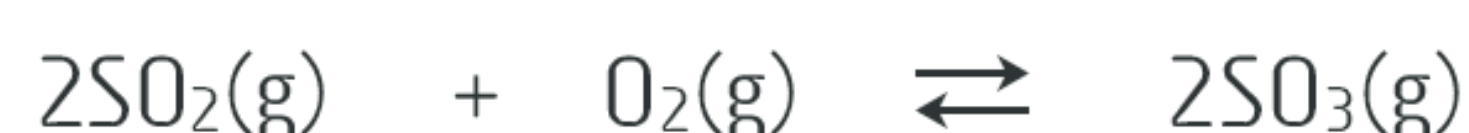
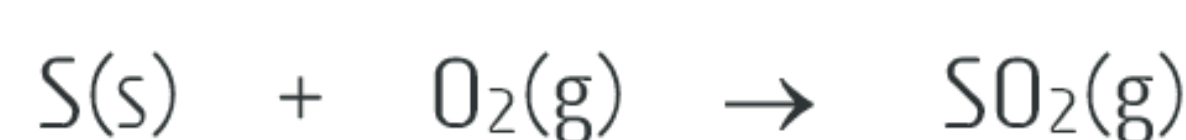
10. The preparation of oxygen in the laboratory can be conveniently achieved by the catalytic decomposition (using  $\text{MnO}_2$ ) of **hydrogen peroxide**.



- What **mass of hydrogen peroxide** is needed to produce 3.47 g of oxygen gas?
- What **mass of hydrogen peroxide solution** is needed if the solution contains 18.5% by weight of hydrogen peroxide? **(E)**

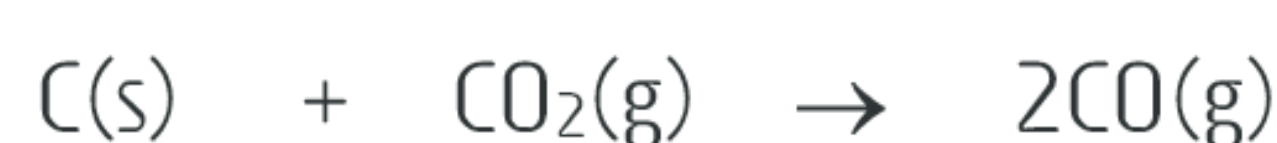


11. Four reactions involved in the manufacture of **sulfuric acid** (Fig 4) are shown here.



- Using appropriate means, add the four equations to produce a **single equation** showing the formation of sulfuric acid from sulfur. (See 6.4 p45.) **(E)**
- Using this equation, determine the **mass of sulfuric acid** that can be produced from 1.250 tonnes of sulfur. (Note: If you could not complete part (a), see p209 for the balanced equation.)

12. Inside a **blast furnace** for the extraction of **iron** from iron ore, many different reactions take place. One important series of reactions for the extraction of iron is shown here. **(E)**



- Write an **overall equation** showing the formation of Fe from  $\text{Fe}_2\text{O}_3$ . (See 6.4 p45.)
- Assuming no other reactions are involved, determine the **minimum mass of carbon** needed for every tonne of iron ore if the ore contains 97%  $\text{Fe}_2\text{O}_3$  by mass.



**FIGURE 4** Pure **sulfuric acid** is a viscous liquid that readily dissolves in water to form a strongly acidic solution. It finds great application in industry, agriculture and around the home. The lead acid battery used in most motor vehicles contains a concentrated sulfuric acid solution. Most of the sulfuric acid manufactured in Australia is used in mineral processing and for the manufacture of superphosphate fertiliser.

## 11.4 Mass to volume calculations

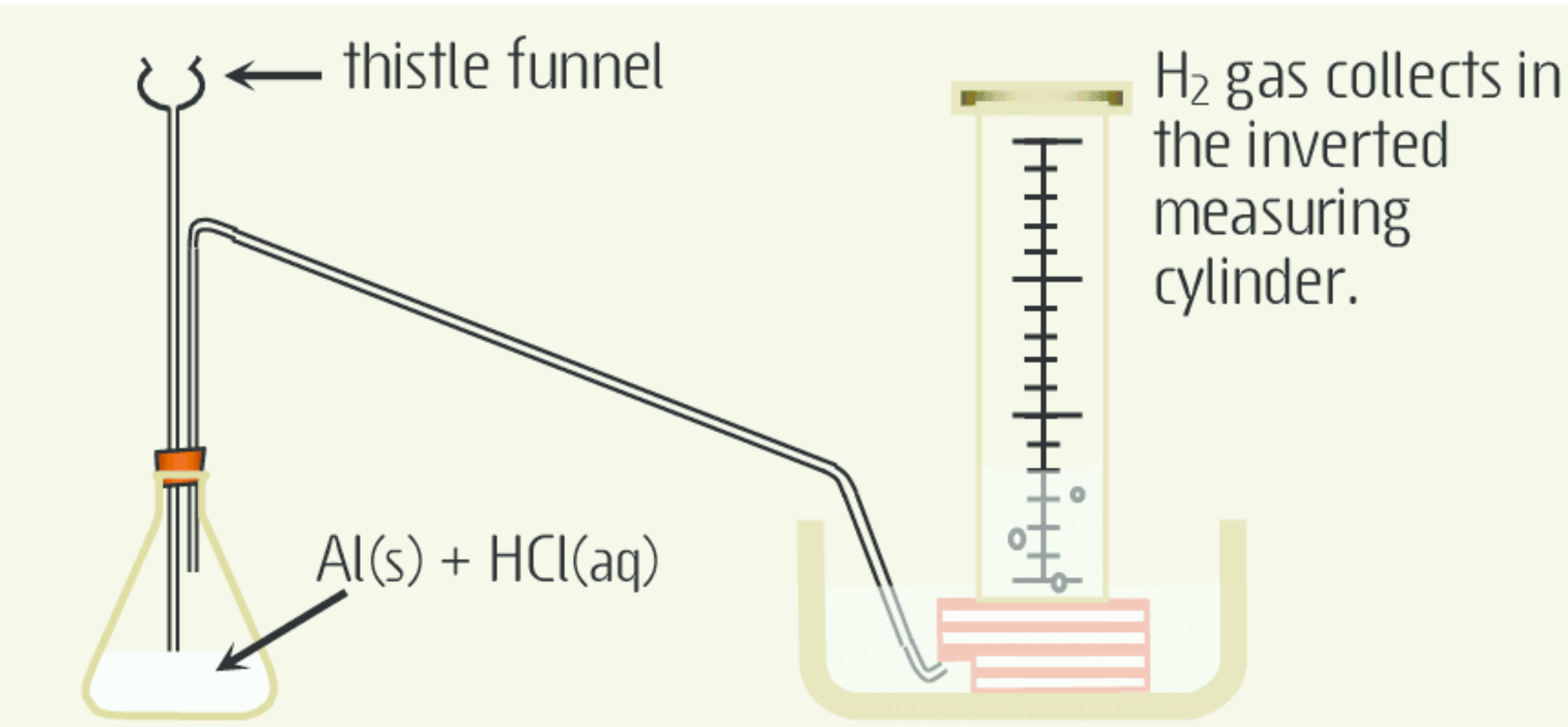
As discussed earlier (see border note) the volume occupied by a gas is related to the molar amount of gas and does not depend on the chemical composition of the gas, thus:

$$V_{\text{stp}} = n(\text{gas}) \times 22.71$$

where:  $n(\text{gas})$  = the moles of gas (mol)  
 $V_{\text{stp}}$  = the STP volume of gas in litres (L)

Using this relationship it is possible to find the volume of a gas involved in a chemical reaction from the mass of another reagent.

**EXAMPLE 5** Excess aluminium (Al) reacts with 1.22 g of hydrochloric acid (HCl) as shown here. What volume of hydrogen gas is formed when measured at STP?



$$n(\text{HCl}) = \frac{m}{M} = \frac{1.22}{36.46} = 3.35 \times 10^{-2} \text{ mol}$$

Find the moles of HCl from the given mass.

$$n(\text{H}_2) = \frac{3}{6} \times n(\text{HCl}) = \frac{3}{6} \times 3.35 \times 10^{-2} = 1.67 \times 10^{-2} \text{ mol}$$

The molar amount of  $\text{H}_2$  involved in the reaction is half (3/6) the molar amount of HCl.

$$V(\text{H}_2 \text{ stp}) = n \times 22.71 = 1.67 \times 10^{-2} \times 22.71 = 0.380 \text{ L}$$

Since at STP the volume of one mole of gas is 22.71 L.

**STP** (Standard temperature and pressure) refers to 100.0 kPa and 273.15 K (0 °C). When a gas volume is measured at these conditions it is possible to determine the molar amount of gas as every 22.71 L corresponds to one mole of it.

This is true for any gas irrespective of its chemical make-up.

Attempt Set 18 # 1, 2 and 3.



## 11.5 Volume to mass calculations

If the volume of a gas involved in a chemical reaction is known then this can be used to determine the mass of other substances involved in the reaction. In order to do this it is essential to convert the given volume of gas to an equivalent molar amount.

$$n(\text{gas}) = \frac{V_{\text{stp}}}{22.71} \quad \text{where: } V_{\text{stp}} = \text{the STP volume of gas in litres L}$$

$$n = \text{the moles of gas in mol}$$

**EXAMPLE 6** Excess hydrochloric acid reacts with a limited amount of Al producing 3.98 L of hydrogen gas measured at STP. What mass of Al was used in the reaction?



$$n(\text{H}_2) = \frac{V_{\text{(stp)}}}{22.71} = \frac{3.98}{22.71} = \mathbf{0.175 \text{ mol}}$$

Since at STP one mole of gas occupies 22.71 L.

$$n(\text{Al}) = \frac{2}{3} \times n(\text{H}_2) = \frac{2}{3} \times 0.175 = \mathbf{0.117 \text{ mol}}$$

The coefficient of H<sub>2</sub> is three, while that of Al is two, thus the molar amount of Al is two thirds (2/3) that of H<sub>2</sub>.

$$m(\text{Al}) = n \times M = 0.117 \times 26.98 = \mathbf{3.15 \text{ g}}$$

Convert the moles of Al to an equivalent mass.

Complete Set 18.

## Set 18 Stoichiometry with mass and gas volumes

- In some vehicles the safety **air bag** is inflated by the rapid decomposition of the compound **sodium azide** (NaN<sub>3</sub>). The impact of collision triggers the reaction shown.



A particular airbag contains 12 g of sodium azide. What **volume** (STP) would the air bag inflate to on collision?

- Cellular respiration**, (see border note) releases energy from sugars like glucose. The overall equation for the respiration of glucose is shown here.



- Determine the **STP volume of oxygen** used to metabolise 8.5 g of glucose, the amount in a typical barley sugar lolly.
- Approximately what **number of breaths** would be needed to supply this much oxygen to your body cells? (**See border note.**)

- Water can be decomposed to form hydrogen gas and oxygen gas by a technique known as **electrolysis**. In this process an electric current passes through water between a pair of electrodes. The resulting reaction is shown here.



- What **volume** of **hydrogen gas** and **oxygen gas** would be formed by decomposing a glass full of water? (Assume a mass of 150 g of H<sub>2</sub>O.) All volumes are measured at STP.
- The 150 g of H<sub>2</sub>O decomposed in part (a) has a volume of 150 mL. However, while the gaseous products also have a combined mass of 150 g they occupy a much greater volume, around 285 L or 1900 times the volume of the decomposed water. Use your knowledge of the kinetic theory to **account** for this large change in volume.

- As carbon dioxide is an acidic gas it readily reacts with basic solutions to form carbonate compounds. What **mass of sodium carbonate** is formed when 1.55 × 10<sup>2</sup> L of carbon dioxide gas measured at STP is absorbed into a sodium hydroxide solution as shown?



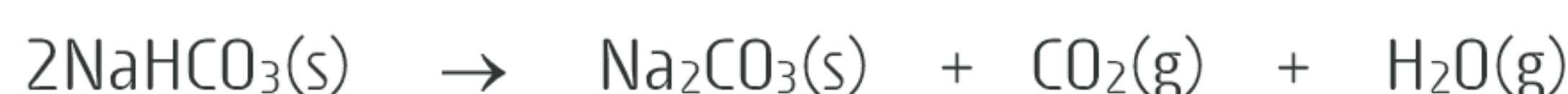
**Respiration** should not be confused with **breathing**. They are two quite different processes. Cellular respiration is a metabolic process (involves a chemical change) where food and oxygen are converted to carbon dioxide and water. During respiration, energy is released allowing body cells to carry out various life processes.

Breathing involves the lungs and diaphragm working together to inhale and exhale air. Breathing allows oxygen gas to be absorbed into the blood stream while carbon dioxide and water are excreted. Oxygen is then available to body cells for the chemical process of respiration.

During normal breathing an adult will, on average, inhale 0.50 L of air per breath. Although oxygen makes up 21% of the inhaled air only a quarter (25%) of this is actually absorbed into the blood stream from each breath.



- 5 The rising of pastries, cakes and bread products is largely due to the addition of **baking soda** ( $\text{NaHCO}_3$ ) to the cake mix or dough. When baked, the baking soda decomposes, releasing carbon dioxide gas. This causes the formation of carbon dioxide bubbles in the dough making it rise (inflate). The baking of a particular loaf of bread causes its volume to inflate by 1.17 L (STP value). What **minimum mass of baking soda** is needed to achieve this? Assume the increase in bread volume is due solely to the carbon dioxide gas produced from the decomposition of baking soda.



- 6 Nitrogen, phosphorus and potassium are the three major elements needed for healthy plant growth. (See Fig 5.) **Urea**  $[(\text{NH}_2)_2\text{CO}]$  is an important nitrogen based **fertiliser**. It can be produced by the direct reaction of ammonia with carbon dioxide at a moderate temperature and a high pressure.



What **mass of urea** can be formed by the complete reaction of  $5.00 \times 10^3$  L (STP) of ammonia and excess carbon dioxide?

- 7 A typical **butane gas lighter** can release 6.50 L of butane gas ( $\text{C}_4\text{H}_{10}$ ) measured at room conditions of 102 kPa and 27 °C. Adjusted for STP conditions this equates to a butane volume of 6.03 L. Determine the **STP volume of oxygen** needed to burn this fuel.



**FIGURE 5** Nitrogen (N), phosphorus (P) and potassium (K) are the three major soil based plant nutrients. For plants to grow successfully these nutrients must be available in the soil in a water soluble form. Ammonium nitrate (35%N), ammonium sulfate (21%N) and urea (47%N) are common nitrogen fertilisers. These all release water soluble ammonium ions when added to moist soil. Plants can gain the nitrogen they need by absorbing ions like ammonium ions  $[\text{NH}_4^+(\text{aq})]$  or nitrate ions  $[\text{NO}_3^-(\text{aq})]$  through their root system.

## 11.6 Limiting reagents: How much is enough (E)

In most situations where a chemical reaction is performed one of the two reagents will be present in **excess**, ie some of it remains when the reaction is finished. The reagent that is fully consumed is known as the **limiting reagent**. This reagent determines the amount of all other substances used or produced in the reaction. The concept of a limiting reagent is similar to many everyday situations. (See Fig 6.)



**Note:** Sections identified in this text with an **(E)** may be considered an extension to the Chemistry Course Units 1 and 2. These cover content considered desirable for developing a good understanding of the Chemistry Course Units 1 or 2 or they lead into content covered later in Chemistry Course Units 3 or 4. Their inclusion is for the convenience of teachers and students.

**FIGURE 6 A party problem?** You are having friends over for a party and need to make as many ham sandwiches as possible. You have 24 slices of bread and 16 slices of ham. Each sandwich needs two slices of bread and one slice of ham.

As a result, there will be enough ingredients for only 12 ham sandwiches with 4 left over slices of ham.

The **limiting ingredient** here was the **bread**. It determined how many sandwiches were able to be made and how much ham was used. The ham was the **excess ingredient**.

## 11.7 Identifying the limiting reagent (E)

If the amount of both reagents in a reaction mixture is known, it is important to determine which one is the limiting reagent. One method for doing this is to compare the **actual ratio** of the molar amounts present in the reaction mixture to the **stoichiometric ratio** of the reagents shown in the balanced equation. (See Example 7.) The limiting reagent may alternatively be found by a method of **trial and error**. (See Example 8.)



$$\frac{24.5}{9.87}$$

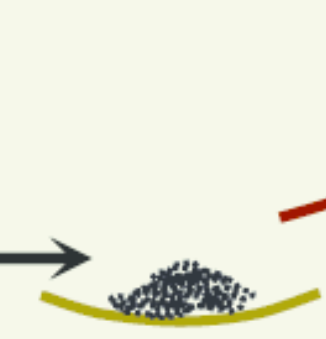
numerator

denominator

**EXAMPLE 7** Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.



9.87 mol of  
aluminium  
metal



24.5 mol of  
hydrochloric  
acid

$$\text{actual ratio} = \frac{n(\text{HCl})}{n(\text{Al})} = \frac{24.5}{9.87} = \mathbf{2.48}$$

Find the actual mole ratio of the two reagents using the amounts given. Either reagent can be the numerator.

$$\text{stoichiometric ratio} = \frac{n(\text{HCl})}{n(\text{Al})} = \frac{6}{2} = \mathbf{3}$$

Find the stoichiometric mole ratio using the equation coefficients. Keep the same numerator.

actual ratio < stoichiometric ratio

∴ **HCl is the limiting reagent.**

If the actual ratio (AR) is greater than the stoichiometric ratio (SR) then the **denominator** (see border note) is the limiting reagent. Alternatively if the AR is less than the SR then the numerator is the limiting reagent.

**EXAMPLE 8** Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.



Let Al be the limiting reagent, then:

Either reagent, Al or HCl is assumed to be the limiting reagent.

$$n(\text{HCl}) = \frac{6 \times n(\text{Al})}{2} = \frac{6 \times 9.87}{2} = \mathbf{29.6 \text{ mol}}$$

Using the assumed limiting reagent, calculate the required amount of the other reagent.

Hence, insufficient HCl for the complete reaction of Al. Thus **HCl is the limiting reagent.**

29.6 mol of HCl would be needed for the complete reaction of 9.87 mol of Al. As only 24.5 mol of HCl is present then it will be fully consumed before the Al runs out.

Attempt Set 19 #1.

## 11.8 Mass to mass calculations with a limiting reagent (E)

When the mass of both reagents in a chemical reaction is given, the **limiting reagent** must first be identified. This can be achieved either by comparing the **actual ratio** to the **stoichiometric ratio** of reagents or by a **trial and error** method. (See examples 7 and 8.) The limiting reagent is then used to calculate the amount of any other substance involved in the reaction.

**EXAMPLE 9** A student adds a 10.50 g piece of zinc metal to a solution containing 10.50 g of hydrochloric acid. Find the mass of zinc chloride formed and determine the amount of excess reagent left unused.



$$n(\text{HCl}) = \frac{m}{M} = \frac{10.50}{36.46} = \mathbf{0.2880 \text{ mol}}$$

Find the moles of HCl from the given mass.

$$n(\text{Zn}) = \frac{m}{M} = \frac{10.5}{65.38} = \mathbf{0.1606 \text{ mol}}$$

Find the moles of Zn from the given mass.

Let Zn be the limiting reagent

Either reagent, Zn or HCl is assumed to be the limiting reagent.

$$n(\text{HCl}) = \frac{2}{1} \times n(\text{Zn}) = \frac{2}{1} \times 0.1606 = \mathbf{0.3212 \text{ mol}}$$

Use the assumed limiting reagent (Zn) to find the required amount of HCl.

Insufficient HCl for complete reaction of Zn

∴ **HCl is the limiting reagent**

Since there is only 0.2880 mole of HCl and 0.3212 mole would be needed to completely react with the 0.1606 mole of Zn.

$$n(\text{ZnCl}_2) = \frac{1}{2} \times n(\text{HCl}) = \frac{1}{2} \times 0.2880 = \mathbf{0.1440 \text{ mol}}$$

Use the limiting reagent to find the amount of ZnCl<sub>2</sub> formed.

$$m(\text{ZnCl}_2) = n \times M = 0.1440 \times 136.28 = \mathbf{19.62 \text{ g}}$$

Convert n(ZnCl<sub>2</sub>) to an equivalent mass.

$$n(\text{Zn used}) = \frac{1}{2} \times n(\text{HCl}) = \frac{1}{2} \times 0.2880 = \mathbf{0.1440 \text{ mol}}$$

Use the limiting reagent to find the amount of Zn used.

$$m(\text{Zn used}) = n \times M = 0.1440 \times 65.38 = \mathbf{9.415 \text{ g}}$$

Convert the moles of Zn used to an equivalent mass.

$$m(\text{Zn remaining}) = m(\text{Zn original}) - m(\text{Zn used}) \\ = 10.50 - 9.415 = \mathbf{1.09 \text{ g}} \text{ (2DP, ie 3 SF)}$$

Originally 10.50 g of Zn was added and only 9.415 g is consumed by the HCl.

Complete Set 19.



## Set 19 Limiting reagent calculations (E)

1. The preparation of **chlorine** in the laboratory is achieved by the reaction between concentrated hydrochloric acid and manganese(IV) oxide (manganese dioxide). **(E)**



In an experiment, a group of students performed this reaction in a fume hood. They used different molar amounts of hydrochloric acid and manganese dioxide. In each case determine the **limiting reagent**.

- 0.600 mol HCl and 0.251 mol of  $\text{MnO}_2$
- $7.08 \times 10^{-2}$  mol HCl and  $1.92 \times 10^{-2}$  mol of  $\text{MnO}_2$
- 0.655 mol HCl and 0.142 mol of  $\text{MnO}_2$

2. Sodium carbonate readily reacts with a hydrochloric acid solution.



This reaction is carried out several times using different quantities of each reagent. In each case determine the **limiting reagent** and find the **mass** of NaCl(s) formed. **(E)**

- 5.00 g of  $\text{Na}_2\text{CO}_3$  and 4.00 g of  $\text{HCl}$
- 1.926 g of  $\text{Na}_2\text{CO}_3$  and 1.205 g of  $\text{HCl}$

3. Sodium hydroxide and sulfuric acid react by the neutralisation reaction shown here:



In a particular experiment a solution containing 5.240 g of sodium hydroxide is added to another solution containing 0.1640 mol of sulfuric acid. Determine the mass of sodium sulfate formed. (E)

4. The compound barium sulfate was produced by combining a solution containing  $1.740 \times 10^{-1}$  g of barium nitrate with another solution containing  $9.260 \times 10^{-2}$  g of sodium sulfate. Determine the **mass of barium sulfate** precipitate and the **mass of the excess reagent** that remains after complete reaction. (E)



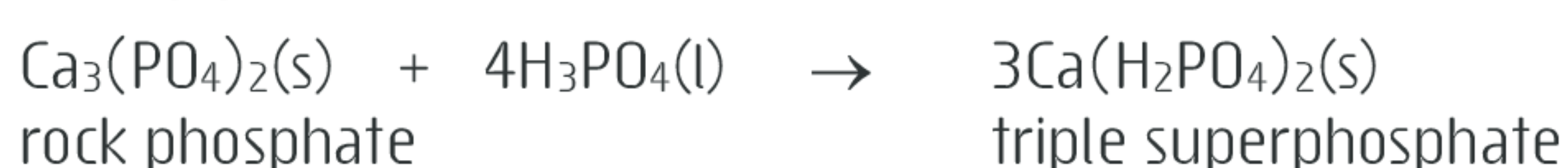
5. Solutions of copper nitrate and potassium carbonate readily react to produce insoluble copper carbonate and a solution of potassium nitrate.



Different amounts of each reagent are combined in several experiments. What **mass of the excess reagent** is left over in each situation? **(E)**

- a. 9.50 g of  $\text{K}_2\text{CO}_3$  and 14.00 g of  $\text{Cu}(\text{NO}_3)_2$   
b.  $3.380 \times 10^{-2}$  g of  $\text{K}_2\text{CO}_3$  and  $5.980 \times 10^{-2}$  g of  $\text{Cu}(\text{NO}_3)_2$

6. Triple superphosphate is a water soluble fertiliser produced by mixing phosphoric acid with insoluble rock phosphate. (See Fig 7.) It is important to add the reagents in the correct stoichiometric ratio so that there is no wastage of rock phosphate and no excess of phosphoric acid in the resulting fertiliser. A particular batch of triple superphosphate is prepared by combining 4.92 tonnes of rock phosphate with 6.67 tonne of phosphoric acid. (E)



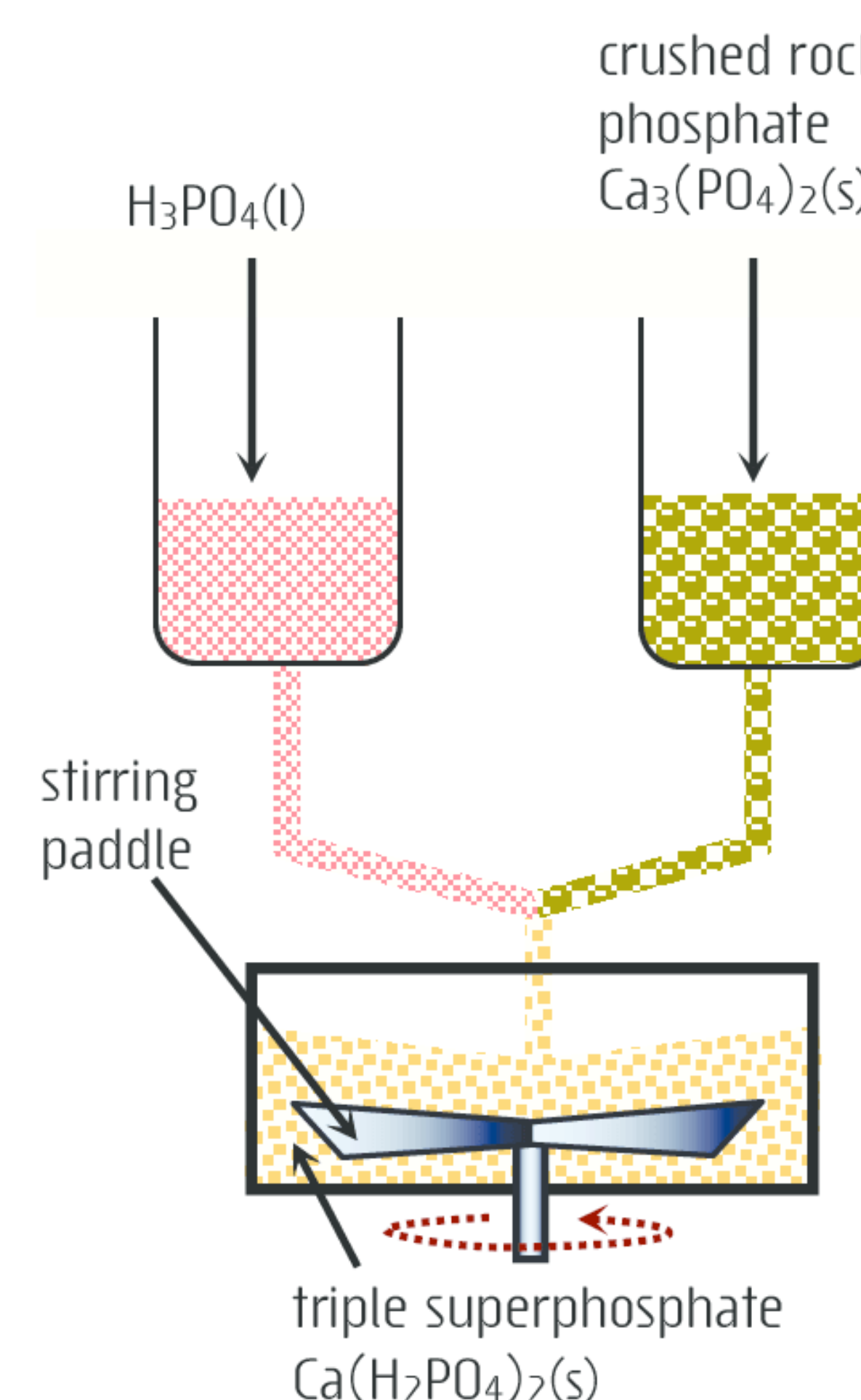
- Determine the **limiting reagent** and calculate **how much more** of this needs to be added so that there is sufficient to completely react with the excess reagent.
- What **mass of triple superphosphate** is formed when the two reagents are present in the stoichiometric equivalent amounts as calculated in (a)?



**Chlorine** is a toxic gas that irritates the eyes, skin and the respiratory system. If this gas is to be produced in the laboratory then suitable ventilation must be used.

Its bleaching and disinfectant properties are used for maintaining hygienic water supplies and swimming pools. The white solid known as '**pool chlorine**' contains compounds like sodium hypochlorite [ $\text{NaClO}(\text{s})$ ] and calcium hypochlorite [ $\text{Ca}(\text{ClO})_2(\text{s})$ ]. These react with water to produce the familiar chlorine ( $\text{Cl}_2$ ) odour found around swimming pools.

**FIGURE 7** Producing water soluble **triple superphosphate** from  $\text{H}_3\text{PO}_4(\text{l})$  and water insoluble rock phosphate  $\text{Ca}_3(\text{PO}_4)_2(\text{s})$ .





# CHAPTER 12 | ORGANIC CHEMISTRY: HYDROCARBONS

## 12.1 Hydrocarbon sources and uses (E)

Hydrocarbons are molecular compounds containing the elements **hydrogen** and **carbon** only. Fossil fuels like **petroleum** (crude oil) and natural gas are the world's major source of hydrocarbons. **Natural gas** consists primarily of methane mixed with ethane and small amounts of propane and butane. Petroleum is a liquid mixture with varying composition and contains literally thousands of different hydrocarbon compounds.

Petroleum refineries use the physical process of **fractional distillation** (Fig 1) to separate the mixture of hydrocarbons from crude oil into 'fractions' that have similar boiling points and molecular mass. These fractions are obtained by vaporising crude oil at temperatures as high as 400 °C, then condensing its vapours at progressively lower temperature ranges. This partial separation relies on the boiling points of hydrocarbon compounds increasing with increasing dispersion forces, ie with increasing molecular mass or number of carbon atoms per molecule. (See p130.)

Some petroleum fractions are used directly while **chemical processes** like steam cracking, catalytic cracking or catalytic reforming (Fig 3 and note p102) are used to produce modified compounds. Ultimately, hydrocarbons are used as fuels, lubricants, solvents and asphalt or converted to other materials such as plastics, synthetic fibres, pharmaceuticals and more.

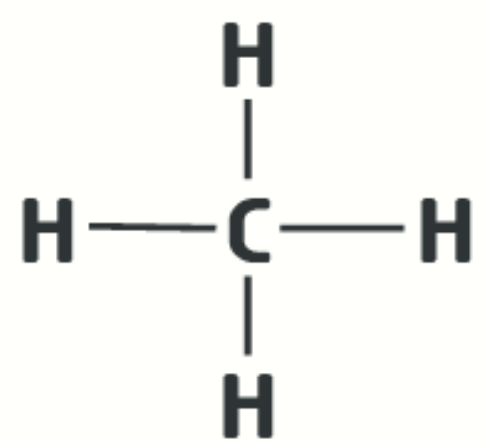

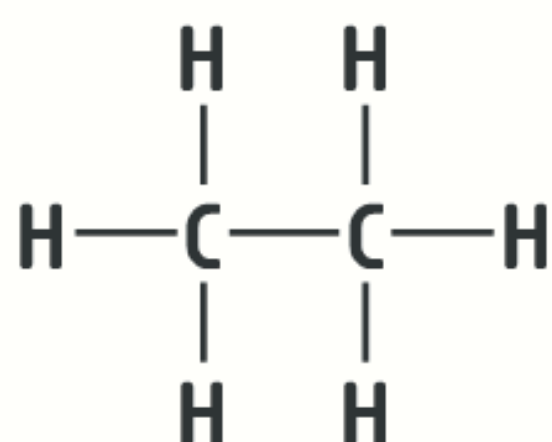
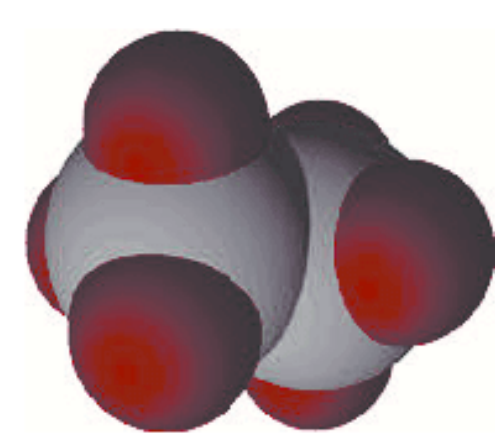
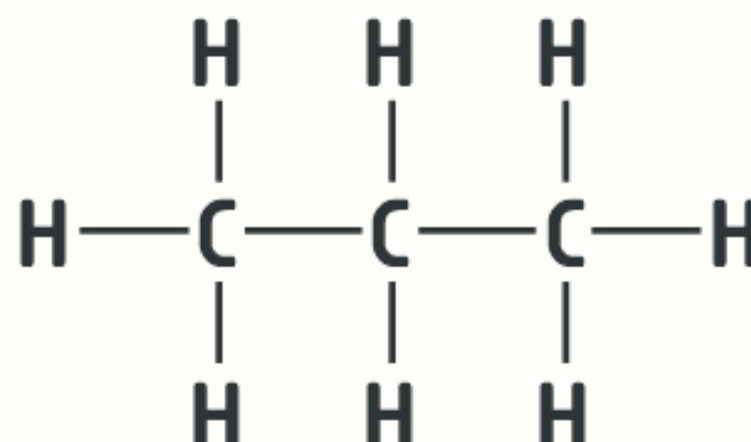
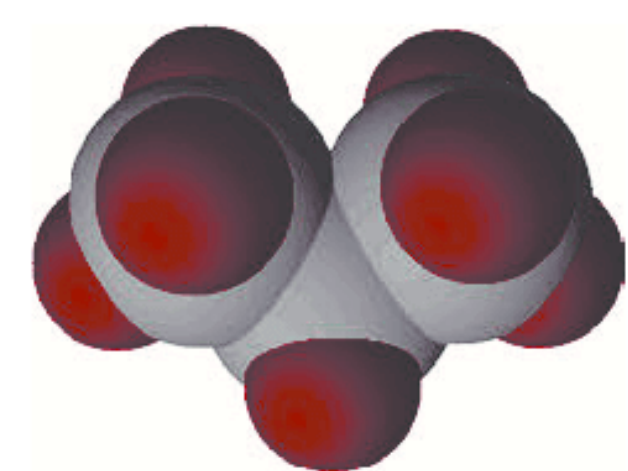
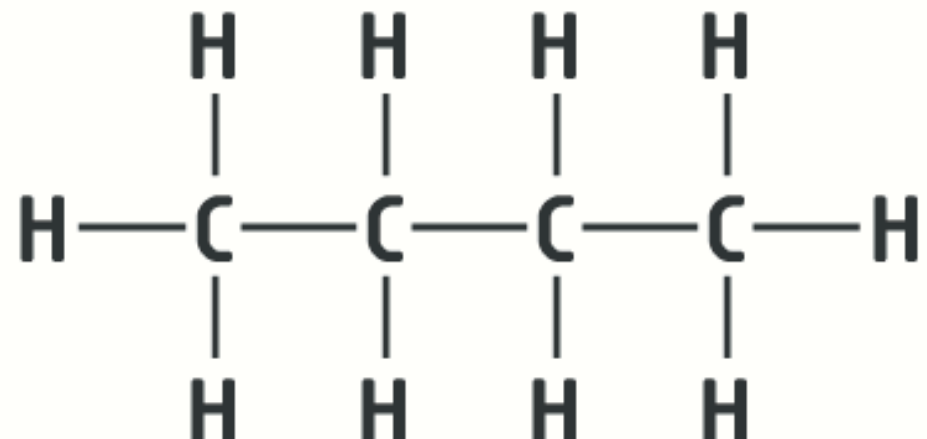
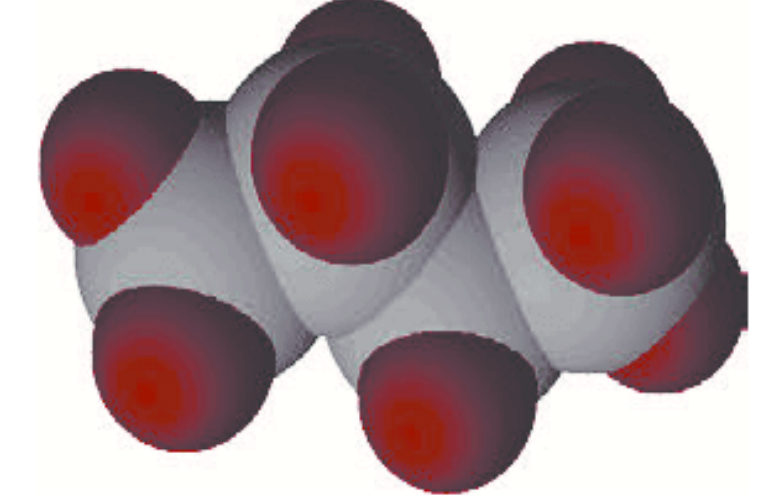
## 12.2 Families of hydrocarbon compounds (E)

Hydrocarbons are classified into various families of compounds based on structural similarities. Some hydrocarbon families include **alkanes**, **alkenes**, **cycloalkanes**, **cycloalkenes** and **aromatics**. We will study some of these families in the following sections.

## 12.3 Alkanes: Structure and nomenclature

Alkanes consist of molecules with the general formula  $C_nH_{2n+2}$ . Their molecules contain **single bonds only** and for this reason are called **saturated** hydrocarbons. Alkane names have the suffix **-ane**. Some alkanes include methane ( $CH_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), butane ( $C_4H_{10}$ ), pentane ( $C_5H_{12}$ ), hexane ( $C_6H_{14}$ ), heptane ( $C_7H_{16}$ ), and octane ( $C_8H_{18}$ ).

TABLE 1 Structure and nomenclature of selected alkanes

Name	Structural formula	Condensed formula	Molecular shape
<b>methane</b> $CH_4$		$CH_4$	
<b>ethane</b> $C_2H_6$		$CH_3CH_3$	
<b>propane</b> $C_3H_8$		$CH_3CH_2CH_3$	
<b>butane</b> $C_4H_{10}$		$CH_3CH_2CH_2CH_3$	

The alkanes shown in Table 1 are all **straight chain** alkanes. Their terminal carbon atoms (ie end ones) are bonded to three hydrogen atoms ( $CH_3$ ) while the inner carbon atoms bond to two hydrogen atoms ( $CH_2$ ). Sometimes alkanes form **branched** structures (see Fig 2) where an inner carbon atom is bonded to three or four carbon atoms and has fewer bonded hydrogen atoms. Structural variations like this contribute to the great variety and number of different alkane compounds, all of the same general formula  $C_nH_{2n+2}$ .

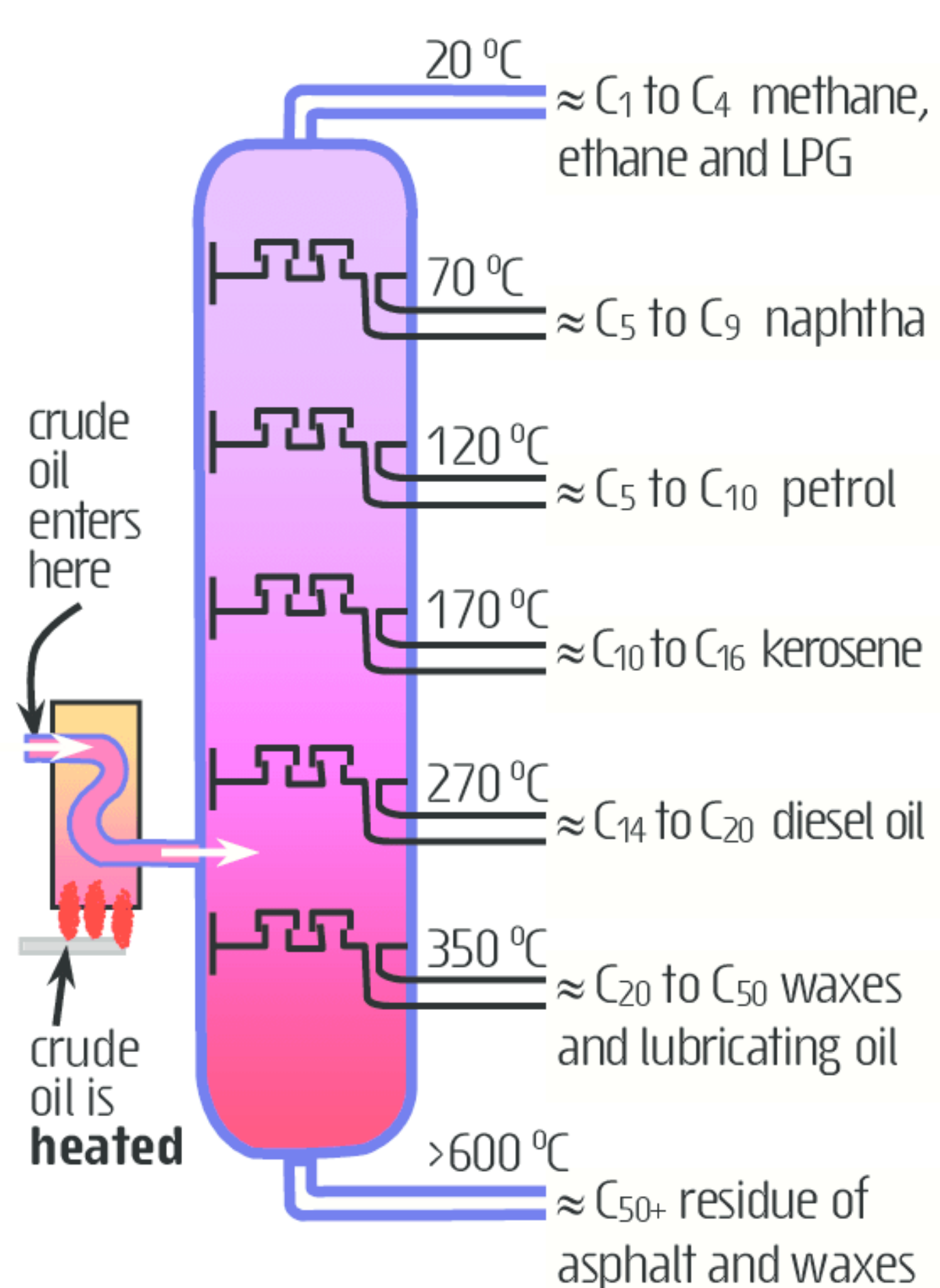


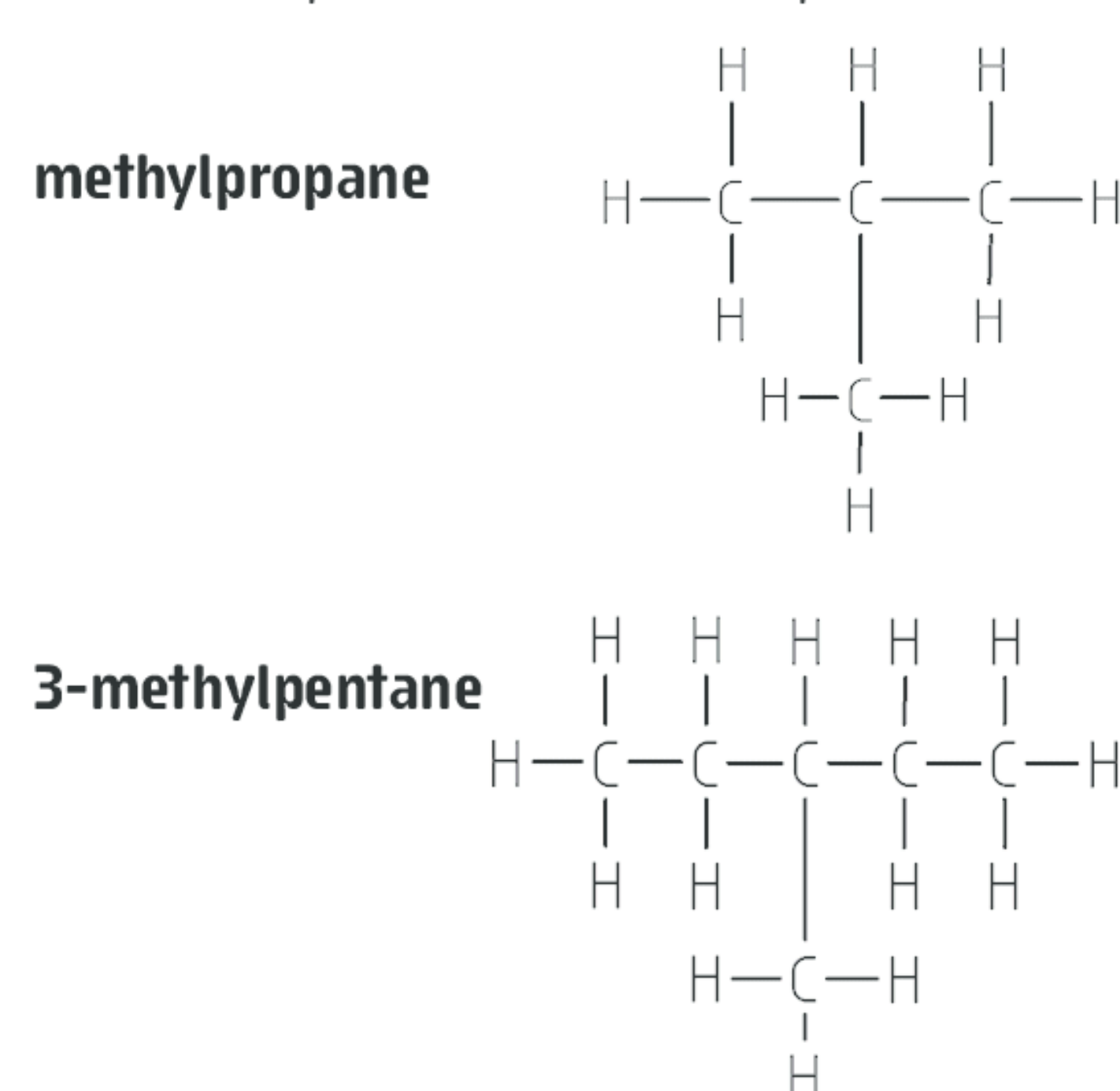
FIGURE 1 Crude oil is separated into various fractions using a fractionating tower like this one. Each **fraction** is a **mixture** of hydrocarbons with its own **boiling point range**. The temperatures and C numbers indicated here for the different fractions are an approximate guide only.

Attempt Set 20 # 1.

The first part of an alkane name indicates the number of carbon atoms in the molecular chain.

**meth**..... 1 carbon atom  
**eth**..... 2 carbon atoms  
**prop** ..... 3 carbon atoms  
**but** ..... 4 carbon atoms  
**pent**..... 5 carbon atoms  
**hex**..... 6 carbon atoms  
**hept**..... 7 carbon atoms  
**oct** ..... 8 carbon atoms  
**non**..... 9 carbon atoms  
**dec** ..... 10 carbon atoms

FIGURE 2 Structures like these **branched alkanes** contribute to the great variety and number of possible alkane compounds.



Attempt Set 20 # 2, 3 and 4.



## 12.4 Alkanes: Structural isomerism (E)

Structural isomers of alkanes are compounds having the same **molecular** formula but a different **structural** formula. This happens when molecules contain the same number and type of atoms but the sequence in which the atoms are bonded is different. (See Table 2.) Structural isomers may have similar chemical and physical properties but they are not identical. (See Fig 3.) Pentane for example boils at 36.1 °C while its structural isomers methylbutane and dimethylpropane boil at 27.9 °C and 9.5 °C respectively.

TABLE 2 Structural and condensed formulas for three structural isomers of C<sub>5</sub>H<sub>12</sub>

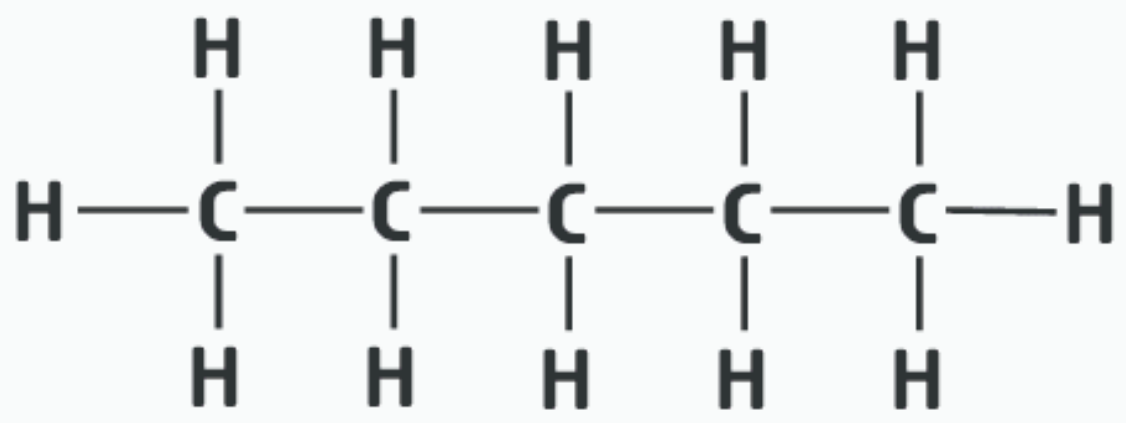
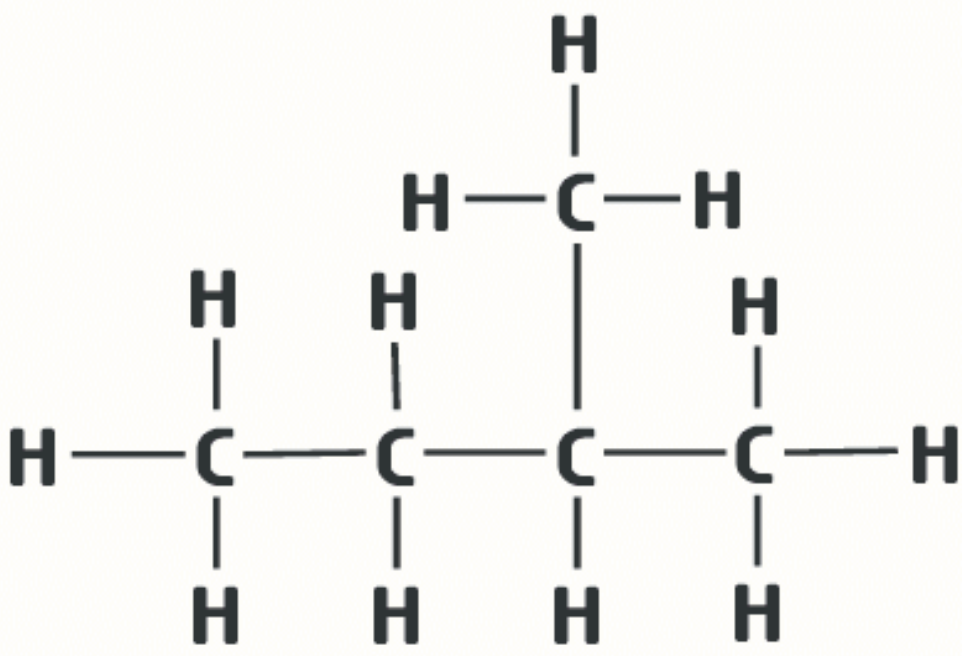
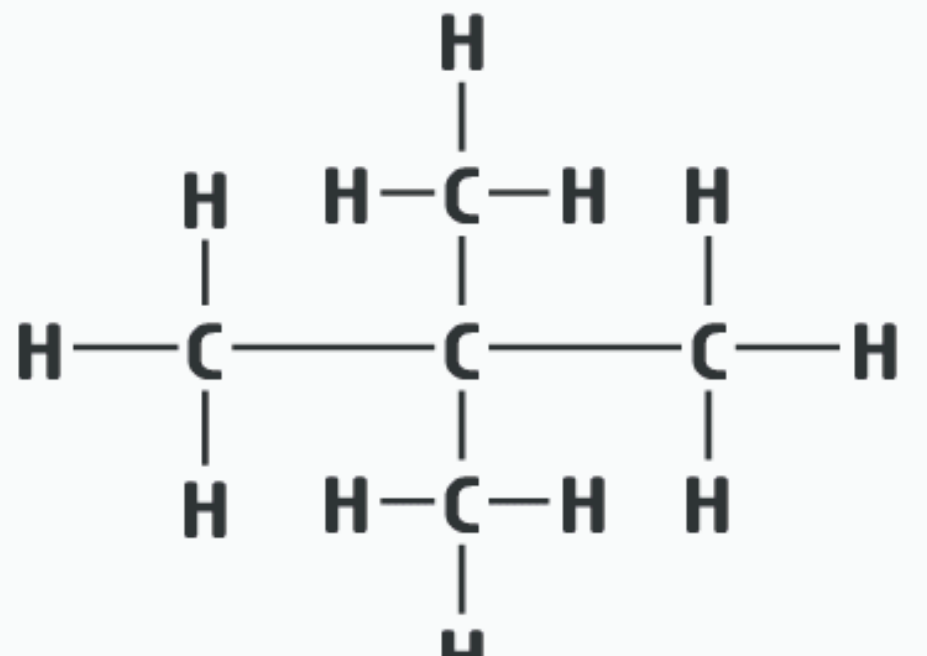
pentane	methylbutane	dimethylpropane
		
CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>	CH <sub>3</sub> —CH <sub>2</sub> —CH(CH <sub>3</sub> )—CH <sub>3</sub>	CH <sub>3</sub> —C(CH <sub>3</sub> ) <sub>4</sub>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>



FIGURE 3 One measure of the combustion characteristics of petrol is its **octane rating**. Depending upon an engine's compression ratio, manufacturers will specify a fuel of a particular octane rating, usually between **87** and **98**. (See p97.)

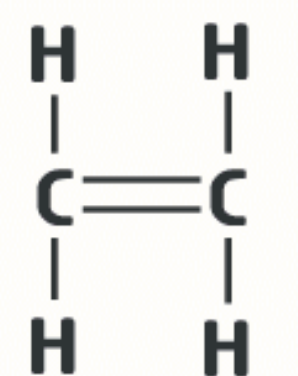
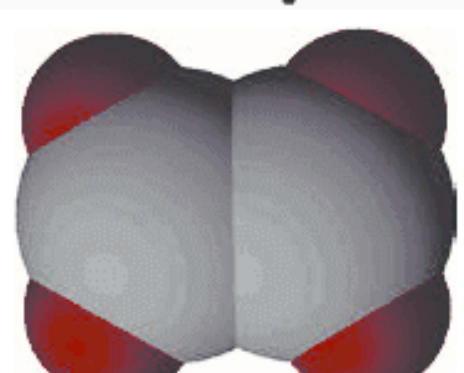
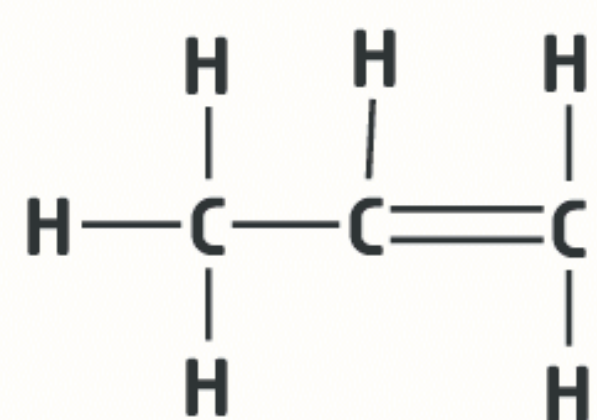
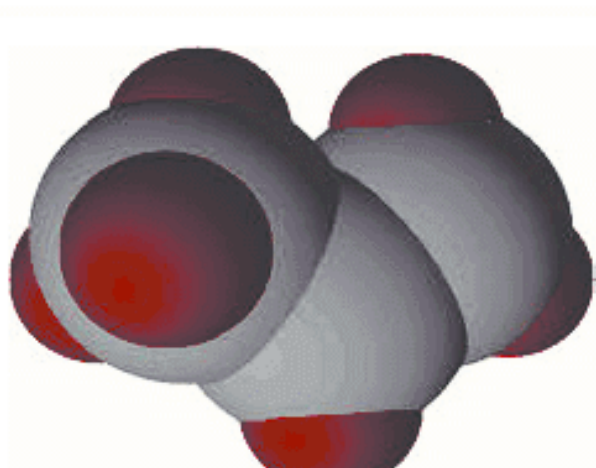
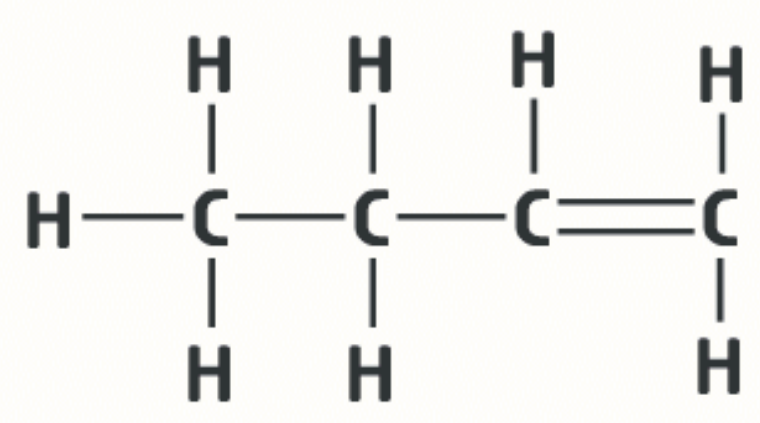
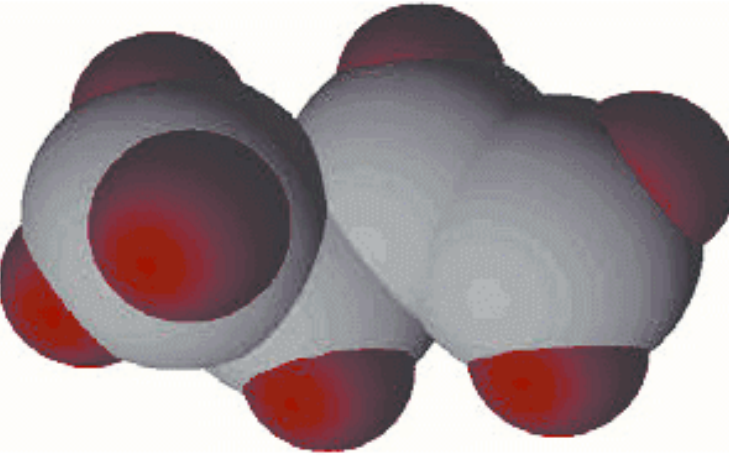
**Catalytic reforming** is one process used in the petroleum industry to produce transport fuels with a higher octane rating. This involves the conversion of **straight chain hydrocarbons** called heavy naphtha, a mixture of molecules with around 6 to 10 carbon atoms, into various **branched isomers** like 2,3,4-trimethyl pentane, a branched isomer of octane. Branched isomers typically have a higher octane rating than straight chain isomers.

Attempt Set 20 # 5.

## 12.5 Alkenes: structure and nomenclature

Alkenes are **unsaturated** hydrocarbons with molecules that contain a carbon to carbon **double bond**. The presence of a double bond means their molecules have two less hydrogen atoms than a corresponding alkane. This is why they are said to be unsaturated. They have the general formula **C<sub>n</sub>H<sub>2n</sub>**. Alkene names have the suffix **-ene**.

TABLE 3 Structure and nomenclature of some alkenes

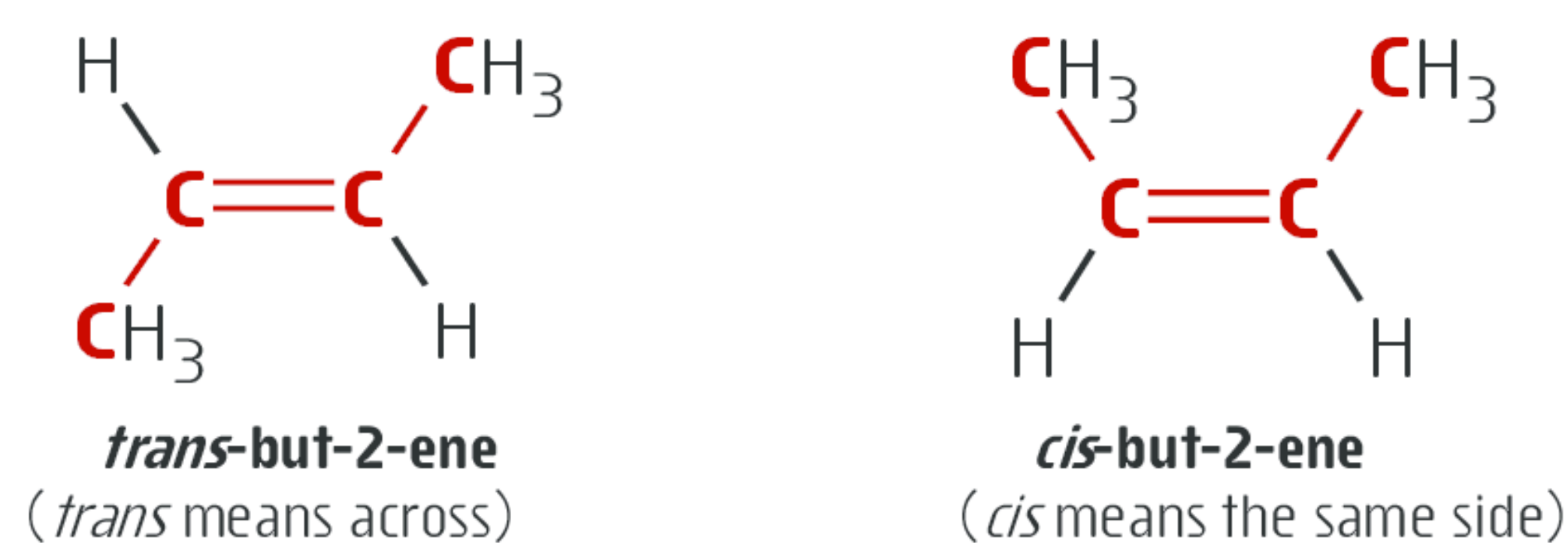
Name	Structural formula	Condensed structural formula	Molecular shape
<b>ethene</b> C <sub>2</sub> H <sub>4</sub>		CH <sub>2</sub> CH <sub>2</sub> or CH <sub>2</sub> = CH <sub>2</sub>	
<b>propene</b> C <sub>3</sub> H <sub>6</sub>		CH <sub>3</sub> CHCH <sub>2</sub> or CH <sub>3</sub> CH = CH <sub>2</sub>	
<b>but-1-ene</b> (1-butene) C <sub>4</sub> H <sub>8</sub>		CH <sub>3</sub> CH <sub>2</sub> CHCH <sub>2</sub> or CH <sub>3</sub> CH <sub>2</sub> CH = CH <sub>2</sub>	

Attempt Set 20 # 6 and 7.

## 12.6 Alkenes: Cis-trans isomerism (E)

Some alkene compounds have **cis-trans isomers** (formerly known as geometric isomers). These are isomers with the same molecular formula and structural formula, ie same sequence of bonding between their atoms, but a **different geometry**. The different geometry is a result of the inability of double bonded carbon atoms to rotate along the axis of their double bond. These geometric forms are known as **cis** and **trans** isomers. (See Fig 5.)

FIGURE 5 These two molecules have the **same sequence** of bonding yet the molecules have a **different geometry**. These substances are the **cis** and **trans** isomers of but-2-ene.



If **either** of the **two** carbon atoms involved in the double bond has **two identical groups** attached to it, then **cis-trans** isomerism will **not** be possible. Thus 1,1-dichloroethene does **not** have **cis-trans** isomerism but 1,2-dichloroethene does.



FIGURE 4 **Fats** and **oils** from animals and plants consist of molecules known as **triglycerides**. These compounds are **NOT** hydrocarbons however they do contain **three carbon chains** as part of each triglyceride molecule. These carbon chains typically have an even number of carbon atoms, usually 12 to 20, in a straight unbranched arrangement.

Liquid triglycerides, like **vegetable oils**, usually contain one or more **double bonds** in these carbon chains. Oils like this are said to be **unsaturated** or **polyunsaturated** (more than one double bond). Olive oil, shown above, contains **monounsaturated** fats.

By comparison, most **animal triglycerides** are solids called **fats**. The carbon chains in these don't usually contain double bonds and are said to be **saturated**.

Nutritionists recognise that fats are an important part of our diet. The risk of developing heart disease does not so much depend upon the amount of fat in our diet as on the type of fat consumed. Unsaturated fats are thought to be much better for our cardiovascular system than saturated fats. In particular, modified unsaturated fats such as those found in margarine and hard stick margarine (used in baking) can contain **trans isomers** of unsaturated fats. These, it seems pose the greatest risk to the health of our cardiovascular system.

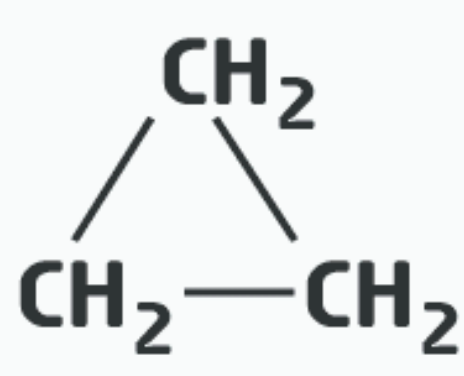
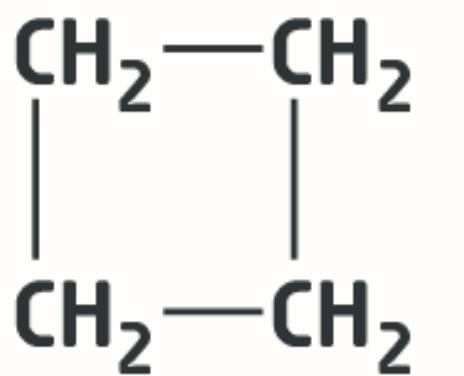
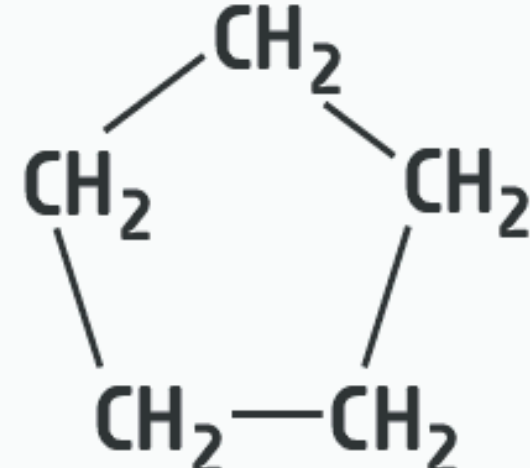
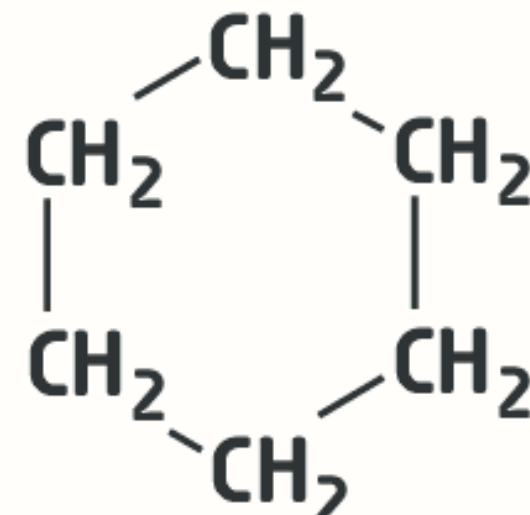

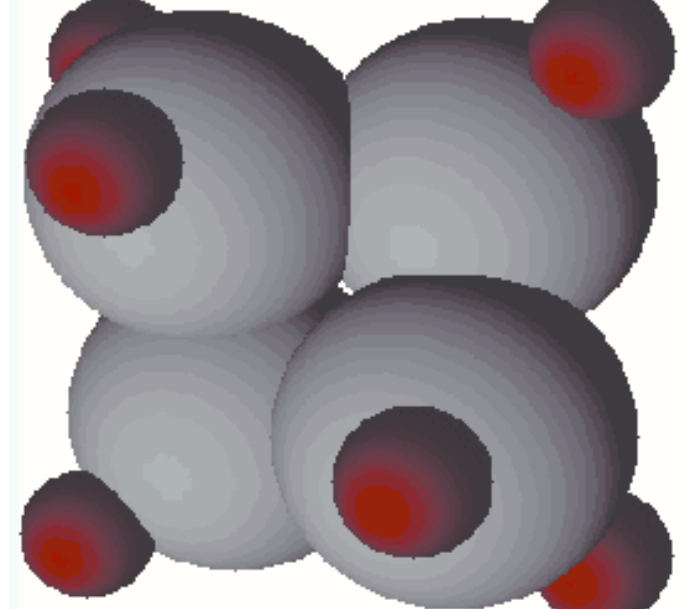
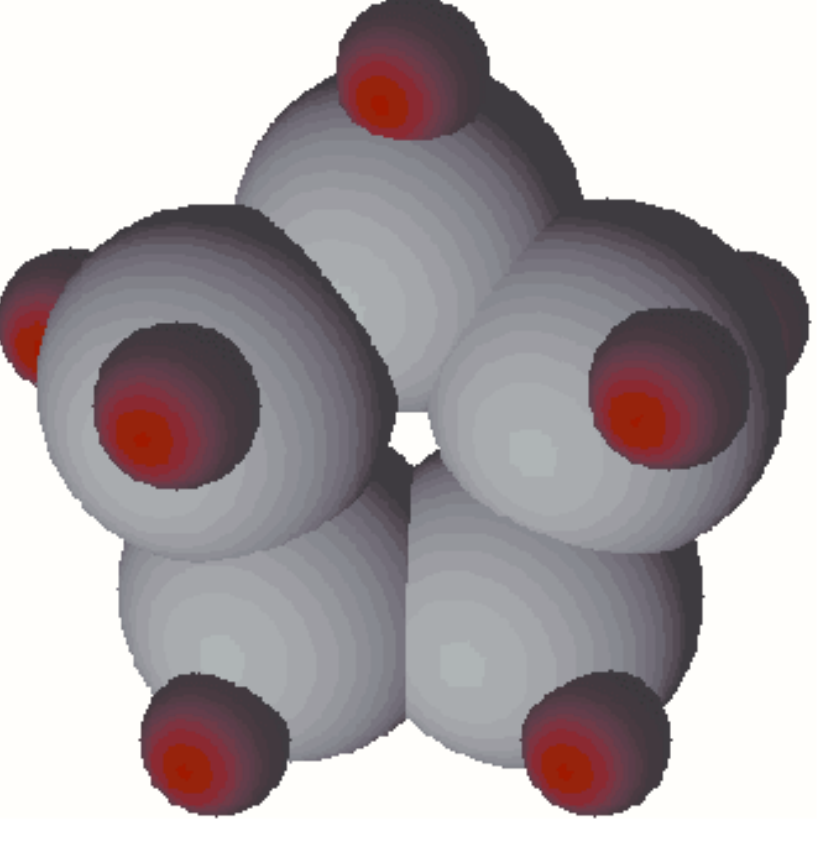
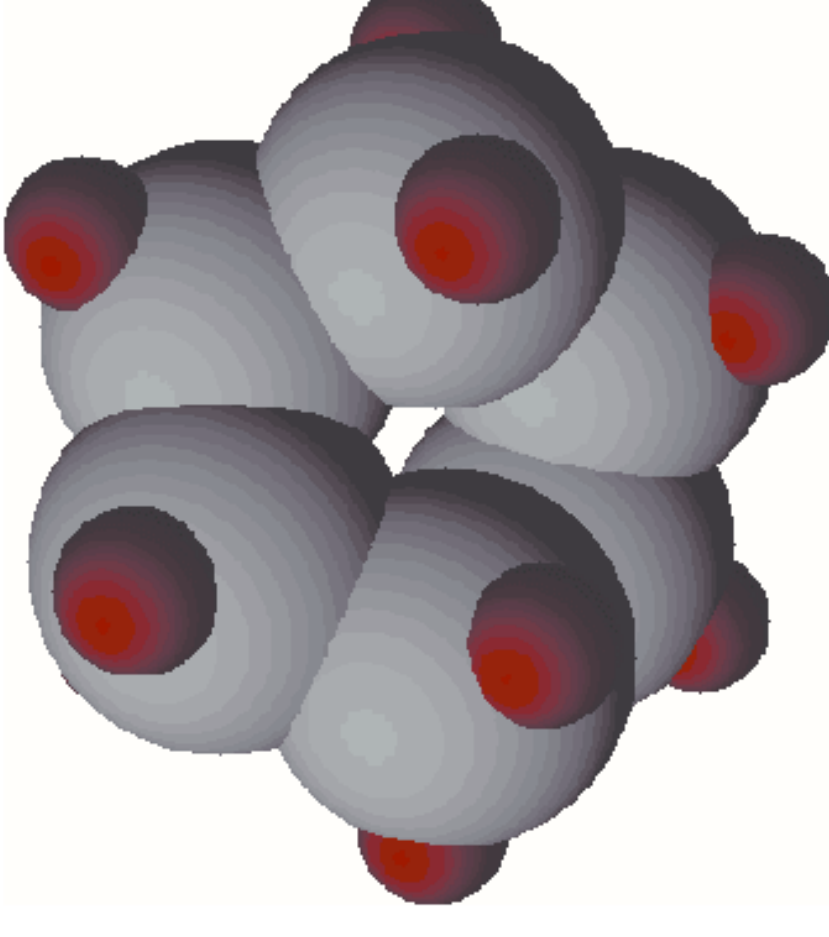
Attempt Set 20 # 8.



## 12.7 Cycloalkanes (E)

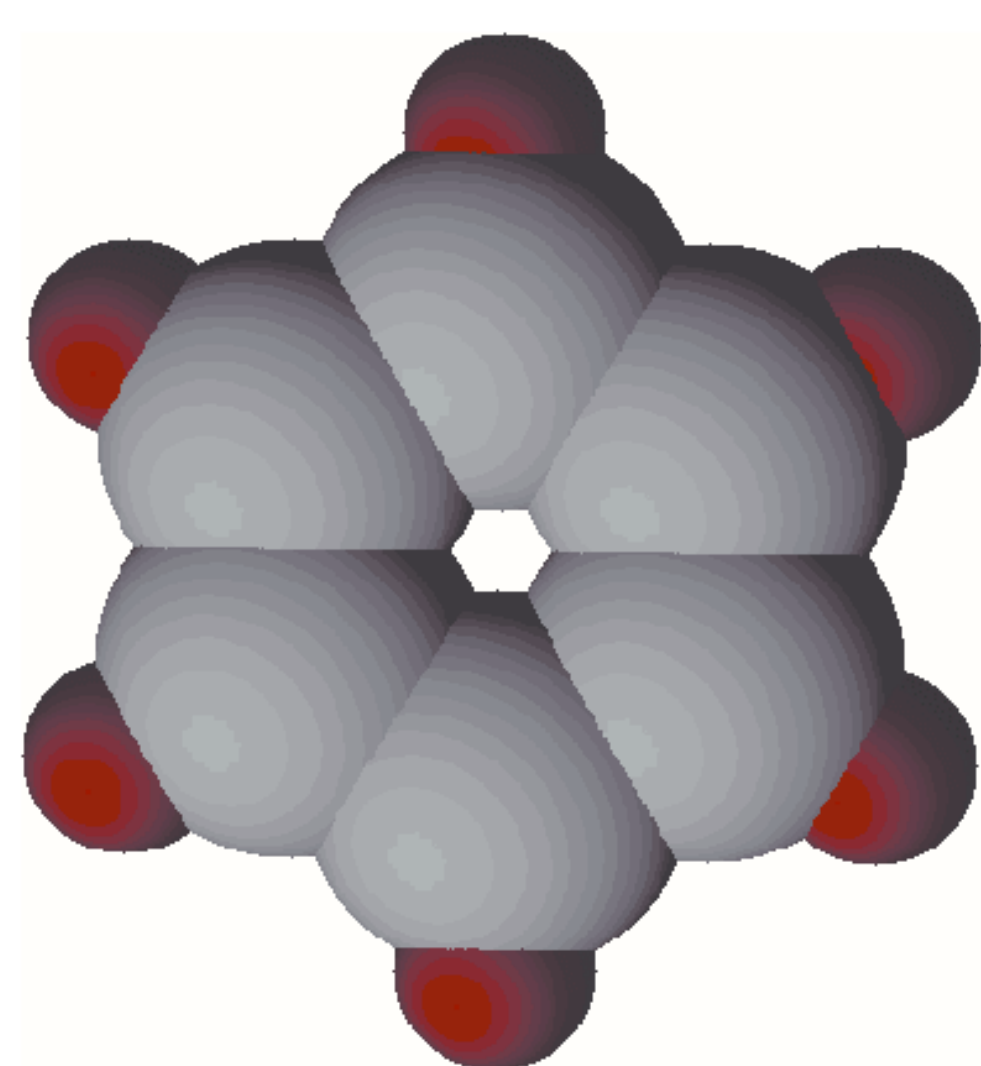
Cycloalkanes consist of three or more carbon atoms arranged into a **ring** structure. Every carbon atom is bonded to two hydrogen atoms and two carbon atoms. (See Table 4.) Due to their cyclic structure they have two less hydrogen atoms per molecule than a corresponding alkane and thus have the general formula  $C_nH_{2n}$ . Cycloalkane names all have the prefix **cyclo-** added to the stem name. As with alkanes these structures may also have attached side chains.

**TABLE 4** Structure and nomenclature of some **cycloalkanes**

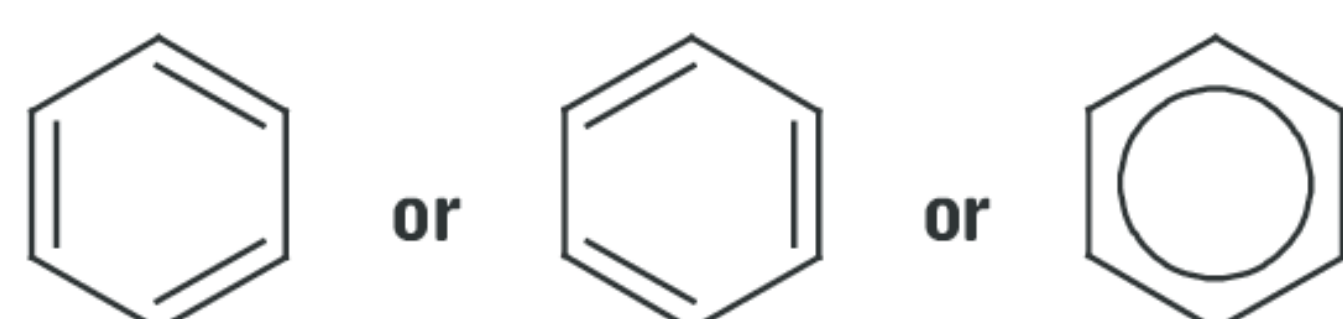
cyclopropane ( $C_3H_6$ )	cyclobutane ( $C_4H_8$ )	cyclopentane ( $C_5H_{10}$ )	cyclohexane ( $C_6H_{12}$ )
			
			

Attempt Set 20 # 9.

**FIGURE 6** The **benzene** molecule ( $C_6H_6$ ) consists of six C atoms arranged into a flat hexagonal ring structure with each C atom bonded to a single H atom.



A benzene molecule can be represented by any one of the following **shorthand notations**.

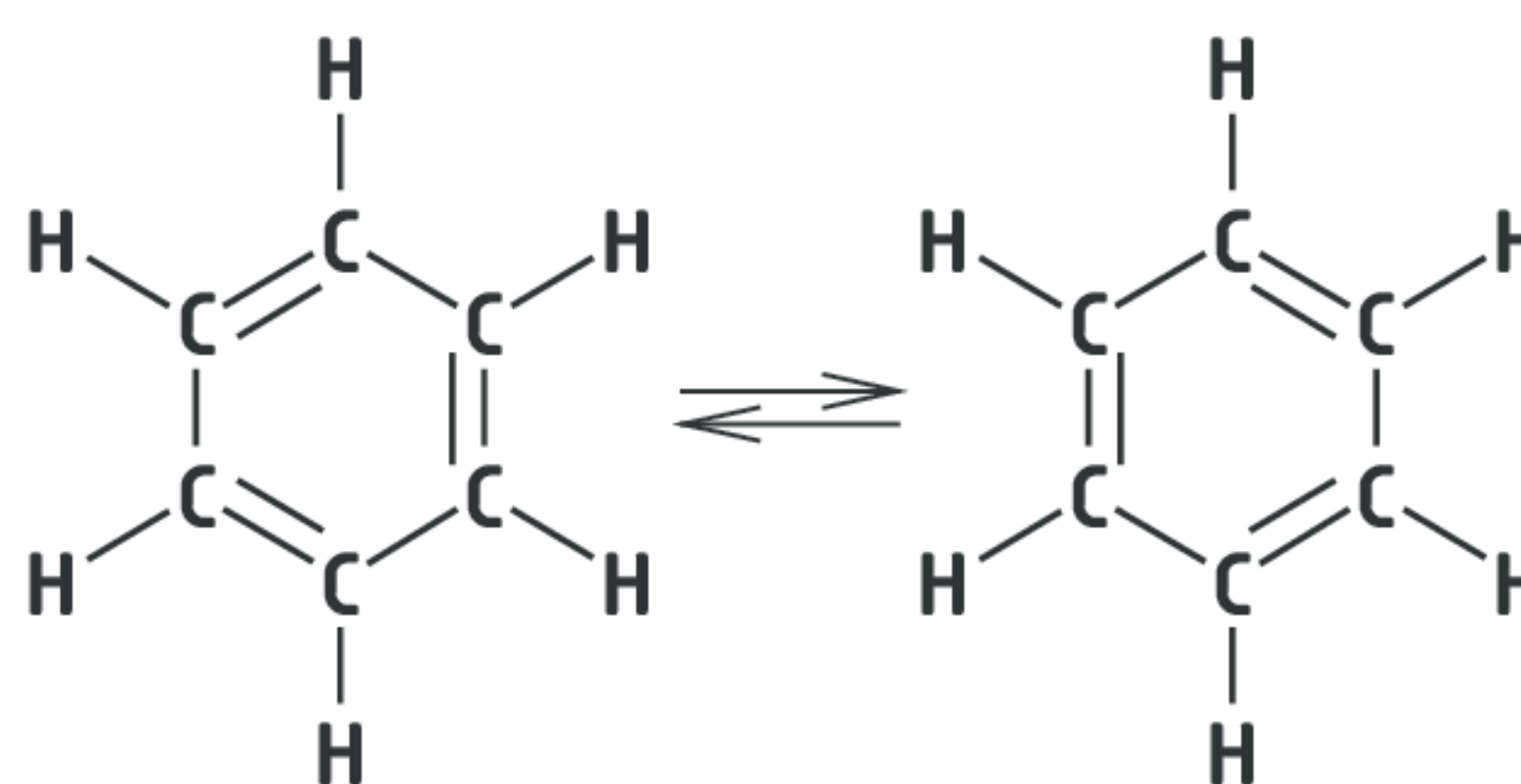


Research has shown benzene and some of its aromatic derivatives to be **carcinogenic** (cancer-causing). Excessive exposure may affect bone marrow and blood production and can lead to leukaemia. Even short-term exposure to high levels of benzene can cause drowsiness, dizziness, unconsciousness and death.

**Petrol** emissions from vehicles is the major source of benzene in the Australian environment. For this reason the benzene content of Australian petrol has been legally limited from January 2006 to 1% by volume.




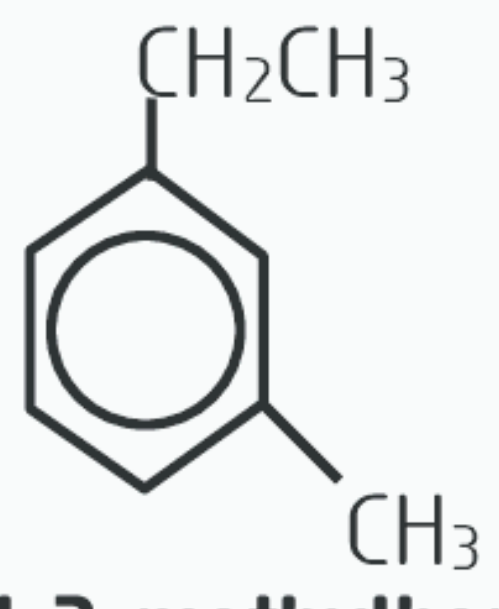
## 12.8 Benzene

**Benzene** has a molecular formula of  $C_6H_6$ , with a particularly stable, flat hexagonal ring structure. (See Fig 6.) All carbon to carbon bonds in benzene are **identical** in nature and **intermediate** in length between a single and double bond. Within the hexagonal ring of six carbon atoms, it is as though each C atom were alternately 'double bonded' to either of its neighbouring C atoms. The benzene structure is said to resonate between the two forms show here.



The benzene ring is a unique structure found incorporated into the molecules of many naturally occurring substances. These benzene based compounds, referred to as **aromatic**, are formed when one or more hydrogen atoms of the benzene ring are replaced with some other atom or group of atoms. (See Table 5.)

**TABLE 5** Structure and nomenclature of some aromatic compounds

			
<b>benzene</b>	<b>methylbenzene (toluene)</b>	<b>ethylbenzene</b>	<b>1-ethyl-3-methylbenzene</b>

Benzene occurs naturally in coal and crude oil and is produced by the burning of natural materials such as in forest fires. Most benzene for industrial use comes from the refining and reforming of crude oil. It is used in the manufacture of plastics, detergents and pesticides. Benzene improves the octane rating of fuels and as such is an important petrol additive. Its use however, is strictly controlled as it is known to be a **carcinogen**.

Attempt Set 20 # 10.



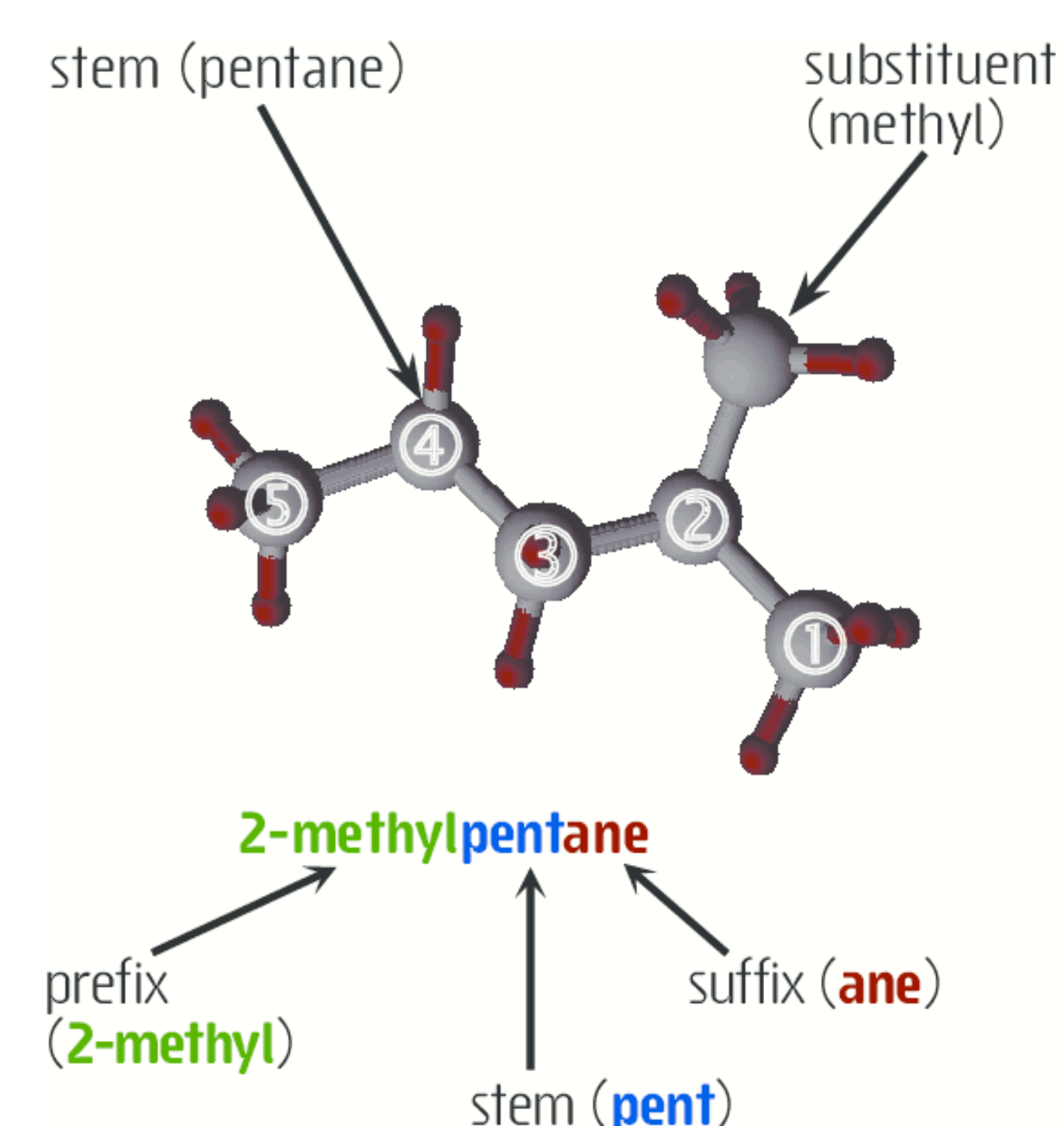
## 12.9 IUPAC nomenclature for alkanes and alkenes

The International Union of Pure and Applied Chemistry, **IUPAC** has the task of devising and maintaining an up-to-date worldwide system for naming compounds. IUPAC names are based on the compound's **parent** or **stem** structure. (See Fig 7.) The name is written by adding **suffixes** and/or **prefixes** onto the name of the parent compound to identify any **substituents** or other features that may be present on, or as part of the parent structure.

The presence of a **double bond** for example is identified using the suffix **-ene**. If only **single bonds** are present then the suffix **-ane** is used. Where an **alkyl** substituent group (a hydrocarbon side chain to the parent molecule) is present these are named as prefixes such as **methyl-**, **ethyl-**, **propyl-** and so on. (See Table 6.) If a **halogen** atom substituent group occurs on a hydrocarbon chain, ie F, Cl, Br or I, its presence is indicated by the prefixes **fluoro-**, **chloro-**, **bromo-** and **iodo-**.

Use the following IUPAC rules when naming simple alkanes and alkenes. (See Example 1.)

- Find the **longest continuous chain of carbon atoms** to which all substituent groups are attached. This is the parent chain and determines the stem name. If a carbon to carbon double bond ( $\text{C}=\text{C}$ ) is present then the parent chain must be chosen to include it; even if this does not give the longest chain.
- Number the carbon atoms** of the parent chain sequentially from either end so that the substituent group has the lowest possible number. If several groups are present then number from the end giving the lowest number to the first encountered substituent. Alkyl groups and halogen groups are treated equally for this purpose.
- If a **double bond** is present it has numbering priority so the parent chain is numbered from the end giving it the lowest number irrespective of the position of alkyl or halogen substituents.
- In the final name, prefixes are **ordered alphabetically** and numbered according to the carbon atom to which they are attached. **Prefixes** di, tri and tetra are used if multiples of a group are present. These do not affect the alphabetic order. Numbers are separated from letters with a **hyphen (-)** while a **comma** is used to separate numbers.



**FIGURE 7** IUPAC names are based on a compound's **parent** or **stem** structure. **Prefixes** and **suffixes** along with **numbers** are used to show the identity and location of substituent groups.

**TABLE 6** Alkyl groups (side chains)

Name	Condensed formula
<b>methyl</b>	$\text{CH}_3-$
<b>ethyl</b>	$\text{CH}_3\text{CH}_2-$
<b>propyl</b>	$\text{CH}_3\text{CH}_2\text{CH}_2-$
<b>butyl</b>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$

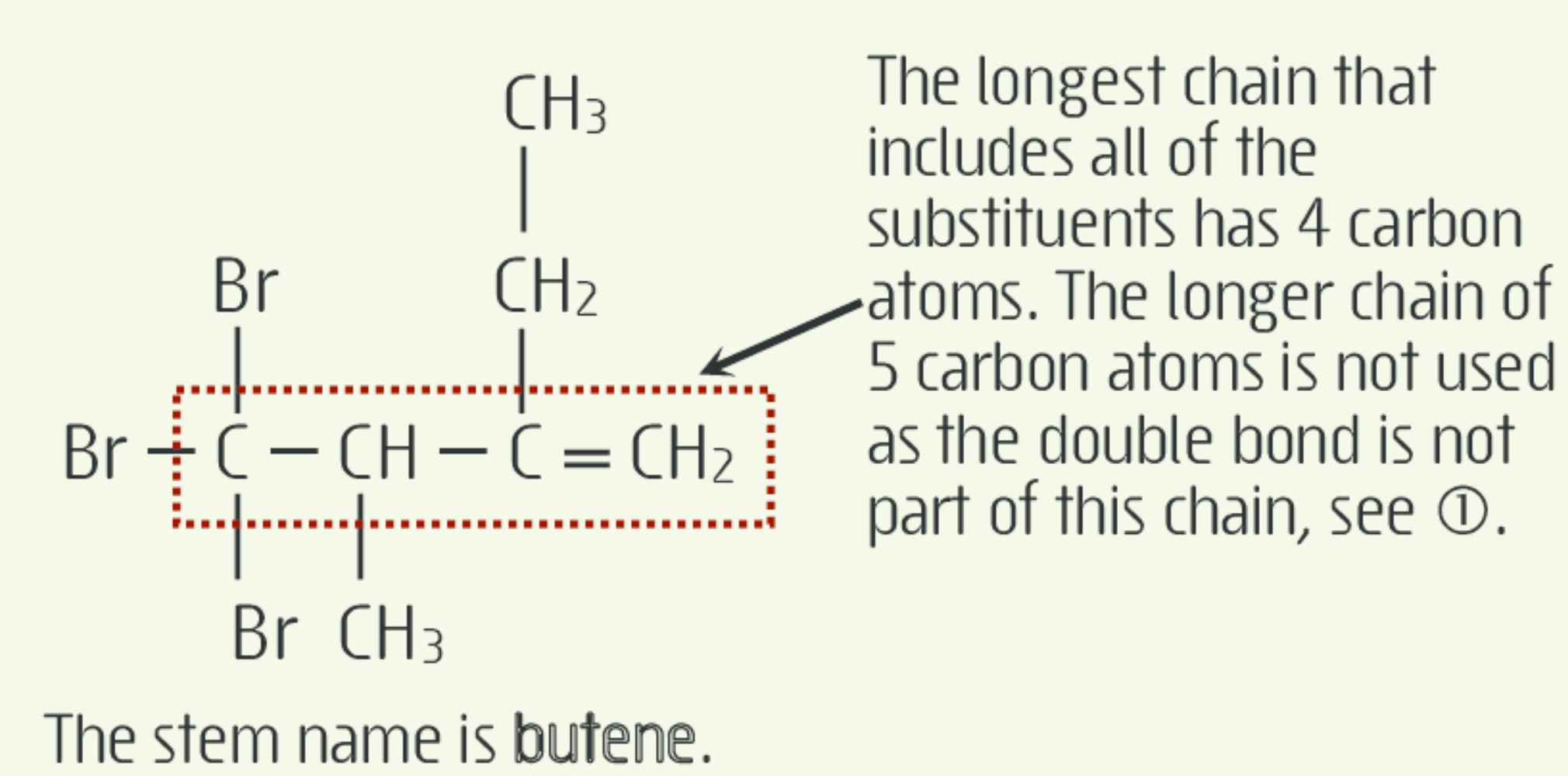
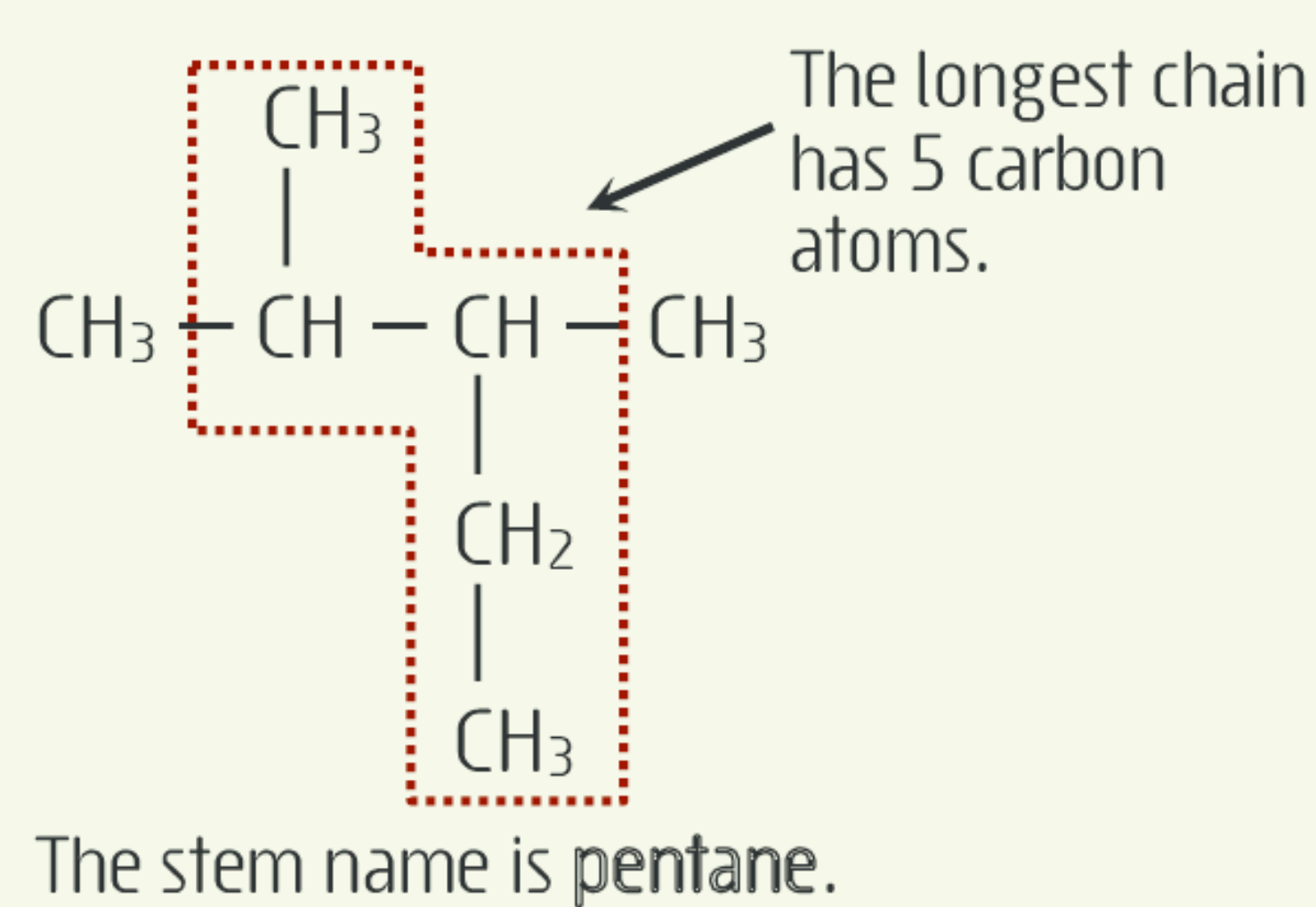
**EXAMPLE 1** Use IUPAC rules to name the organic compounds shown in Problems 1 and 2.

### Procedure

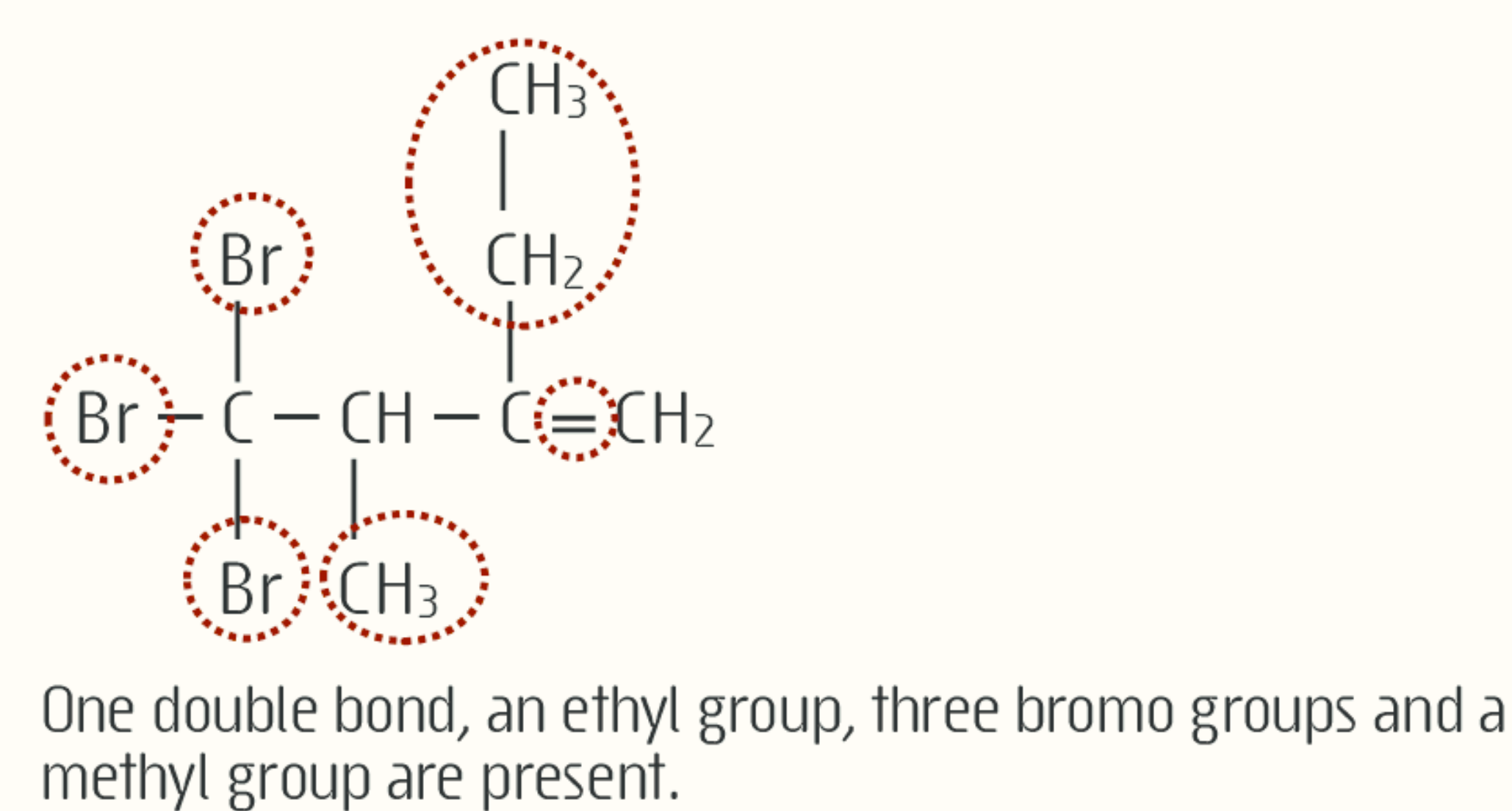
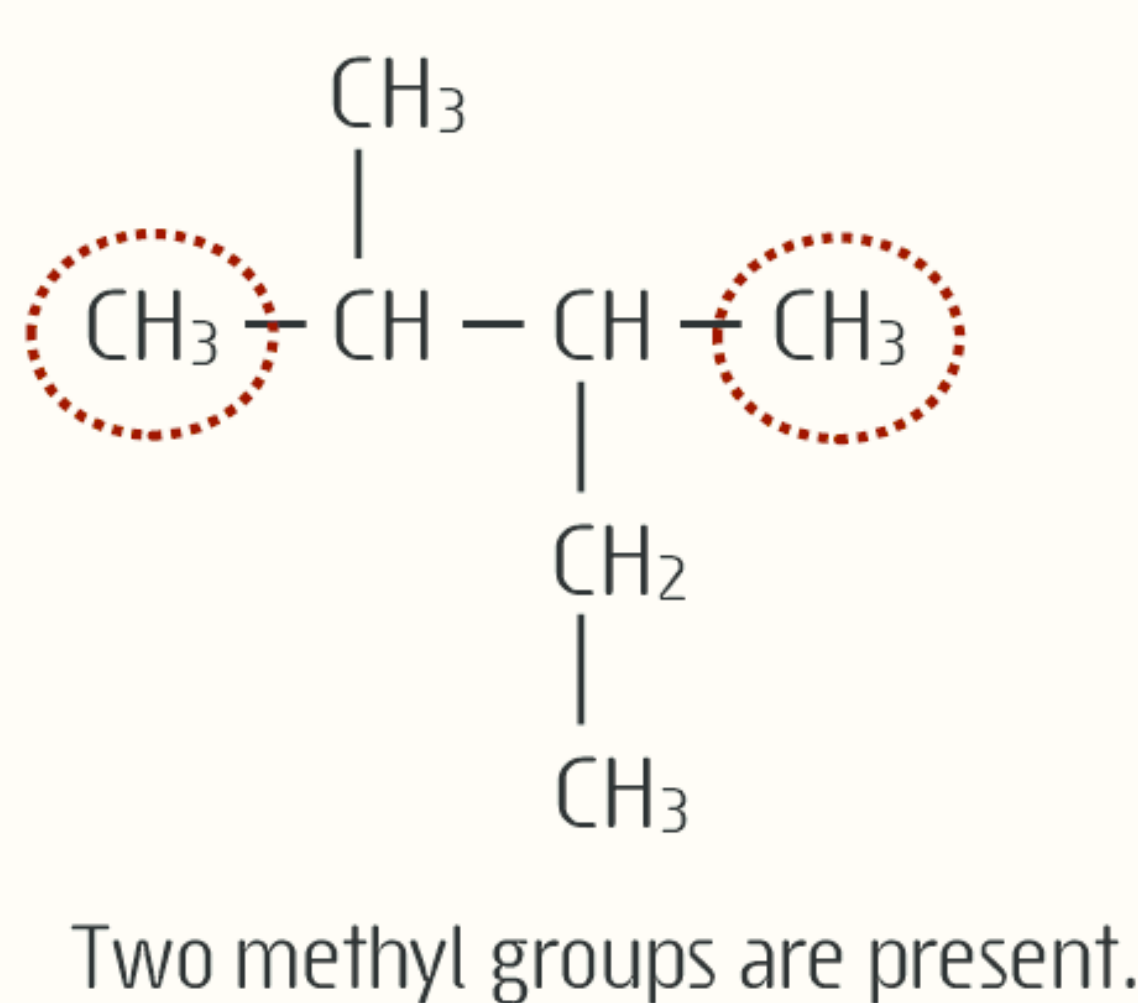
#### Problem 1 (a hydrocarbon)

#### Problem 2 (a haloalkene, ie contains a halogen group)

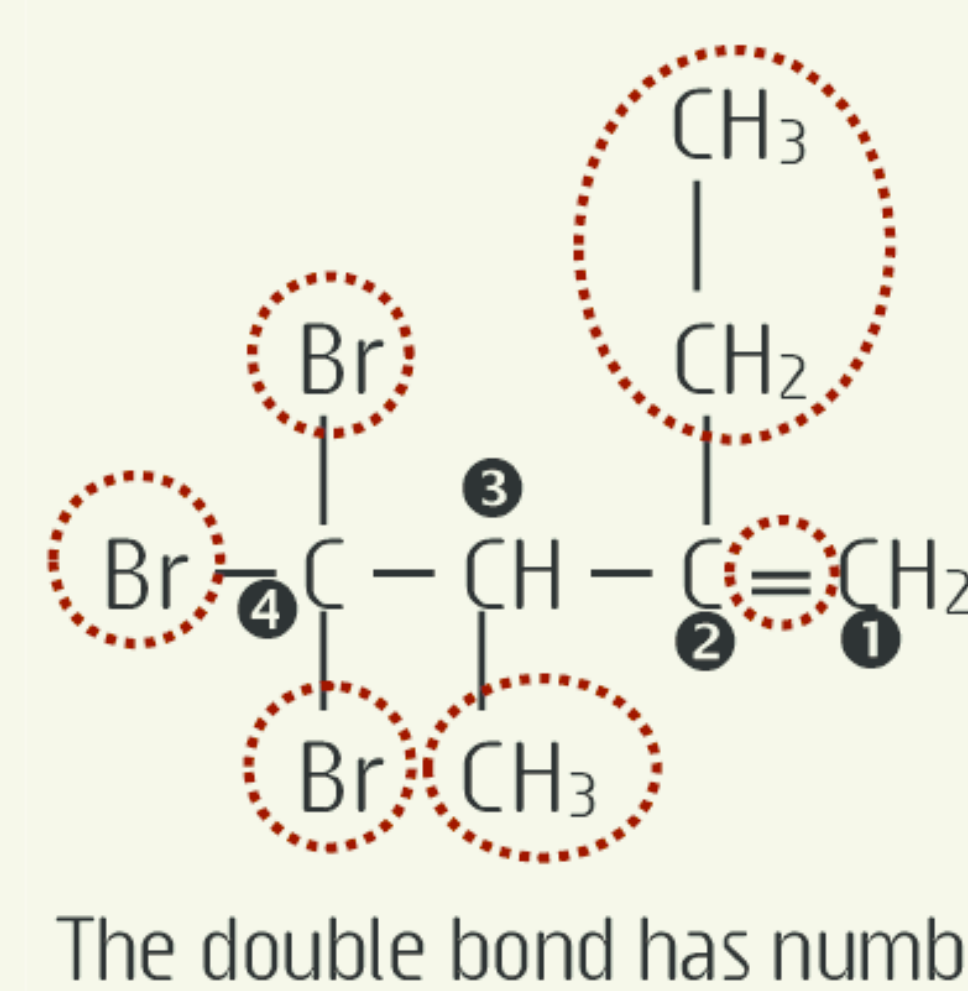
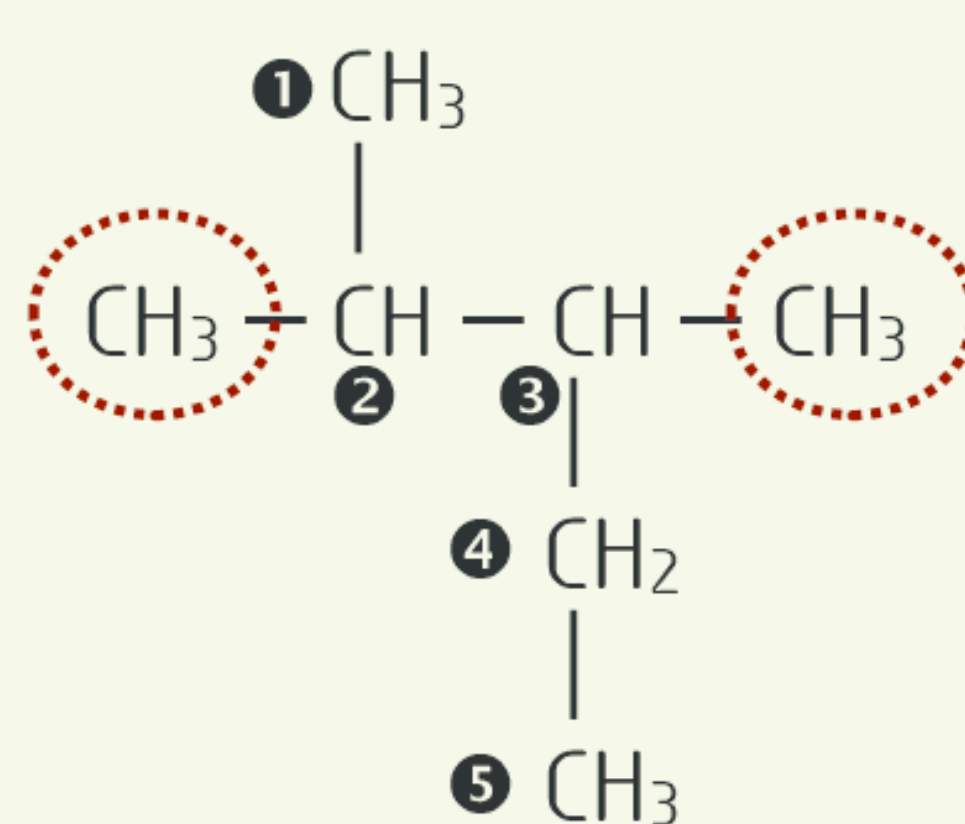
Identify the **longest continuous chain** of carbon atoms (see boxed area) which has the substituent groups attached. The number of carbon atoms in this chain determines the stem name.



Identify any **substituents** attached to the main chain. (These have been circled.)



**Number each carbon sequentially** from the end of the stem that gives the attached group the lowest possible number. If two or more groups are present, number from the end that gives the lowest number to the first encountered group. (See rule 2 above.)



Write the name of the substance. All prefixes are in alphabetical order.

**2,3-dimethylpentane**

**4,4,4-tribromo-2-ethyl-3-methylbut-1-ene**

Complete Set 20.



## Set 20 Hydrocarbons: Nomenclature and structure

carbon  
mixtures  
methane  
ethane  
natural gas  
fibres  
hydrogen  
carbon atoms  
fuels  
cracking  
molar mass  
petroleum  
plastics  
molecule

The **wax** found naturally occurring on apple skins is a straight chain **paraffin** of molecular formula  $C_{27}H_{56}$ .



1. Use the list of terms given to complete the following passage. **(E)**

Hydrocarbons are molecular compounds composed of the elements (a) \_\_\_\_\_ and (b) \_\_\_\_\_ only. The major sources of hydrocarbons are (c) \_\_\_\_\_, (d) \_\_\_\_\_ and coal. Natural gas consists mostly of (e) \_\_\_\_\_ with some (f) \_\_\_\_\_ and smaller amounts of propane and butane. Petroleum or crude oil is a complex mixture of various hydrocarbons.

At petroleum refineries, crude oil is separated into fractions of similar (g) \_\_\_\_\_ in a process called fractional distillation. These fractions are not pure compounds but rather they are (h) \_\_\_\_\_ of hydrocarbons with similar numbers of carbon atoms per (i) \_\_\_\_\_. The fractional distillation process works because the boiling point of hydrocarbons shows a general increase with the number of (j) \_\_\_\_\_ per molecule.

Various chemical processes like catalytic reforming and catalytic (k) \_\_\_\_\_ are sometimes used to produce modified hydrocarbon compounds. These and other hydrocarbon fractions are used as (l) \_\_\_\_\_, lubricating oils and for asphalt. They are also a valuable source of raw materials in the petrochemical industry for the manufacture of detergents, pharmaceuticals, solvents, fertilizers, pesticides and polymers like (m) \_\_\_\_\_, (n) \_\_\_\_\_, elastomers and resins.

2. Give the **IUPAC** name for the straight chain hydrocarbons of formula:

a.  $C_2H_6$                       b.  $C_4H_{10}$                       c.  $C_6H_{14}$                       d.  $C_8H_{18}$

3. **Paraffin wax**, used in candle making, refers to a variety of alkanes with 20 to 40 carbon atoms per molecule. Use the alkane general formula ( $C_nH_{2n+2}$ ) to write the **molecular formula** for the paraffins having 20, 24 and 28 carbon atoms per molecule.

4. Distinguish between **straight chain** and **branched chain** alkanes. Use the compounds of molecular formula  $C_4H_{10}$  to illustrate your answer.

5. There are five **alkanes** all with the same molecular formula of  $C_6H_{14}$ .

a. Draw all of these structures for  $C_6H_{14}$ .  
b. What is the general name given to compounds like these? **(E)**

6. What is the structural difference between an **alkane** and an **alkene**? Explain how this affects the general formula of an alkene. Use propane and propene to support your answer.

7. Give the **molecular formula** and **structural formula** for the compounds named here.

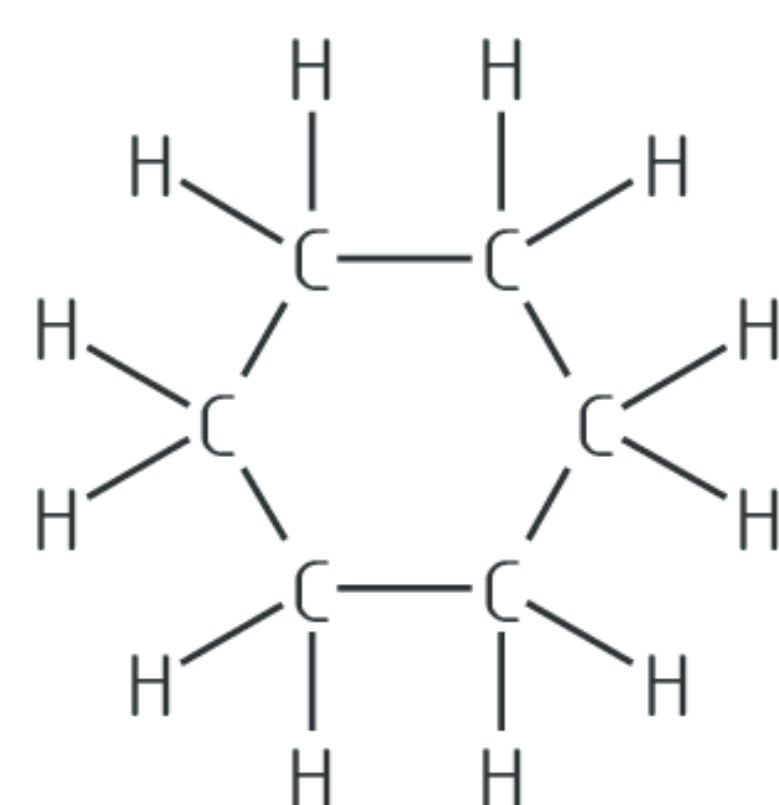
a. ethene                                      b. but-1-ene                                      c. pent-1-ene

8. Consider the two alkenes pent-2-ene and pent-1-ene, do these substances have **cis-trans isomers**? If so draw their structures and identify them as *cis* or *trans* isomers. **(E)**

9. Draw the structural formula for **pentane** ( $C_5H_{12}$ ) and **cyclopentane** ( $C_5H_{10}$ ). Account for their different molecular formula with reference to their structural formula. **(E)**

10. The structure drawn at left, in Fig 8, represents a molecule of the hydrocarbon **cyclohexane**,  $C_6H_{12}$ . The molecular structure of the substance called **benzene** has some similarities and some significant differences to cyclohexane. Draw the structure for benzene and describe these similarities and differences.

FIGURE 8 A molecule of **cyclohexane** ( $C_6H_{12}$ ).



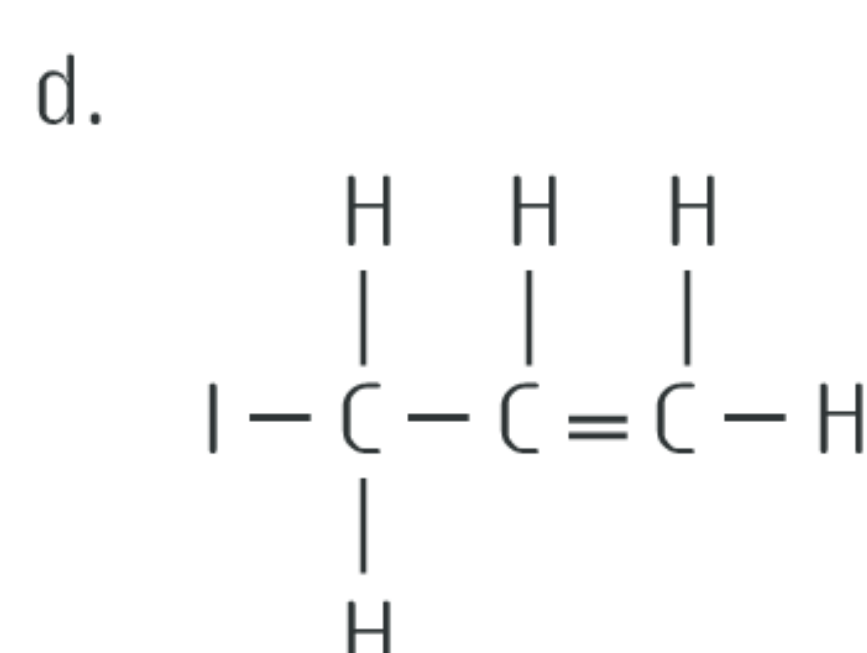
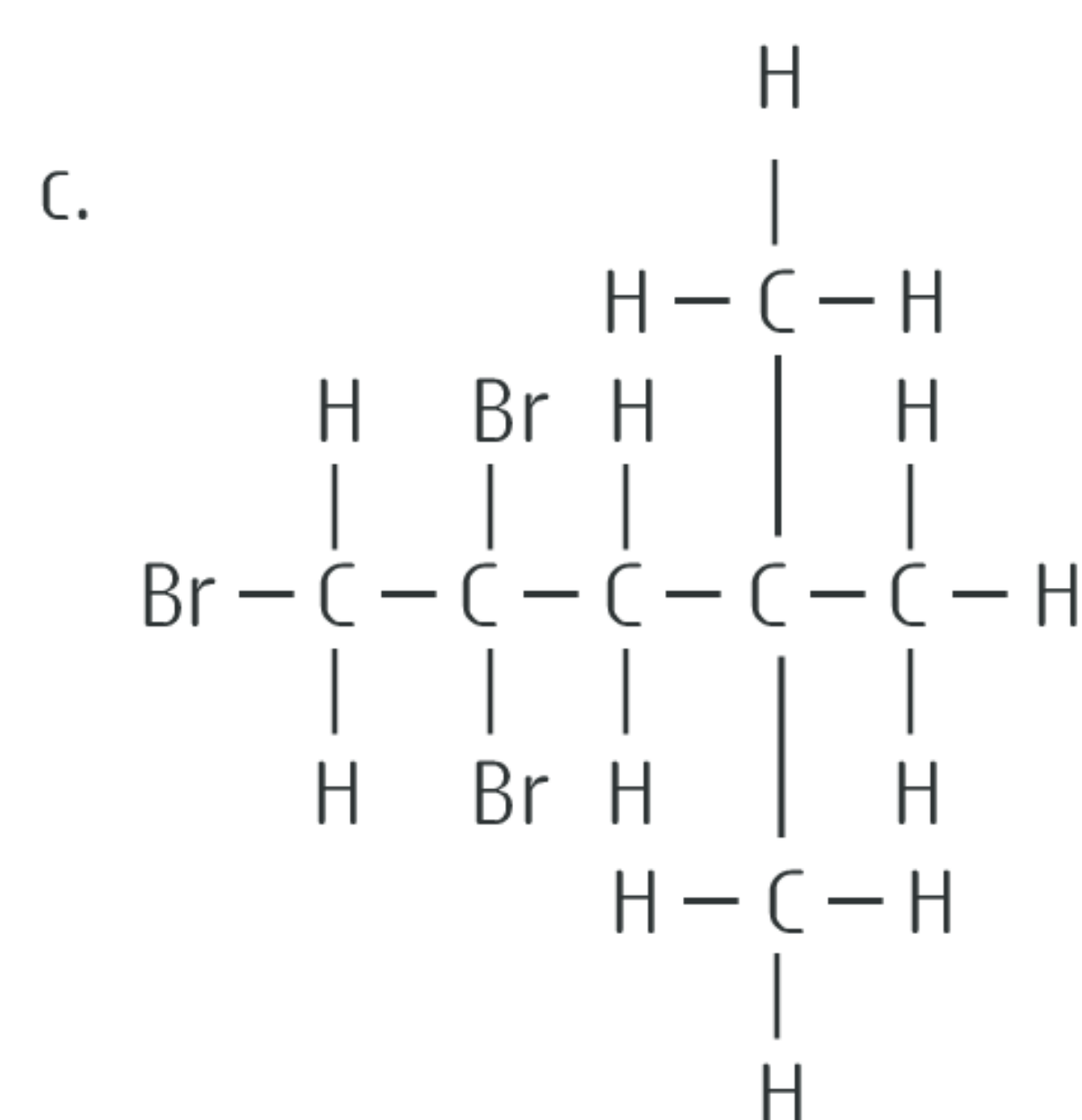
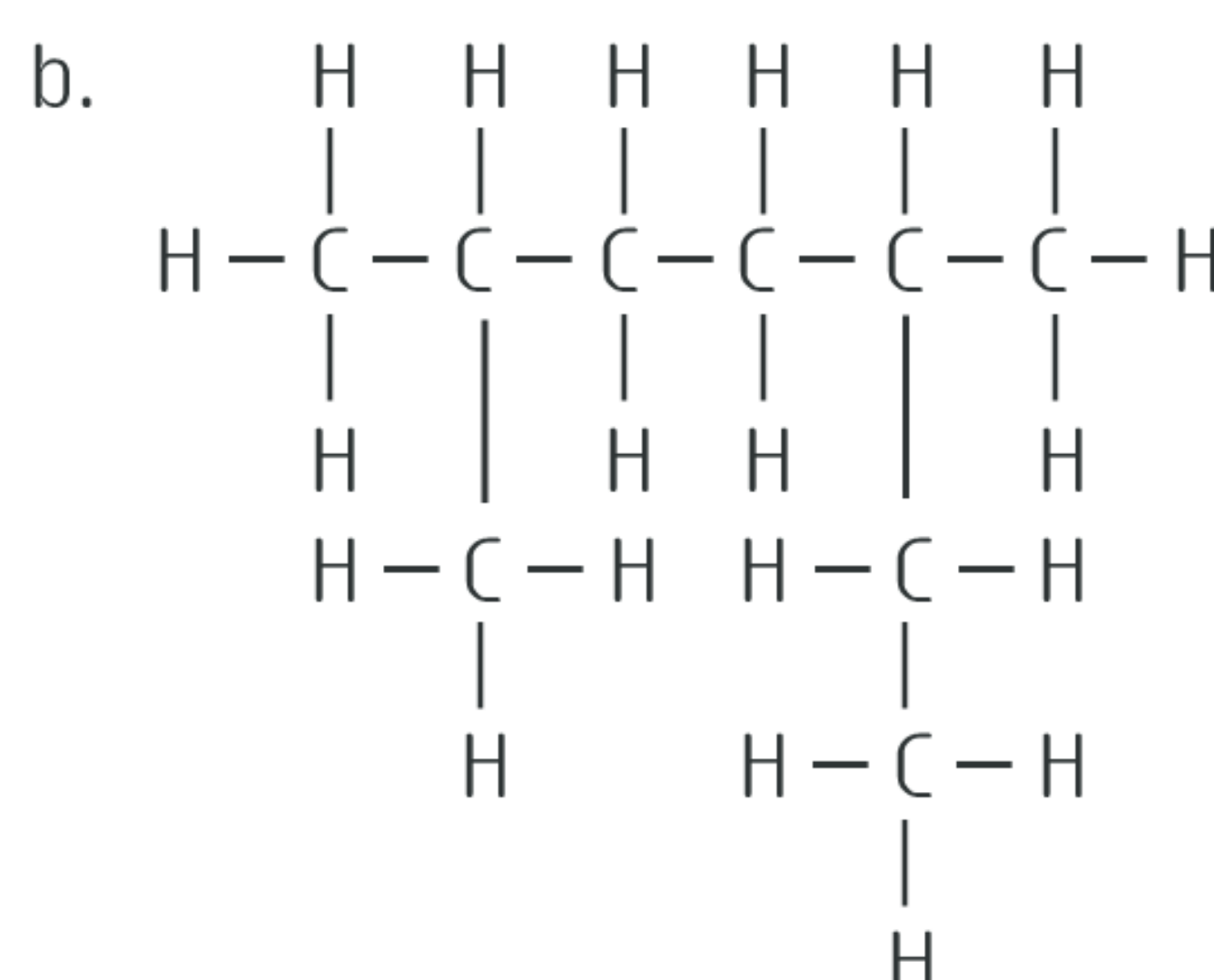
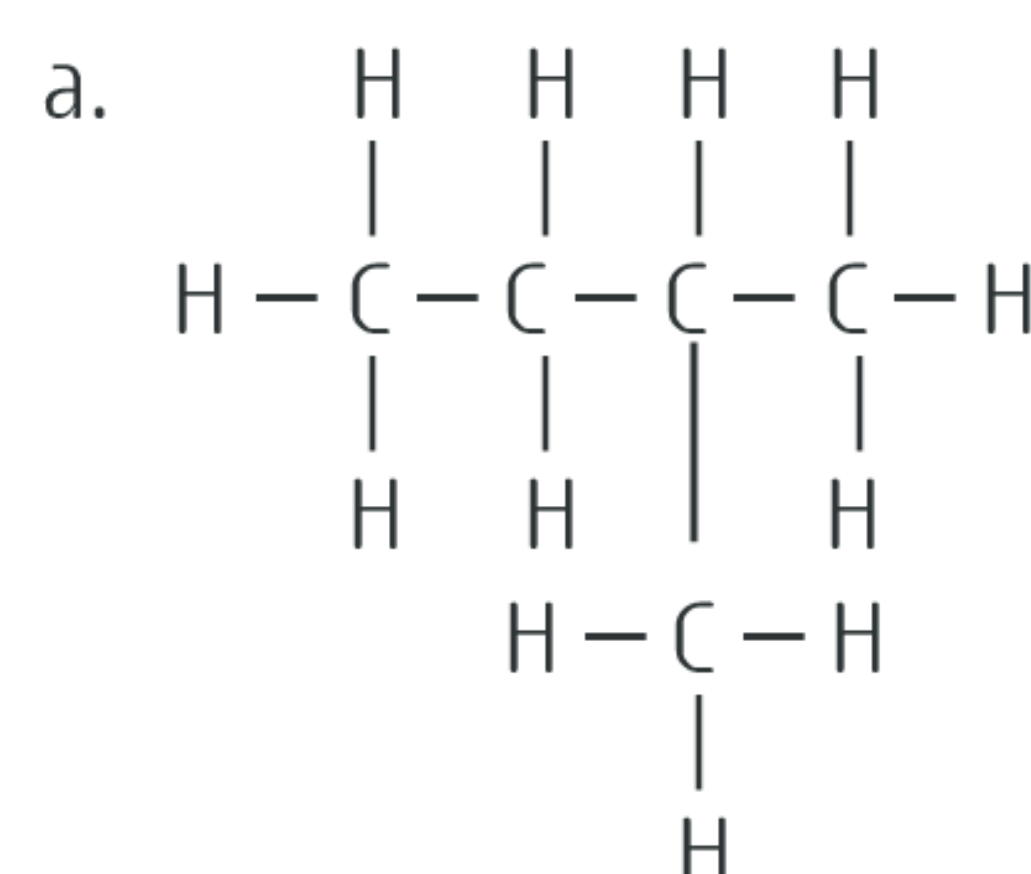


11. Draw **full structural formula** for the following hydrocarbons and other **halogenated** compounds. (See border note.) **Show all bonds**.

- |                             |   |
|-----------------------------|---|
| a. methylpropane            | f. 4,4-dipropylhept-2-ene                   |
| b. 2,3-dimethylbutane       | g. 4,5-difluoro-2-methylpent-1-ene          |
| c. 1-chloro-3-ethylpentane  | h. <i>cis</i> -1,2-dibromoethene <b>(E)</b> |
| d. 1,1,3-tribromopent-1-ene | i. <i>trans</i> -but-2-ene <b>(E)</b>       |
| e. 1,2-dichlorohexane       | j. 1-fluoro-3-methylbenzene <b>(E)</b>      |

**Halogenated hydrocarbons** are a most useful class of organic compound. (See border note p101.) They are formed when one or more of the hydrogen atoms of a hydrocarbon are replaced with a halogen atom (ie **F**, **Cl**, **Br** or **I**).

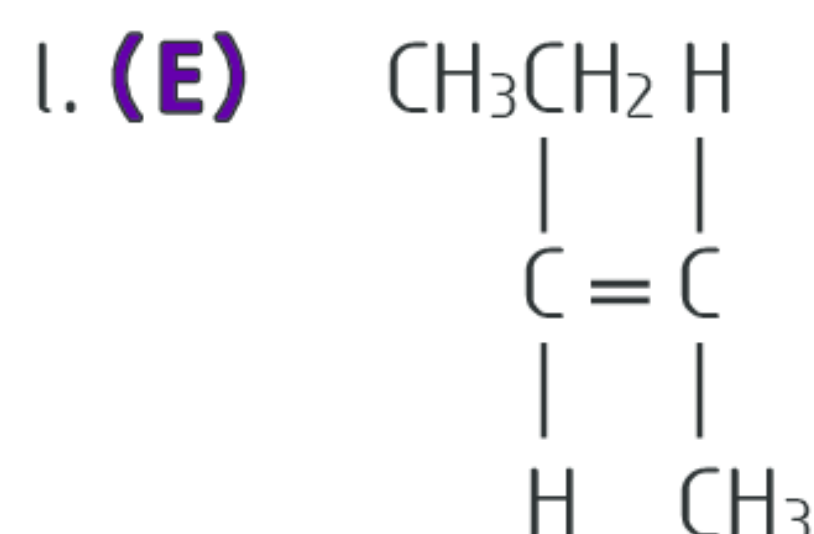
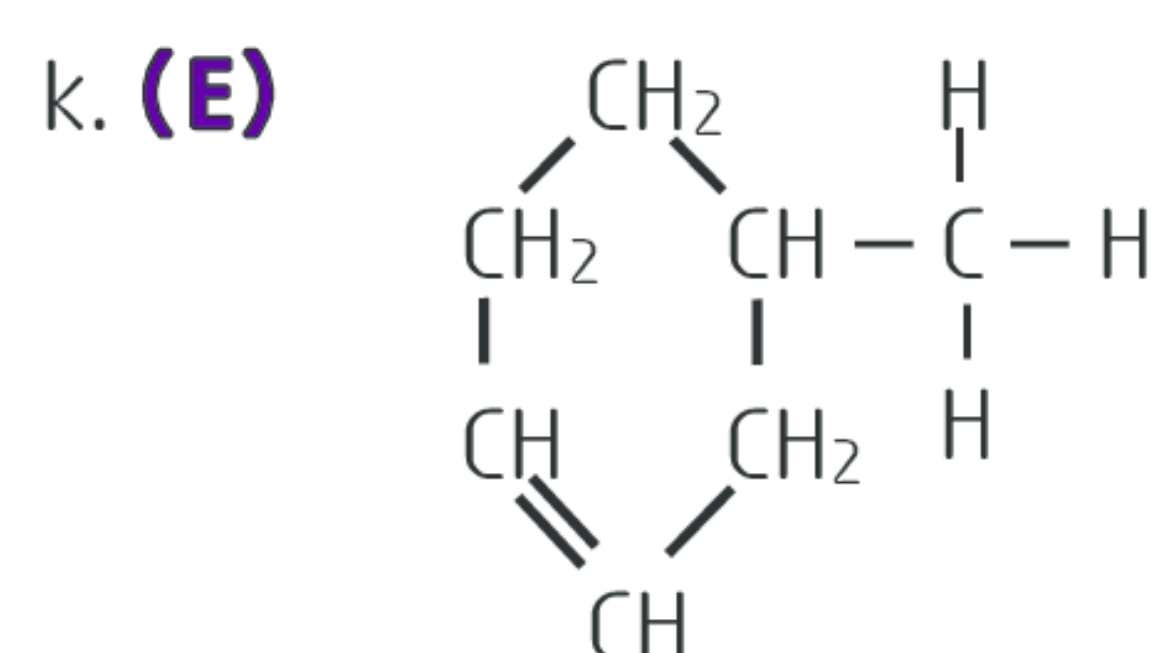
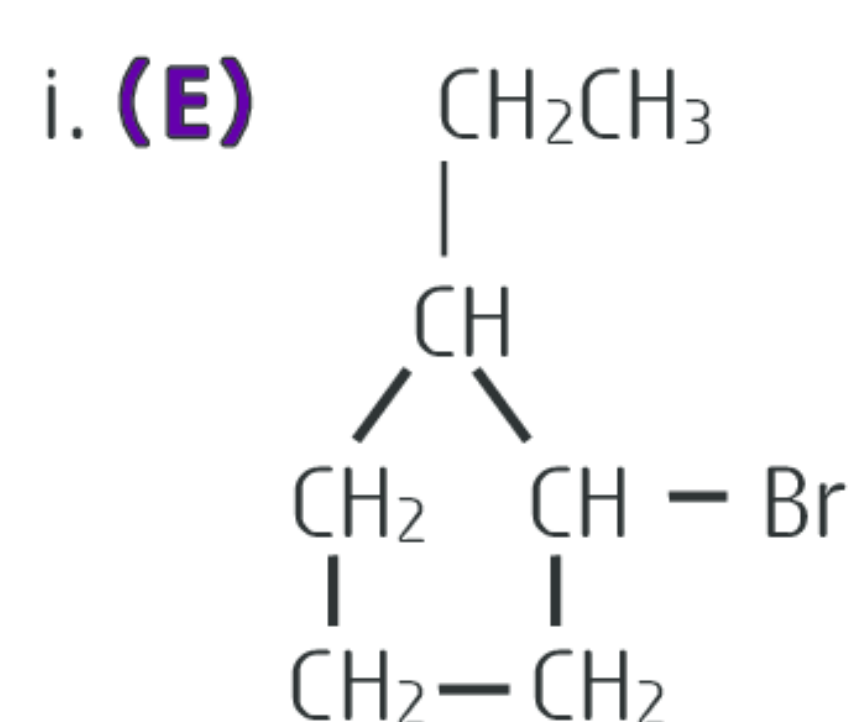
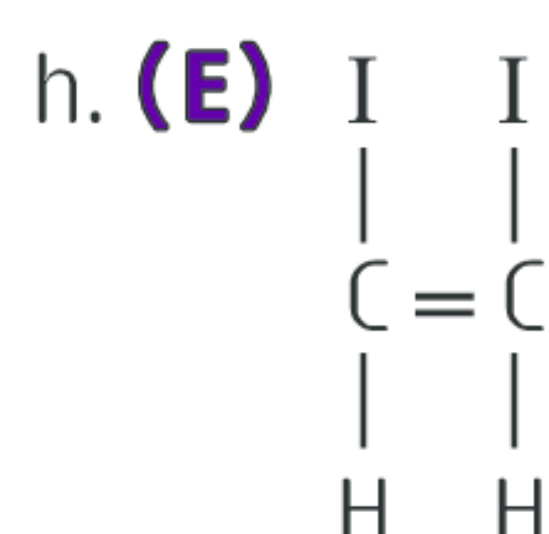
12. Give the **IUPAC name** for the substances with the molecular structures shown below.



e.  $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHCHCH}_3$   
(**Hint**: Draw the structural formula first.)

f.  $\text{CH}_3(\text{CH}_3)_2\text{CCH}_2\text{CHCH}_2$

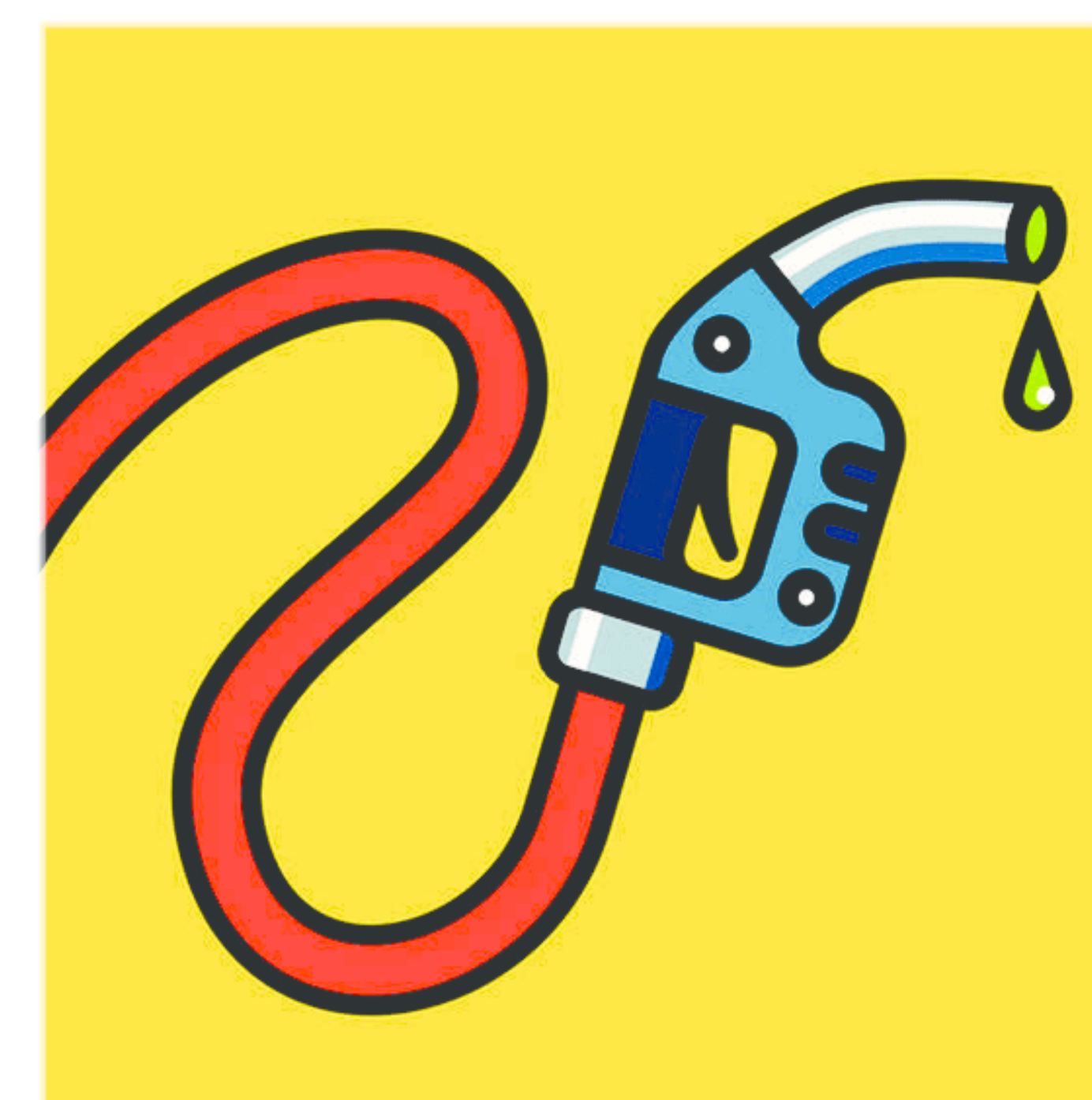
g.  $\text{Cl}_2\text{CHCH}_2\text{CHCH}_3\text{CHBrCH}_3$   
(**Hint**: Draw the structural formula first.)



13. Consider the **octane rating** (Fig 9) of the three hydrocarbon fuels listed here.

heptane, **0**      2,2-dimethylpentane, **89**      2,2,3-trimethylbutane, **113**

- Draw the structural formula of these compounds. How are these compounds related? Justify your answer.
- Describe one factor that affects the octane rating of a hydrocarbon fuel. (See Fig 9.) Use the data provided to support your answer.



**FIGURE 9** Petrol is a complex mixture of many different hydrocarbon compounds. One measure of the combustion characteristics of petrol is its **octane rating**. This measures a fuel's tendency to resist exploding when pressure is applied to its vapour and is known as its **anti-knock quality**. Depending upon an engine's compression ratio, manufacturers will specify a fuel of a particular octane rating, usually between 87 and 98.

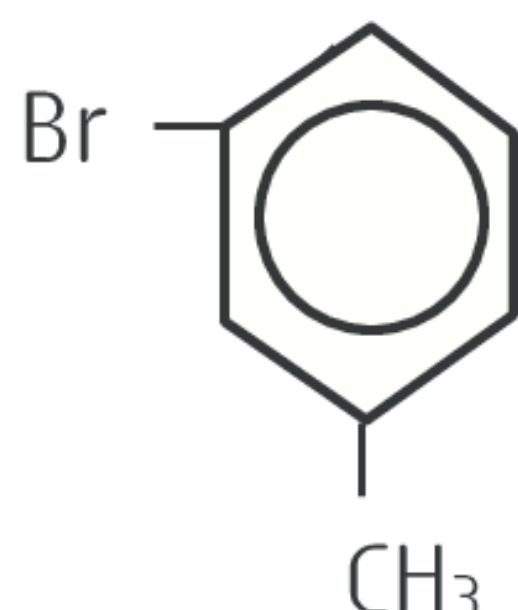
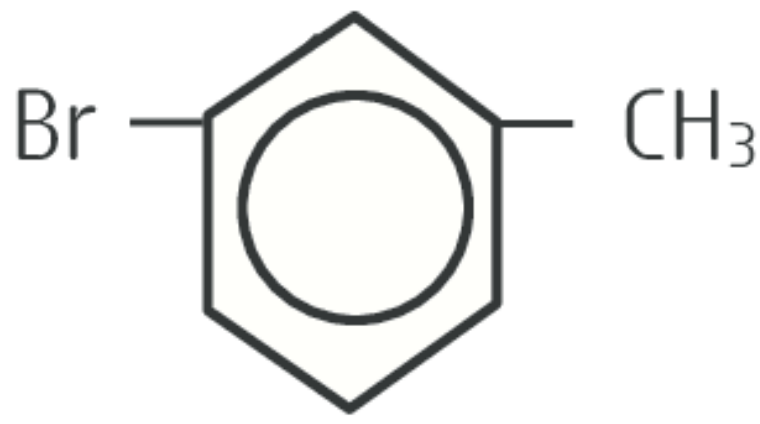
By definition, the octane rating of **heptane** ( $\text{C}_7\text{H}_{16}$ ) is **0** and the octane rating of **2,2,4-trimethylpentane** is **100**. Octane ratings of different petrol blends are found by matching their anti-knock combustion performance in a test engine to that of a mixture of these two reference fuels.

For example, by definition a fuel mixture containing 5% heptane and 95% 2,2,4-trimethylpentane has an octane rating of 95. If a particular petrol blend when used in a test engine has similar knocking characteristics as this 95 octane rating fuel then the petrol blend is assigned a 95 octane rating.



**Isomers** are compounds with the same molecular formula but a different structural formula. Compounds like this may have similar chemical and physical properties but they are not the same.

14. A student was given several different molecular formulas and asked to draw two different structures representing two different compounds for each of the molecular formulas. The 'different structures' he drew and their molecular formula are shown below. Which of the pairs of structures are **actually different compounds** and which are simply different ways of drawing the **same compound**? Naming the structures will help, ie if the two structures have the same IUPAC name then they actually are the same compound, otherwise they are different. (See border note.)

Molecular formula	Structure 1		Structure 2
a. <b>C<sub>4</sub>H<sub>10</sub></b>	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad   \\  \quad \quad \quad \text{H}-\text{C}-\text{H} \\  \quad \quad \quad   \\  \quad \quad \quad \text{H}  \end{array}  $	and	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $
b. <b>C<sub>6</sub>H<sub>14</sub></b>	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad   \quad \text{H} \quad \text{H} \\  \quad \quad \quad \text{H}-\text{C}-\text{H} \\  \quad \quad \quad   \\  \quad \quad \quad \text{H}  \end{array}  $	and	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad   \quad \text{H} \\  \quad \quad \quad \text{H}-\text{C}-\text{H} \\  \quad \quad \quad   \\  \quad \quad \quad \text{H}  \end{array}  $
c. <b>C<sub>6</sub>H<sub>14</sub></b>	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad   \quad \text{H} \\  \quad \quad \quad \text{H}-\text{C}-\text{H} \\  \quad \quad \quad   \\  \quad \quad \quad \text{H}  \end{array}  $	and	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $
d. <b>C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub></b>	$  \begin{array}{c}  \text{Cl} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{H} \\    \quad   \\  \text{H} \quad \text{Cl}  \end{array}  $	and	$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{H} \\    \quad   \\  \text{Cl} \quad \text{Cl}  \end{array}  $
e. <b>C<sub>7</sub>H<sub>16</sub></b>	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{CH}_3 \\    \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{CH}_3  \end{array}  $	and	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad   \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{CH}_3 \quad \text{H}  \end{array}  $
f. <b>C<sub>3</sub>H<sub>5</sub>Br<sub>2</sub> (E)</b>	$  \begin{array}{c}  \text{Br} \quad \text{H} \\    \quad   \\  \text{C} = \text{C} \\    \quad   \\  \text{H} \quad \text{CH}_3  \end{array}  $	and	$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{C} = \text{C} \\    \quad   \\  \text{Br} \quad \text{CH}_3  \end{array}  $
g. <b>C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> (E)</b>	$  \begin{array}{c}  \text{H} \quad \text{Br} \\    \quad   \\  \text{C} = \text{C} \\    \quad   \\  \text{Br} \quad \text{H}  \end{array}  $	and	$  \begin{array}{c}  \text{Br} \quad \text{H} \\    \quad   \\  \text{C} = \text{C} \\    \quad   \\  \text{Br} \quad \text{H}  \end{array}  $
h. <b>C<sub>7</sub>H<sub>7</sub>Br (E)</b>		and	



15. Louise named several organic compounds as indicated below. Unfortunately, although each name specifies a correct structure, the name given does not correctly follow the IUPAC system of nomenclature. Use the given name to determine the structure and hence give the **correct IUPAC name** for each compound.

- |                      |                                  |
|----------------------|----------------------------------|
| a. 4-methylpentane   | d. 2,2-diethylbutane             |
| b. 2-methylbut-3-ene | e. 1-bromo-5-methylbenzene       |
| c. 1-methylpropane   | f. 1,2-dichloroethene <b>(E)</b> |

16. Some of the following structures have *cis-trans* (geometric) isomerism. Where this is possible, **draw** the two structures and **name** each compound. **(E)**

- |   |  |
|---|--|
| a. $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ | d. $\text{CH}_2=\text{CHCl}$                       |
| b. $\text{CH}_2=\text{CCl}_2$             | e. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$ |
| c. $\text{CHCl}=\text{CHCl}$              | f. $\text{CH}_2\text{BrCH}_2\text{Br}$             |

17. **Fats** and **oils** consist of compounds known as triglycerides. (See Fig 4 p93.) **Triglycerides** are produced from the reaction of a **fatty acid** and **glycerol** ( $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ ). The **carbon chain** of a fatty acid may contain several carbon to carbon double bonds (called polyunsaturated), one carbon to carbon double bond (called monounsaturated) or no double bonds (called saturated). Examine the **carbon chain only** (red bold section) of these three fatty acids and classify the carbon chains as **saturated**, **monounsaturated** or **polyunsaturated**. Justify your answer.

**$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$**   
stearic acid

**$\text{CH}_3(\text{CH}_2)_4(\text{CH})_2\text{CH}_2(\text{CH})_2(\text{CH}_2)_7\text{COOH}$**   
linoleic acid

**$\text{CH}_3(\text{CH}_2)_7(\text{CH})_2(\text{CH}_2)_7\text{COOH}$**   
oleic acid

18. **Name** an organic compound that matches each description.

- This compound has a molecular formula of  $\text{C}_3\text{H}_6$  and is unsaturated.
- A branched, saturated hydrocarbon with four carbon atoms per molecule.
- A high octane fuel of molecular formula  $\text{C}_6\text{H}_{14}$  that has two methyl groups per molecule.
- An aromatic hydrocarbon produced from the catalytic reforming of certain petroleum fractions. It contains seven carbon atoms per molecule and eight hydrogen atoms.



hex-1-ene

$\text{Br}_2(\text{aq})$

A few seconds of mixing turns the  $\text{Br}_2(\text{aq})$  layer colourless.

Attempt Set 21 # 1.

It is sometimes possible to distinguish between **saturated** and **unsaturated** hydrocarbons by their reaction with bromine water. Unsaturated hydrocarbons, ie alkenes **rapidly discolour** bromine water by an addition reaction. By comparison, saturated hydrocarbons and benzene **slowly discolour** bromine water. This is due to the much slower rate of the substitution reaction.

Attempt Set 21 # 2.



**FIGURE 11** Methane ( $\text{CH}_4$ ) is the major component of natural gas (NG). This is an important fuel for electric power generation and is used in the home for heating and cooking.

Attempt Set 21 # 3.

## 12.10 Addition reactions of hydrocarbons

Alkenes are known as **unsaturated** hydrocarbons as their bonding capacity is not fully utilised, ie their molecules have the capacity to bond to more atoms. For this reason they readily undergo **addition** reactions where the double bond ( $C=C$ ) is replaced by bonds to other atoms like H, F, Cl, Br or I. Alkanes and benzene do **not** undergo addition reactions.

Reagents used in addition reactions include  $\text{H}_2$  (with a Pt catalyst),  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$ . In the laboratory it is most convenient to use  $\text{Br}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  in aqueous solution form, ie  $\text{Br}_2(\text{aq})$  and  $\text{Cl}_2(\text{aq})$ . These are known as bromine water and chlorine water respectively. (See Fig 10.)

**TABLE 7** Addition reactions of alkenes

<p><b>Example</b></p> $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCHBrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ <p><b>hex-1-ene</b>                                  <b>1,2-dibromohexane</b></p> $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCHBrCH}_2\text{CH}_2\text{CH}_3$ <p><b>hex-2-ene</b>                                  <b>2,3-dibromohexane</b></p> $\text{CH}_2=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl}$ <p><b>ethene</b>                                      <b>chloroethane</b></p> $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CHClCH}_3^*$ <p><b>propene</b>                                    <b>2-chloropropane</b></p>	<p><b>Observation</b></p> <p>In each case two immiscible layers form. With mixing, the bromine water changes colour from <b>orange</b> to <b>colourless</b>. (See Fig 10.)</p>       <p>In both cases two colourless gases react to form a colourless liquid.</p>
---	--

\* Interestingly only **2-chloropropane** is formed, ie 1-chloropropane does not form. When HCl, HBr or HI gases react by addition, 'the added **hydrogen** atom will attach to the carbon of the double bond already having the **most** attached **hydrogen** atoms'. This is known as Markovnikov's rule.

## 12.11 Substitution reactions of hydrocarbons

Substitution reactions occur when an **alkane** or **benzene** is combined with **Cl<sub>2</sub>** or **Br<sub>2</sub>**. This results in the replacement (ie substitution) of one or more H atoms with Cl or Br atoms. The number of replaced H atoms depends upon the reaction conditions. With **excess** Cl<sub>2</sub> or Br<sub>2</sub> **complete** substitution can occur.

Under similar conditions, **substitution** reactions are much **slower** than **addition** reactions. (See border note.) Ultra violet light (UV) and/or heat may be used to speed this reaction. Only alkanes and benzene compounds undergo substitution reactions. Alkenes will instead undergo addition with similar reagents.

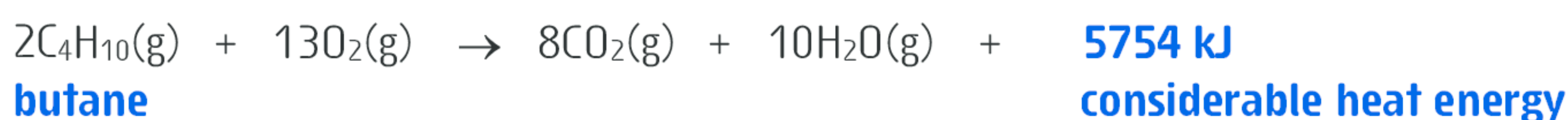
TABLE 8 Substitution reactions of alkanes and benzene

Example*	Observation
$\text{CH}_3\text{CH}_3 + \text{Br}_2(\text{aq}) \xrightarrow{\text{UV}}$ $\text{CH}_3\text{CH}_2\text{Br} + \text{HBr}$ <b>ethane</b> <b>bromoethane</b>	Bromine water [ie Br <sub>2</sub> (aq) ] slowly changes colour from <b>orange</b> to <b>colourless</b> .
$\text{C}_6\text{H}_6 + \text{Cl}_2(\text{aq}) \xrightarrow{\text{UV}}$ $\text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ <b>benzene</b> <b>chlorobenzene</b>	Chlorine water slowly changes colour from <b>pale yellow</b> to <b>colourless</b> .

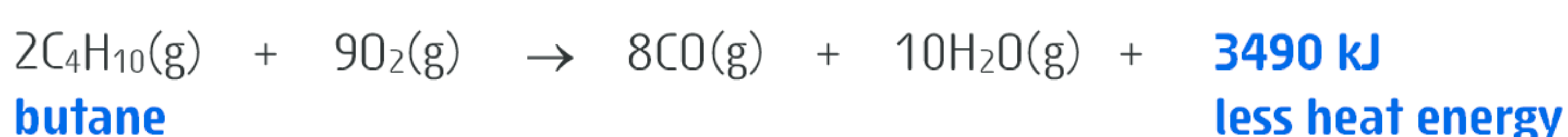
\*Note: If **excess** Br<sub>2</sub> or Cl<sub>2</sub> is present in the reaction mixture then substitution of hydrogen atoms will continue until complete. This would result in the formation of **hexabromoethane** (C<sub>2</sub>Br<sub>6</sub>) and **hexachlorobenzene** (C<sub>6</sub>Cl<sub>6</sub>).

## 12.12 Combustion reactions of hydrocarbons

Hydrocarbons are excellent **fuels**. (See Fig 11.) When ignited in excess air ( $O_2$ ) they produce carbon dioxide, water vapour and release considerable amounts of heat energy.



**Incomplete combustion** occurs if the air ( $O_2$ ) supply is limited (insufficient). Carbon monoxide and even soot  $[C(s)]$  can be produced. (See Fig 12.)



Incomplete combustion is an inefficient way to burn hydrocarbon fuels as it produces significantly less energy than complete combustion.



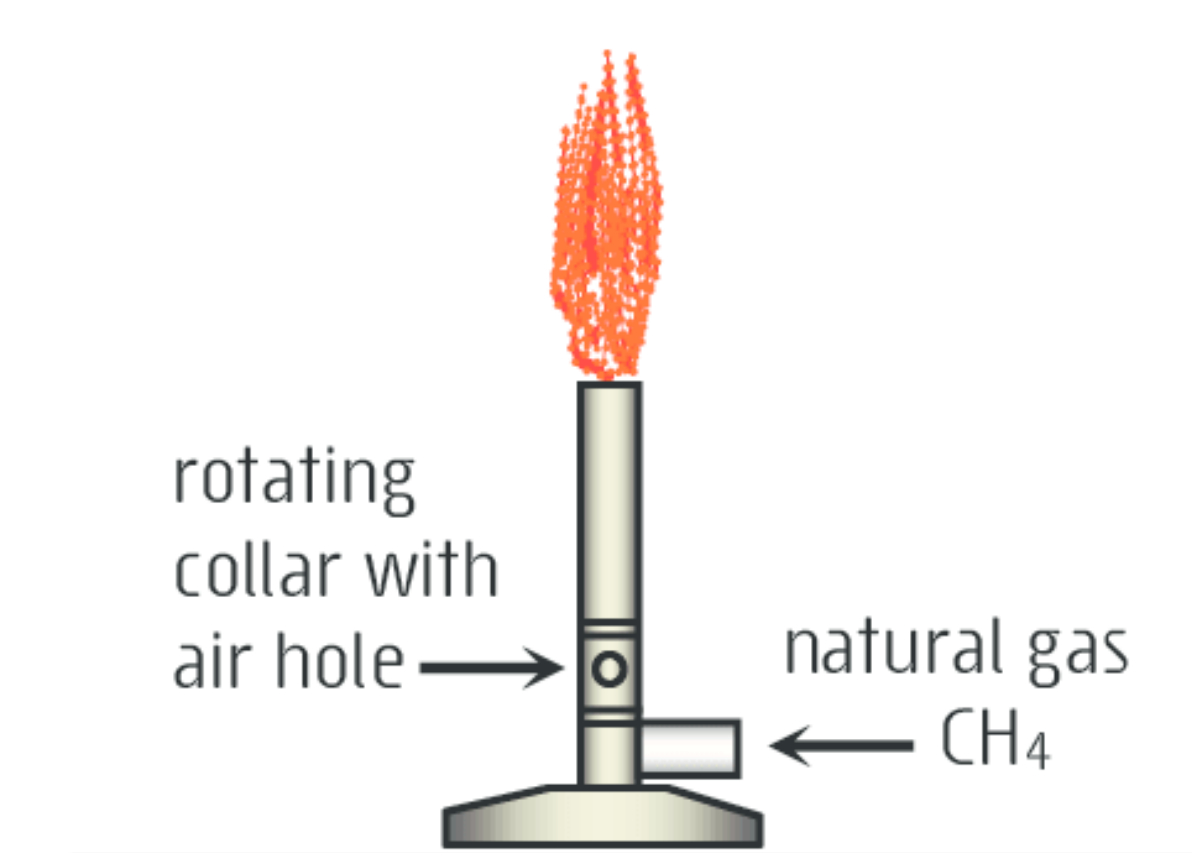
More importantly, incomplete combustion is a potential health hazard due to the toxic products formed. Inhaled carbon monoxide molecules have the ability to attach to haemoglobin molecules in blood. They do so around two hundred times more strongly than oxygen molecules. Inhaling even relatively low concentrations of carbon monoxide can lead to **hypoxia**, a condition where cells are deprived of an adequate oxygen supply. Symptoms include headache, mental confusion, agitation, nausea, vomiting and if untreated may lead to death. As carbon monoxide is a colourless and odourless gas its presence may initially go unnoticed. For this reason it is essential to provide adequate ventilation when burning hydrocarbon fuels in confined spaces.

Indoor gas heating in Western Australia is currently regulated by the Department of Commerce. It stipulates the maximum allowed gas heater size for an unflued (no chimney for exhaust gases) indoor heater is 25 MJ. Any room fitted with a gas bayonet point must have two fixed ventilation points each of 250 cm<sup>2</sup> area, one at floor level and one at ceiling height. The vents ensure sufficient air flow into the room thus maintaining an adequate oxygen concentration needed for the complete combustion of heater gases. This is essential for the prevention of incomplete combustion and carbon monoxide formation.

Complete Set 21.

## Set 21 Reactions of hydrocarbons

- Write a balanced equation for each of the **addition** reactions described here.
  - $\text{CH}_2 = \text{CH}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{_____?}$
  - $\text{CH}_2 = \text{CH}_2(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{_____?}$
  - $\text{CH}_2 = \text{CHCH}_3(\text{g})$  is combined with  $\text{H}_2(\text{g})$ .
  - Propene gas is bubbled through bromine water.
  - Chlorine water is mixed with cyclopentene.
  - Propene gas is bubbled into an  $\text{HBr}(\text{aq})$  solution.
- Write a balanced equation for each of the following **substitution** reactions. Assume the reaction conditions permit **single substitution only**, unless otherwise indicated.
  - $\text{CH}_3\text{CH}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{_____} + \text{_____}$
  - A mixture of  $\text{CH}_4(\text{g})$  and **excess**  $\text{Br}_2(\text{g})$  is exposed to ultraviolet radiation. (Assume complete substitution occurs.)
  - A few drops of bromine water is mixed with **excess** liquid hexane.
  - A few drops of bromine solution and **excess** benzene are mixed and exposed to ultraviolet radiation.
  - Ethane gas and **excess** chlorine gas are combined and react until **no further** reaction occurs.
- Write **balanced equations** for the combustion of the following fuels. Assume an excess air supply (complete combustion) unless otherwise stated. (See border note.)
  - Burning methane in a Bunsen flame (Fig 12),  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{_____} + \text{_____}$
  - Incomplete combustion of propane, a major component of LPG.  
 $\text{C}_3\text{H}_8(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{_____} + \text{_____}$
  - $\text{C}_{24}\text{H}_{50}(\text{s})$ , a wax, is burnt with a limited air ( $\text{O}_2$ ) supply.
  - Burning octane, a major component of petrol. Assume complete combustion.
  - Acetylene ( $\text{C}_2\text{H}_2$ ) in an oxyacetylene torch and excess oxygen is ignited.
  - Complete combustion of benzene, an important petrol additive.



**FIGURE 12** The heat produced from a Bunsen burner comes from the combustion of natural gas (essentially methane,  $\text{CH}_4$ ). A rotating collar surrounding the air hole can be adjusted to vary the amount of air mixing with methane. Less air results in **incomplete combustion** forming  $\text{CO}$ ,  $\text{C}$  (soot) and less heat.

The **yellow-orange** colour of a Bunsen flame is caused by the presence of unburnt carbon particles (soot) within the flame. This happens when the air holes are fully closed as **insufficient air** ( $\text{O}_2$ ) is present for complete combustion to occur.

Sometimes the effect of incomplete combustion can be seen when diesel powered cars or trucks accelerate quickly producing plumes of black exhaust. The black smoke (particulate pollution) consists of unburnt carbon particles.

### Hint!

Having trouble visualising the reaction products? Try drawing full structural formula for the organic reactant and its product.

Substitution reactions can be used to produce **chlorinated hydrocarbons**. These are a most useful class of organic compound. They have application in the manufacture of rubbers, plastics, insecticides and as industrial solvents.

Chloroethene ( $\text{CH}_2=\text{CHCl}$ ), also known as vinyl chloride, for example is used in the manufacture of **polyvinylchloride**, the plastic known as vinyl or PVC. Dry cleaning fluid or **tetrachloroethene** ( $\text{Cl}_2\text{C}=\text{CCl}_2$ ) is excellent for dissolving grease and oil. It can be used for **dry-cleaning** clothes that would otherwise be damaged by soap or water.

A wide variety of **hydrocarbon fuels** are available for different specific applications.

**methane** ( $\text{C}_1$ ) (major component of NG) home heating and cooking

**acetylene** ( $\text{C}_2$ ) (ethyne) high temperature flames

**LPG** ( $\text{C}_{3-4}$ ) (mainly propane and butane) motor cars and portable cookers

**petrol** ( $\text{C}_{5-10}$ ) motor cars

**jet fuel** ( $\text{C}_{8-16}$ ) aircraft

**diesel** ( $\text{C}_{10-15}$ ) heavy vehicles

**wax** ( $\text{C}_{20-40}$ ) candles



**Steam cracking** is used in the petrochemical industry to convert light fractions of crude oil (those with less than 6 atoms of carbon in each molecule) into **ethene**. The light crude fraction along with steam is heated to between 750 °C and 950 °C. The resulting reactions convert long chain molecules into smaller molecules (ie cracking) and introduce double bonds into some. Ethene is one product of this process. It is separated from the resulting mixture of compounds by high pressure distillation.

**Catalytic cracking** by comparison involves various decomposition reactions of heavy crude oil residues. The process uses controlled pressure and temperature (450–500 °C) with the aid of an  $\text{Al}_2\text{O}_3/\text{SiO}_2$  catalyst to convert **large hydrocarbon molecules** to a variety of **smaller molecules**. The resulting compounds are suitable for use in petrol and other fuels and as a chemical feedstock.

**Fluorine ( $\text{F}_2$ )** reacts explosively with all hydrocarbons causing both addition and substitution.

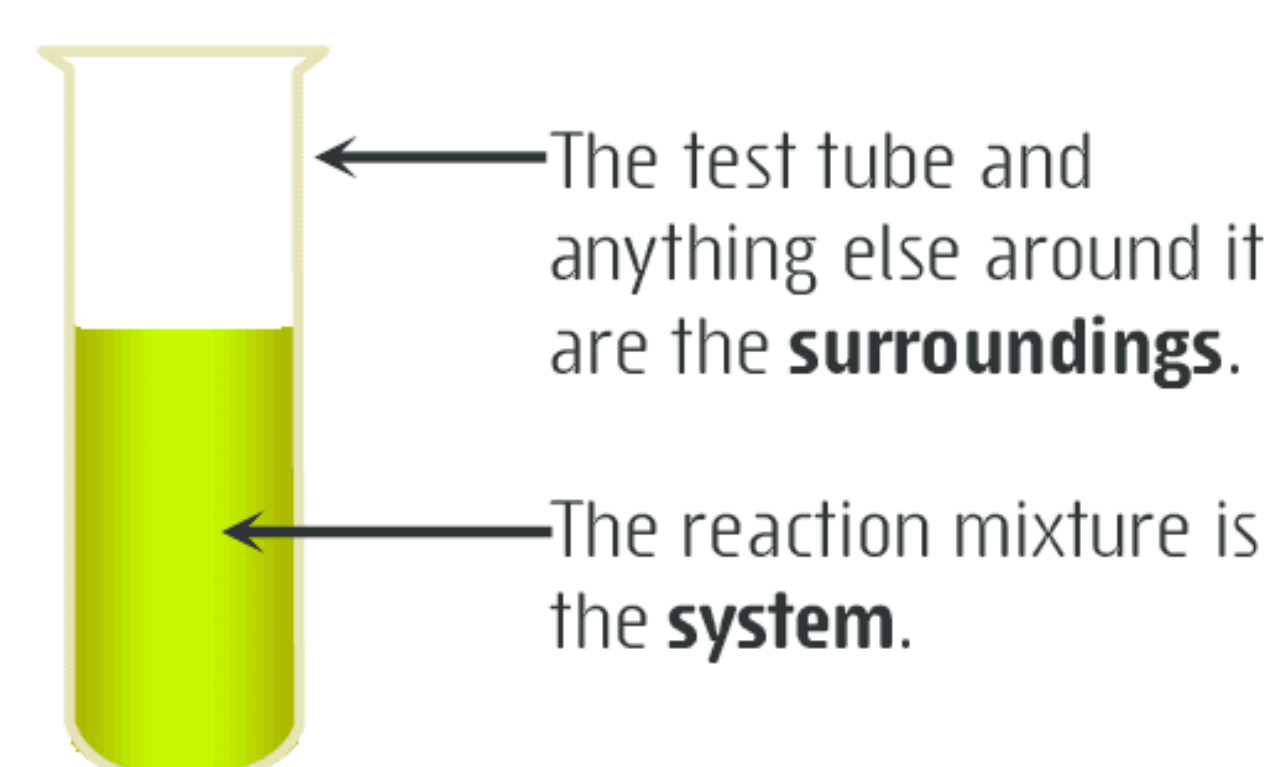
**Iodine ( $\text{I}_2$ )** shows no tendency to undergo addition or substitution reactions with hydrocarbons.

4. Ethane extracted from natural gas can be converted to ethene by a process called **steam cracking**. (See border note.) This is an important petrochemical process for the production of ethene. A steam and ethane mixture is heated to between 750 °C and 950 °C. This produces ethene and a valuable by-product, hydrogen gas. Steam plays no part in the chemical reaction itself.
  - a. Use the information given to write an equation for this reaction. How does this reaction compare with the process of addition of hydrogen to an alkene?
  - b. Very briefly state the advantage of heating the mixture to such a high temperature.
  - c. Why is ethene such an important hydrocarbon?
5. **Catalytic reforming** is an important chemical process used in the petrochemical industry for the production of quality automotive fuels. Generally this involves straight run heavy naphtha (a crude oil distillate mixture consisting mostly of  $\text{C}_6$  to  $\text{C}_{10}$  hydrocarbons) being converted to aromatic compounds and various branched hydrocarbons. The reforming process may involve reactions like the conversion of straight chain saturated hydrocarbon compounds such as heptane to 2,2-dimethylpentane or to aromatic compounds like methylbenzene. Hydrogen gas is a valuable by-product of this process.
  - a. With reference to this information, explain the meaning of the phrase, '**converted to aromatic compounds and various branched hydrocarbons**'.
  - b. Use the information given to write an overall equation for the formation of methyl benzene during catalytic reforming. What is the by-product of this reaction?
  - c. Briefly, what is the purpose of carrying out this catalytic reforming process? (See Fig 9 p97.)
6. Ali carried out a variety of reactions using different hydrocarbons as outlined below. In each case determine whether he will observe a reaction and if so state:
  - i. the **type of reaction** (addition, substitution or combustion)
  - ii. the **names** of the expected **products** (an equation is **not** required)
  - iii. the **observations** that Ali would notice.
  - a. Ethane gas is bubbled through bromine water and exposed to sunlight (UV radiation).
  - b. A mixture of ethene and oxygen is ignited.
  - c. A mixture of benzene and chlorine water is exposed to sunlight.
  - d. Hydrogen chloride gas is bubbled through pent-1-ene.
7. Addition and substitution reactions can be used to make halogenated compounds. This is done by reacting a suitable hydrocarbon with an appropriate halogen ( $\text{F}_2$ ,  $\text{Cl}_2$  or  $\text{Br}_2$ ) or an appropriate hydrogen halide ( $\text{HCl}$ ,  $\text{HBr}$  or  $\text{HI}$ ). **Name the starting materials** that you could use to make each of the following organic compounds. Also **state the type of reaction** involved. There is no need to give the equation or describe the reaction conditions.
 

a. chloroform, $\text{CHCl}_3$	c. 2-chlorobutane
b. 1,2-dibromobutane	d. bromobenzene
8. It is sometimes possible to **distinguish** between **saturated** and **unsaturated** hydrocarbons by their reaction with **bromine water**. Unsaturated hydrocarbons rapidly discolour a bromine water solution (an addition reaction), while saturated hydrocarbons have a slow reaction with bromine water (a substitution reaction) and usually need UV light to speed up the reaction. Can bromine water be used to distinguish between the following pairs of compounds? Explain your answer.
  - a. ethane gas and ethene gas
  - b. ethene gas and propene gas
  - c. hexane and benzene
  - d. methylcyclopentane and 3-methylcyclopentene
  - e. hexene and benzene
  - f. the two isomers of  $\text{C}_3\text{H}_6$  **(E)**

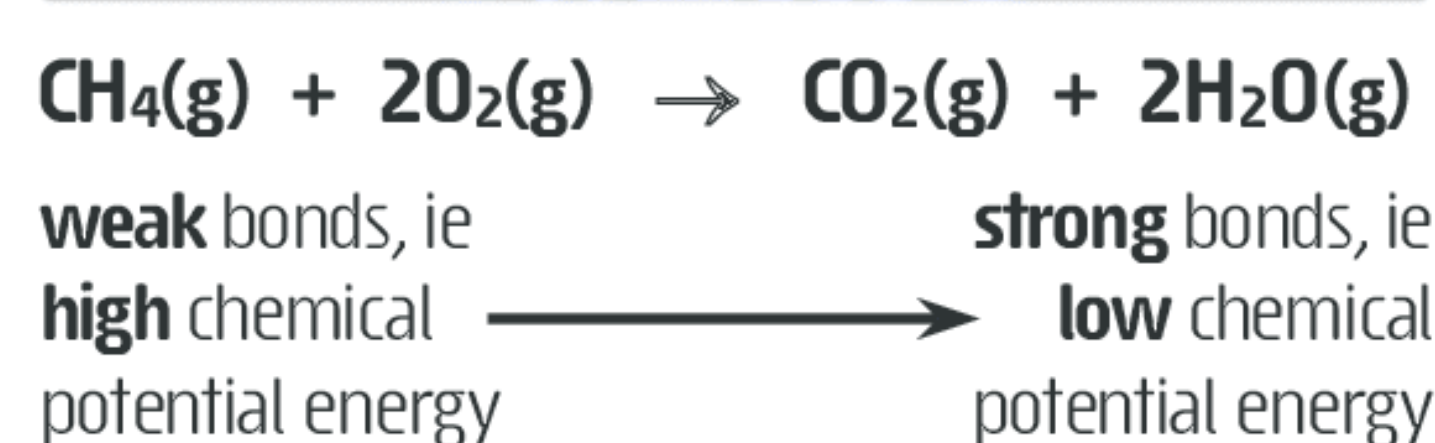
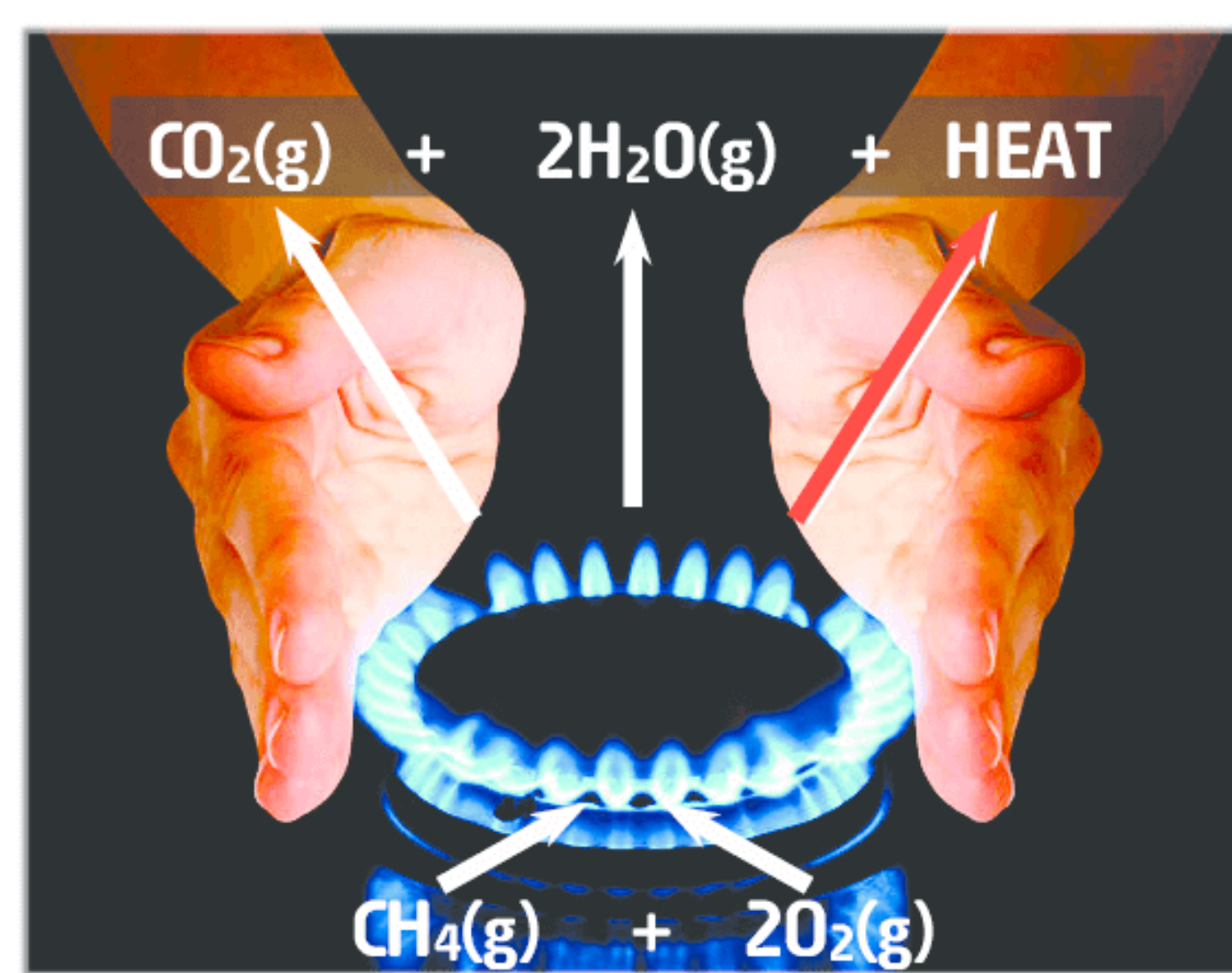


# CHAPTER 13 | ENERGY FLOW AND CHEMICAL CHANGE

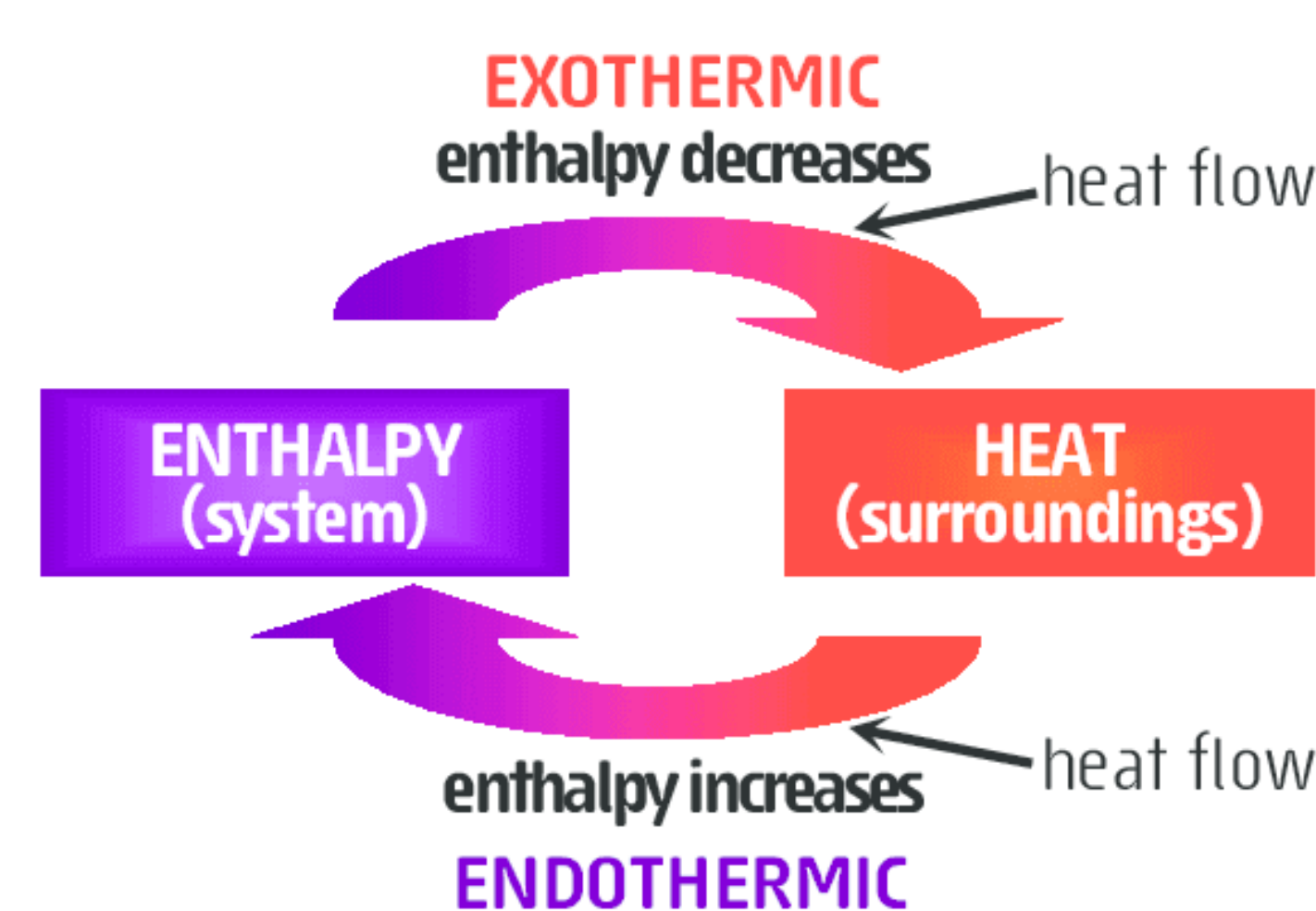


**FIGURE 1** When analysing energy changes in a chemical reaction it is convenient to define the **reaction mixture** as the **system** and its container and everything else around it as the **surroundings**.

**FIGURE 2** A combustion reaction like that in a gas burner releases heat to the surroundings. This happens as the total energy stored in the bonds of the products is less than that of the reactants. The energy difference appears as heat in the reacting system causing its temperature to rise. Heat then flows out of the hot reacting system (gas flame) and into the cooler surroundings (air and hands). Overall **energy is conserved**.



**Exothermic** reactions convert chemical potential energy (purple), into increased particle kinetic energy (red). This means the temperature of the system (reaction mixture) rises and consequently **heat flows out of** the system (hot) to the surroundings (cool). Overall, the reacting system loses energy to the surroundings thus its **enthalpy decreases**.



**Endothermic** reactions convert particle kinetic energy ('heat') into stored chemical potential energy. The loss of particle kinetic energy within the reacting system (converted to chemical potential energy) causes the system's temperature to fall. As the system cools, **heat then flows into it** from the warmer surroundings. Thus the system gains energy from the surroundings and its **enthalpy increases**.

Attempt Set 22 # 1, 2, and 3.

## 13.1 Understanding energy

**Energy** can be described as the capacity to do work or cause change. It is measured in **joules**. Some forms of energy are heat, chemical, electrical, light, kinetic and potential. The various forms of energy are interchangeable. However, the total amount of energy present is always constant. This means whenever one form of energy disappears or reduces in quantity then another form of energy will appear or increase in quantity so that the total amount of energy present is unchanged. Thus, if the energy present in a given **system** falls then there will be a corresponding rise in the energy of its **surroundings** so that the total energy in the **system + surroundings** remains constant. (See Fig 1.) This idea is known as the **law of conservation of energy**.

## 13.2 Energy changes in chemical reactions

During a chemical change the system and its surroundings are often seen to heat up or cool down simply because of the chemical change that has occurred. These heating or cooling effects are a result of a change in the enthalpy present in the products of the reaction compared to enthalpy in the reactants. The **enthalpy** of a substance is the **total energy** present in the substance. It includes (but is not limited to) the energy stored in chemical bonds, known as **chemical potential energy** plus the energy due to particle motion, ie the **kinetic energy** of its particles. Remember, particle kinetic energy rises with rising temperature. (See p2.) Also, the chemical potential energy of a bond is high for a weak bond and low for a strong bond.

During a chemical change some bonds are broken and new ones are formed and so there will inevitably be a change (increase or decrease) in the amount of stored chemical potential energy. As energy must be conserved, any change in chemical potential energy must be balanced by an opposite change in some other form of energy, usually particle kinetic energy ('heat'). This means the **temperature** of the reaction system will rise or fall and cause **heat** energy to flow into or out of the reaction system. (See Fig 2.) Remember heat always flows from hot regions to cooler ones. This flow of heat changes the enthalpy (total energy) of the reacting system. The resulting **enthalpy change**,  $\Delta H$  is defined as:

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

where: **H** = enthalpy

$\Delta H$  = change in enthalpy

For chemical changes that happen at **constant pressure**, such as in an **open** beaker or test tube, the **heat gain or loss** of the system **equals its change in enthalpy** ( $\Delta H$ ). In these situations  $\Delta H$  is also referred to as the **heat of reaction**.

## 13.3 Endothermic and Exothermic reactions

Reactions that **lose heat to the surroundings** (eg combustion, see Fig 2) are called **exothermic** reactions. These have a **negative** value for  $\Delta H$ , ie enthalpy **decreases** during the course of the reaction. In an exothermic reaction some of the chemical potential energy stored in bonds is converted to particle kinetic energy, ie resulting in an increase in the system's temperature. Overall energy is conserved with chemical potential energy becoming 'heat' energy. However, as this change raises the reacting system's temperature so heat then flows out of the hot system and into the cooler surroundings. (See Fig 2.) The loss of heat energy from the system to the surroundings then means the system's enthalpy (total energy) has reduced and hence  **$\Delta H$  is negative**.

Reactions that **gain heat from the surroundings** are called **endothermic** reactions. These reactions have a **positive** value for  $\Delta H$ , ie enthalpy **increases** during the course of the reaction. This will happen if some of the particle kinetic energy in the reacting system is converted into chemical potential energy stored in bonds. Overall there is no change in enthalpy. However, as a consequence of the reduced particle kinetic energy the reacting system's temperature will fall. Heat then flows from the warmer surroundings into the cooler reacting system. This now increases the reacting system's total energy (enthalpy) and hence  **$\Delta H$  is positive**. (See border note.)

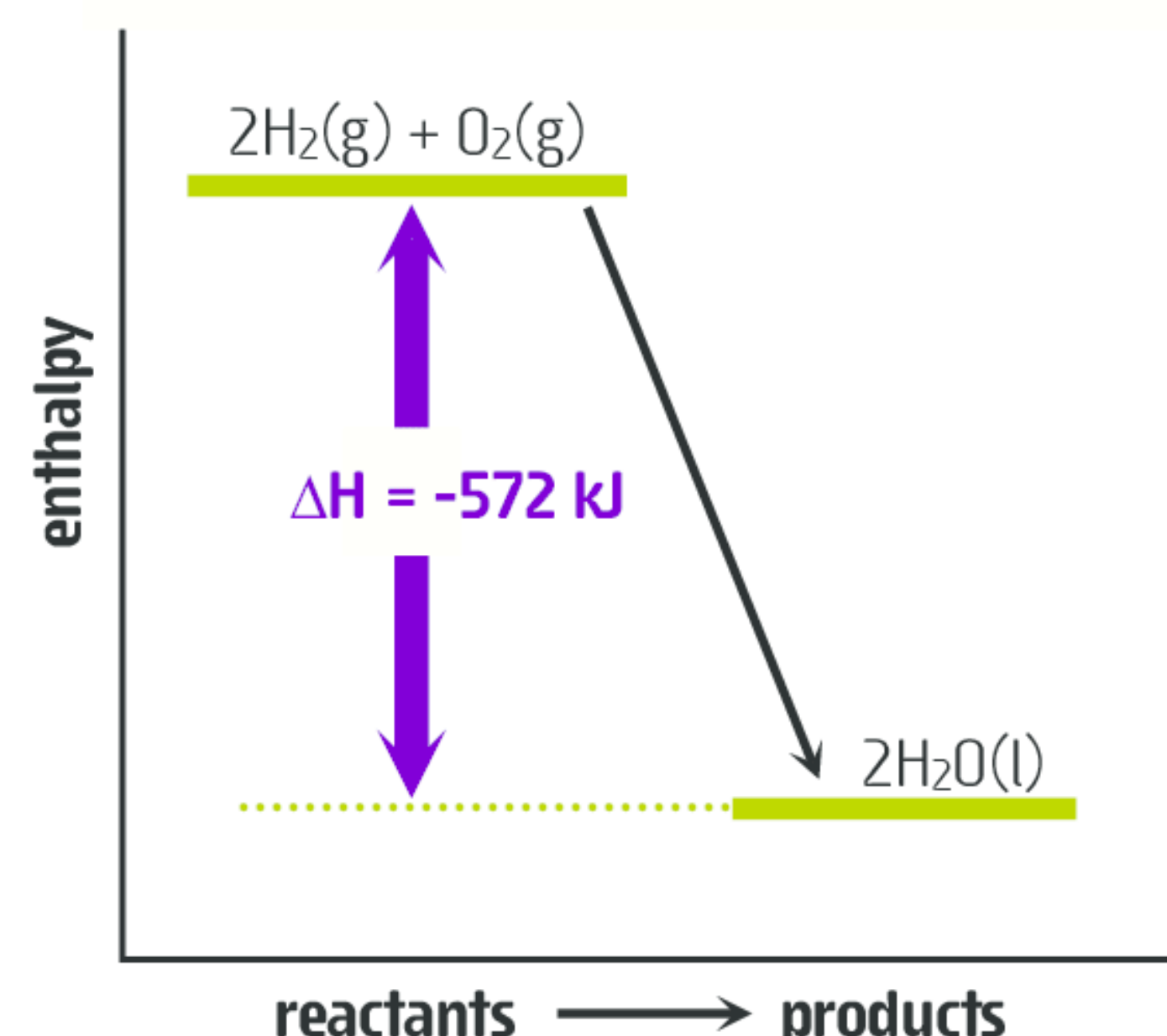


## 13.4 Representing energy changes in chemical reactions

The enthalpy change,  $\Delta H$  for a chemical reaction can be shown graphically using an **energy profile diagram** or it can be written along with the **chemical equation**. Sometimes the **heat** absorbed or released during the reaction is written into the equation rather than giving the enthalpy change. (See Fig 3.)

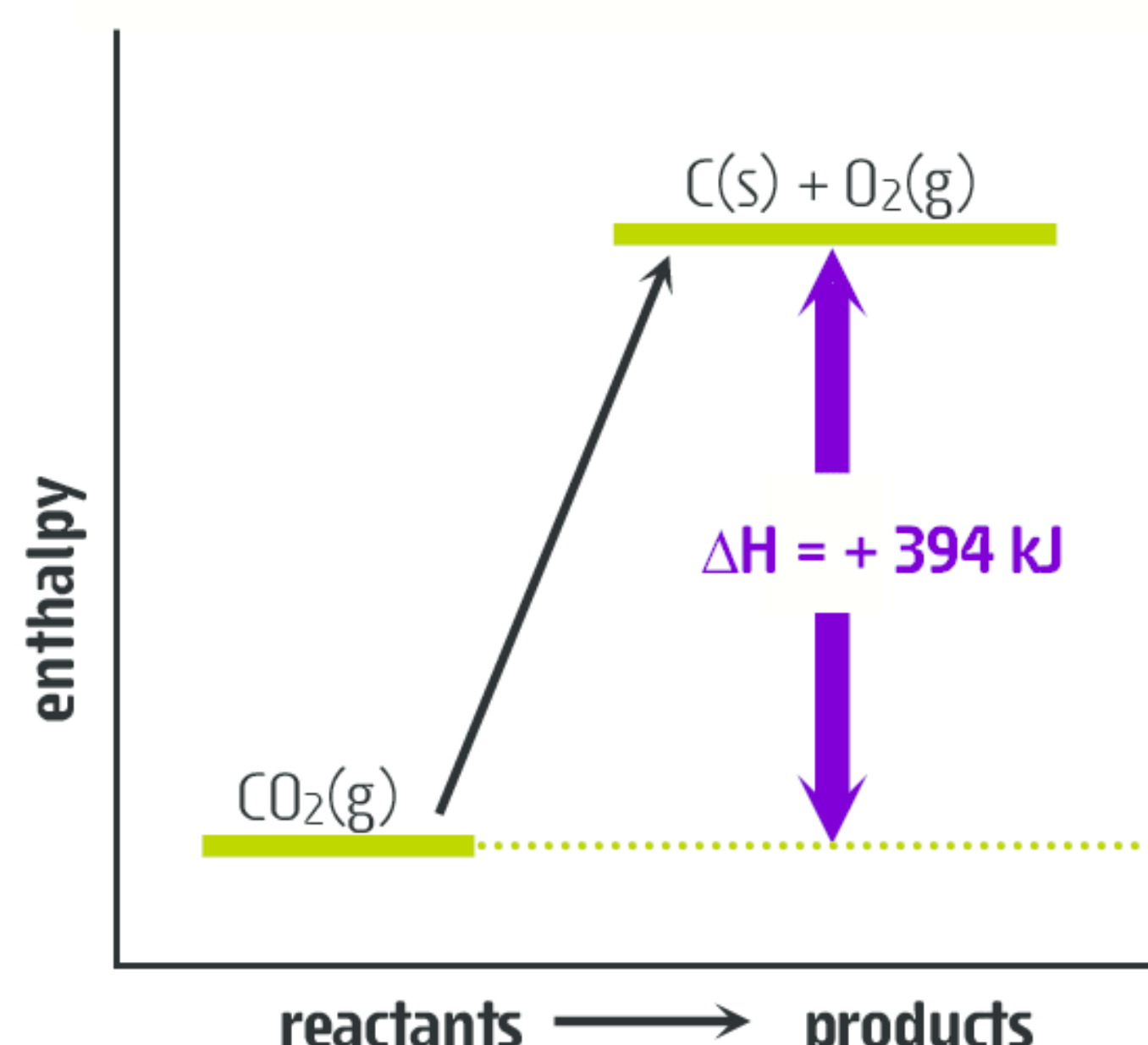
### (A) Exothermic reaction

In this reaction **enthalpy reduces** by 572 kJ ( $\Delta H = -572$  kJ) and so 572 kJ of heat is released to the surroundings.



### (B) Endothermic reaction

In this reaction **enthalpy increases** by 394 kJ ( $\Delta H = 394$  kJ) and so 394 kJ of heat is absorbed from the surroundings.



**FIGURE 3** The energy profile diagram (A) shows the reduction in enthalpy for an **exothermic** reaction. In the **endothermic** reaction (B) there is an increase in enthalpy as products have more enthalpy than reactants.

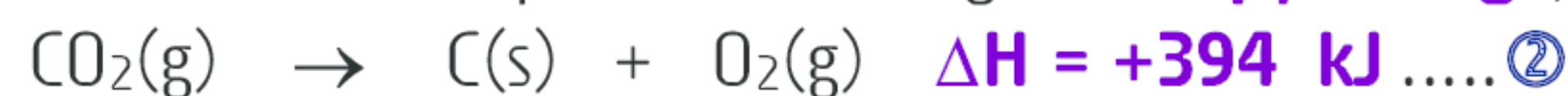
For convenience  $\Delta H$  can be written along with the balanced equation, as shown for ① and ②. (See below.) Alternatively the **heat** absorbed or released in the reaction can be written into the equation, as shown for ③ and ④. (See below.)

The following equations show how the energy change involved in a chemical reaction can be written along with the equation in terms of the **enthalpy change** ( $\Delta H$ ), as in equation ① and ②, or the associated **heat** flow, as in equation ③ and ④.

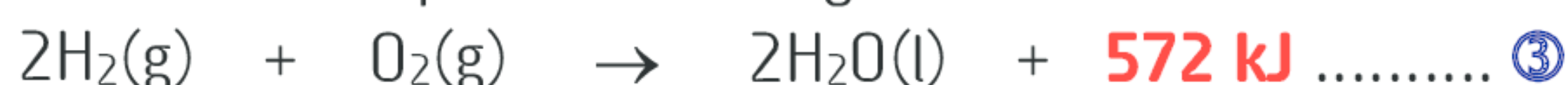
**Exothermic** equation showing **enthalpy change**,  $\Delta H$



**Endothermic** equation showing **enthalpy change**,  $\Delta H$



**Exothermic** equation showing **heat released**



**Endothermic** equation showing **heat absorbed**



Attempt Set 22 # 4 and 5.

## 13.5 Energy effects of making and breaking bonds

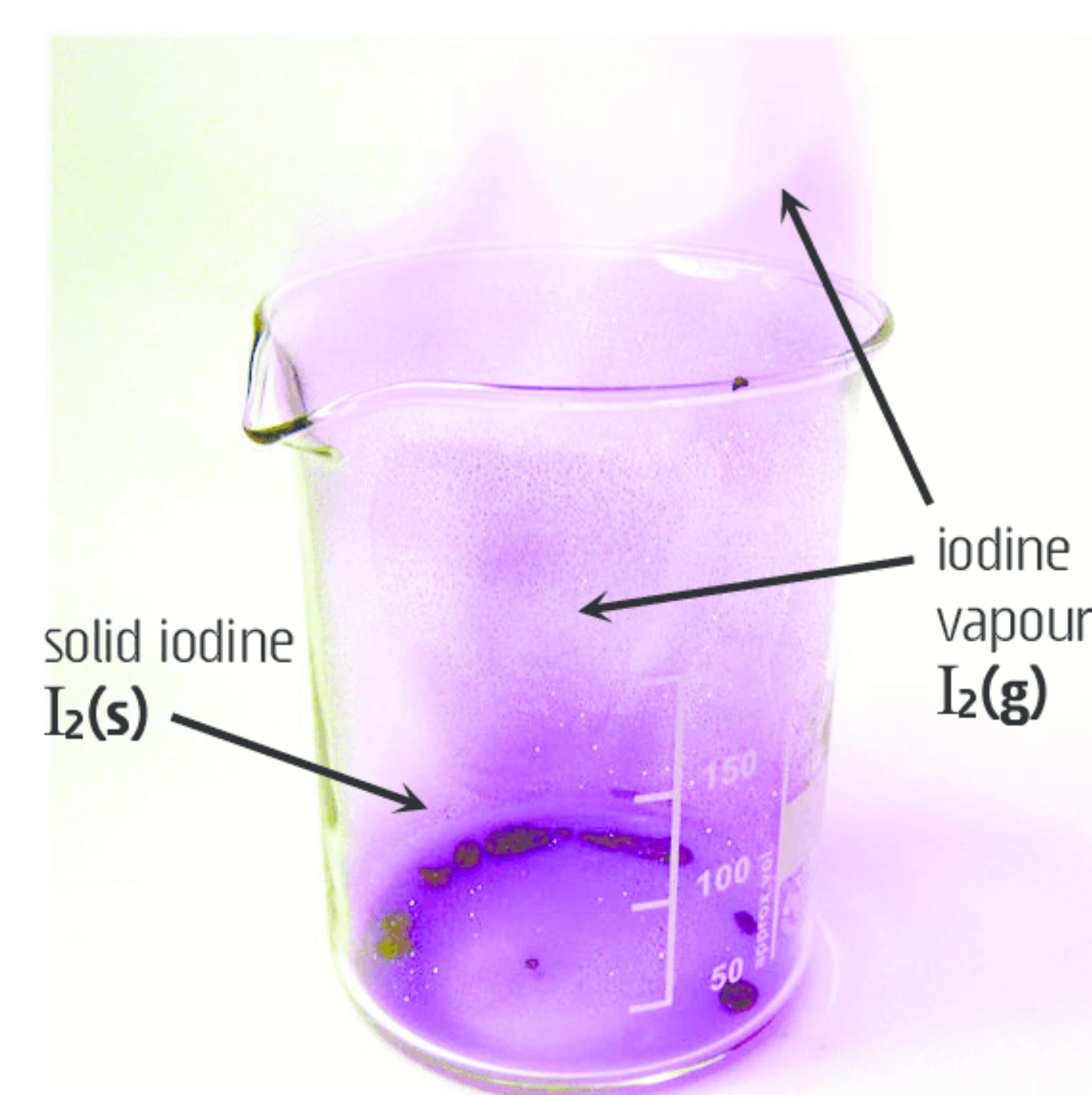
Another way to interpret energy changes during chemical reactions is in terms of **bond breaking** and **bond making**. It must be understood that **bond breaking** requires an input of energy, ie is **endothermic** (raises enthalpy). Typically, the stronger the bonds to be broken the more energy that needs to be absorbed to achieve this. By contrast, **bond making** releases energy, ie is **exothermic** (lowers enthalpy). The stronger the bonds that are formed the greater is the energy released in forming them.

The **sublimation** of solid iodine,  $\text{I}_2(\text{s})$  to form iodine vapour,  $\text{I}_2(\text{g})$  (Fig 4 and reaction ①) is endothermic as it involves the breaking of bonds. The **weak intermolecular forces** (IMFs) between neighbouring iodine molecules in the solid phase are broken to form unbonded iodine molecules in the gas phase. The reverse reaction, equation ②, is exothermic as it involves the formation of bonds (weak IMFs) between iodine molecules.



Equation ① shows 62 kJ of heat are needed for each mole of solid iodine that sublimates to form iodine gas. The reverse reaction ②, ie the formation of solid iodine from its vapour, is exothermic releasing 62 kJ of heat per mole of iodine solid formed.

**FIGURE 4** When heated, **solid iodine** changes directly into a **vapour** phase. This process, known as **sublimation**, is **endothermic**. It involves breaking the weak attractive forces (intermolecular forces) between neighbouring iodine molecules in the solid phase to form individual iodine molecules in the gas phase.



Attempt Set 22 # 6.

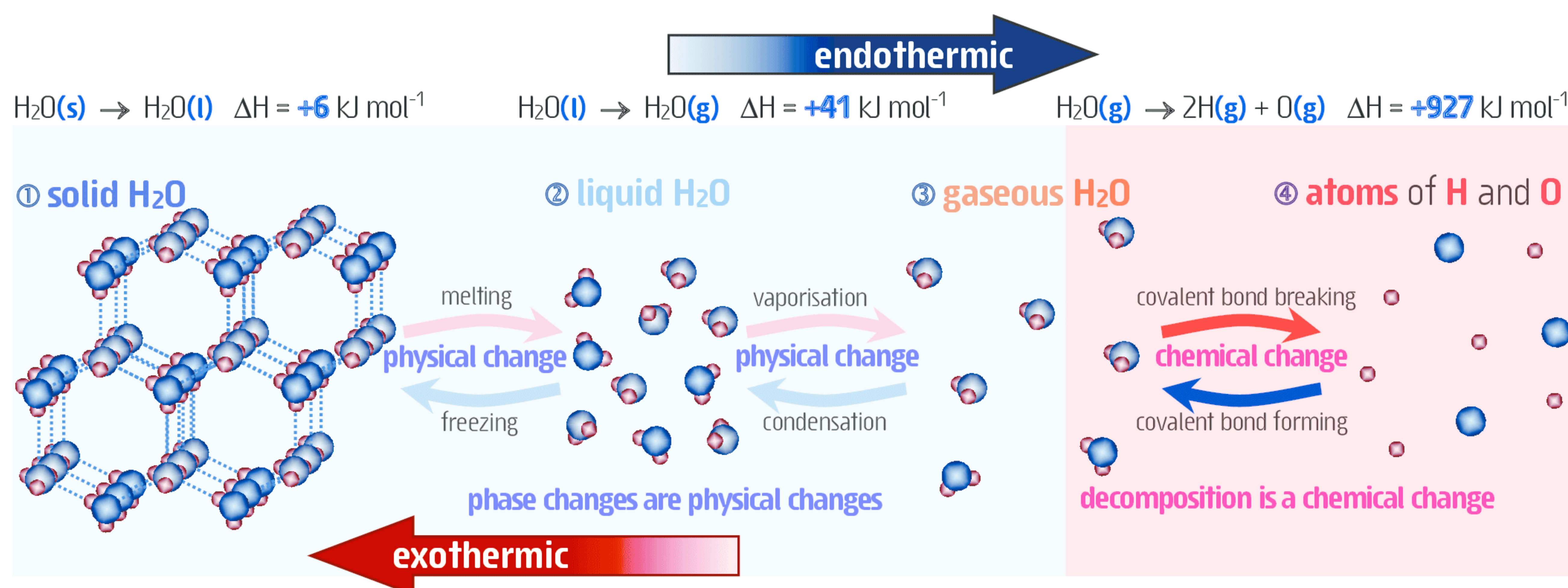
## 13.6 Comparing energy in physical and chemical changes

**Phase changes** like the sublimation of iodine are **physical changes** and as such involve the breaking or making of **weak bonds** only. For this reason, phase changes involve relatively small amounts of energy. By comparison **chemical changes** involve breaking or making **strong** chemical bonds like the covalent bonds in an iodine molecule. This is why chemical changes involve relatively large amounts of energy. Equations ③ and ④ show how much more energy is involved in breaking and forming the covalent bonds of an iodine molecule, than is involved in breaking or forming the weak bonds (IMFs) during its sublimation, ① and ②.





Typically the energy changes involved in physical processes like **melting**, **vaporisation** or **sublimation** are much less than that for a chemical process. Figure 5 shows the processes involved when ice is heated and changes phase to a liquid, then gas and ultimately, if the temperature is high enough, it undergoes **chemical decomposition** into free hydrogen and oxygen atoms. Notice how the energy involved in the chemical change of decomposing water molecules is so much greater than in the physical changes.

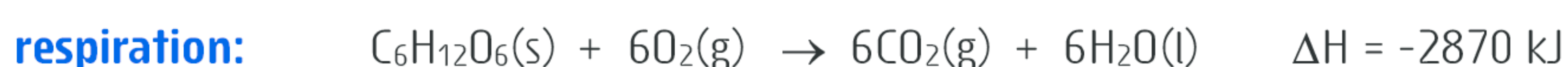


**FIGURE 5** Ice,  $\text{H}_2\text{O}(\text{s})$  consists of water molecules bound into a regular array, ① by **weak intermolecular forces** (shown here as dotted lines). Heating ice above its melting point,  $0^\circ\text{C}$  causes the weak attractive forces to be partially overcome. As a result the water molecules move freely in the liquid phase, ②. Further heating above  $100^\circ\text{C}$  causes the liquid to form a gas, ③ where water molecules are far apart and move in random straight lines. These phase changes are **physical processes** that involve much **less energy** than **chemical changes**. If the water temperature is raised to well above  $2000^\circ\text{C}$  then a significant number of the  $\text{H}_2\text{O}$  molecules will **decompose** forming unbonded **H atoms** and **O atoms**, ④. The decomposition of water requires a very high temperature as it is a **chemical process** involving the breaking of strong covalent bonds between hydrogen and oxygen atoms in water molecules.

Attempt Set 22 # 7 and 8.

## 13.7 Energy for you (E)

**Carbohydrates** are the major dietary source of energy that our bodies rely upon. **Fats**, **oils** and to a lesser extent **proteins** are also a cellular energy source. The equation here shows the overall reaction for the **aerobic respiration** of the carbohydrate **glucose**,  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ .



In the human body respiration (above) is catalysed by enzymes found in the cytoplasm and mitochondria of all cells. Energy released in this reaction is vital for maintenance of bodily functions and life processes.

The food we eat is a **renewable energy source**, a biological fuel, originating from plants that collect solar energy (light) and store it as **chemical potential energy** in various carbohydrates, oils or proteins. Plants initially collect light energy in a reaction called **photosynthesis** (below), this is essentially the reverse of respiration. Ultimately, the energy and  $\text{CO}_2(\text{g})$  absorbed in this endothermic reaction is returned to the environment when cells carry out respiration.



## 13.8 Fuels: The energy source for a modern economy

Fuels are substances that release heat energy when burnt, ie react with oxygen. Energy released in this reaction can be used directly for heating and cooking or to produce electricity or for powering motor vehicles or aircraft. Two types of fuels in use today are **fossil fuels**, which include **coal**, **oil** and **natural gas**, and **biofuels** like **biodiesel**, **bioethanol** and **biogas**. The following equations show the combustion of ethanol, methane and octane which are the major components of bioethanol, natural gas and petrol respectively.



These fuels produce varying amounts of **energy** and **carbon emissions** ( $\text{CO}_2$ ).

Attempt Set 22 # 9.



**FIGURE 6** Our daily energy intake needed to maintain regular physical activity and basic metabolic functions varies with age, level of activity and gender. A 17 year old male, for example, who is moderately active will need around 13.7 MJ per day and a female 10.8 MJ per day.

All of this energy originates from the metabolism of carbohydrates, lipids (fats and oils) or proteins. The energy in these compounds can be traced back to the light energy absorbed by plants during photosynthesis where atmospheric carbon dioxide and water are converted into sugars.

**Respiration** occurring in the cells of our body releases the energy in sugars and **returns carbon dioxide** to the environment from where plants originally absorbed it during **photosynthesis**.

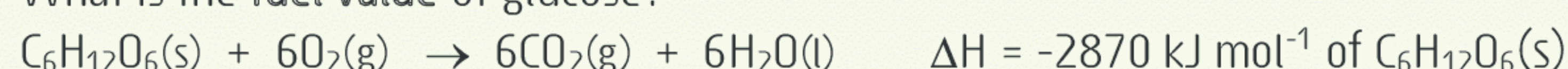


## 13.9 Comparing fossil fuels: Emissions and fuel values

Two important aspects of a fuel are its **fuel value**, sometimes called **heating value**, and its **carbon emissions**. (See Fig 7.) Fuel values are a convenient way of comparing the energy available from the complete combustion of equal masses or volumes of different fuels. The higher the fuel value the greater the energy available from a given mass of the fuel. It can be expressed in a variety of units such as **kJ g<sup>-1</sup>**, **MJ kg<sup>-1</sup>** or **MJ L<sup>-1</sup>**. For pure compounds this can be calculated from the standard heat of combustion for the fuel,  $\Delta H_c$ . (See Example 1.) Most fossil fuels and biofuels however, are complex mixtures whose composition may vary. For this reason the heating value of these fuels is best obtained experimentally and the values will vary depending upon the actual composition of the fuel and the nature (ie phase) of the combustion products. (See Table 1 p108.)

$$\text{Fuel value}_{(\text{compound})} = \frac{\Delta H_c}{M} \quad \text{where: } \Delta H_c = \text{standard heat of combustion of 1 mol of the fuel} \\ M = \text{the molar mass of fuel (ie the mass that is burnt, 1 mole)}$$

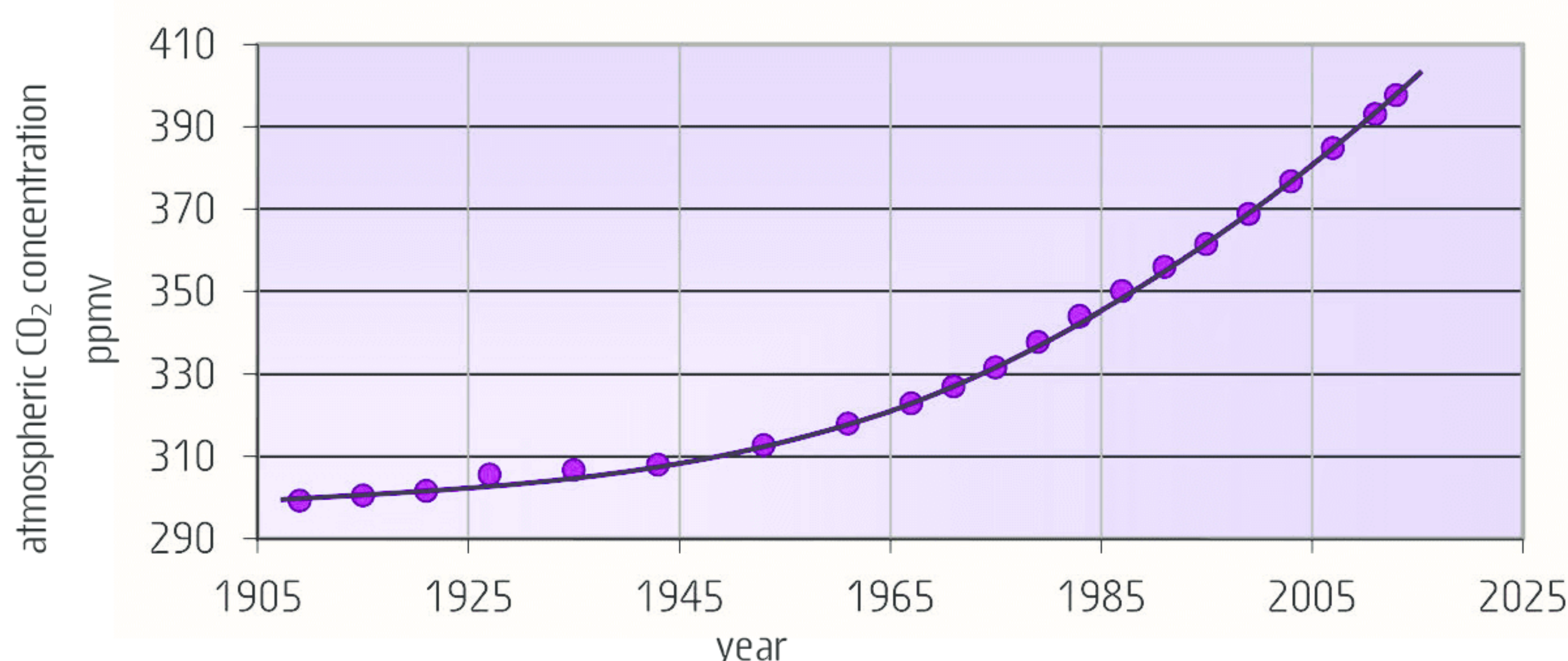
**Example 1** What is the fuel value of glucose?



$$\text{Fuel value} = \frac{\Delta H_c}{M} = \frac{2870}{180.156} = 15.9 \text{ kJ g}^{-1} \quad \text{This tells us to expect 15.9 kJ of heat energy to be released for every gram of glucose that is burnt.}$$

For a given use it is most desirable to choose fuels with a **higher fuel value** (heating value) as this will require the handling (mining, transport or processing) of smaller masses of fuel for the same energy output.

**Carbon emissions**, ie  $\text{CO}_2(\text{g})$ , resulting from the combustion of a fuel are an important issue as carbon dioxide is a known greenhouse gas. **Greenhouse gases** like carbon dioxide and methane, for example, contribute to a warmer atmosphere by reabsorbing heat that would otherwise be radiated from the Earth's surface and out into space. The presence of greenhouse gases in the atmosphere helps prevent the Earth's surface temperatures from plunging to below zero. However, it is now understood that the increasing atmospheric  $\text{CO}_2$  concentration (see Fig 8) is contributing to rising average global temperatures which in turn are resulting in climate change.



**FIGURE 8** The graph at left shows the atmospheric concentration of  $\text{CO}_2$  in parts per million by volume (**ppmv**). Data from 1910 till 1953 is from the **Siple Station ice core** in Antarctica. Data from 1953 onwards is from **Mauna Loa** in Hawaii.

A clear trend is evident showing an increased rate of growth in the atmospheric  $\text{CO}_2$  concentration. The current rate of increase is around **2 ppmv per year**, equivalent to  $2 \times 10^{10}$  tons of  $\text{CO}_2$  per year!

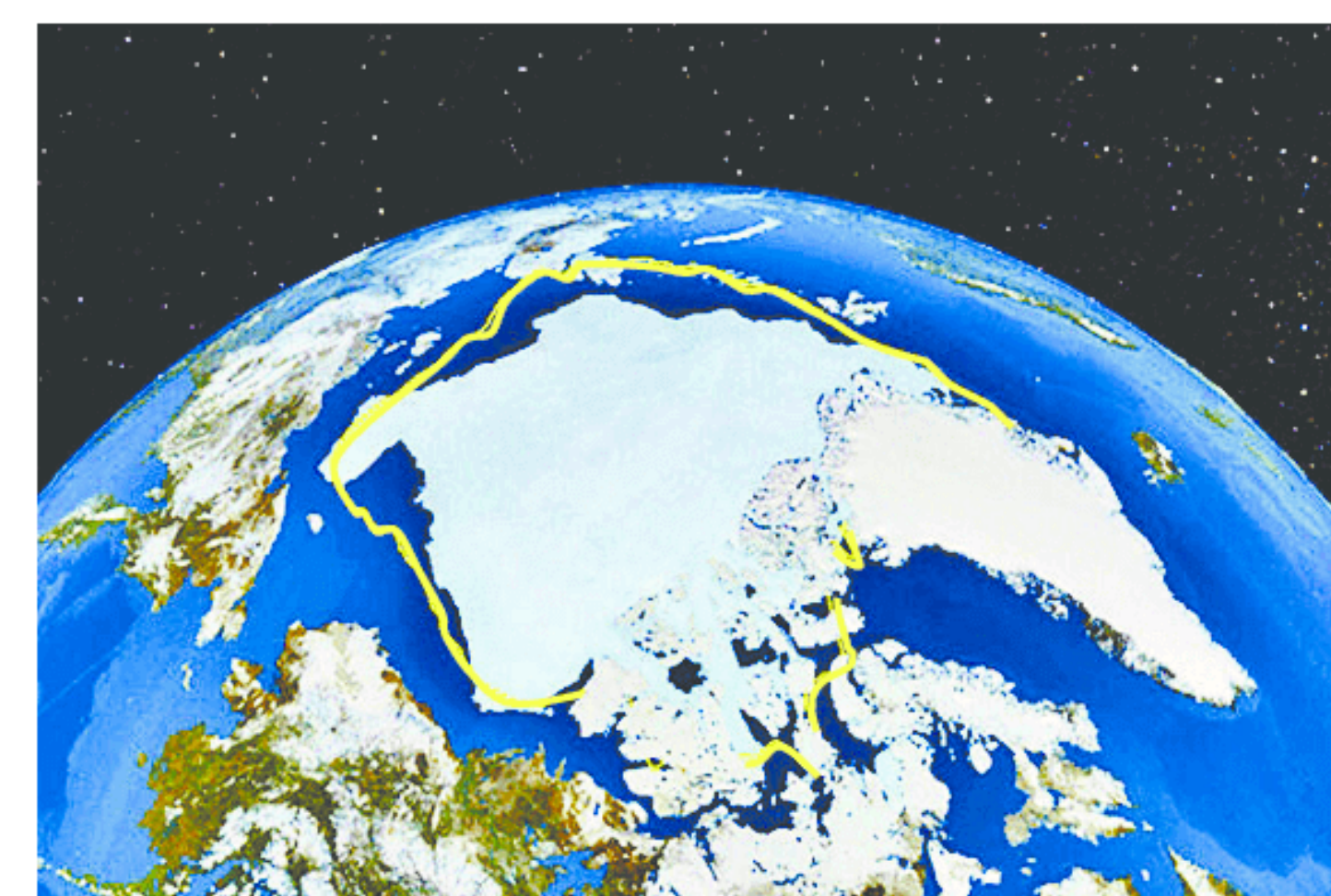
Note: The y axis starts at 290 ppmv.

For the latest data see: <http://www.esrl.noaa.gov/gmd/ccgg/trends/>

The **United Nations**, through the United Nations Framework Convention on Climate Change, **UNFCCC** (see border note) has set itself the ultimate objective of 'stabilisation of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous **anthropogenic** (ie human-induced) interference with the climate system.'

Understanding the carbon emission characteristics of different fuels is essential to making valid judgements about fuel choice for minimising these emissions. **Carbon emission values** can be helpful in this regard as they compare the amount of carbon dioxide a given fuel produces for a given amount of energy released. They are usually expressed as the mass of carbon dioxide produced in grams per megajoule of energy released when the fuel is burnt, ie **g( $\text{CO}_2$ ) MJ<sup>-1</sup>**. (See Table 1.) Scientific information about carbon emissions and fuel values helps nations like Australia, which are signatories to the **Kyoto Protocol**, (border note) achieve set targets for reductions in carbon emissions. One way to achieve this is to move to fuels with lower rates of carbon emissions.

**Coal** (Fig 9) is the most abundant and cheapest of the fossil fuels. However, it also has the highest rate of carbon emissions, eg Australian black coal produces 90-95 g( $\text{CO}_2$ ) MJ<sup>-1</sup>. (See Table 1.) For this reason, there is a global move to replace coal used for electricity generation with **natural gas (NG)**, a lower carbon emitting fuel producing only 51 g( $\text{CO}_2$ ) MJ<sup>-1</sup>.



**FIGURE 7** Carbon emissions in the form of  $\text{CO}_2(\text{g})$  are believed to contribute to global warming. One clearly visible effect of this is the well documented annual reduction in the area of summer Arctic sea ice. The image here shows the extent of Arctic sea ice on Sept. 12, 2013, the day before NSIDC estimated it hit its annual minimum. The yellow line shows the 30-year average minimum. The lowest ever recorded sea ice coverage occurred on **September 16, 2012**. This equalled an area about **half the thirty year average** summer minimum.

The image data was provided by the Japan Aerospace Exploration Agency from their GCOM-W1 satellite's AMSR2 instrument.

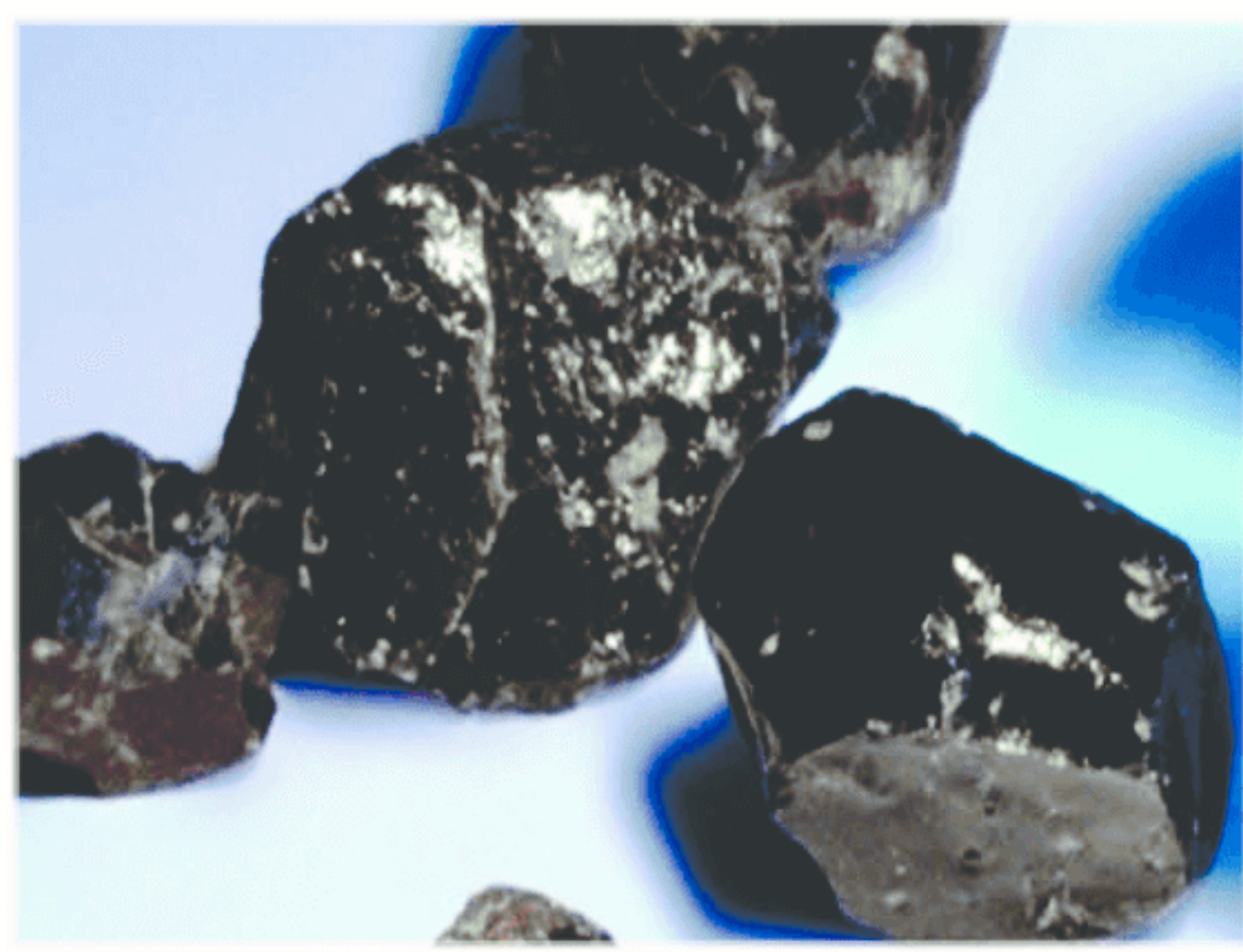
Image Credit: NASA Goddard's Scientific Visualization Studio/Cindy Starr.

The **United Nations Framework Convention on Climate Change** (UNFCCC) entered into force in 1994 with the aim to consider remedies to limit average global temperature increases and the resulting climate change.

Today, it has near-universal membership with 195 countries party to the convention. To assist in achieving its objective, the **UNFCCC** has implemented international agreements such as the **Kyoto Protocol**, which sets binding emission reduction targets for 37 industrialised countries (those largely responsible for the current high levels of atmospheric greenhouse gas emissions).

More recently, in December 2015, the 195 member nations reached an historic agreement to combat climate change and take actions and investment towards a low carbon, resilient and sustainable future. A major aim of this agreement is to keep global temperature rise this century to well below 2 degrees Celsius and to drive efforts to limit the temperature increase even further to 1.5 degrees Celsius above pre-industrial levels. (See <http://newsroom.unfccc.int/>)





**FIGURE 9** The fossil fuel coal consists mainly of carbon chemically combined to varying amounts of hydrogen, oxygen, sulfur and nitrogen. Its carbon content can vary considerably. Anthracite coal for example (shown above) may contain up to 98% carbon by mass while lignite contains as little as 50% carbon.

Coal is the source of energy for around 41% of the electricity generated world wide. Currently Australia is the world's second largest exporter of coal and in 2011-2012 coal fired power stations produced 69.4% of Australia's electric power.

According to research by the WWF-Australia, one third of Australia's carbon dioxide emissions come from electricity generation. Although the concentration of this gas in our atmosphere is very low, currently less than 0.04% by volume, its concentration is steadily increasing. (See Fig 8.) This is a significant issue as CO<sub>2</sub> is a known greenhouse gas that is believed to contribute to global warming and climate change.

Attempt Set 22 # 10, 11 and 12.



**FIGURE 10** Transperth operates free CAT Bus services in Perth, Fremantle and Joondalup, WA. The fleet was introduced in 2005 and now consists of 39 CAT buses; 31 fuelled by CNG and 8 by diesel.

The CNG engines run at a higher temperature than do diesel engines. This reduces the service life of certain engine components and leads to higher maintenance costs for CNG powered buses.

According to the international European emission standards, Transperth CNG bus emissions are rated **Euro 4**, while the new generation **diesel** CAT buses are rated **Euro 5** (less harmful emissions). As CNG is no longer the best fuel to assist in the reduction of Transperth's carbon footprint, there are no plans to expand the CNG fleet. Image courtesy of Transperth.

**TABLE 1** Some **fossil fuel types**, their **heating value** (blue) and **carbon emissions** (green)

**Coal (24-30 MJ kg<sup>-1</sup> (Australian black coal) 90-95 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** Coal is a black to light brown solid containing carbon (50% to 98%) and varying amounts of hydrogen, oxygen, sulfur and nitrogen. Brown coal is a low grade coal containing 60-80% carbon (after drying) and considerable moisture (H<sub>2</sub>O). Its heating value can be as low as a quarter that of black coal which has a much higher carbon content and lower moisture content. Both black and brown coal deposits are extensively mined in Australia.

**Natural gas (NG) and compressed natural gas (CNG) (47 MJ kg<sup>-1</sup>/0.039 MJ L<sup>-1</sup>, 51 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** NG occurs in underground deposits on its own or along with petroleum. It is a gas mixture of mainly methane (typically 85 - 90%), with progressively lesser amounts of ethane, propane, butane and so on. Impurities like N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and sulfur compounds are also present. Some applications use CNG. This is made by compressing NG to 250 times normal atmospheric pressure.

**Liquefied natural gas (LNG) (49 MJ kg<sup>-1</sup> 51 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** LNG is obtained by cooling NG to between -159 °C to -162 °C. In the process impurities are removed as they condense (liquefy) at higher temperatures. The higher molar mass hydrocarbons are extracted (see LPG) and sold separately.

**Liquefied petroleum gas (LPG) (49 MJ kg<sup>-1</sup>/26 MJ L<sup>-1</sup> 59 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** This is the generic name for hydrocarbon mixtures of propane and butane stored in the liquid state at moderate pressure. LPG is extracted from NG by cooling or obtained as a by-product of petroleum refining.

**Petrol (46 MJ kg<sup>-1</sup>/34 MJ L<sup>-1</sup> 66 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** Petroleum (crude oil) refining involves fractional distillation to produce various boiling range mixtures of hydrocarbons. (See 12.1 p92.) Further chemical treatments such as catalytic cracking, reforming and blending are then used to produce the mixture of hydrocarbons called petrol. Petrol typically contains a range of hydrocarbon isomers with 4-12 carbon atoms per molecule. Octane, C<sub>8</sub>H<sub>18</sub> is often used as an 'average' representation of the compounds in petrol.

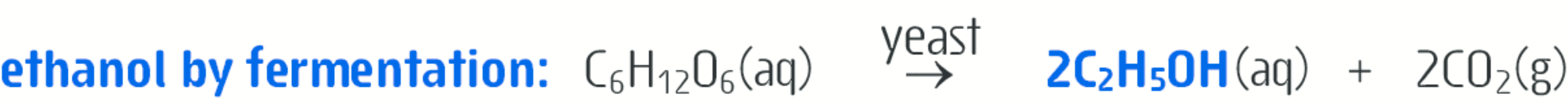
**Diesel (46 MJ kg<sup>-1</sup>/39 MJ L<sup>-1</sup> 70 g(CO<sub>2</sub>) MJ<sup>-1</sup>):** As with petrol, diesel is a fuel derived from the fractional distillation of petroleum. It is a mixture of higher molar mass hydrocarbons with 10-15 carbon atoms per molecule.

Data source: Bush, S., Harris, J. and Ho Trieu, L. 1997, Australian Energy Consumption and Production: Historical Trends and Projections to 2009-10, ABARE Research Report 97.2, Canberra.

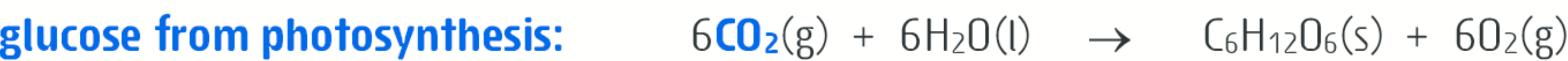
While NG is suitable for power generation, its low energy density as a gas, 39 MJ m<sup>-3</sup> is clearly problematic for transportation uses. While some commercial vehicles do operate using **compressed natural gas** (CNG, Fig 10) its widespread use is hampered by the dangers of using a flammable gas that is stored at around 200-250 times atmospheric pressure. A better transport alternative has been the use of **LPG** as it has similar low emission characteristics (59 g(CO<sub>2</sub>) MJ<sup>-1</sup>) but has a much higher boiling point range and so can be stored as a liquid at much lower pressures. A disadvantage of LPG though, is its lower fuel value, 26 MJ L<sup>-1</sup> when compared to petrol, 34 MJ L<sup>-1</sup>, for this reason LPG tanks must have a larger volume. Also, for safety reasons these tanks can only be filled to around 80% of capacity.

### 13.10 Biofuels: A low emission alternative

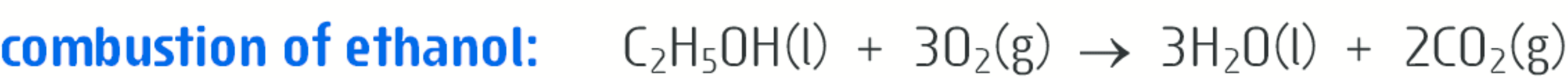
**Biofuels** like bioethanol, biogas (Fig 11) and biodiesel are produced from **biomass** and are considered fossil fuel alternatives. These fuels are a renewable resource as they all originate from organic matter (biomass) and their use results in lower carbon emissions than fossil fuels. The biofuel ethanol, C<sub>2</sub>H<sub>5</sub>OH(l) for example can be produced by the fermentation of plant sugars such as in the conversion of **glucose** to **ethanol** by **yeast**.



It is important to note that glucose is a product of plant photosynthesis (below) and thus all of the carbon present within glucose originates from the absorption of atmospheric CO<sub>2</sub>.



Ultimately, all of the atmospheric CO<sub>2</sub> absorbed during plant photosynthesis is recycled to the atmosphere during fermentation (above) or by its combustion as a fuel (below).



For this reason, biofuels like ethanol **might** be considered '**carbon neutral**' as their production and combustion merely recycles back to the atmosphere the same amount of CO<sub>2</sub> that was originally removed during photosynthesis. A full **life cycle analysis** of a biofuel's **carbon emissions**, however, must also take into account any extra emissions resulting from the use of **fossil fuels** in the biofuels manufacture or transportation.



This could include CO<sub>2</sub> emissions due to fossil fuel use in biomass farming, fertiliser manufacture, fuel synthesis and transportation. While the extent of this extra CO<sub>2</sub> emission will vary for different situations, it shows the use of biofuels is not necessarily carbon neutral. For comparison purposes, it must be noted that fossil fuels such as coal, petrol or diesel also involve extra 'life cycle' CO<sub>2</sub> emissions. These result from the use of fossil fuels in mining and exploration, refining and processing and fuel transportation. This means the motor vehicle tailpipe CO<sub>2</sub>(g) emissions only represent part of a fossil fuel's full life cycle emissions.

A further advantage of biofuels such as ethanol and biodiesel is their typically negligible or extremely low **sulfur content** compared to fossil fuels. The combustion of sulfur containing fuels is an environmental issue as it leads to the emission of **sulfur dioxide**; a respiratory irritant that impacts human health and also leads to acid rain. (See Fig 3 p86.) For this reason the Australian Government has legislated the reduction of average sulfur in fuels from a maximum permissible level of 1300 ppm in 1999 to a current maximum of 10 ppm for diesel, 50ppm in premium unleaded and a 150ppm maximum for standard petrol.

### 13.11 Biofuel production

Biofuels being produced on a commercial scale with current technology are known as **first generation biofuels**. This includes the production of:

- bioethanol by the **fermentation** of waste sugar (molasses) or waste wheat starch from crops like sugarcane or wheat,
- biodiesel by the **trans-esterification** of oilseed crops like soy and rapeseed or from waste animal fats.

A significant issue for the **sustainable** use of first generation biofuels on a large scale is the need for large tracts of agricultural land for growing the biofuel crops. Agricultural land and water are a finite resource with most of the readily available resources already allocated to food production. It would be undesirable for food costs to rise as a result of biofuel crop production competing with food production. The growth in first generation biofuel use in Australia will rely on new crops like agave, jatropha or various GM crops that can be grown without irrigation or on less fertile soils not currently used for agriculture.

New technologies currently in research and development involve the use of other **thermal** or **biochemical processes** to convert non-edible fibrous or woody portions of plants (ie **lignocellulosic** material) and **algae** into biofuels. These processes involve enzymes and micro-organisms that convert lignocellulose present in the biomass into sugar prior to its fermentation into ethanol. Biofuels produced this way are referred to as **second generation biofuels**. Commercialisation of second generation technologies offers the prospect of using a new range of bioenergy feedstock such as waste from agriculture and forestry or from farming algae in saline lakes. Neither of these approaches appear to compete for traditional agricultural resources and in some cases may complement current agricultural practices by turning farming waste into valuable biofuel.

Bioenergy production is most efficient where cheap or '**negative-cost**' residues or wastes (negative if a waste disposal cost is avoided) are available and used to produce biofuels onsite. This can happen at locations such as at sewage treatment facilities, paper mills, sawmills or sugar mills or at waste landfill sites. Most bioenergy production in Australia occurs in small to medium **cogeneration plants** built at sugar mills and other food processing plants that have access to significant low cost biomass waste streams. In Australia, CSIRO's Energy Flagship is conducting research into creating a sustainable future with renewable energy production and storage for electricity generation and transport.

Another important issue for consideration in the production of a biofuel is the amount of energy expended in producing the biofuel and in growing specific crops for biofuel production. This can potentially mean that more energy in the form of fossil fuels is expended in biofuel production than is returned when the biofuel is used. One recent paper (Environ. Sci. Technol., 2006, 40 (6), p1744-1750) estimates the **energy return,  $r_e$**  for producing ethanol from starch (corn) as between **0.84** and **1.65**. An  **$r_e < 1$**  means more energy goes into producing the ethanol than is available from its use as a fuel. In practice  **$r_e$**  must be significantly greater than one for biofuel production to be worthwhile.

**FIGURE 11** Biogas is essentially a mixture of methane, CH<sub>4</sub> and carbon dioxide CO<sub>2</sub> that is formed from the anaerobic digestion (bacterial decomposition without oxygen) of biomass (plant matter). In Australia biogas is harvested from landfill sites, sewage treatment plants, livestock feedlots and agricultural wastes such as bagasse from sugarcane refining.

The image below is of a small biogas plant. The dome shaped tanks are the anaerobic digesters where bacteria convert organic matter into biogas (CH<sub>4</sub> and CO<sub>2</sub>).



Gas from plants like these can be used directly to produce heat or electricity or converted to conventional fuels like natural gas or compressed natural gas, CNG.



**FIGURE 12** The **Kwinana Cogeneration Plant** is primarily fuelled by **natural gas** from Western Australia's gas fields, north of Perth. This cogeneration plant supplies otherwise waste steam directly to the nearby BP Australia Kwinana Oil Refinery. Also its proximity to the refinery minimises energy loss due to transmission distances. The remaining electrical energy is supplied to the state grid.

**Conventional power stations** may convert as little as 35% of the available energy stored in fuel into electricity. Much of the available energy is lost to the environment as waste heat. One of the aims of modern cogeneration plants is to utilise as much of the otherwise waste heat as possible, either directly within the plant or in nearby homes or industries.

Image courtesy of GDF SUEZ Australian Energy.

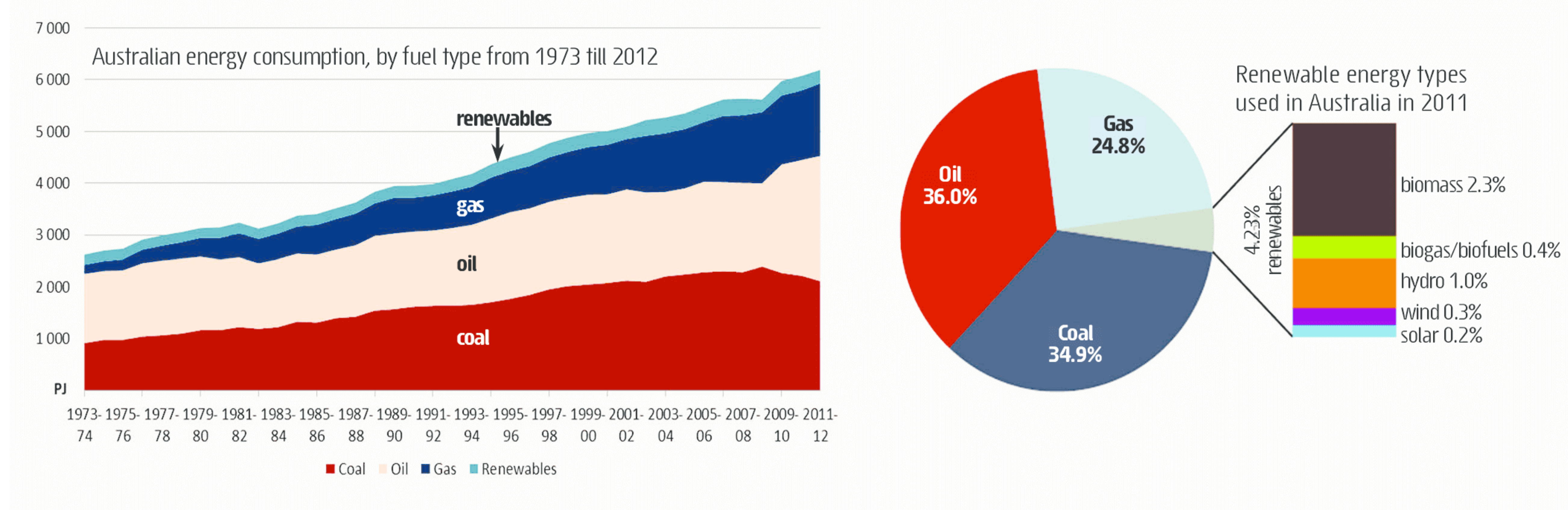
Attempt Set 22 # 13.



## 13.12 Fuel use in Australia

The rapid evolution of technology that has taken place since the industrial revolution has given us seemingly endless ways to use ever greater amounts of energy. In 2011–2012 Australia recorded a total energy consumption of **6,194 petajoules** ( $6,194 \times 10^{15}$  joules). This was the total amount of energy used for that year in agriculture, mining, manufacture and construction, transport, commercial and residential use and included energy losses due to energy conversions, transmission and distribution.

**FIGURE 13 Australian energy consumption by fuel type** (Source: 2013 Energy in Australian (May 2013), BREE, Canberra.)



**FIGURE 14** Since 2002 the Australian Government has been encouraging the industrial production of ethanol in Australia through the 'Ethanol Production Grants (EPG) program'. Ethanol producers receive a grant of around 38.1 cents per litre of ethanol produced, if the ethanol is to be used in transportation.

Ethanol produced from biomass, such as waste from the sugar industry, known as bagasse, has the advantage of being a renewable energy source while potentially reducing greenhouse emissions as a partial petrol replacement. The manufacture of biofuels such as ethanol can pose environmental and social issues. Large scale production would require vast amounts of agricultural land, fertilisers and water resources. These issues are minimised if agricultural waste products like bagasse can be used instead of cropping specifically for biofuel production.

These graphs show a clear trend towards increasing energy consumption in the Australian economy and reveal its heavy reliance on fossil fuels like coal, oil and natural gas. This reflects a similar global trend and the resulting need for ever greater extraction rates of diminishing **non-renewable** resources. Although global oil production, for example, is still rising due to new discoveries and improved technology, the peak production (called **peak oil**) is thought to be only a matter of decades away. This is one reason why fossil fuel use is considered **unsustainable**. Another is due to the carbon emissions it produces, namely, **carbon dioxide** gas,  $\text{CO}_2(\text{g})$ . Although  $\text{CO}_2(\text{g})$  is a natural part of the Earth's atmosphere its concentration is known to be increasing steadily (Fig 8 p107) and contributing to climate change. For these reasons, the search for **sustainable alternative fuels** is now paramount.

The graph in Fig 13 shows **renewable energy sources** accounted for only 4.23% of the energy used in Australia in 2011. Of this, 2.7% was in the form of **renewable fuels** including biomass, 2.3% (which includes wood, wood waste and other plant fibre) and biofuels, 0.4% (which includes biodiesel, bioethanol and biogas). Other **non-fuel** (ie non-combustible) renewable energy sources included hydro, wind and solar.

Ultimately the decision to use biofuels or other renewable fuels will depend upon factors such as cost, availability, suitability of the fuel for the particular purpose, environmental issues and social attitudes as well as political influences including legislation and international agreements. (See border note p107) The Australian Federal and State Governments, for example have a number of programs and initiatives that support the production, distribution and use of alternative transport fuels. Current initiatives include the 'Ethanol Production Grants' program (Fig 14), 'The Energy Grants (Cleaner Fuels) Scheme', 'The LPG Vehicle Scheme' and the 'Advanced Biofuels Investment Readiness' (ABIR) program. These programs offer tax concessions or direct financial grants which are aimed at encouraging the development of sustainable fuel options into the future.

As well as these programs the Australian Government has established **The Australian Renewable Energy Agency** (ARENA) to make renewable energy solutions more affordable and increase the amount of renewable energy used in Australia. Currently ARENA has a significant budget to fund renewable energy projects, to support research and development activities, and to support activities to capture and share knowledge in this area. (Want to know more? See: <http://arena.gov.au/>)



## Set 22 Fuels and energy in chemical systems

1. The concepts of **enthalpy** and **heat** are easily confused. These terms actually refer to quite different aspects of the energy of a system. Complete the table (**yes** or **no**) which compares enthalpy and heat.

	Enthalpy	Heat
a. A measure of energy		
b. Measured in joules		
c. The total energy of a chemical system		
d. The energy transferred between two objects at a different temperature		
e. Can be changed into other forms of energy		
f. Always conserved so it can neither be created nor destroyed		
g. Represented by the symbol H as in $\Delta H$		
h. Includes chemical potential energy that is stored in chemical bonds		

2. During a chemical reaction there can be a change in the total enthalpy of reactants compared to that of the products. This change in enthalpy is represented by  $\Delta H$ . In an exothermic reaction  $\Delta H$  has a negative value and the temperature of the reaction mixture will increase. What is the significance of the negative value of  $\Delta H$  and why should this lead to an increase in temperature for the reaction mixture?
3. When barium hydroxide solid is mixed with solid ammonium chloride a chemical reaction takes place causing the reaction mixture to cool down. The drop in temperature is due to the loss of heat energy. Since energy can neither be created nor destroyed how can we **account** for the lost heat energy? **Explain** your answer. (See Fig 15.)
4. Oxyacetylene welding uses the combustion of **acetylene** [ $C_2H_2(g)$ ] in pure oxygen gas as a means of producing temperatures high enough to melt many metals and cut through steel. The reaction produces carbon dioxide gas and water vapour as the only products.
- Is this reaction endothermic or exothermic? **Explain**.
  - Write an **equation** for the combustion of acetylene in excess oxygen gas.
  - Include **heat** in your equation given that each mole of acetylene releases 1.255 megajoules of heat energy when burnt this way.
  - Now write your equation to include the enthalpy change,  $\Delta H$ .
  - Draw an **enthalpy change diagram** for this reaction. Label the axes, reactants, products, enthalpy of reactants, enthalpy of products and  $\Delta H$  (heat of reaction).
5. The commonly used sports cold pack (Fig 15) contains  **$NH_4Cl(s)$**  and **water** in separate compartments. When struck sharply the two substances mix, resulting in a cooling effect. The mixing allows water to dissolve the solid  $NH_4Cl$ .
- Is this reaction endothermic or exothermic? **Explain**.
  - Write an **equation** for this reaction.
  - Include **heat** in your equation given the dissolving of one mole of  $NH_4Cl(s)$  absorbs 1.4 kilojoules of heat energy when dissolved. (See border note at right and Fig 16.)
  - Include the enthalpy change,  $\Delta H$  in your equation.
  - Draw an **enthalpy change diagram** for this reaction. Label the axes, reactants, products, enthalpy of reactants, enthalpy of products and  $\Delta H$ .

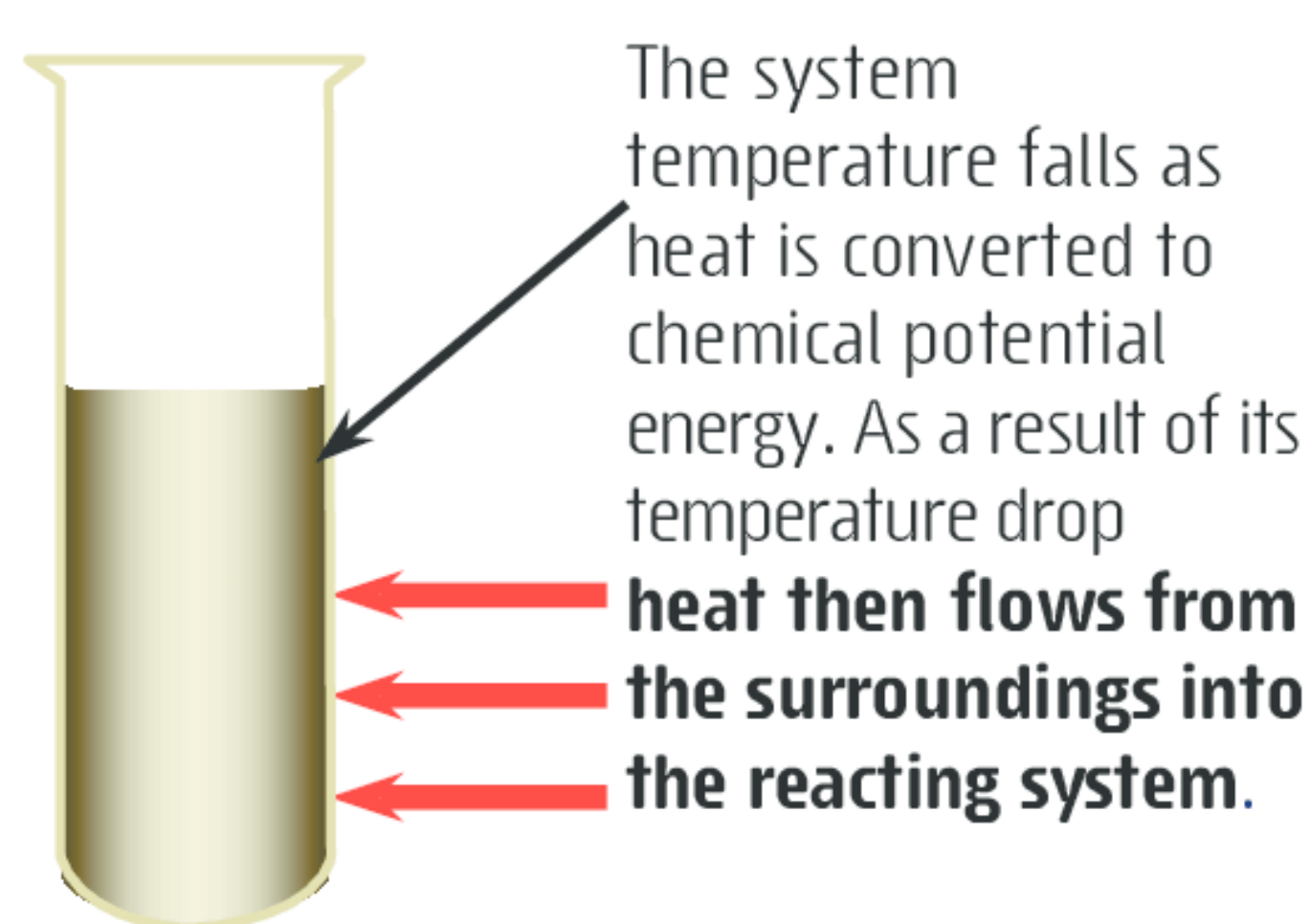


**FIGURE 15** Instant sports cold packs like these use an **endothermic** reaction to produce freezing temperatures. Sports hot packs use an **exothermic** reaction to produce a heating effect.

The statement, '**the reaction absorbs 1.4 kJ of heat,**' is easily misunderstood. You may think absorbing this much heat energy into a system should cause an increase in its temperature when actually the temperature of the system will decrease!

In reality the reaction is converting 1.4 kJ of heat energy (particle kinetic energy) from within the reacting system into increased stored energy (chemical potential energy) within the reacting system. This loss of heat energy causes a fall in the system's temperature and results in the flow of heat into the system from the surroundings, ie the absorbed heat. (See Fig 16 next page.)



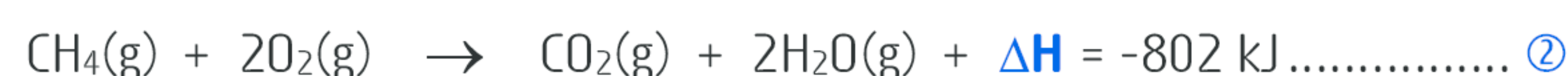
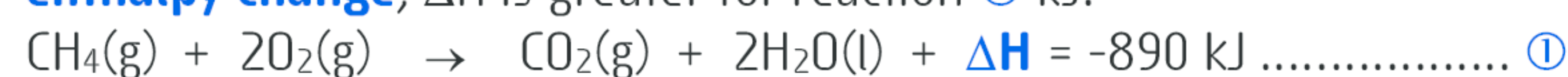


**FIGURE 16** An **endothermic** reaction converts heat (particle kinetic energy) into chemical potential energy so the reacting systems temperature falls. Heat then flows into the reacting system from the surroundings.

6. Use your knowledge of the energy effects of **bond breaking** and **bond forming** to decide if the following reactions are endothermic or exothermic. **Justify** your answer.
  - a. Boiling of water,  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$
  - b. Sublimation of gaseous carbon dioxide to its solid phase,  $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$
  - c. Decomposition of molecular sulfur to atomic sulfur,  $\text{S}_8(\text{g}) \rightarrow 8\text{S}(\text{g})$

7. Choose from the following pairs of substances, the one having the **highest enthalpy**.
  - a. equal masses of  $\text{H}_2\text{O}(\text{l})$  and  $\text{H}_2\text{O}(\text{g})$  , both at  $100\text{ }^\circ\text{C}$
  - b. equal masses of  $\text{CO}_2(\text{s})$  and  $\text{CO}_2(\text{g})$  , both at the same temperature
  - c. equal masses of  $\text{H}_2\text{O}(\text{s})$  and  $\text{H}_2\text{O}(\text{l})$ , both at  $0\text{ }^\circ\text{C}$
  - d. equal masses of  $\text{H}_2\text{O}(\text{l})$  at  $10\text{ }^\circ\text{C}$  and  $\text{H}_2\text{O}(\text{l})$  at  $80\text{ }^\circ\text{C}$

8. These two equations both represent the combustion of methane. Explain why the **enthalpy change**,  $\Delta\text{H}$  is greater for reaction ① kJ.



9. Consider the chemical changes described here and **complete the following table**.

**Natural gas** is essentially methane ( $\text{CH}_4$ ). The heating effect of a gas stove and gas heater rely on the combustion of this gas as shown in the following equation.



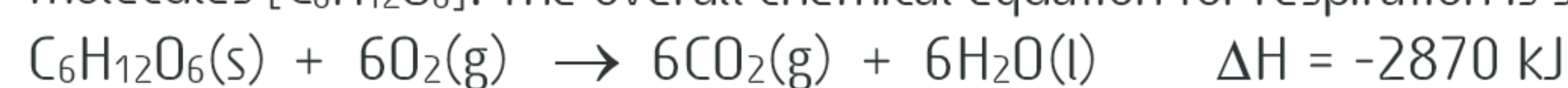
**Ethanol** is a key ingredient found in many window cleaners. One of its advantages is that it evaporates easily leaving a clear, smear free finish on glass surfaces. The equation shows its evaporation.



**Ice** is an excellent cooling agent and is often used to cool drinks. The equation shows the melting of ice.



**Respiration** is a chemical process occurring in the cells of all living organisms. It provides the energy needed for all life processes by releasing the enthalpy stored in chemical bonds of sugar molecules [ $\text{C}_6\text{H}_{12}\text{O}_6$ ]. The overall chemical equation for respiration is shown here.



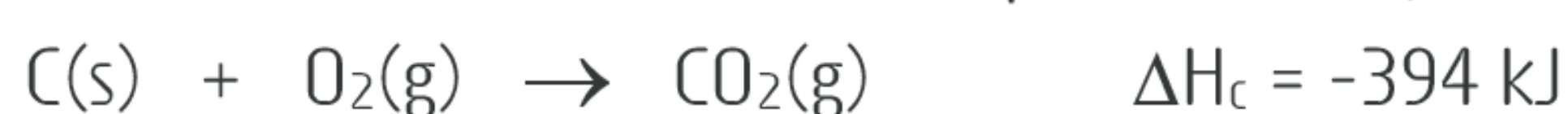
**Photosynthesis** is essentially the reverse of respiration. (See above.) During photosynthesis green plants convert carbon dioxide and water into sugar and oxygen. This process absorbs energy present in sunlight and stores it as enthalpy in sugar.

	Gas oven burning natural gas	Glass cleaner, ethanol evaporating from a window	Ice melting in a glass of soft drink	Respiration, where cells release energy from sugar	Photosynthesis, where plants produce sugar using solar energy
Is the reaction endothermic or exothermic?					
Is enthalpy increased or decreased?					
Is there an increase or decrease in temperature?					
Is there an increase or decrease in the heat energy present?					
Is the total energy of the system and surroundings increased, decreased or unchanged?					
Overall, which have the stronger bonds, reactants or products?					



10. The fossil fuel **coal** (Fig 17) is the source of energy for around 41% of the world's electricity production. Coal is rich in **carbon** containing from 50% to 98% carbon.

- a. Use the information given in the combustion equation for carbon (below) to determine the **fuel value** for pure carbon, ie **MJ kg<sup>-1</sup>**.



- b. Use the information given in the combustion equation for carbon in part (a) to determine the amount of CO<sub>2</sub> produced in grams for every MJ of heat released from the burning of pure carbon, ie carbon emissions in **g(CO<sub>2</sub>) MJ<sup>-1</sup>**.
- c. **Compare** the values obtained in part (a) and (b) for **carbon** with those quoted in Table 1 p108 for **coal**. Comment briefly on any differences in fuel value and rate of carbon emissions for coal compared to carbon.

11. In 2011–2012 around 70% of Australia's electricity came from **coal fired power stations**. Carbon dioxide emissions from this sector represented a significant part of Australia's total emissions in that year. **Natural gas** (essentially methane, CH<sub>4</sub>) is now the preferred fuel for power generation as it produces less greenhouse gas emissions. Answer the following questions with reference to the above information and the information given in Table 1 p108.

- a. What is the **average rate of emission** of CO<sub>2</sub> when burning coal to produce heat? Answer in **g(CO<sub>2</sub>) MJ<sup>-1</sup>**. (See Table 1 p108.)
- b. If **coal** had been completely replaced with **natural gas** would carbon emissions have increased or decreased? Explain.
- c. Determine the reduction in carbon emissions that could be achieved if **NG** totally replaced **coal** for the purpose of electric power generation? Give the reduction as a **percentage** of the current emissions produced by coal.

12. Road transport relies heavily on the use of **petrol** and **diesel** as a fuel. These are strong greenhouse gas emitters and both are becoming increasingly expensive due to dwindling world supplies of crude oil. Other more abundant petroleum products are being increasingly used as replacements. Some alternatives include **CNG** and **LPG**.

- a. Which of the two fuels, **CNG** or **LPG**, is the better fuel in terms of minimising greenhouse gas emissions? See Table 1 p108.
- b. What major **problem** is associated with the use of CNG as a transport fuel? Why is this not such a serious issue with LPG use?
- c. Which of the two fuels LPG or petrol has the lower **energy density** in terms of **MJ L<sup>-1</sup>**? (See border note and Table 1.) Why is this difference an issue when replacing petrol with LPG as a transport fuel?

13. **Bioethanol** (C<sub>2</sub>H<sub>5</sub>OH) is one fuel being used as a **petrol** replacement. It is touted as being a renewable fuel source while petrol is not. The standard enthalpy of combustion of ethanol is shown here. (See border note.)



- a. Ethanol is referred to here as a **biofuel**. What does this mean?
- b. **Comment** on the statement, '**bioethanol is a renewable energy source while petrol is not.**'
- c. The equation above shows the complete combustion of the biofuel ethanol. Use the information shown to determine its **fuel value** in **megajoules per gram, MJ g<sup>-1</sup>**.
- d. Ethanol has a density of 789 g L<sup>-1</sup>. Use this information and your answer to part (c) to determine its **fuel density** in **MJ L<sup>-1</sup>**. Does its fuel density impact on the use of ethanol as a petrol replacement?



**FIGURE 17** The carbon content of coal can vary considerably. The form of coal known as **anthracite** for example may contain up to 98% carbon by mass while **lignite** contains as little as 50% carbon. **Coal** is the source of energy for around 41% of the electricity generated world wide.

**Energy density** of a fuel may be defined as the energy available per unit volume of the fuel (eg **kJ L<sup>-1</sup>** or **MJ L<sup>-1</sup>**). It depends upon the **fuel value** and the **fuel's density** ( $d=m/v$ ). Thus, for a given amount of energy, the higher the energy density of a fuel, the smaller its volume will be. For this reason, energy density is an important property of fuels, especially those used in transport. The higher the fuel's energy density, the smaller the required fuel tank.

The standard enthalpy of combustion  $\Delta H_c$  of a fuel gives  $\Delta H$  for the complete combustion of 1 mole of the fuel at 25 °C and 101.3 kPa.





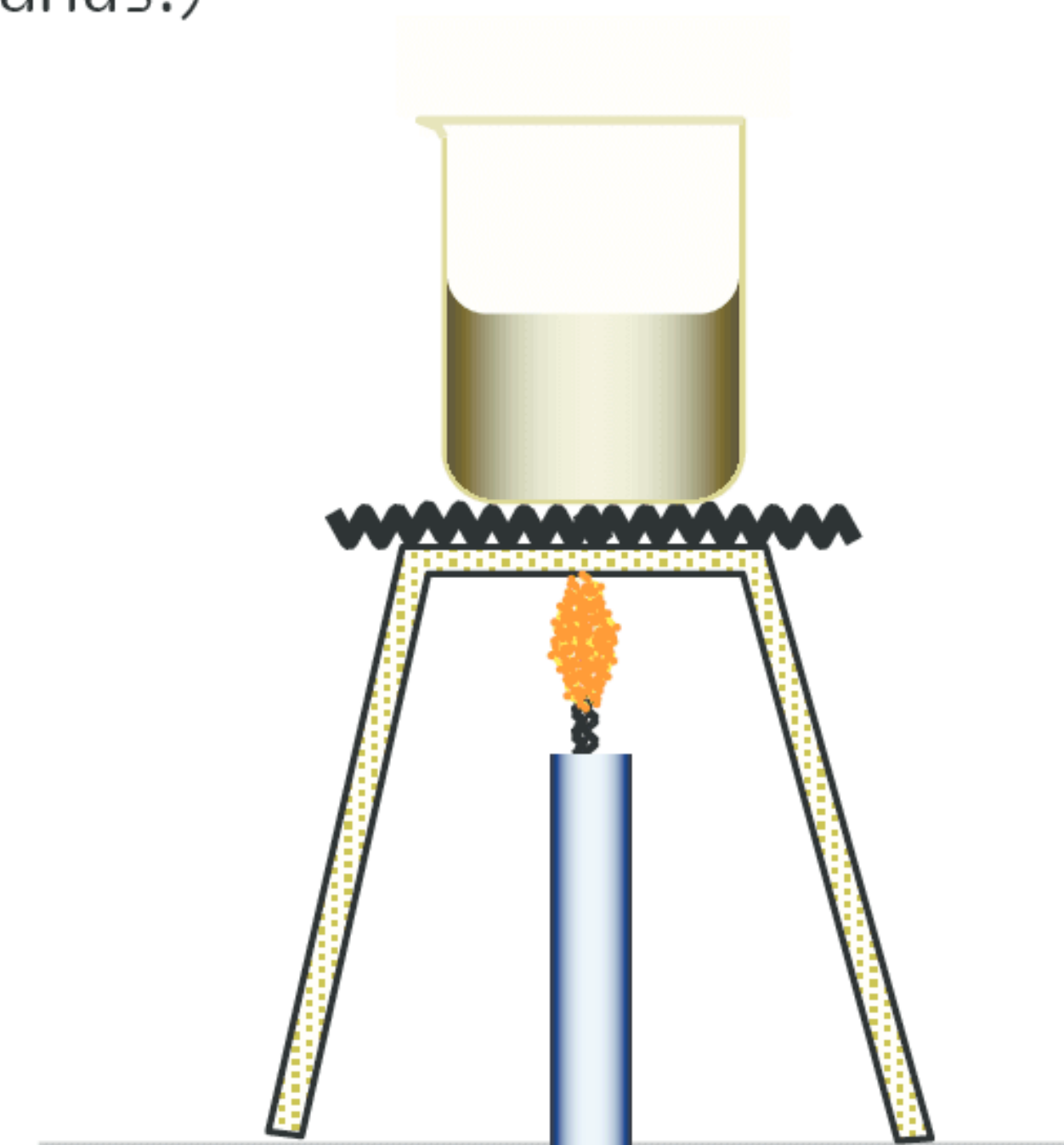
**FIGURE 18** In Europe and the US, **E85** flexible vehicles are commercially available and can operate on biofuel blends as high as **85% ethanol** and 15% fossil fuel. Ethanol use in Australia occurs mainly on the East Coast, close to where it is manufactured. Here ethanol is available as an **E10** blend consisting of 10% ethanol and 90% petrol.

The Australian government has legislated to restrict the use of higher ethanol blends due to vehicle manufacturer warranties on locally available cars.

14. **Biofuels** are said to have the advantage of not contributing to increased levels of the atmospheric greenhouse gas **carbon dioxide**. This statement can appear confusing as the combustion of biofuels does release  $\text{CO}_2(\text{g})$  into the atmosphere. The following questions refer to the use of biofuels and their  $\text{CO}_2(\text{g})$  emissions.
  - a. The combustion of both ethanol and petrol releases about 1.5 mole of  $\text{CO}_2(\text{g})$  per megajoule of heat energy produced. Despite this it can be argued that the combustion of ethanol does not increase the concentration of the atmospheric greenhouse gas  $\text{CO}_2$  while petrol combustion does. **Justify** this statement.
  - b. A full life cycle analysis of the biofuel ethanol shows it can contribute to anthropogenic (human induced) carbon emissions. **Explain** how this can happen.
  - c. Ethanol/petrol blends like E10 (Fig 18) are available in some parts of Australia as petrol alternatives. What is E10 and why aren't blends like E85 generally used in Australia?
  - d. Why does the Australian Government promote the use of ethanol petrol blends like E10 via programs like the Ethanol Production Grants (EPG) program?

15. Matt and Erin conducted an investigation to determine the heating value and molar heat of combustion,  $\Delta H_c$  of beeswax. This involved burning a beeswax candle and using the heat released to warm a measured amount of water in a beaker above the candle. (See Fig 19.) From the **temperature rise** and **mass of water** used they calculated **625 kJ** of heat was released from the burning candle. Before burning, the candle had a mass of **85.59 g** and after burning its mass was **63.04 g**. Assume the wax undergoes complete combustion and the chemical composition of beeswax to be myricyl palmitate,  $\text{C}_{46}\text{H}_{92}\text{O}_2$ . (Although it is actually a mixture of similar compounds.)

**FIGURE 19** As the beeswax candle burns it heats water in the beaker above the flame. The heat gained by the water can be calculated from its temperature rise.



- a. Write an **equation** for the complete combustion of the wax,  $\text{C}_{46}\text{H}_{92}\text{O}_2$ .
- b. Determine the heat that would be produced by burning one mole of wax. This gives the molar heat of combustion of the wax, ie  $\Delta H_c$ .
- c. Rewrite your combustion equation showing both the **heat** involved and the **enthalpy change**. You may assume the lost enthalpy appears as heat only.
- d. Matt and Erin's investigation has several potential sources of error. Answer the following which are about these possible sources of error.
  - i In particular, it is unlikely the beaker of water will capture all of the heat released by the burning candle. **Justify** this statement.
  - ii Is the error described above a **systematic** or **random** error? **How** will this error affect their calculated value of  $\Delta H_c$ ?
  - iii **Suggest** how they might modify their procedure in order to reduce this error.
  - iv After the experiment was completed Matt noticed that a lot of **black residue** had formed on the bottom of the beaker. Suggest the chemical composition of this residue and what is its significance regarding their calculated value of  $\Delta H_c$ .



# CHAPTER 14 | REACTION RATE



**FIGURE 1** Although the rate of reaction between the reagents in a safety match is extremely slow, once the reaction starts it then proceeds rapidly, almost explosively.

Reactions like those occurring in a burning match are heterogeneous reactions.

**Heterogeneous** reactions involve reactants that are in two **separate** phases, eg solid/solid, solid/liquid, solid/gas, liquid/gas or liquid/liquid (ie two immiscible liquids).

In these reactions the reaction rate increases with increasing **surface area** or **state of subdivision** of the reactants. For this reason **powdered** magnesium reacts much more rapidly with a hydrochloric acid solution than a **single piece** of magnesium of the same mass. This happens as the powdered magnesium has a greater surface area in contact with the acid.

## 14.1 Reactions fast and slow: Introducing rate

Adding a piece of magnesium ribbon to some dilute hydrochloric acid solution results in a moderately fast reaction. Using concentrated hydrochloric acid makes this reaction extremely vigorous. By comparison, under normal conditions, the rate of reaction between the reagents in a safety match is so slow that it appears as if no reaction is occurring at all. If, however, the match is struck, then an extremely rapid, almost explosive reaction is seen. (See Fig 1.)

Typically the **rate** or **speed** of reactions like these **increase** with **increasing temperature**, **concentration**, **pressure** and **state of sub-division**. (See border note.) As well as these factors, the presence of a **catalyst** in a reaction mixture will also increase the rate of reaction. Catalysts are unique substances which are involved in a reaction without appearing to be consumed by the reaction. Thus the amount of catalyst present in a reaction mixture does not change as the reaction proceeds.

Attempt Set 23 # 1 and 2.

## 14.2 Measuring reaction rate

Just how fast or slow a reaction proceeds can be described in terms of the rate of **formation of products** or the rate of **consumption of reactants**. Thus the rate of a chemical reaction can be calculated using:

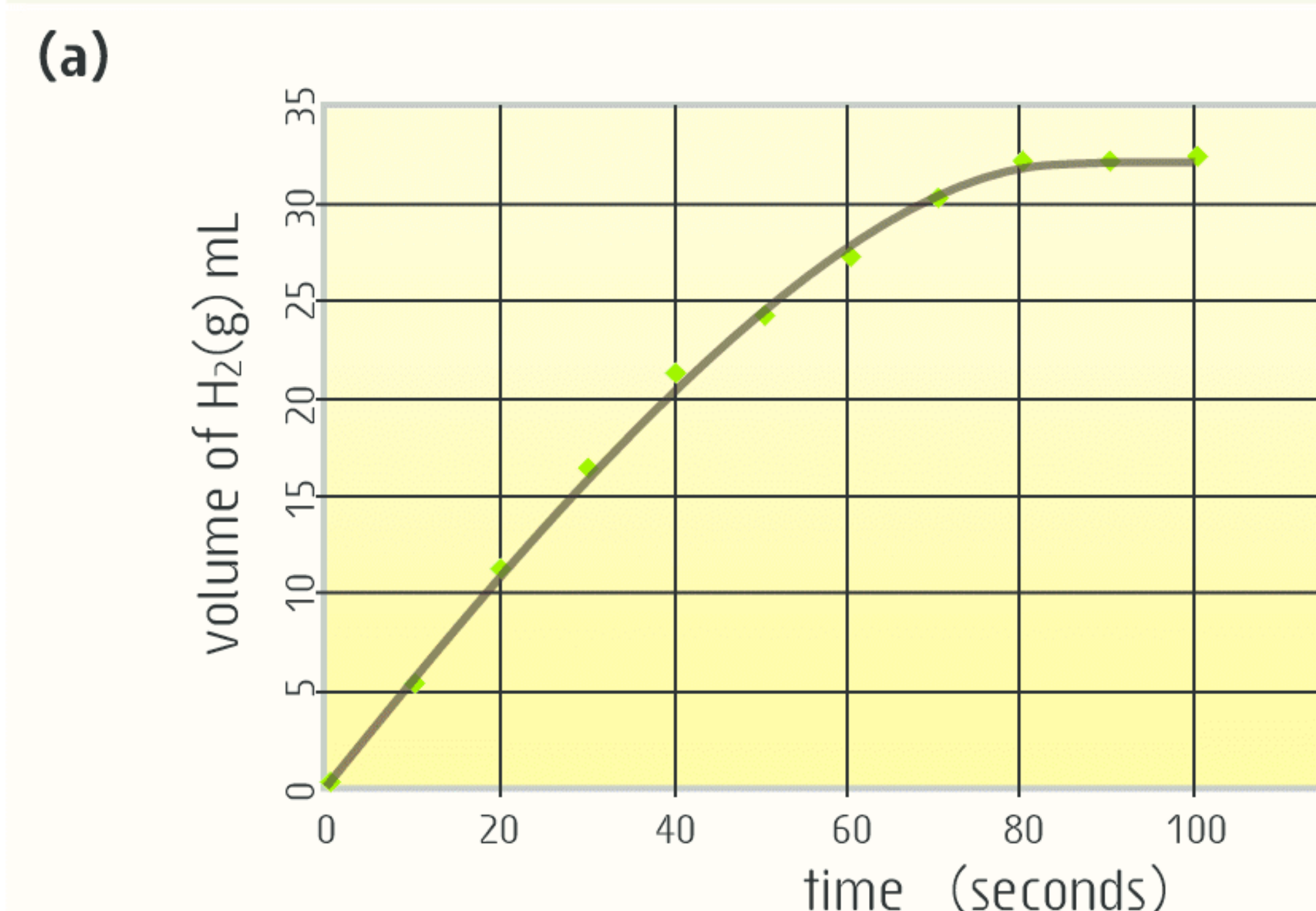
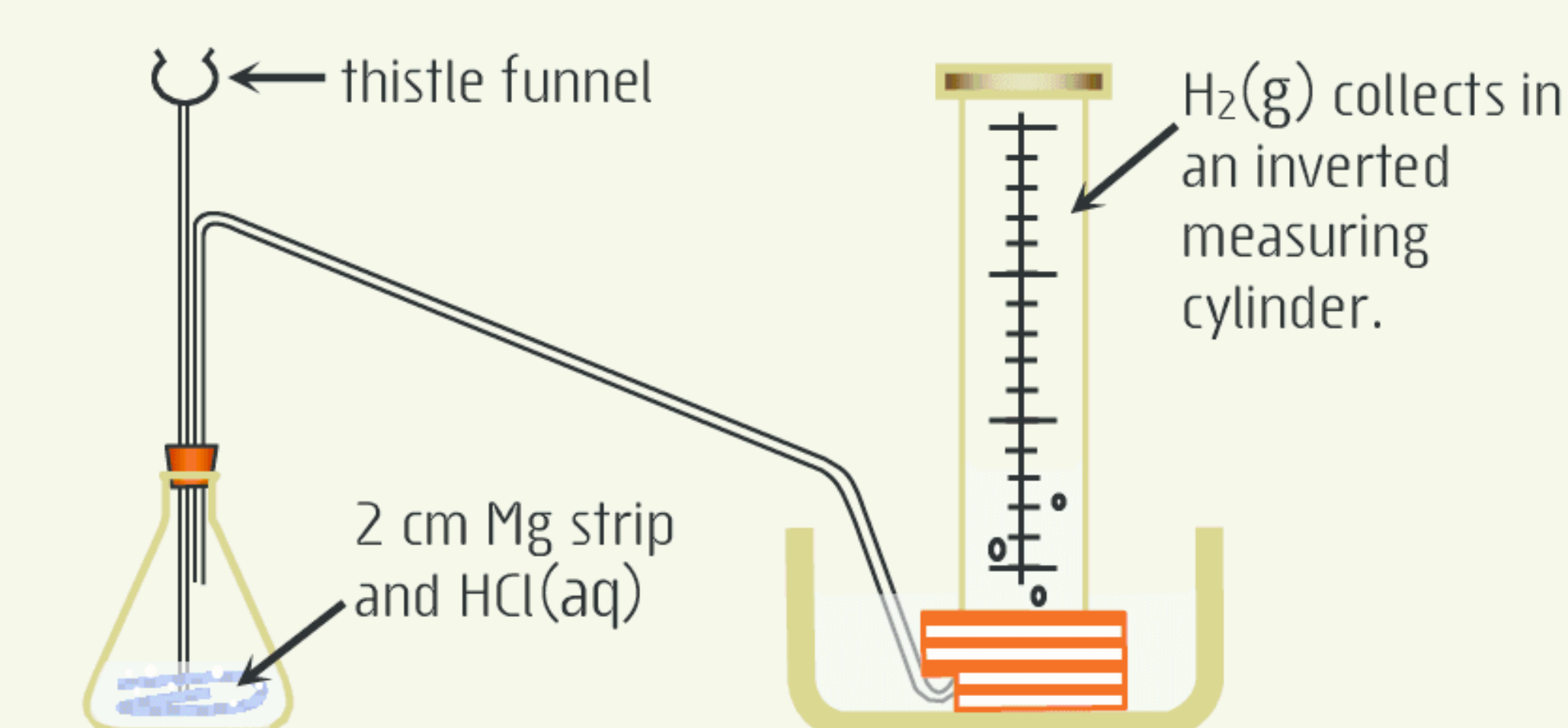
$$\text{rate of reaction} = \frac{\text{amount substance used or produced}}{\text{time taken}}$$

Various units can be used to express rate; eg moles per second ( $\text{mol s}^{-1}$ ), grams per second ( $\text{g s}^{-1}$ ) or millilitres per second ( $\text{mL s}^{-1}$ ). The units are chosen to suit the reaction being investigated and the method used to collect data. Often, rather than calculating rate, it may be more convenient to visualise reaction rate by **graphing** the amount of substance used or produced against **time**. When this is done the rate is indicated by the slope or **gradient** of the graph; the steeper the gradient the greater the reaction rate. (See Example 1 and 2.)

**EXAMPLE 1** A student wanted to investigate how the rate of the acid-metal reaction between magnesium and hydrochloric acid would change over time. He hypothesised '**the rate of reaction between magnesium and hydrochloric acid will decrease uniformly with time as the reaction progresses to completion**'. To test his hypothesis he investigated the reaction between 20.0 mL of  $0.8 \text{ mol L}^{-1} \text{ HCl(aq)}$  and a 2 cm strip of magnesium (Mg) ribbon. Using the apparatus shown at right he was able to collect data on the volume of  $\text{H}_2(\text{g})$  produced as the reaction progressed to completion.

volume of $\text{H}_2(\text{g})$ (mL)	0	5	11	16	21	24	27	30	32	32	32
time (s)	0	10	20	30	40	50	60	70	80	90	100

- Construct a graph of volume of hydrogen gas produced against time.
- Examine the gradient of this graph and comment on the rate of formation of hydrogen gas as the reaction proceeded to completion.
- On the basis of these experimental results, comment on the validity of the student's hypothesis. You may assume the experiment was conducted carefully with negligible experimental errors.



- The rate of this reaction is shown by the gradient of the graph for the formation of hydrogen gas with time. As the gradient is fairly constant for the first 50-60 seconds then this means the reaction rate is also constant for the first 50-60 seconds. From 60 seconds onwards to the end of the reaction at 100 seconds, the gradient for the formation of hydrogen gradually reduces to zero (graph becomes horizontal). This shows the rate steadily decreases to zero during the last 40 seconds of the reaction.
- The student's hypothesis predicts 'the reaction rate will decrease uniformly as it progresses to completion'. These results partially support the student's hypothesis as they do show the reaction rate slowly falls to zero during the latter part of the reaction. However, during the first 50-60 seconds of the reaction, the rate is fairly constant. This constant rate is not predicted by the student's hypothesis.



The graph in Figure 2 shows how the total volume of  $\text{H}_2(\text{g})$  collected increases during the course of the reaction. As discussed, it is the **gradient** of this graph that gives the actual or **instantaneous rate** of the reaction at any particular point in time. As can be seen at right, the gradient reduces over time until it is zero (ie graph becomes horizontal) meaning the reaction has stopped. Using the data from Example 1 it is possible to calculate the average rate of reaction over any given period of time during the reaction. See Example 2.

**EXAMPLE 2** Use the student data from Example 1 to calculate the average rate of reaction, ie rate of evolution of hydrogen gas, for the following time intervals.

total volume of $\text{H}_2(\text{g})$ (mL)	0	5	11	16	21	24	27	30	32	32	32
time (s)	0	10	20	30	40	50	60	70	80	90	100

(a) For the first 30 seconds, ie from  $t = 0 \text{ s}$  to  $t = 30 \text{ s}$ .

(b) The last 30 seconds of the reaction, ie from  $t = 50 \text{ s}$  to  $t = 80 \text{ s}$ .

$$(a) \text{ rate} = \frac{\text{amount produced}}{\text{time taken}} = \frac{16}{30} = 0.53 \text{ mL s}^{-1}$$

The data table shows 16 mL of  $\text{H}_2(\text{g})$  is collected from the start to 30 seconds.

$$(b) \text{ volume of } \text{H}_2(\text{g}) \text{ collected} = 32 - 24 = 8 \text{ mL}$$

$$\text{rate} = \frac{\text{amount produced}}{\text{time taken}} = \frac{8}{30} = 0.27 \text{ mL s}^{-1}$$

Since 24 mL of  $\text{H}_2(\text{g})$  have been collected by 50 s and a total of 32 mL are collected by 80 s.

### 14.3 Collision theory

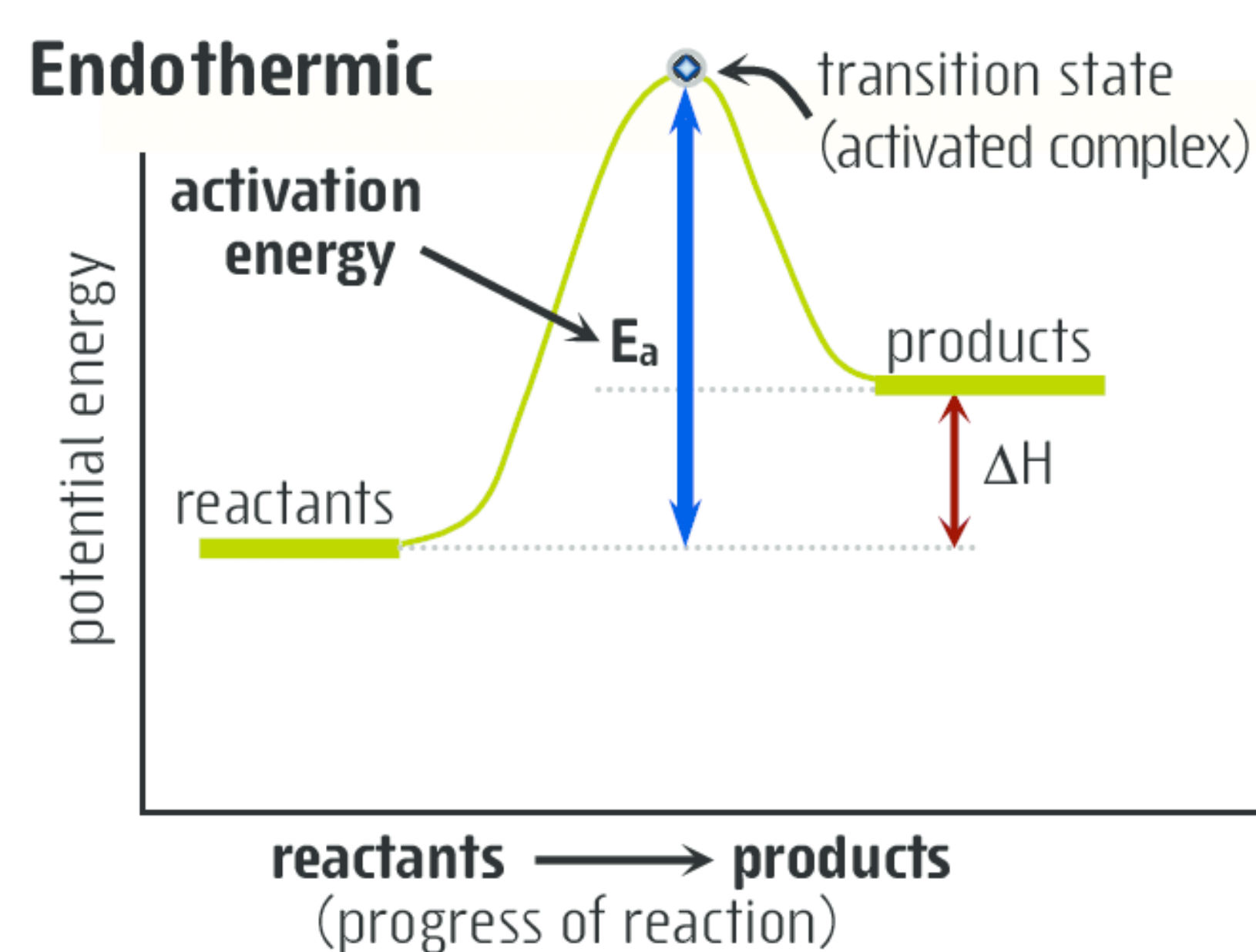
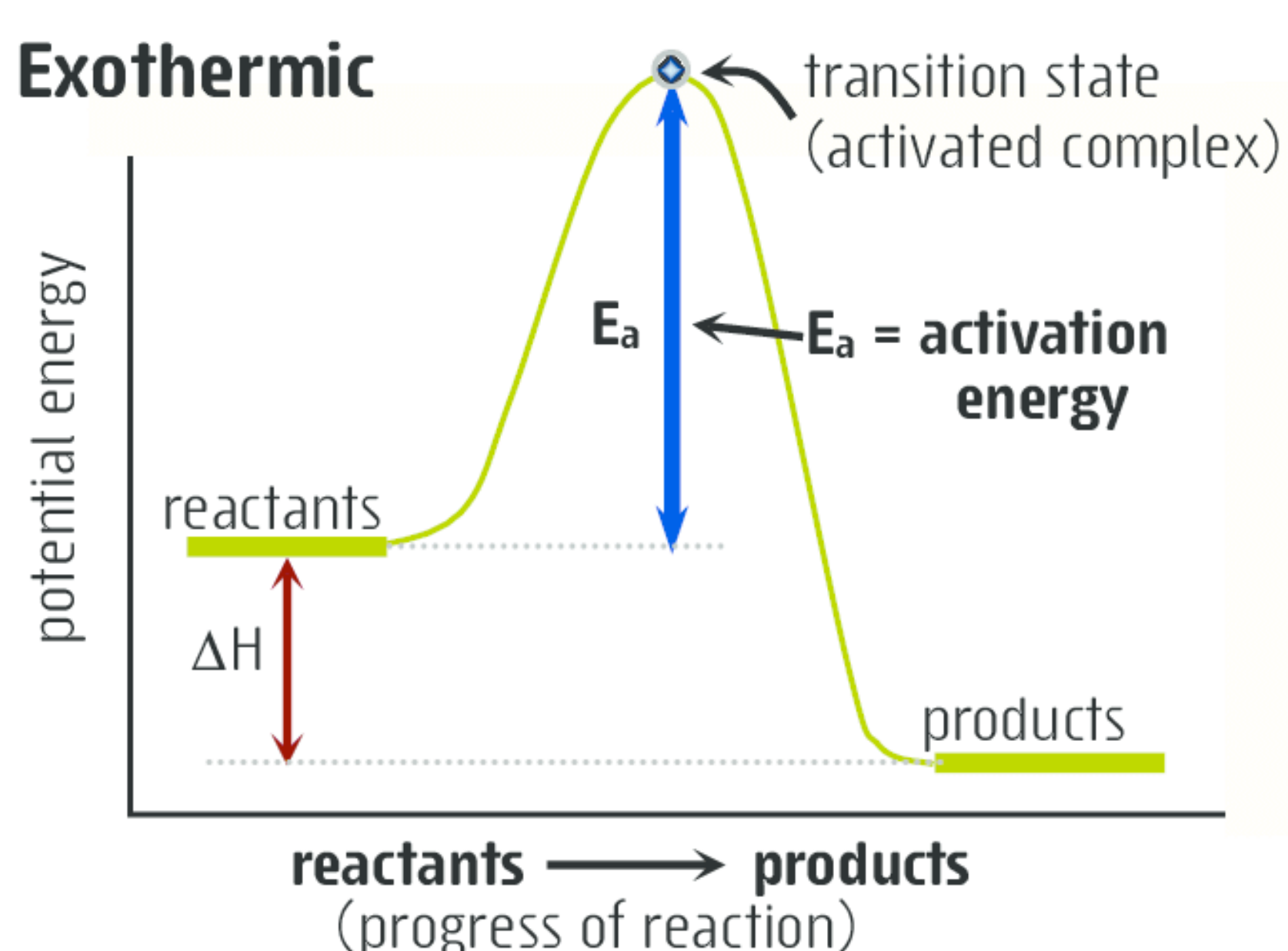
The **collision theory** gives us an insight into what is occurring at the particle level during a chemical reaction. It gives us a way to understand and explain how the various factors of concentration, pressure, temperature, catalysts, state of sub-division and nature of reactants affect reaction rate. The collision theory describes chemical reactions in terms of collisions between individual reacting **particles** (atoms, ions or molecules). According to this theory, for a reaction to occur, **all** of the following conditions must be met.

- Individual particles of the reacting substances must **collide**. (See Fig 3.)
- The collision energy must be equal to or greater than a certain minimum amount known as the **activation energy,  $E_a$** . (See Fig 4.)
- The reacting particles must collide with a suitable **orientation**. (See Fig 3.)

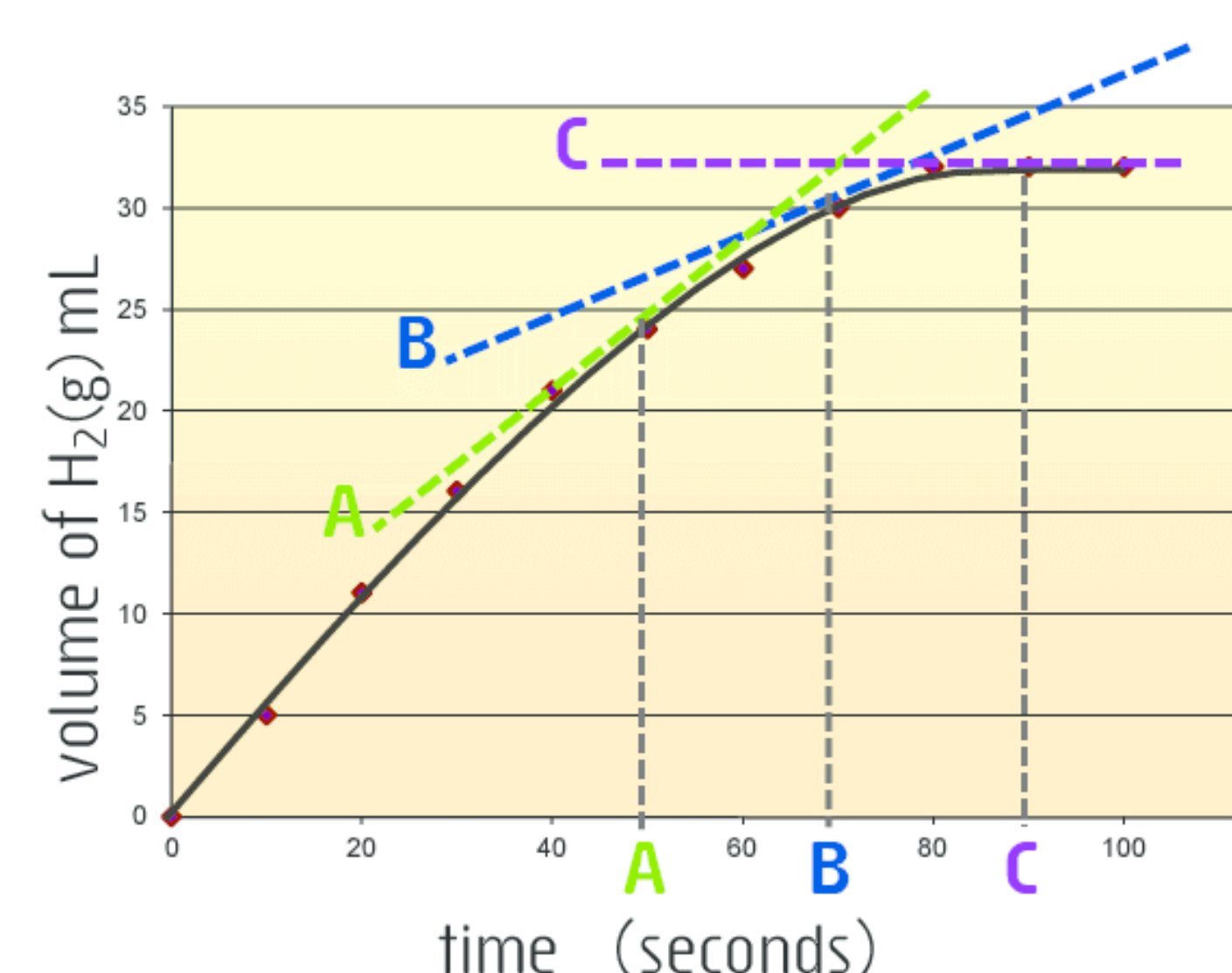
If the reacting particles collide with sufficient energy and a suitable orientation then they can form a transition state. Here the original bonds are breaking while new bonds are forming. The transition state exists for a very short time only and when it decomposes it may lead to the formation of new products or may reform to the original reactants.

### 14.4 Potential energy profile

As reacting particles randomly approach each other, repulsive forces between their electron clouds cause them to slow down and lose speed, ie lose kinetic energy. The lost kinetic energy then reappears as increased potential energy. If the colliding particles have sufficient kinetic energy they can approach close enough (collide) to form a **transition state**, (see Fig 3) also known as the **activated complex**, the highest potential energy state for the reaction. The transition state is a point in the reaction where the original bonds are breaking and new ones are forming. It is an **unstable** arrangement that decomposes quickly to form either the original reactants or new products. The minimum collision energy required to form the transition state is known as the **activation energy  $E_a$** . (See Fig 4.) Typically, the activation energy for a reaction is **higher** when the bonds of the reactants are stronger or more numerous as it is these bonds that must first be broken or rearranged if the reaction is to proceed.



**FIGURE 2** Formation of  $\text{H}_2(\text{g})$  from Example 1.

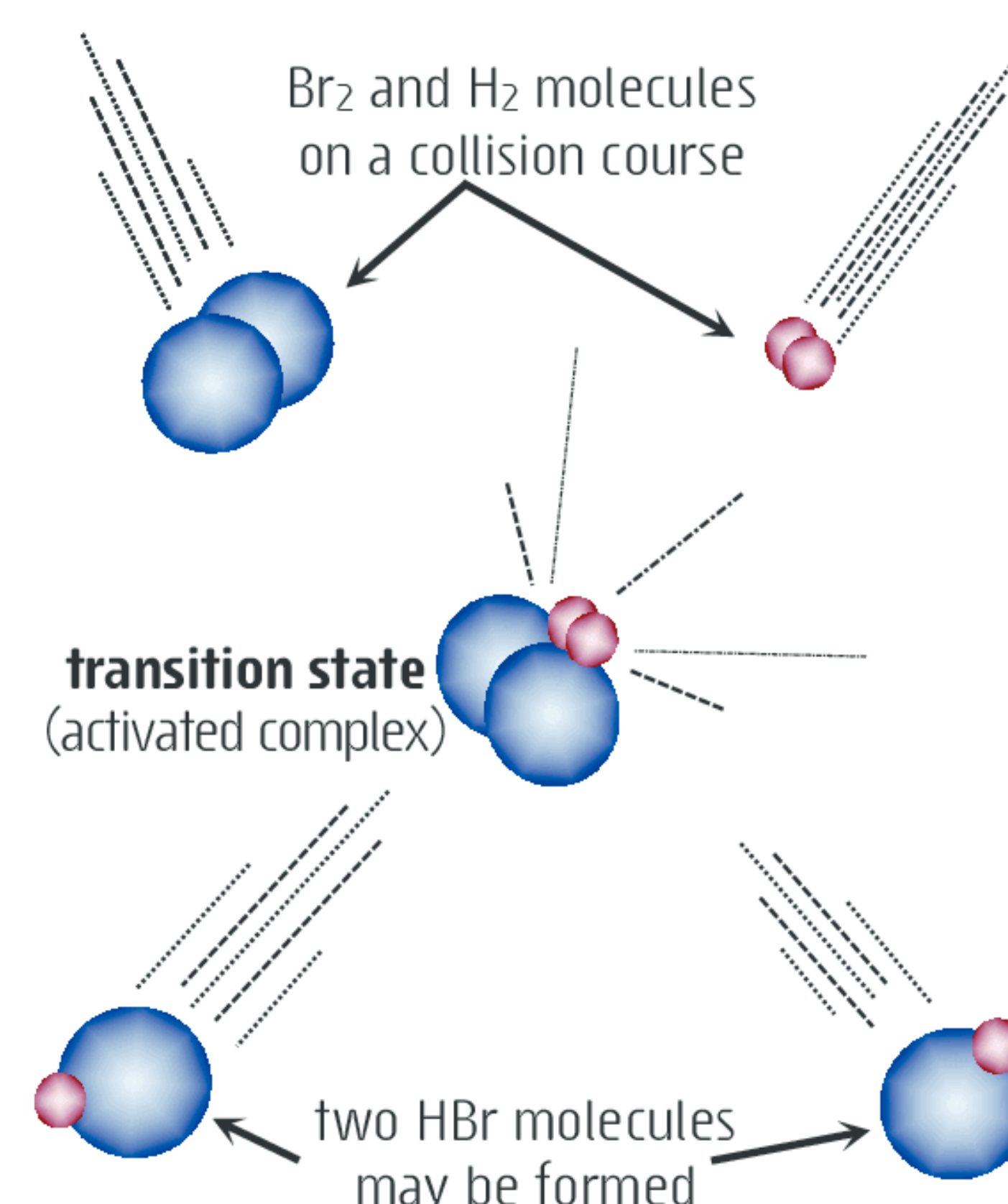


This graph shows the total volume of  $\text{H}_2(\text{g})$  produced over time for the reaction in Example 1. Its gradient at any point in time gives the instantaneous rate of the reaction at that time. The gradients of the **green**, **blue** and **purple** lines give the rate of this reaction at times **A** (50 s), **B** (70 s) and **C** (90 s) respectively.

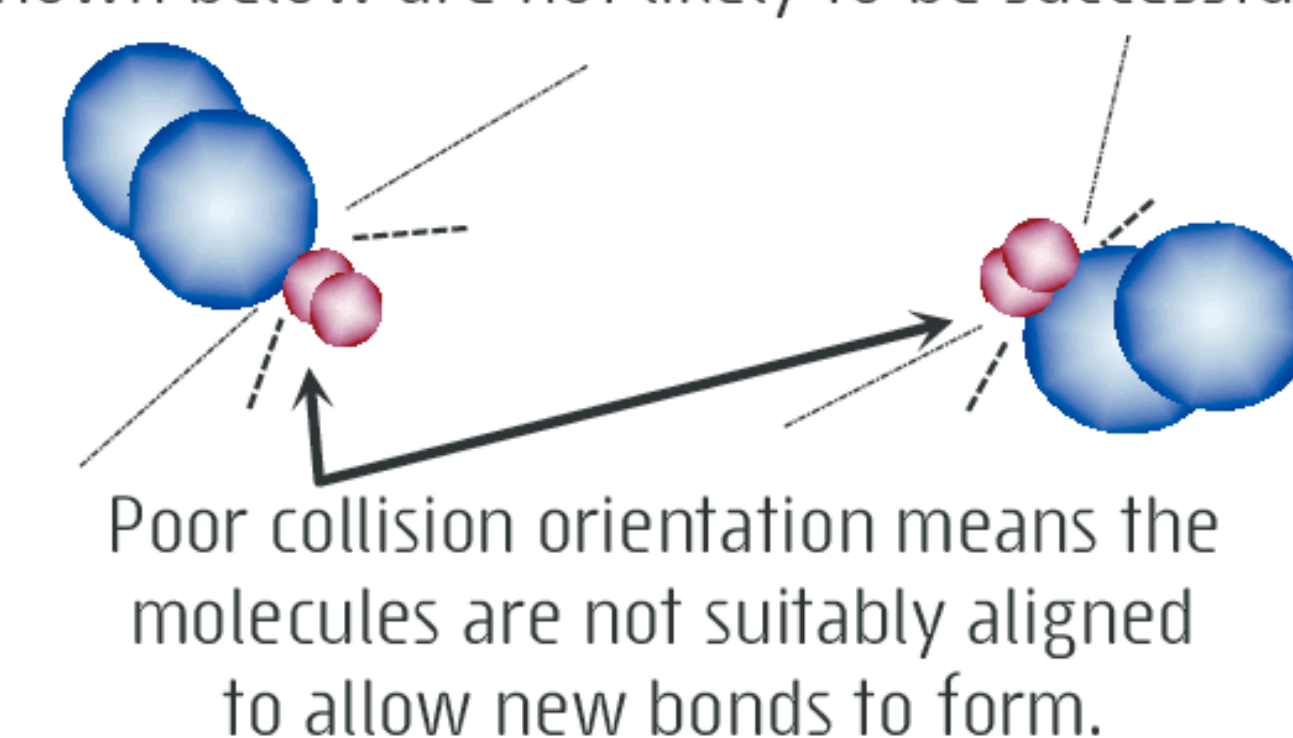
Attempt Set 23 # 3, 4 and 5.

**FIGURE 3** According to the **collision theory**, chemical reactions like the one shown here,  $\text{Br}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$

involve a collision between particles. In this example, a  $\text{H}_2$  molecule and a  $\text{Br}_2$  molecule collide to form a **transition state** that may then decompose to form the product **HBr**.



The transition state shows how the **orientation** at collision is important for a successful reaction. The collision orientations shown below are not likely to be successful.



**FIGURE 4** A **potential energy profile** shows the change in potential energy for reacting particles as they approach and form an activated complex. If the colliding particles have too little kinetic energy they will rebound before the activated complex forms and so there would be no reaction. The minimum collision energy needed to form an activated complex is the **activation energy**. This is labelled  **$E_a$** .

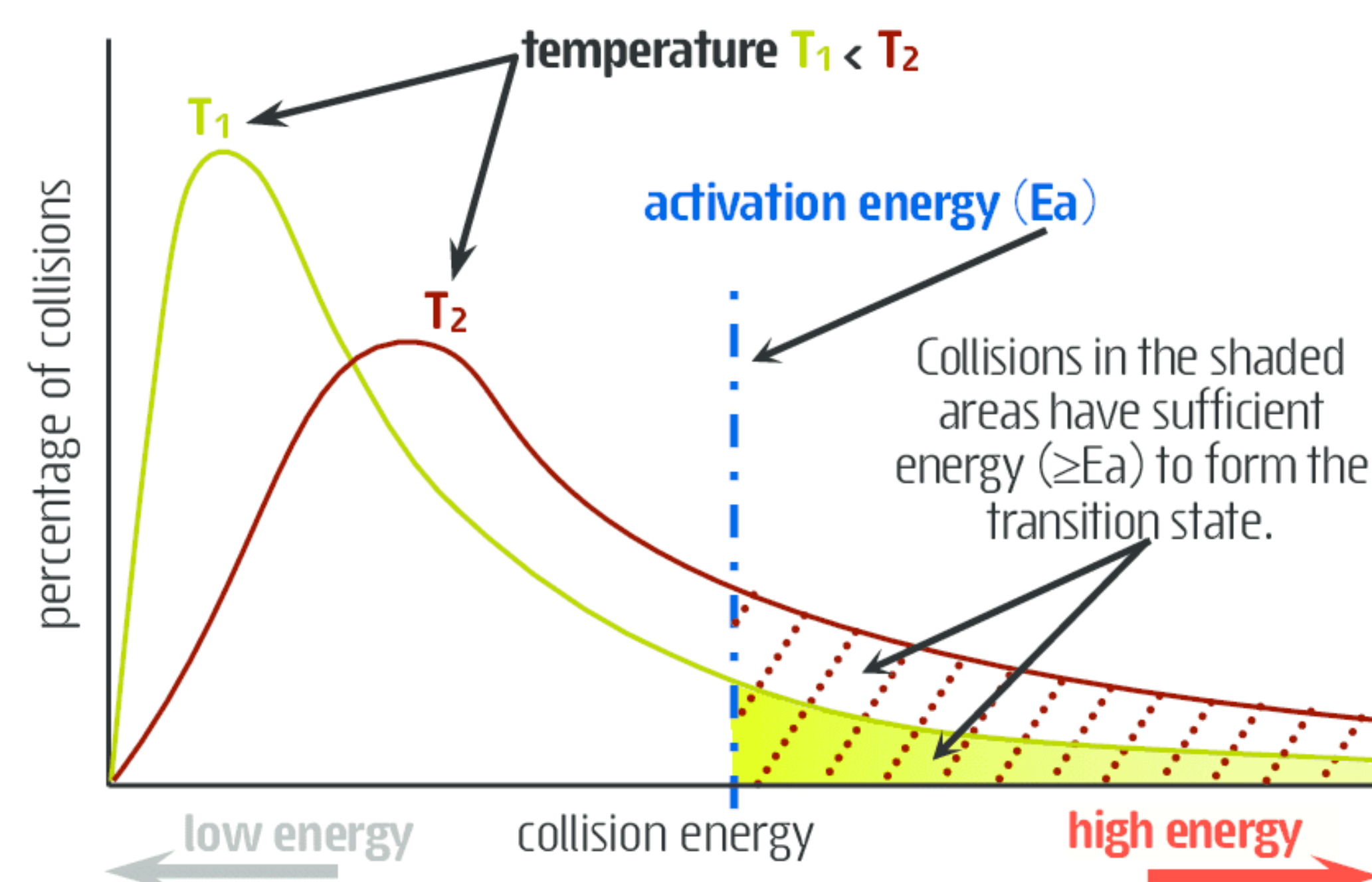
Attempt Set 23 # 6 and 7.



## 14.5 Collision energy and temperature

**Temperature** is a measure of the **average kinetic energy** ( $E_k = \frac{1}{2}mv^2$ ) of the particles of a substance. As the temperature of a substance rises so does the average kinetic energy of its particles. Thus at a higher temperature the **average collision energy** of the reacting particles in a reaction mixture increases. (See Fig 5.)

**FIGURE 5** The distribution of collision energies for the particles in a reaction mixture depends upon its temperature. At the higher temperature  $T_2$ , a greater percentage of collisions have collision energy greater than activation energy,  $E_a$ . This is shown by the diagonally shaded area. The green shaded area shows a smaller percentage of collisions have **collision energy  $\geq E_a$**  at the lower temperature  $T_1$ .



Attempt Set 23 # 8.

## 14.6 Understanding the factors that affect reaction rate

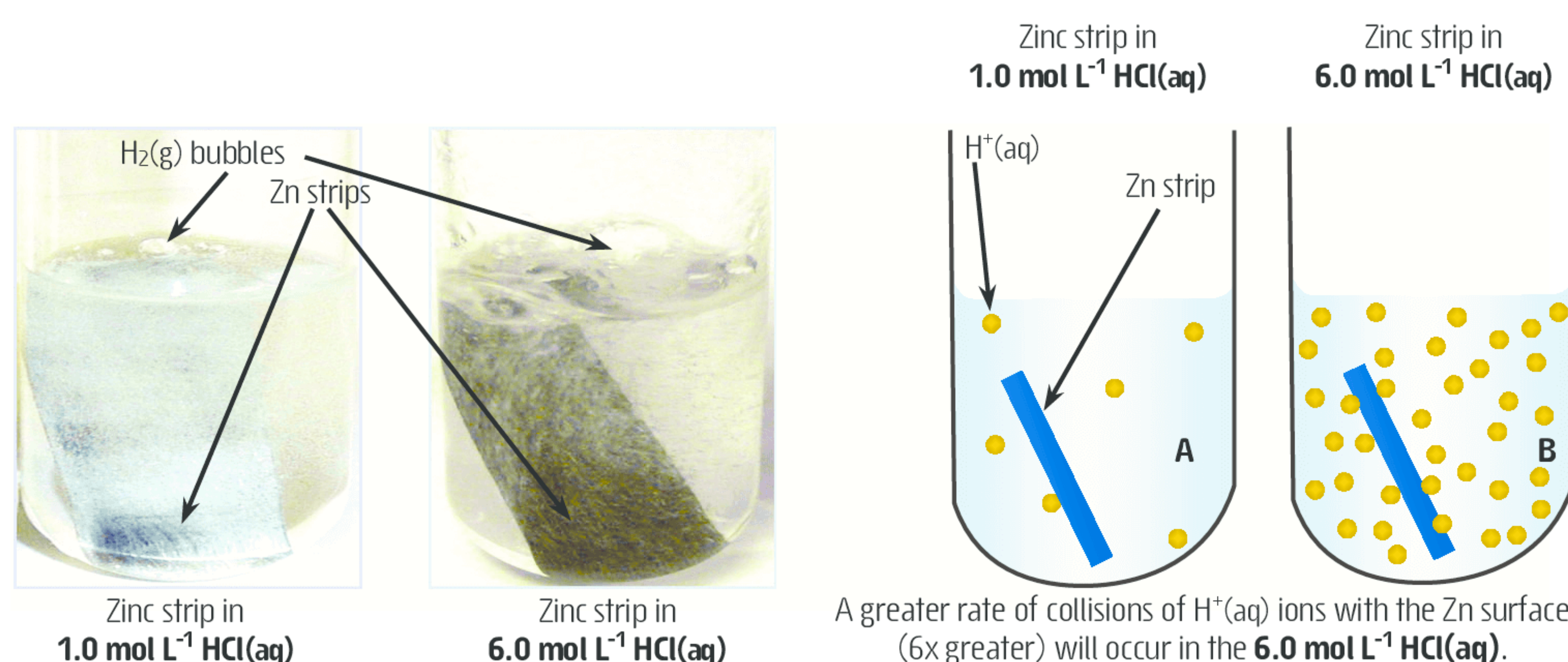
The collision theory gives us a basis for **understanding** and **explaining** the effects of concentration, temperature, pressure, state of sub-division and catalysts on reaction rate.

- **Concentration:** Raising the concentration of an aqueous reagent increases the reaction rate. Typically doubling the concentration of a reagent will usually (but not always) double the reaction rate. The collision theory provides an explanation for this observation in terms of **collision rate**. A higher concentration of reacting particles causes an increase in the rate of collisions between the reacting particles, hence an increase in rate of reaction. (See Fig 6.)

**FIGURE 6** Concentration affects the rate of reaction between  $Zn(s)$  and  $HCl(aq)$ .



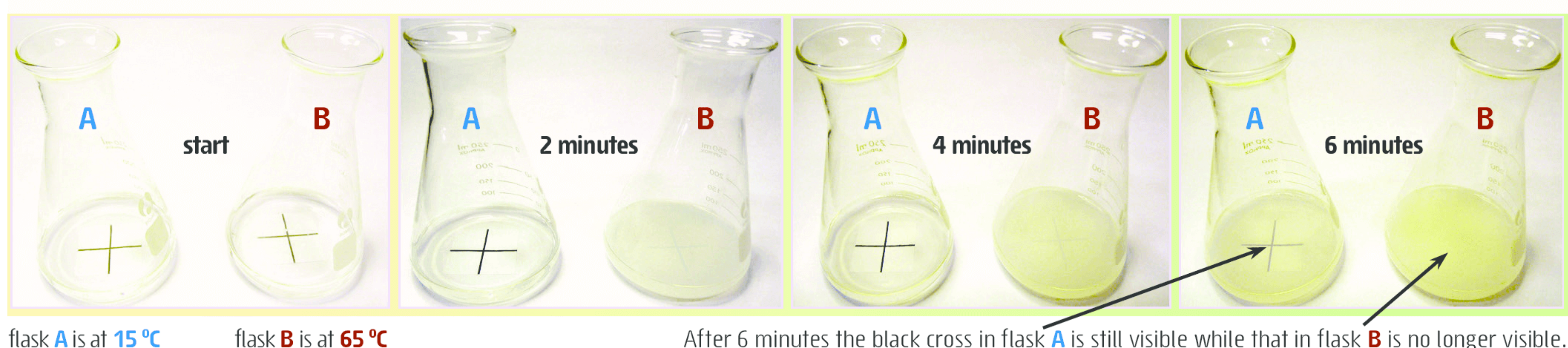
Notice the rate of evolution of hydrogen gas is much greater in the right hand test tube with the higher concentration of  $HCl(aq)$ . According to the collision theory, this is due to a greater rate of collisions between  $HCl(aq)$  [specifically  $H^+(aq)$ ] and  $Zn$  atoms on the zinc surface in the more concentrated solution. This is visualised at the particle level by **diagram A**, low  $H^+(aq)$  concentration and **diagram B**, high  $H^+(aq)$  concentration.





▪ **Temperature:** Raising the temperature of reagents increases the reaction rate. (See Fig 8.) Using the collision theory it is possible to explain this in terms of **successful collisions**. At a higher temperature, particles on average have a **greater kinetic energy**. This means a higher percentage of collisions have energy equal to or greater than the activation energy. (See Fig 5.) Thus a greater percentage of the collisions are successful and hence the reaction rate increases.

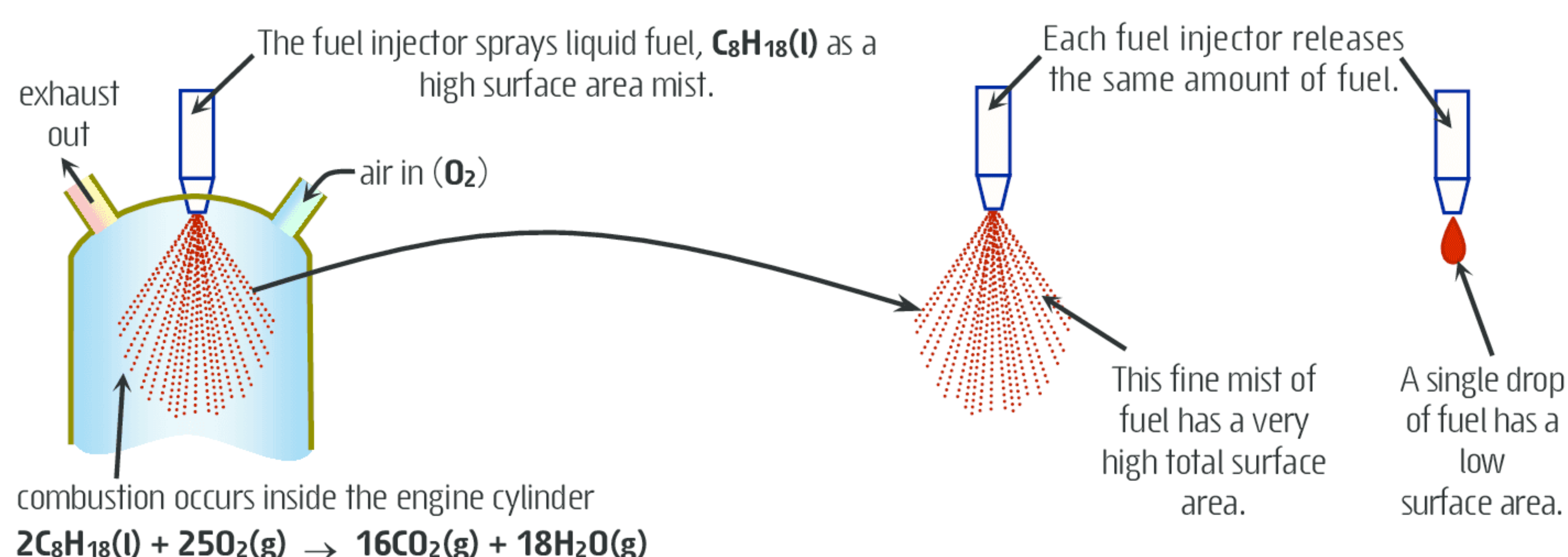
**FIGURE 8** The series of images below show the reaction between **sodium thiosulfate** ( $\text{Na}_2\text{S}_2\text{O}_3$ ) and **hydrochloric acid**:  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{S}(\text{s}) + \text{SO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$  at **15 °C** (flask A) and **65 °C** (flask B). The speed of this reaction can be visually monitored as it produces elemental sulfur, **S(s)** which turns the clear mixture cloudy yellow. Notice how the black cross disappears much more quickly in flask B, the warmer flask. The rate of this reaction is much greater at the higher temperature as a greater percentage of the collisions between thiosulfate ions,  $\text{S}_2\text{O}_3^{2-}(\text{aq})$  and hydrogen ions,  $\text{H}^+(\text{aq})$  have a collision energy equal to or greater than the activation energy.



It is also true, that higher temperatures mean an increased rate of collision between reacting particles. While this does contribute very slightly to an increased rate of reaction, its effect is known to be **minor** compared to the effect of increased collision energy.

▪ **State of subdivision: Heterogeneous** reactions involve reactants that are in two separate phases, eg solid/solid, solid/liquid, solid/gas, liquid/gas or two immiscible liquids. In these reactions the reacting particles can only collide at the **surface boundary** where the separate phases make contact. Increasing the surface area exposes a greater amount of reacting particles to the possibility of a collision. This results in an increased **rate of collision** between reacting particles and hence increases the reaction rate. (See Fig 9.)

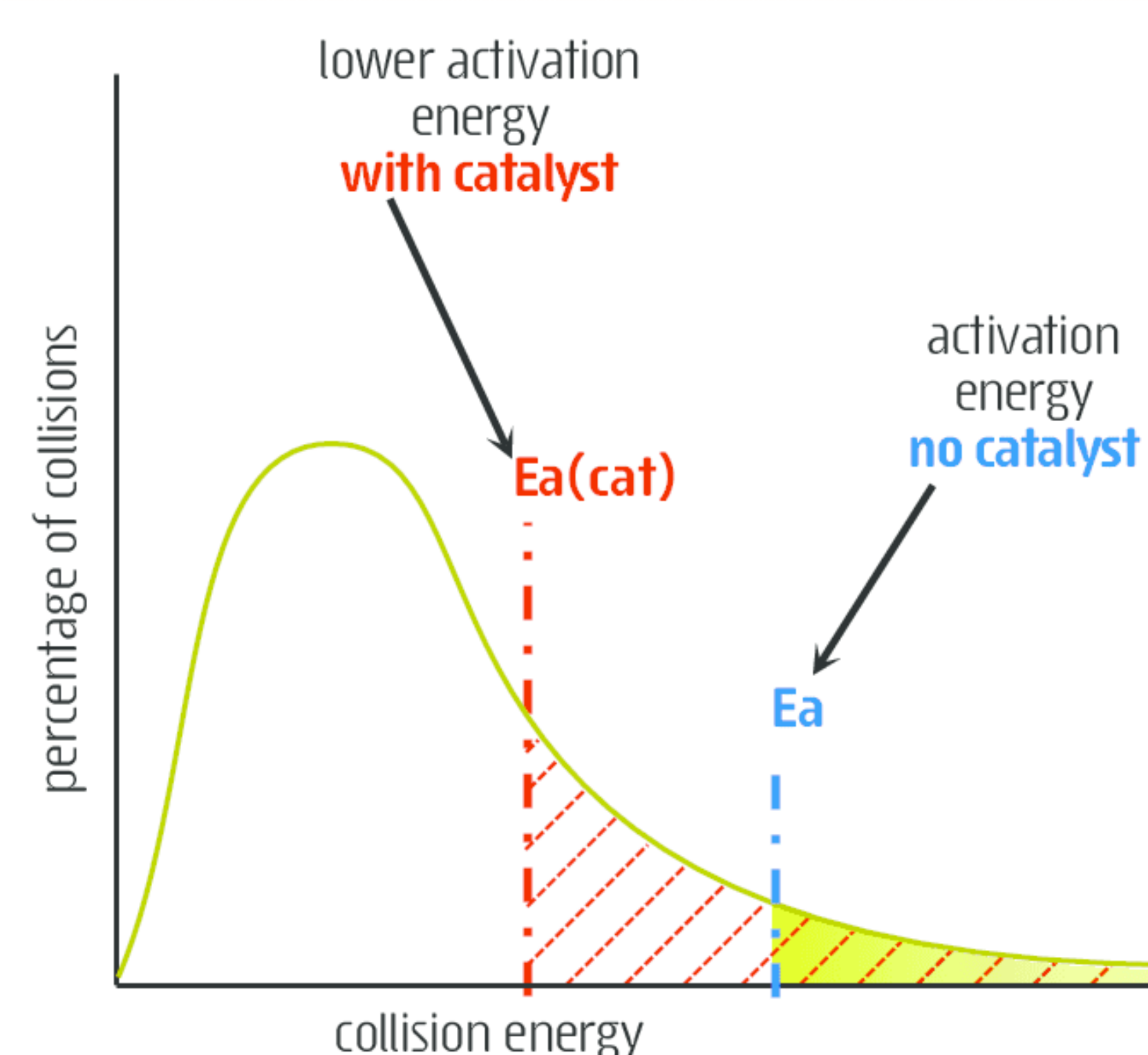
**FIGURE 9** Car engine fuel injectors spray liquid fuel into the combustion chambers (cylinders) forming a fine mist of fuel (high surface area). This increases the rate of collision between oxygen molecules (gas phase) and the fuel molecules (liquid phase), thus increasing the rate of fuel combustion.



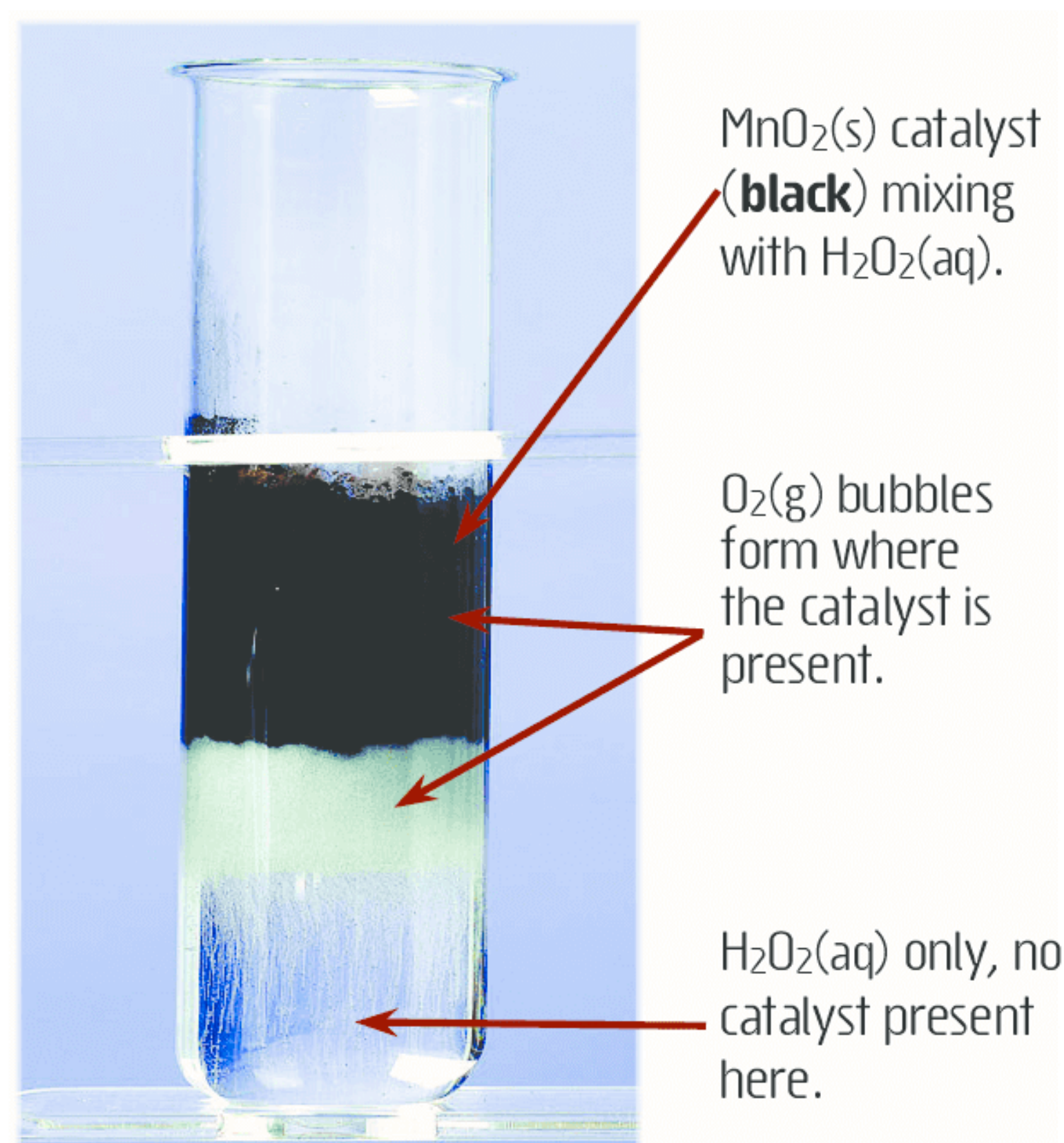
▪ **Catalysts:** Certain chemical substances, known as catalysts, have the ability to speed up chemical reactions while they remain chemically unchanged at the end of the reaction. That is, even though the catalyst might take part in the reaction there is no net consumption of the catalyst during the course of the reaction. Many transition metal elements like Mn, Pt, Pd, Au, Rh and their compounds show strong catalytic effects in certain reactions. The presence of a small amount of manganese dioxide,  $\text{MnO}_2(\text{s})$  for example, rapidly increases the rate of decomposition of hydrogen peroxide to oxygen and water. (See Fig 11.)

Catalysts increase the rate of reaction by providing a reaction pathway; a series of changes by which reactants change to products, with a **lower activation energy**. Thus when a catalyst is present a greater percentage of collisions will have an energy equal to or greater than the activation energy. (See Fig 10.) As a result a greater percentage of collisions are successful and so the rate of reaction increases.

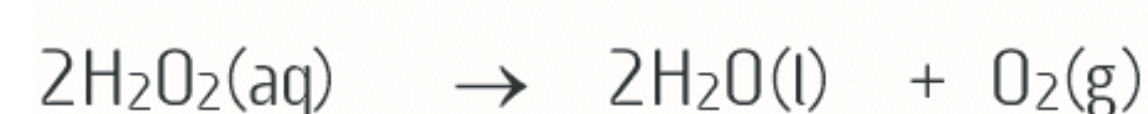
**FIGURE 10** A catalyst reduces the activation energy. The shaded areas (red hatched and green) show a greater percentage of collisions have energy  $\geq E_a$  (activation energy) when a catalyst is present.



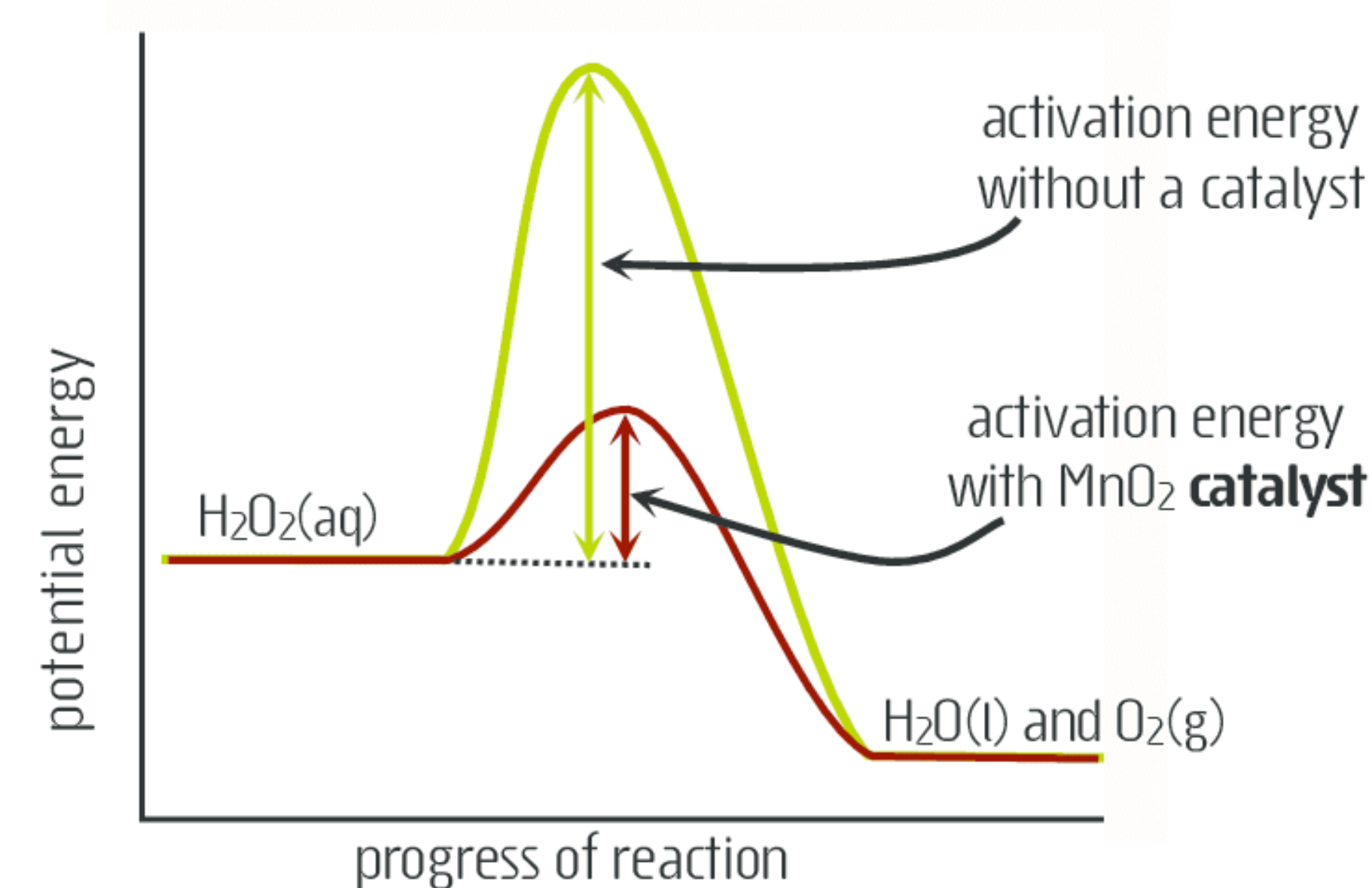




**FIGURE 11** The **uncatalysed** and **catalysed** potential energy profile for the decomposition of  $\text{H}_2\text{O}_2(\text{aq})$  (at left).



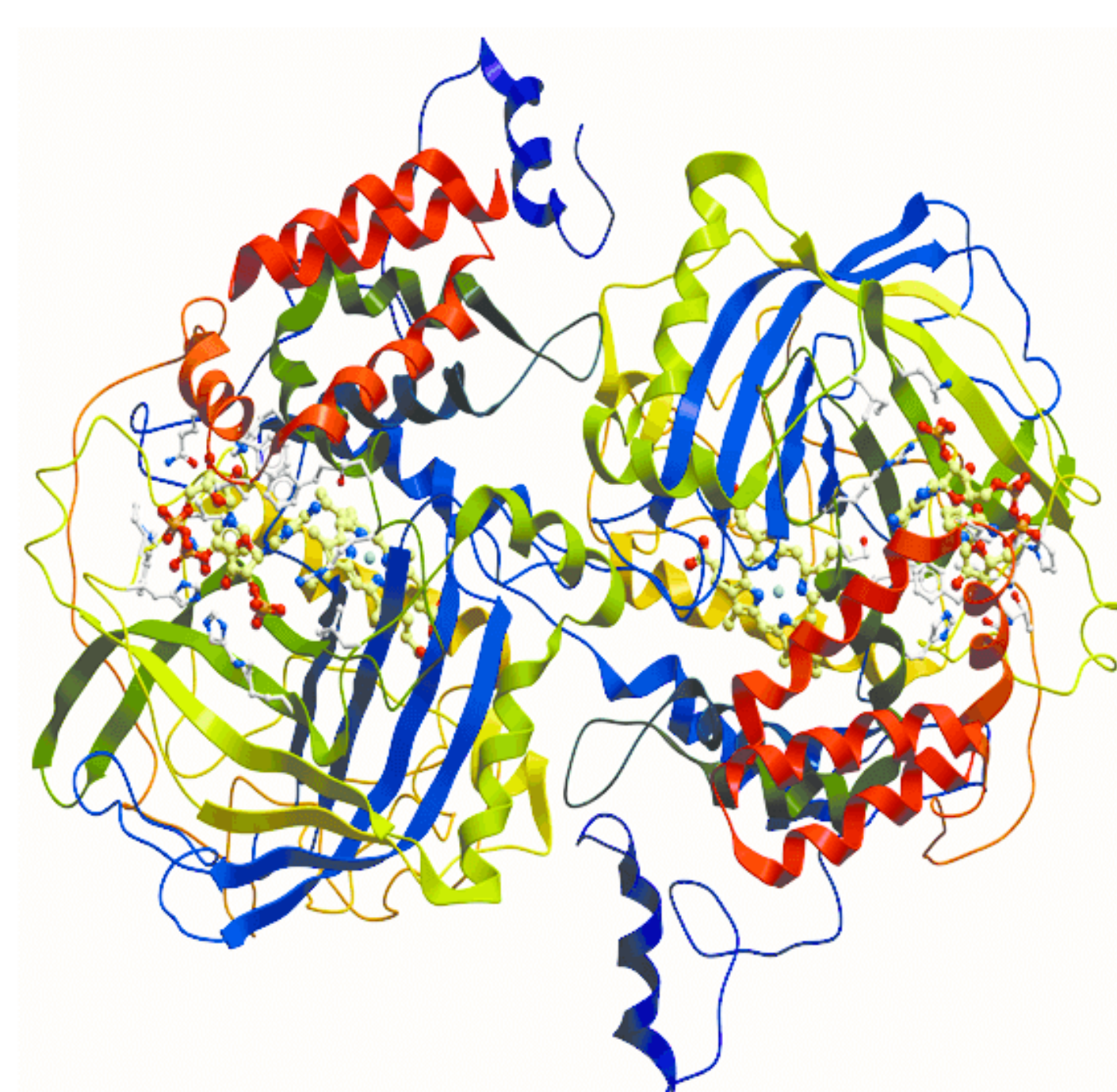
A high activation energy makes this reaction slow under normal laboratory conditions. Adding a catalyst like  $\text{MnO}_2(\text{s})$  provides the reaction with a pathway of lower activation energy. Thus with the catalyst present a greater percentage of collisions between  $\text{H}_2\text{O}_2$  molecules have sufficient energy to form the activated complex. Such collisions may go on to produce  $\text{H}_2\text{O}(\text{aq})$  and  $\text{O}_2(\text{g})$ . As a result the rate of decomposition of  $\text{H}_2\text{O}_2(\text{aq})$  is much greater with a catalyst present.



Attempt Set 23 # 9, 10 and 11.

**FIGURE 12** Hydrogen peroxide,  $\text{H}_2\text{O}_2$  also occurs naturally in the human body as a **waste** product of many normal metabolic processes. Because it is extremely toxic to cell tissue it must be removed rapidly before causing cell damage or death.

In the human body and the tissue of almost all living organisms an **enzyme** called **catalase** is responsible for the rapid catalytic decomposition of  $\text{H}_2\text{O}_2$ . Catalase is one of the **fastest acting catalysts known**. A single molecule can decompose several million  $\text{H}_2\text{O}_2$  molecules per second. The schematic model below shows the complex structure of the catalase molecule.

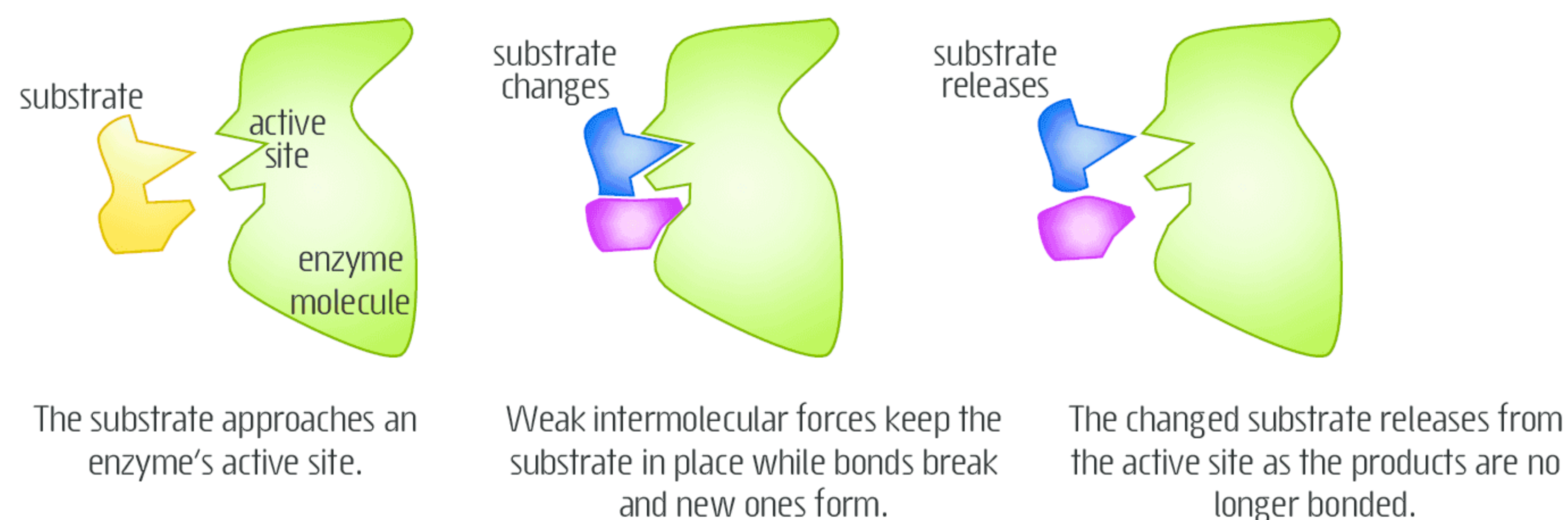


Attempt Set 23 # 12.

## 14.7 Enzymes: Biological catalysts

Catalysts like platinum and manganese dioxide are known as **inorganic catalysts**. They include various metal elements or their simple ionic compounds. However, another type of catalyst is found in living systems. These **biological catalysts** are proteins which are known as **enzymes**. Unlike inorganic catalysts enzymes tend to be very specific in the reactions they catalyse and much faster acting. (See Fig 12.) Often it is their complex structure and particularly their shape that allows a specific reagent molecule (or molecules) called the **substrate**, to fit onto or 'dock' with a specific **active site** on the enzyme surface. It is for this reason that a particular enzyme will often only catalyse a specific reaction. This is known as **enzyme specificity**. Once in place the enzyme forms various weak intermolecular forces with the substrate thus holding it in place at the active site. While the substrate is in this position, bonds are more easily rearranged leading to the quick formation of products. Once the substrate has undergone chemical changes the new products disengage from the enzyme surface leaving the enzyme in its original form. This simple model for enzyme action is called the **lock and key model**. (See Fig 13.)

**FIGURE 13** Schematic representation of the **lock and key model** of enzyme action.



## 14.8 Catalysts contributing to sustainability

The economic synthesis of many valuable chemical substances requires otherwise slow reactions to be sped up. Even though high temperatures and pressures can be effective they require the use of large amounts of energy which has associated economic costs, environmental costs and sustainability issues. The ability of **catalysts** however, to speed up otherwise slow chemical reactions, can offer a solution which is **sustainable**, has low energy input and minimises environmental impact. It is estimated that over 90% of modern materials, from petroleum products to plastics and fertilisers to pharmaceuticals involve the use of catalysts at some stage in their manufacture. As an example, modern day nitrogen based fertilisers, such as  $\text{CO}(\text{NH}_2)_2$  (urea),  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$ , are only possible due to the catalytic synthesis of ammonia,  $\text{NH}_3$  in the Haber-Bosch process. Although this reaction shown below, is spontaneous, it is **uneconomically slow** even when performed at high pressure and temperature.



The discovery of a suitable method for promoting this reaction is attributed to the German chemist **Fritz Haber**. Haber's method essentially hinged on his discovery published in 1905, that iron could be used to catalyse the reaction of nitrogen,  $\text{N}_2(\text{g})$  with hydrogen,  $\text{H}_2(\text{g})$  to produce ammonia,  $\text{NH}_3(\text{g})$ . So significant was this discovery that the **Nobel Prize** in Chemistry 1918 was awarded to Fritz Haber 'for the synthesis of ammonia from its elements'.

**FIGURE 14** The high productivity of modern agriculture has only become possible with the advent of cheap and abundant amounts of nitrogen based fertilisers. The single largest artificial source of these nitrogen based fertilisers comes from the **catalytic** production of ammonia in the **Haber-Bosch process**.





Soon after this discovery, the famous chemist and engineer **Carl Bosch** was successful in adapting Haber's synthesis into an industrial process for the manufacture of ammonia. Today, this process, known as the 'Haber-Bosch' process, is vital for the manufacture of ammonia with around 200 million tonnes produced globally in 2012.

Another important example of the use of catalysts can be seen in the **motor vehicle catalytic converter**. (See Fig 15.) This device is fitted to the exhaust system of all new vehicles sold in Australia and most other countries. Its operation relies on the catalytic ability of metals like platinum, palladium and rhodium to **rapidly** convert toxic and polluting vehicle **exhaust gas** into harmless nontoxic substances. The exhaust gases are in contact with the catalytic surfaces inside the honeycomb structure of the catalytic converter for around 100 to 400 ms. In this very short time 90% of the toxic nitrogen oxides,  $\text{NO}_x$  in the exhaust are converted into harmless  $\text{N}_2$  and 80% of the unburnt hydrocarbons, HCs and poisonous carbon monoxide CO are converted into  $\text{H}_2\text{O}$  and  $\text{CO}_2$  respectively.

To achieve this remarkably rapid conversion, two different types of catalyst are employed. A reduction catalyst, usually platinum or palladium, situated at the front part of the catalytic converter catalyses the conversion of  $\text{NO}_x$  and some CO to  $\text{N}_2$  and  $\text{CO}_2$ . Another catalyst rhodium, an oxidation catalyst, is positioned at the back end of the converter and rapidly converts unburnt HCs and the remaining CO into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

The type of catalysis used in both the Haber-Bosch process and the catalytic converter is known as **heterogeneous catalysis**, so called because the catalysts and the reagents are in two different phases. In these examples the catalysts Fe, Pt, Pd and Rh are in the solid phase and the reactants are in a gas phase. For these reactions to be catalysed the reagent gases must first **adsorb** onto the catalyst surface. While in this adsorbed state their bonds are more easily rearranged. This is why the activation energy for the reaction is lowered when the catalyst is present. Bonds amongst the adsorbed atoms and molecules quickly rearrange to form new products that readily release from the catalytic surface, thus also regenerating the catalyst in its original unchanged form.

As catalytic materials can be very expensive and since heterogeneous catalysis can only take place on the catalyst surface then for minimum cost and maximum rate, the catalyst must have a very **high surface area**. In the automotive catalytic converter (Fig 15) this is achieved by having the catalyst present as fine particles spread over the surface of a supporting structure called a ceramic honeycomb monolith. Typically less than 10 grams of the catalytic metals are present in the form of fine particles deposited on channel surfaces that run through the honeycomb monolith structure. The catalysed reactions happen rapidly as exhaust gases pass through the monolith channels in less than half a second.

## 14.9 Nanoform catalysts

One aspect of nanomaterials is their very **large surface to volume** ratio compared to bulk materials. This makes catalysts in the form of nanoparticles a very attractive proposition. One promising area of research involves using nanocatalysts to develop improved electrodes for the hydrogen-oxygen fuel cell. This cell shows great potential as a low polluting energy converter for transport such as in motor vehicles. It uses a pair of electrodes in an electrochemical cell to convert  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  into  $\text{H}_2\text{O}(\text{l})$  while producing electrical energy to operate the vehicle.

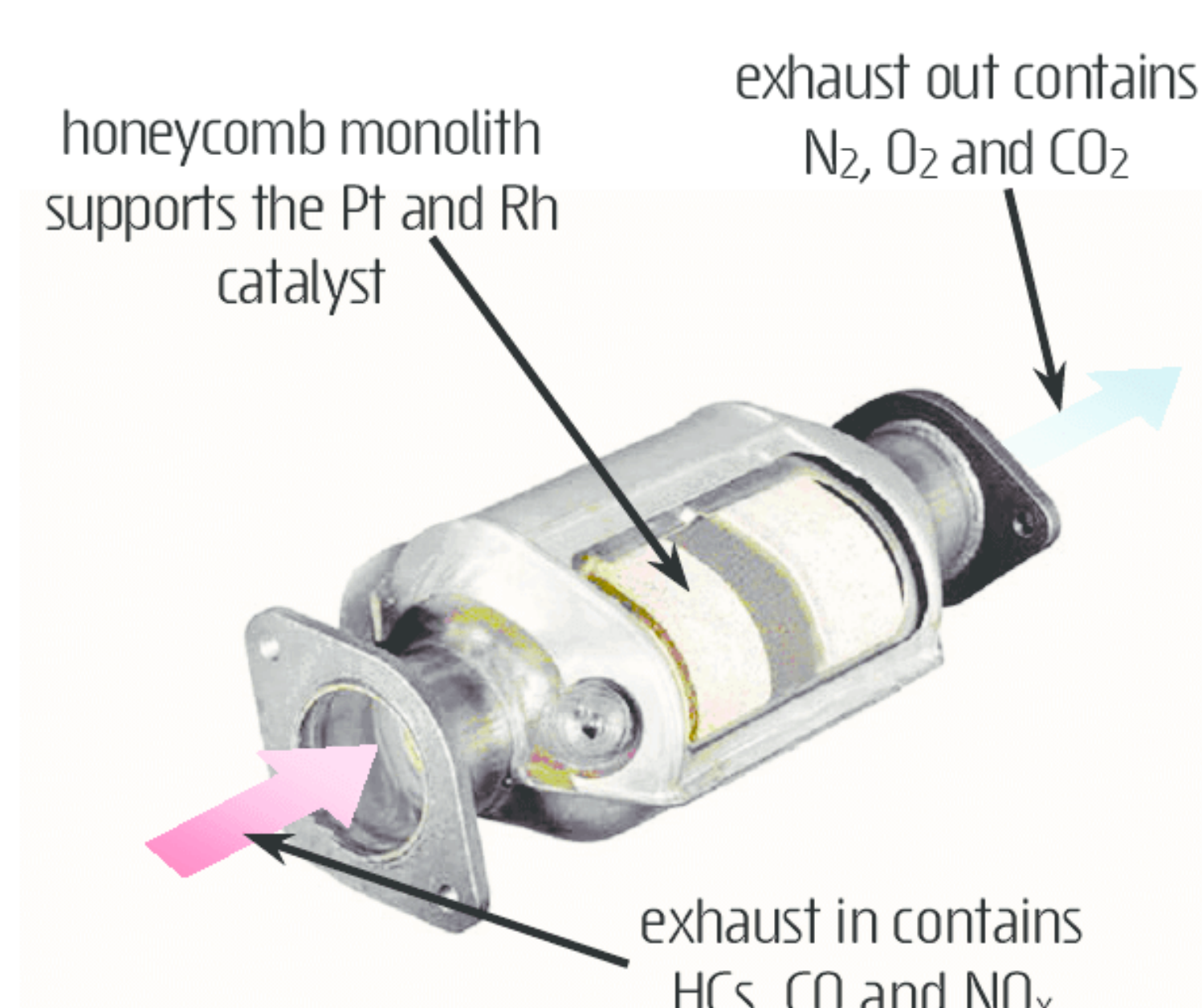
At present the widespread commercial use of these cells is limited. A major reason for this is the ease with which the platinum electrode surfaces become poisoned by the presence of carbon monoxide gas,  $\text{CO}(\text{g})$ . This gas is typically present in the hydrogen fuel obtained from the **catalytic reforming** of hydrocarbons. **Catalytic poisoning** occurs as  $\text{CO}(\text{g})$  molecules attach very strongly to the catalyst surface. This prevents the catalyst from interacting with  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  and catalysing their conversion into  $\text{H}_2\text{O}(\text{l})$ . A current but expensive and environmentally unfavourable solution involves removal of most of the CO from the hydrogen fuel and then operating the fuel cell at high temperatures of around 150–220 °C. Under these conditions catalyst poisoning is greatly reduced but clearly this is an inefficient and high energy option.

A solution currently being researched (Fig 16) involves the use of electrodes made from **core-shell nanocatalyst** particles. These catalytic nanoparticles consist of a ruthenium core coated with a double layer shell of platinum atoms. In this nanoparticle form, the metals have an exceptional surface area for their total mass and excellent catalytic effects on the electrode reactions but most importantly are not prone to CO poisoning. Core-shell nanocatalysts potentially open the door for the widespread commercialisation of low-temperature fuel cells that use inexpensive hydrogen from hydrocarbon reforming (ie  $\text{H}_2$  with CO impurity) as the fuel.

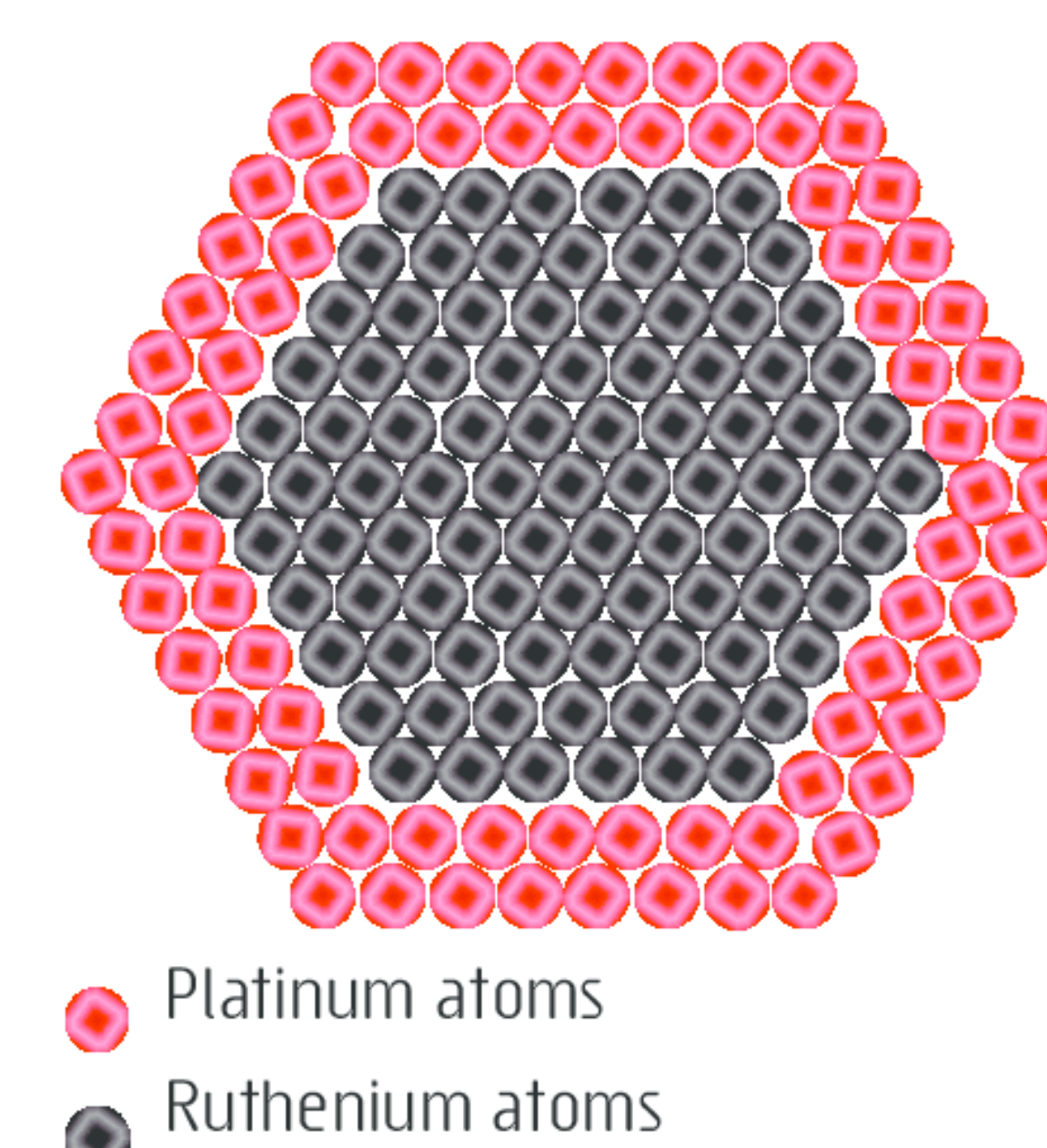
**FIGURE 15** Motor vehicle exhaust contains a number of harmful gases such as carbon monoxide (CO) nitrogen oxides ( $\text{NO}_x$ ) and various unburnt hydrocarbons (HCs). CO is a **toxic gas** while  $\text{NO}_x$  and HCs contribute to an effect known as **photochemical smog**.

Photochemical smog is a toxic cocktail of various chemical pollutants produced when sunlight interacts with car exhaust gases. The introduction of the **catalytic converter** into new motor vehicles sold in Australia since 1986 has greatly reduced these pollutants.

A catalytic converter is integrated into the vehicle's exhaust system. This open view shows the honeycomb monolith through which the exhaust flows. Metals like **platinum, palladium** and **rhodium** are coated onto the channel surfaces within the honeycomb structure. The catalysed reactions occur on the surfaces within the monolith structure.



**FIGURE 16** Researchers at Brookhaven National Laboratory have developed a new type of nanocatalyst that shows great potential in advancing the versatility of the **hydrogen oxygen fuel cell**. The catalytic nanoparticles they created consist of a ruthenium core coated with a double layer shell of platinum atoms. A model of their **core-shell nanocatalyst** particle is shown here.



The researchers also developed an inexpensive 'green' technique suitable for large scale manufacture of these nanoparticles. Fuel cell electrodes made from these would have several advantages over conventional platinum electrodes:

- have exceptional surface area to mass ratio
- require much less of the very expensive catalyst platinum
- not poisoned by CO typically present in low cost hydrogen fuels from reformed methane
- can be manufactured on a large scale using an inexpensive 'green' method of production.

Complete Set 23.



## Set 23 Reaction rate

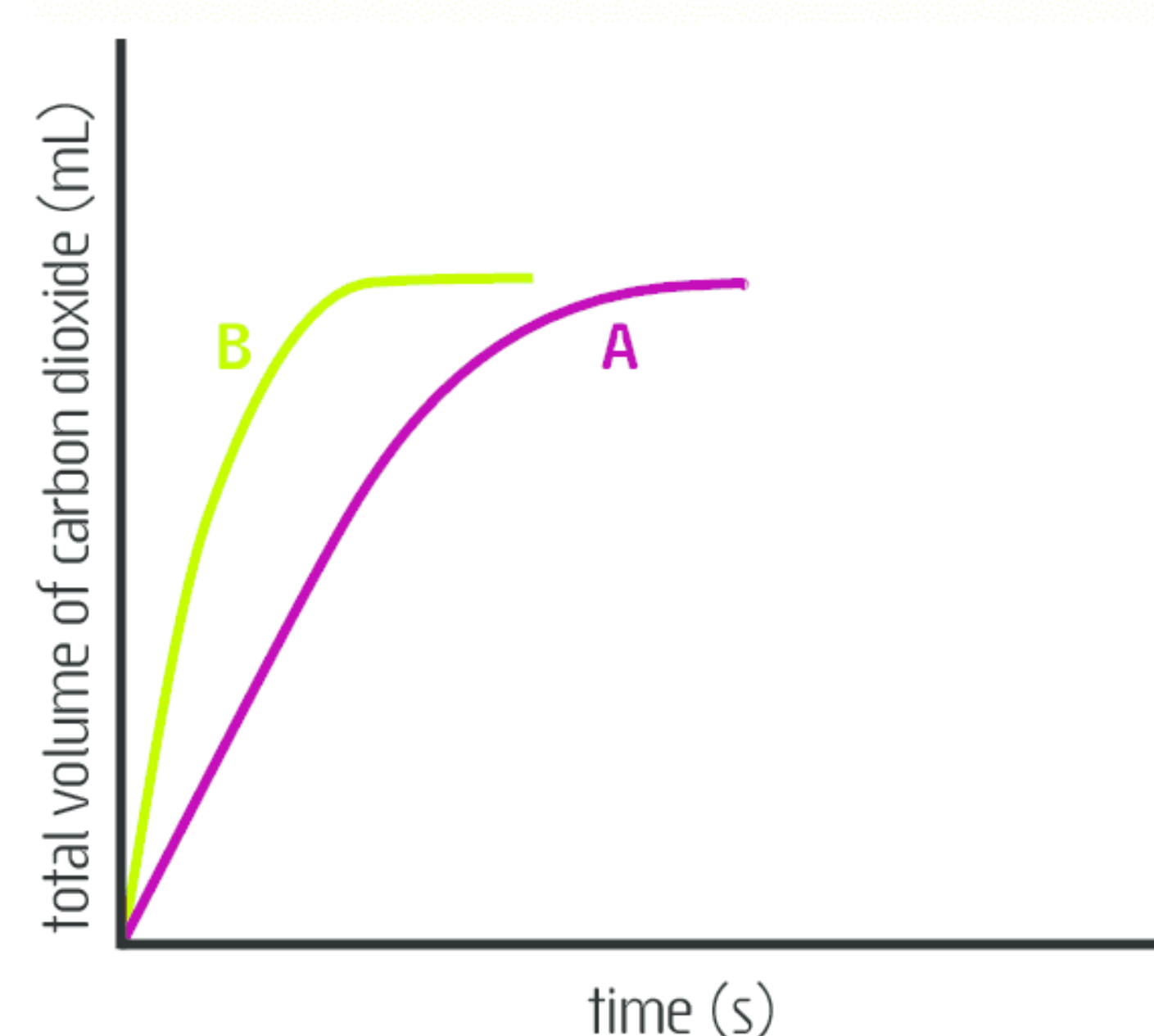
**FIGURE 17** Steel is an alloy consisting mainly of iron. Its reaction with oxygen from air is normally very slow. Corrosion of this steel bicycle chain for example is a slow almost imperceptible reaction.



If, however, a piece of steel is cut with an angle grinder then the hot, fine pieces of steel that are formed react rapidly with air producing a characteristic shower of sparks.



**FIGURE 18** This graph shows the total volume of carbon dioxide produced over time when nitric acid reacts with sodium



- The following examples describe a chemical reaction where the alteration of some factor changes the reaction rate. In a few words **describe** the factor that is altered and **state** its effect on the reaction rate. The first example has been done.

**Example:** Some  $2.0 \text{ mol L}^{-1}$  hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution shows some evidence of a colourless gas forming when left standing at room temperature for ten minutes. A small amount of finely powdered manganese dioxide ( $\text{MnO}_2$ ) is then added to the solution. This results in a rapid and sustained evolution of colourless gas. The black powdered manganese dioxide does not seem to be consumed over time.

**Answer:** The altered factor is the addition of the catalyst manganese dioxide. This resulted in an increased reaction rate.

- A piece of zinc added to a  $1.0 \text{ mol L}^{-1}$  hydrochloric acid solution produced 2 mL of hydrogen gas per minute. When using  $5 \text{ mol L}^{-1}$  hydrochloric acid with a similar piece of zinc, 40 mL of hydrogen gas is produced per minute.
- Some milk left on the laboratory bench for a day curdled and went sour. In a second experiment a similar sample of milk was left in a **refrigerator** and appeared unchanged when tasted a week later.
- A **large piece** of coal is not easily ignited and when it does burn the reaction is quite slow. In the form of **coal dust** (fine particles of coal) a single spark may be sufficient to ignite the coal which then burns explosively.
- A single piece of aluminium added to a  $1.0 \text{ mol L}^{-1}$  hydrochloric acid solution produces very little evidence of a reaction. Adding a few drops of **copper sulfate** solution results in moderate bubbling of hydrogen gas. The blue colour of the added copper sulfate shows no evidence of changing over time.
- Steel normally shows no apparent reaction with air. If a steel section is cut with an angle grinder (Fig 17) the fine pieces of steel rapidly ignite and burn.

- State **three alterations** that could increase the rate of the reaction shown here.



- The graphs in Fig 18 show the **total volume** of carbon dioxide gas formed over **time** for the reaction of sodium hydrogen carbonate with dilute nitric acid.



Graph **A** shows the result when using **20.0 mL** of  $0.50 \text{ mol L}^{-1}$   $\text{HNO}_3\text{(aq)}$  at **25 °C**. Graph **B** is for the same reaction performed at a different **temperature**.

- To obtain the result in Graph **B**, was the temperature increased or decreased? Refer to the **gradients** of Graph **A** and Graph **B** and **explain** in terms of reaction rate.
- This reaction is repeated once more using **100.0 mL** of  $0.10 \text{ mol L}^{-1}$   $\text{HNO}_3\text{(aq)}$  at **25 °C**. Show on Fig 18 (at left) how the rate of formation of carbon dioxide would now appear. **Account** for the shape of your graph.

- A student is asked to test the following hypothesis about rate and concentration.

**'The rate of a chemical reaction is directly proportional to the concentration of any aqueous reagent in the reaction'.**

To do this she devised an experiment using the following reaction.



The investigation involved using a  $1.0 \text{ cm}^3$  cube of calcite (pure  $\text{CaCO}_3$ ) placed into a 250 mL conical flask containing 150.0 mL of  $0.50 \text{ mol L}^{-1}$   $\text{HCl(aq)}$ . The mass of the cube plus the conical flask with acid were measured before the reaction started and also as the reaction progressed. (See Fig 19.) The student recorded the time taken for the reaction mixture to lose 0.30 g in mass. The experiment was repeated several times with different concentrations of acid. The results are shown in the following table.



4. (continued)

concentration of HCl(aq) (mol L <sup>-1</sup> )	0.50	1.2	1.9	3.2	5.0
time to lose 0.30 g mass (s)	1490	231	102	35	14
reaction rate [g(CO <sub>2</sub> ) s <sup>-1</sup> ]					

The following questions relate to this investigation.

- Briefly account** for the mass loss that occurs during the course of the reaction.
  - Calculate the average reaction rate in grams of carbon dioxide produced per second, **g(CO<sub>2</sub>) s<sup>-1</sup>**. Do this for each acid concentration and thus complete the table.
  - If a cotton wool plug is not used (see Fig 19), some solution may be lost due to its vigorous fizzing. How would the loss of solution cause an error in the determination for the mass of CO<sub>2</sub>(g) produced? Would this be a **systematic** or **random** error and how would it affect the calculated rate of reaction for each experiment? **Explain**.
  - Construct a **graph** of rate of reaction against concentration of HCl(aq). You may assume the rate of evolution of CO<sub>2</sub>(g) is zero when the concentration of HCl(aq) is zero.
  - Do the processed results as seen in your graph support the student's hypothesis?
  - The procedure the student used involved allowing the reaction mixture to lose 0.20 g in mass, equivalent to an STP volume of CO<sub>2</sub> of ≈200 mL, before she started timing for the 0.30 g weight loss. **Suggest** a reason why it was important to do this. Remember carbon dioxide gas is much denser than air.
5. A student has a choice of investigating a single factor that might affect the rate of the reaction between zinc and hydrochloric acid. In order to do this she will need to **monitor** the **rate** of this reaction under different conditions. Describe how rate can be measured and briefly outline one way to monitor the rate of this reaction.

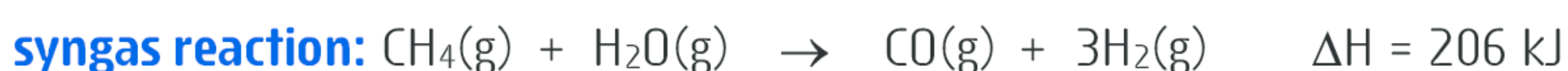


6. The following passage describes the events taking place at the particle level when hydrogen gas, H<sub>2</sub>(g) and oxygen gas, O<sub>2</sub>(g) are mixed in a sealed container and react to form water, H<sub>2</sub>O(g). Use the terms listed to complete the passage. Some terms may be used more than once.

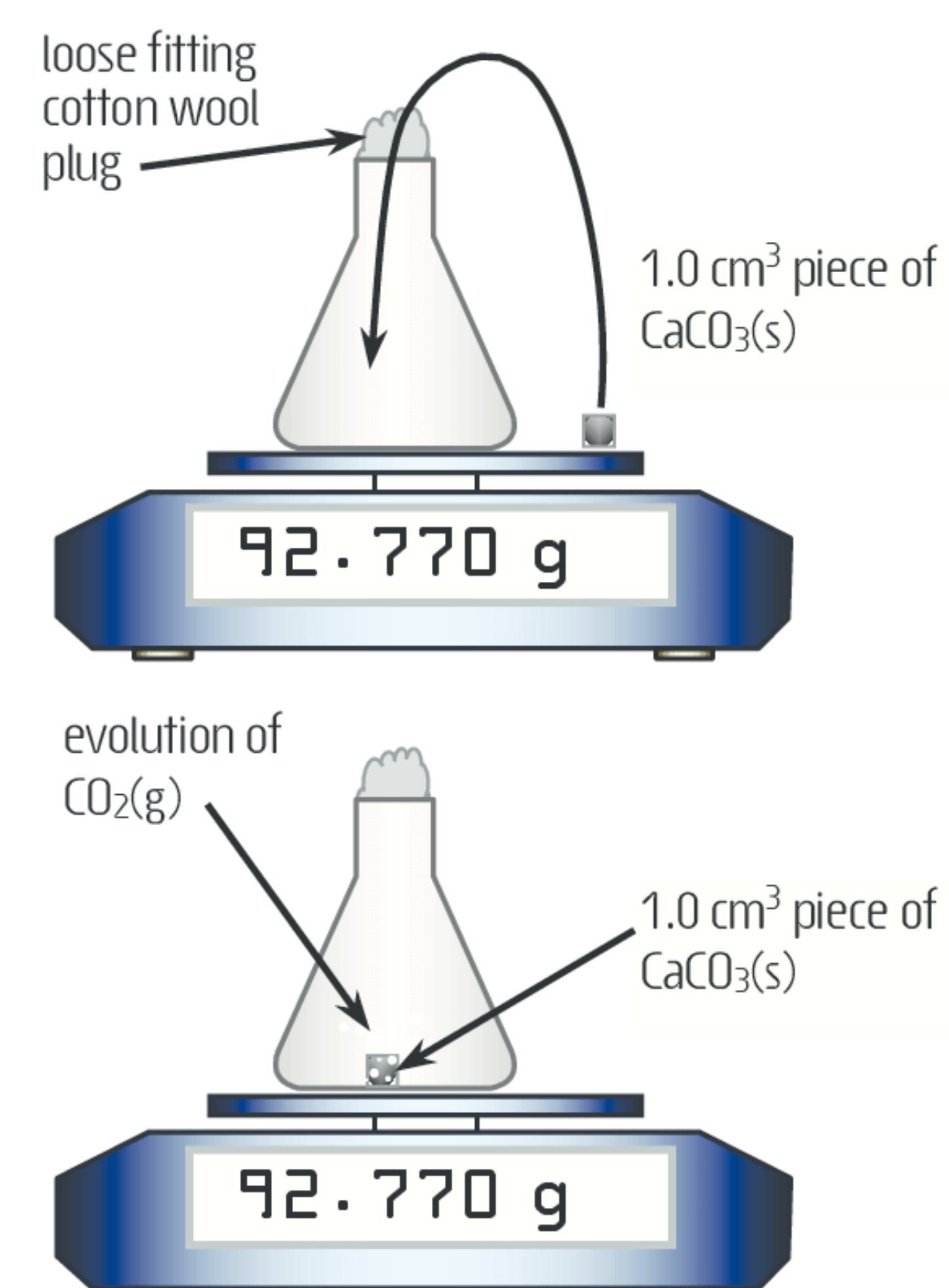
Hydrogen and oxygen (a) \_\_\_\_\_ move (b) \_\_\_\_\_ within the mixture of two gases. Occasionally a molecule of hydrogen gas will (c) \_\_\_\_\_ with a molecule of oxygen gas. When they collide the negatively charged (d) \_\_\_\_\_ of the two molecules will partially overlap causing the molecules to (e) \_\_\_\_\_ one another and slow down. If the molecules collide with sufficient (f) \_\_\_\_\_ so that the collision energy is greater than or equal to the (g) \_\_\_\_\_ and the collision has a favourable (h) \_\_\_\_\_ then a reaction may occur.

Once the molecules of hydrogen and oxygen have collided with sufficient energy they form a single but unstable unit called an (i) \_\_\_\_\_. In this structure the original bonds present within the hydrogen molecules and oxygen molecules are (j) \_\_\_\_\_ while new bonds between oxygen atoms and hydrogen atoms are (k) \_\_\_\_\_. This activated complex or transition state is a short lived arrangement of loosely bonded atoms that will rapidly (l) \_\_\_\_\_ to form either the original (m) \_\_\_\_\_ or (n) \_\_\_\_\_.

7. Synthetic petroleum products like petrol can be manufactured from natural gas (CH<sub>4</sub>) by a chemical process known as the **Fischer-Tropsch** process. The first step in this process involves producing a hydrogen gas-carbon monoxide gas mixture via a **syngas** step. The equation for the **syngas** reaction is shown.



- Suggest** a reason for converting natural gas to synthetic petrol.
- The syngas reaction has a high activation energy and so can be quite slow. **Sketch a potential energy profile** for this reaction. On the profile indicate reactants, products, ΔH and activation energy.
- Briefly explain what the **high** activation energy of the syngas reaction indicates about the nature of the **bonds** in the reactants of this reaction.
- Why is the activation energy of this reaction significant from an **industrial synthesis** point of view?



**FIGURE 19** Carbon dioxide gas has a very low solubility in acid solutions. Thus as CO<sub>2</sub>(g) forms it leaves the solution and escapes from the flask. Hence the mass loss of the reaction mixture and flask can be assumed to be equal to the mass of CO<sub>2</sub>(g) produced.

Using a cotton wool plug in the mouth of the flask helps reduce loss of liquid by spattering while still allowing CO<sub>2</sub>(g) to escape.

**breaking**  
**collide**  
**repel**  
**reactants**  
**orientation**  
**water**  
**kinetic energy**  
**activation energy**  
**randomly**  
**activated complex**  
**forming**  
**electron clouds**  
**molecules**  
**decompose**



8. Briefly **explain** why reaction rate increases with increasing temperature. You should refer to average collision energy and activation energy.
9. A high temperature is used to help increase the rate of the syngas reaction from Question 7. Describe two other conditions that could increase the speed of this reaction. **Justify** your choice of conditions with reference to the collision theory.
10. Two students working together on an investigation into reaction rates decide to focus on the heterogeneous reaction of nickel solid with an hydrochloric acid solution. They intend to make several changes which they hypothesise will affect the rate of reaction. Complete the table indicating any rate changes you might expect them to observe. Use **increase, unchanged** or **decrease**. Also in the final column state how the collision theory supports your predictions.



The original reaction conditions used were as follows:

- a. 45 mL of 1.0 mol L<sup>-1</sup> HCl(aq)
- b. one 4.0 g ball bearing shaped piece of nickel
- c. conducted in a 100 mL open beaker at 25 °C and atmospheric pressure of 101.3 kPa.

Alteration to conditions used: all other conditions remain unchanged	Predicted change to initial reaction rate	Use the collision theory to account for your predictions
a. Cool the mixture to 2 °C		
b. Use 90 mL of acid		
c. Use 2.0 mol L <sup>-1</sup> HCl(aq)		
d. Add 45 mL of distilled water		
e. Use smaller pieces of nickel (same total mass)		
f. Heat the reaction to 95 °C		

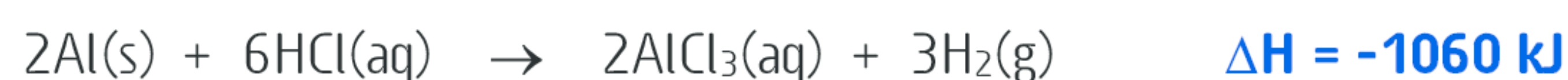
11. **Hydrogen peroxide** is the active ingredient in some household hair bleaches and antiseptics. The compound is unstable and slowly decomposes to produce both water and oxygen gas. In a laboratory investigation 0.85 g of the black solid MnO<sub>2</sub> was added to a 50.0 ml sample of 5% hydrogen peroxide bleaching solution. Upon adding MnO<sub>2</sub>(s) the bleaching solution fizzed rapidly and became quite hot. When the reaction appeared to have stopped the remaining **MnO<sub>2</sub>(s)** was carefully filtered, dried and weighed and found to have not changed significantly in mass.
- a. What is meant by the phrase, '**not changed significantly in mass**'?
  - b. Refer to the collision theory to **account** for the experimental observations.
  - c. Sketch a **potential energy profile** for this reaction. On the profile show the reaction path with and without the MnO<sub>2</sub>(s). Label **reactants, products, ΔH** and **activation energy** with and without MnO<sub>2</sub>(s).
  - d. What is **catalase** (Fig 12 p120) and how is its action related that of MnO<sub>2</sub>(s)?



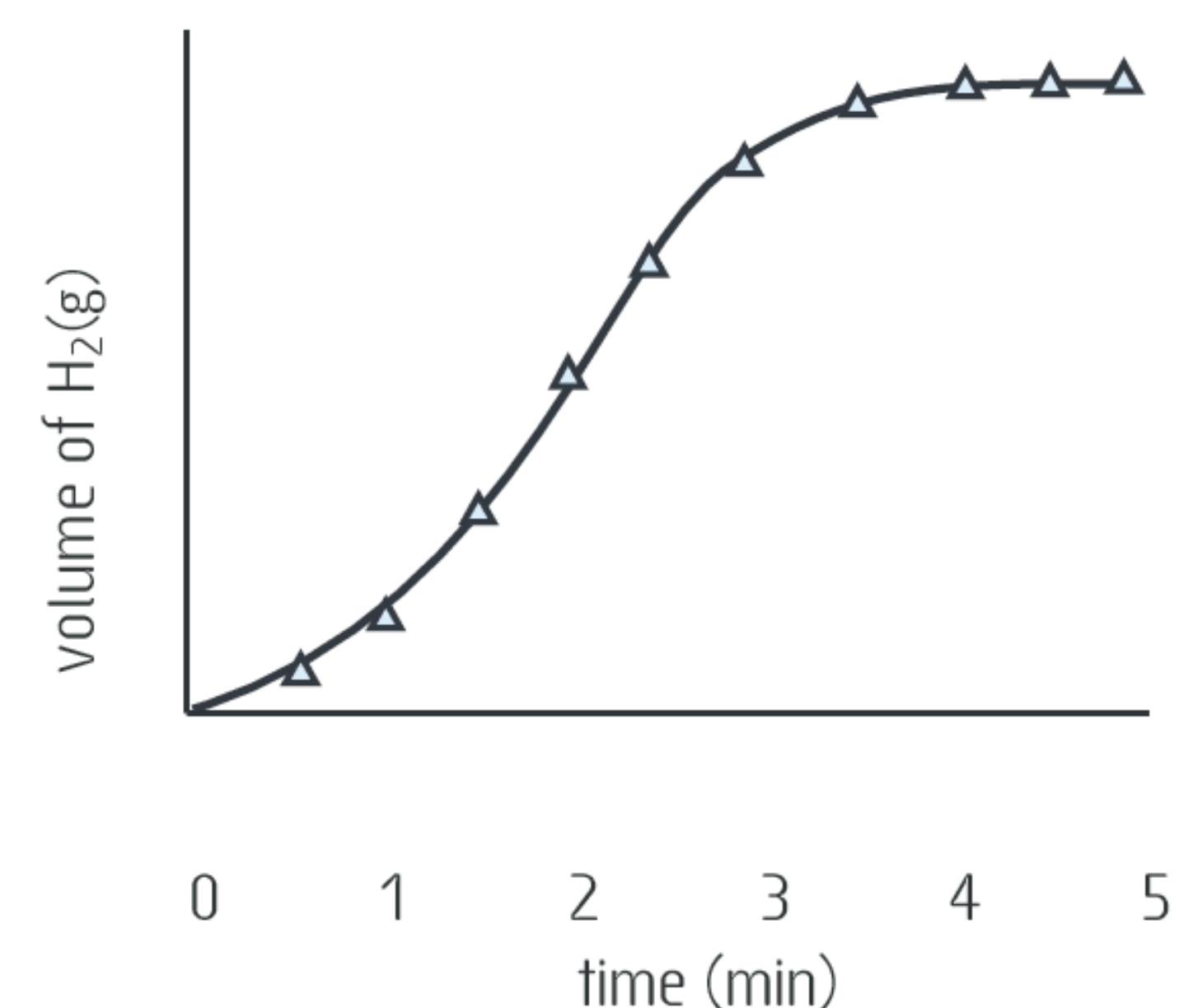
12. **Glucose** is the main source of energy used by living cells. In the human body, glucose,  $C_6H_{12}O_6$  is obtained from the digestion of carbohydrates and is stored in the liver as a polysaccharide called **glycogen**,  $(C_6H_{12}O_6)_n$ . A simplified equation for the conversion of glucose to glycogen is represented here.



- What is the role of the **enzyme** shown in this equation?
  - In the equation above, the enzyme is written above the arrow. Why isn't it included as a reactant or product?
  - How is the action of an enzyme different to that of inorganic catalysts?
13. A student explored the rate of reaction between **aluminium** and a **hydrochloric acid** solution. She used a 3.5 g piece of aluminium foil placed into 65 mL of  $3.5 \text{ mol L}^{-1} \text{ HCl(aq)}$  initially at  $21^\circ\text{C}$ . As the reaction proceeded, the hydrogen gas formed was collected by the downward displacement of water. The total volume of hydrogen gas produced was recorded every thirty seconds for a 5 minute period. Her results are graphed in Fig 20. The equation for this reaction is shown here.

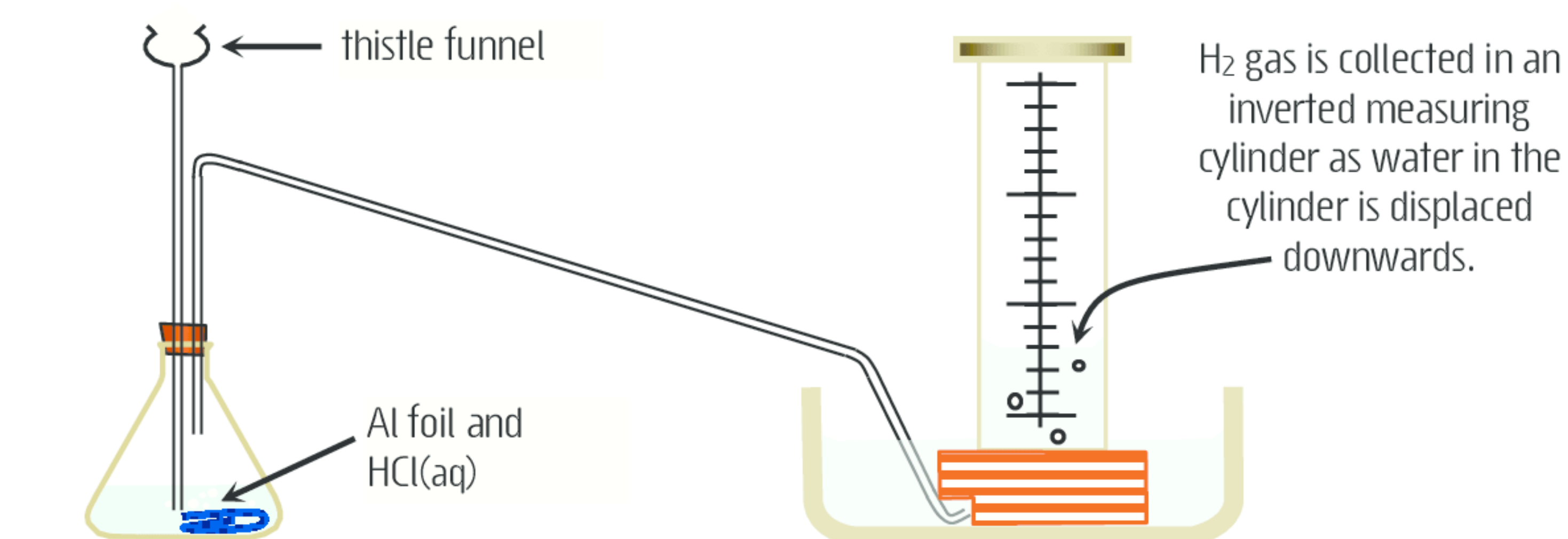


- Suggest a reason for using a **thistle funnel** as part of the apparatus. (See Fig 21.)
- The student did not place the gas collecting cylinder in position until after the required amount of acid had been fully added to the flask. Why is it important to do this in this order?
- Refer to the graph in Fig 20 and describe how the rate of reaction changes during the first two minutes and during the last two minutes of the experiment. Use your knowledge of factors that affect reaction rate to **account** for the observed changes in rate.



**FIGURE 20** Shows how the rate of formation of hydrogen gas changes during the course of the reaction.

**FIGURE 21** Initially the flask contains aluminium foil only. The reaction commences when  $\text{HCl(aq)}$  is added via the **thistle funnel**.  $\text{H}_2$  gas from the reaction of  $\text{HCl(aq)}$  with  $\text{Al(s)}$  is then collected by the downward displacement of water. An inverted measuring cylinder is used here to measure the volume of hydrogen produced as the reaction proceeds.



14. The exhaust system of all motor vehicles is fitted with a device known as a **catalytic converter**. (See Fig 22 and p121.) This device reduces harmful exhaust emissions by eliminating nitrogen oxides ( $\text{NO}_x$ ), unburnt hydrocarbons (HCs) and carbon monoxide (CO) from the car's exhaust stream. It does this by converting these substances to nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ).

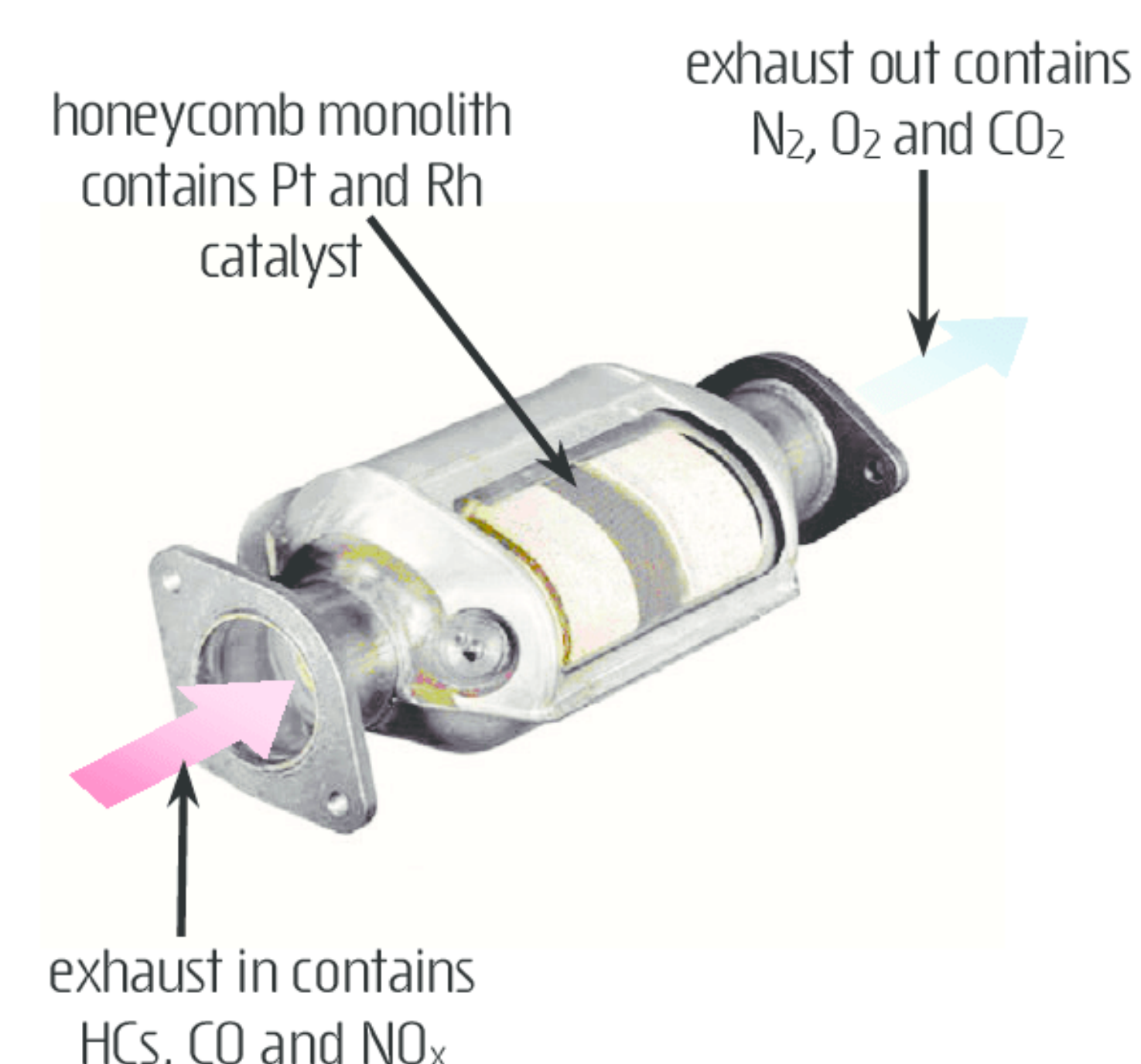
- The main component of the catalytic converter is a porous honeycomb ceramic structure coated with the metals **platinum** (Pt) and **rhodium** (Rh). As nitrogen oxides ( $\text{NO}_x$ ) in the exhaust pass through the honeycomb section their molecules become temporarily bonded to the metals. During this time the atoms in  $\text{NO}_x$  molecules rearrange to form  $\text{N}_2$  and  $\text{O}_2$  molecules which become released back into the exhaust stream. These two reactions can be visualised as shown.



Write an **overall equation** for these two reactions (see 6.4 p45) and **justify** the statement that platinum is acting as a catalyst.

- The catalysts in a catalytic converter are contained within the fine honeycomb passages of the monolith structure. The surface of these passages is **coarse** and **bumpy** and coated with the metallic catalysts. Use your knowledge of the collision theory to **explain** the advantage of having the catalyst arranged this way.
- Catalytic converters were first introduced into Australian petrol vehicles in 1986 along with the introduction of **unleaded petrol**. Prior to this time all petrol types contained lead additives. Vehicles with a catalytic converter must not use leaded petrol as lead has a strong tendency to permanently adsorb to the catalytic surface. This effect is known as 'catalyst poisoning'. **Suggest** why this type of catalytic poisoning renders the catalytic converter useless.

**FIGURE 22** An automotive **catalytic converter**

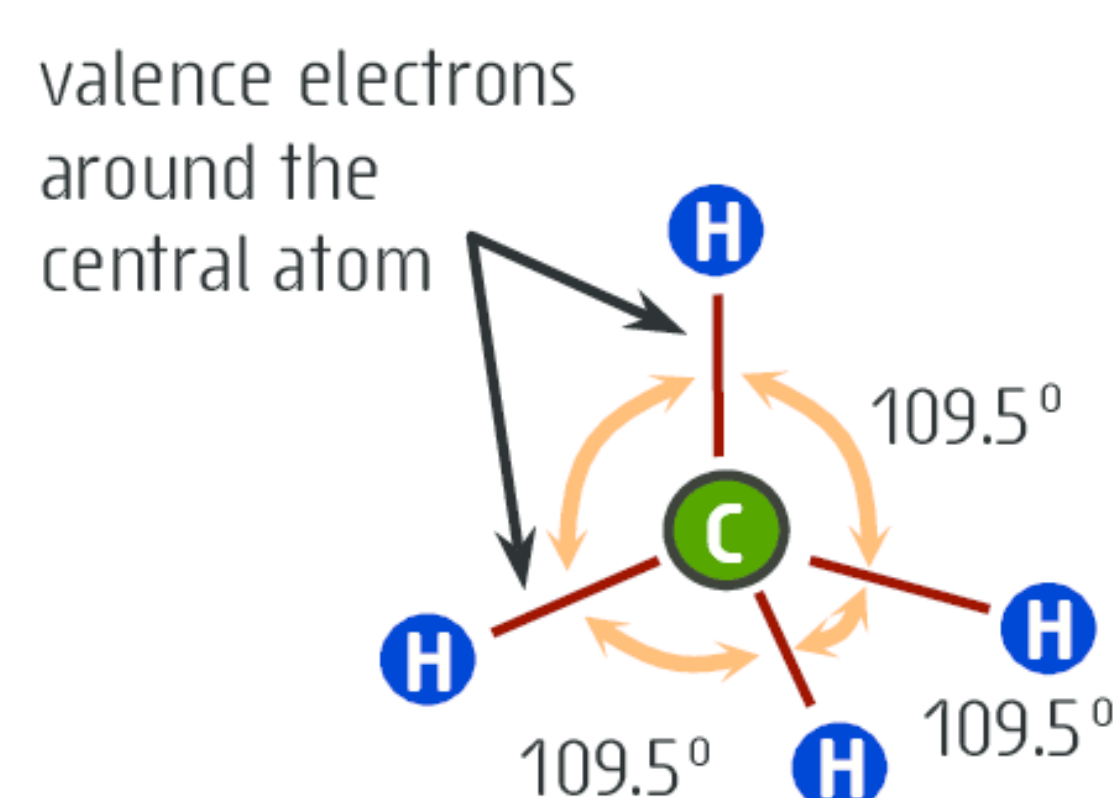




# CHAPTER 15 | INTERMOLECULAR FORCES

## 15.1 Molecular shape

**FIGURE 1** The preferred **shape** of a molecule is one that allows the greatest angular separation between each of the valence shell electron groups around the central atom. For example, in methane ( $\text{CH}_4$ ), the highest angular separation for the four groups of valence electrons of the carbon atom is  $109.5^\circ$ . This gives the methane molecule a **tetrahedral shape**.



In a methane molecule the angle between the central carbon atom (green sphere) and any two bonded hydrogen atoms (blue spheres) will be  $109.5^\circ$ . This angle is known as the **bond angle** for methane.

Shapes of simple molecules include linear, triangular planar, tetrahedral, pyramidal and bent.



Molecular shape, according to valence shell electron pair repulsion theory (**VSEPR**), results from **repulsion** between groups of **electrons**, both bonding and non-bonding, in the **valence shell** of the **central atom** (the atom to which other atoms are bonded) in a molecule. By VSEPR, a molecule's optimum shape allows the valence shell electron groups around the central atom to have the greatest possible angle of separation. (See Fig 1.) For this reason, a molecule's **shape** depends upon the number of groups of valence electrons on its central atom. Although the central atom will usually have 8 valence electrons (octet rule) these electrons are not necessarily distributed as four groups of two electrons. The number of groups of valence electrons is found from the **Lewis structure** for the molecule. When counting groups of valence shell electrons around the central atom:

- each **single** covalent bond (2 electrons) = **1 group** of electrons
- each **double** covalent bond (4 electrons) = **1 group** of electrons
- each **triple** covalent bond (6 electrons) = **1 group** of electrons
- each **lone pair** of electrons (2 electrons) = **1 group** of electrons.

As can be seen a group of electrons may consist of 2, 4 or 6 valence electrons. This is reasonable as all 4 electrons of a double bond must occupy the same region between the same pair of bonded atoms. Similarly the 6 electrons of a triple bond must also occupy the same region between the same pair of bonded atoms. As the central atom becomes increasingly crowded with groups of electrons so the angular separation between these groups of electrons must decrease and the molecular shape changes. The resulting molecular shapes are as follows:

Key:

- central atom
- other attached atoms
- covalent bond(s) (2, 4 or 6 electrons)
- ⋯ lone pairs (2 valence electrons)

**Pyramidal** and **bent** (V shape) molecular shapes are versions of the tetrahedral arrangement where one or two atoms respectively are missing and a lone pair of electrons is in its place.

- **1 or 2** groups of electrons gives a **linear shape** with a  $180^\circ$  bond angle.....
- **3** groups of electrons and none of these are lone pairs gives a **triangular planar** shape with  $120^\circ$  bond angles .....
- **4** groups of electrons and none of these are lone pairs gives a **tetrahedral** shape with  $109.5^\circ$  bond angles .....
- **4** groups of electrons and **one** of these is a **lone pair** gives a **pyramidal** shape with bond angles a few degrees less than  $109.5^\circ$  .....
- **4** groups of electrons and **two** of these are **lone pairs** gives a **bent** or **V** shape with bond angles several degrees less than  $109.5^\circ$  .....

Example 1 (next page) shows the **ideal bond angles** for each of these molecular shapes. These are the bond angles that would give all the bonding and non-bonding valence electron groups the largest equal angle of separation. These angles assume that all valence electrons repel one another equally. However, it is known that repulsion between lone pairs of valence electrons is greater than that between bonding groups of valence electrons. Consequently, if one or two lone pairs of electrons are present on the central atom then **actual bond angles** will be reduced as shown in Example 1.

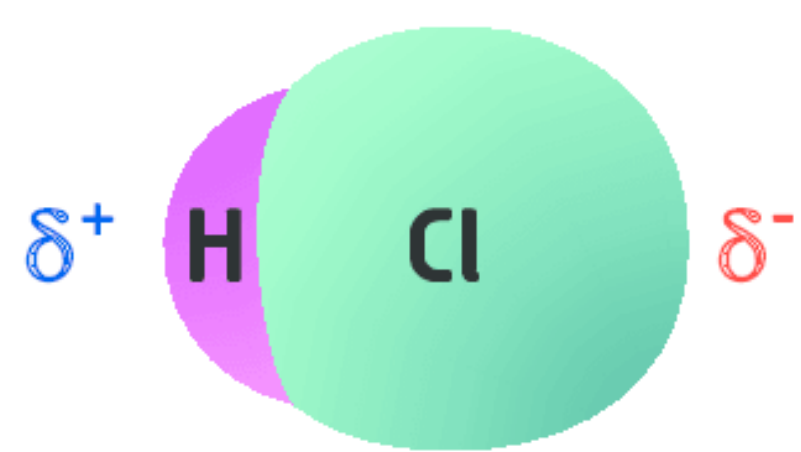


Substance	Lewis structure	Central atom + number and type of valence electron groups	Shape	Molecular appearance	Bond angle
carbon dioxide CO <sub>2</sub>		C has 2 groups of valence shell electrons and none of these are lone pairs.	linear O = C = O		180°
hydrogen cyanide HCN		C has 2 groups of valence shell electrons and none of these are lone pairs.	linear H — C ≡ N		180°
methanal H <sub>2</sub> CO		C has 3 groups of valence shell electrons and none of these are lone pairs.	triangular planar 		120°
methane CH <sub>4</sub>		C has 4 groups of valence shell electrons and none of these are lone pairs.	tetrahedral 		109.5°
silicon bromide SiBr <sub>4</sub>		Si has 4 groups of valence shell electrons and none of these are lone pairs.	tetrahedral 		109.5°
ammonia NH <sub>3</sub>		N has 4 groups of valence shell electrons and one of these is a lone pair.	pyramidal 		ideal: 109.5° actual: 107°
water H <sub>2</sub> O		O has 4 groups of valence shell electrons and two of these are lone pairs.	bent 		ideal: 109.5° actual: 104.5°

Intermolecular forces 127



**FIGURE 4** The presence of a bond dipole in the HCl molecule causes it to be **polar**. Molecules like this have an uneven distribution of electrons so that one side of the molecule has a permanent **slight negative charge** ( $\delta^-$ ) while the other end has a permanent **slight positive charge** ( $\delta^+$ ).



## 15.3 Polar and non-polar molecules

**Polar molecules** are those with **slight positive** ( $\delta^+$ ) and **slight negative** ( $\delta^-$ ) charged ends to the molecule. (See Fig 4.) Molecules like this are said to have a **net dipole** (di = two, pole = opposites). This occurs in all molecules with a single bond dipole. If a molecule has several bond dipoles then these may act to reinforce one another or they may cancel each other's effect. This will depend upon the strength and direction of the individual bond dipoles. (See Example 2.)

The **polarity** of a molecule is found by drawing its **shape** and identifying all of its bond dipoles. If the bond dipoles are of equal size and act in symmetrically opposing directions, then they cancel each other's effect and the molecule has a **zero net dipole** and is **non-polar**. Alternatively, if the bond dipoles are **non-symmetrically** arranged then they add to produce a **net dipole** and the molecule is **polar**. (See Example 2.)

**EXAMPLE 2** The individual bond dipoles of a molecule add together to produce a net dipole. When adding bond dipoles their direction and size must be considered.

Molecule	CO <sub>2</sub>	H <sub>2</sub> O	CCl <sub>4</sub>	CHCl <sub>3</sub>	H <sub>2</sub> CO
Shape and bond dipoles (arrows)					
Bond dipole symmetry	symmetrical	not symmetrical	symmetrical	not symmetrical	not symmetrical
Net dipole (large arrow)					
Molecular polarity	non-polar	polar	non-polar	polar	polar

Complete Set 24.

## Set 24 Molecular shape and polarity

- The following passage explores how the **VSEPR** theory can be used to find the shape of a molecule. Use the list of terms to complete the passage.

When two or more atoms covalently bond to one another they can form a tightly bound cluster known as a (a) \_\_\_\_\_. The shape of a simple molecule describes the arrangement of atoms around the (b) \_\_\_\_\_ atom of the molecule. From the valence shell electron pair repulsion theory or (c) \_\_\_\_\_, we understand that molecular shape depends upon the number of (d) \_\_\_\_\_ of electrons present in the (e) \_\_\_\_\_ of the central atom. These groups of electrons may consist of (f) \_\_\_\_\_ (non-bonding electrons) of the central atom or bonding electrons from single, double or triple bonds. Each group of valence shell electrons may consist of two, four or (g) \_\_\_\_\_ electrons.

Molecules form a (h) \_\_\_\_\_ shape when the central atom has two groups of valence shell electrons. Three groups of valence shell electrons on the central atom result in a (i) \_\_\_\_\_ shape. If the central atom has four groups of valence shell electrons but only (j) \_\_\_\_\_ atoms attached to it then this results in a pyramidal shape. Similarly four groups of valence shell electrons and only two attached atoms results in a (k) \_\_\_\_\_ shape. With four groups of valence shell electrons and four attached atoms the molecular shape will be (l) \_\_\_\_\_.

### VSEPR

lone pairs  
molecule

six

linear

three

central

bent

valence shell

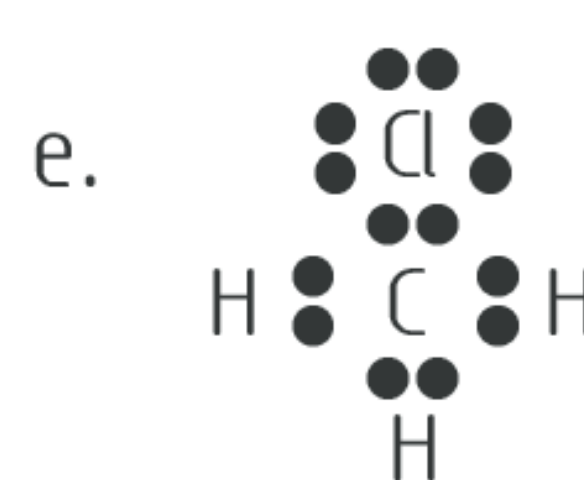
triangular planar

groups

tetrahedral



2. Refer to the Lewis structure for the following compounds and determine their **molecular shape**. (See Fig 5.)



3. Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (see Question 2) consist of molecules with two atoms bonded to a central atom yet their shapes are different.  $\text{CO}_2$  is linear while  $\text{H}_2\text{O}$  is bent. **Explain** in terms of valence shell electron pair repulsion (**VSEPR**) why this should occur.
4. The covalent bond between hydrogen and fluorine in hydrogen fluoride ( $\text{HF}$ ) is said to have a bond dipole whereas the covalent bond between fluorine atoms in fluorine gas ( $\text{F}_2$ ) has no bond dipole. Use these two examples to **show your understanding** of bond dipoles and how they occur.

5. Molecules of chloromethane ( $\text{CH}_3\text{Cl}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and trichloromethane ( $\text{CHCl}_3$ ) all have a net dipole moment, ie they are polar molecules yet the compounds methane ( $\text{CH}_4$ ) and tetrachloromethane ( $\text{CCl}_4$ ) both have a zero dipole moment, ie are non-polar. These molecules contain the same polar  $\text{C}-\text{Cl}$  or  $\text{C}-\text{H}$  covalent bonds. Use your knowledge of molecular polarity to **account** for the difference in net molecular polarity of these molecules. You should **include diagrams** as part of your answer.

6. **Draw** a **Lewis structure** for each of these substances and hence determine their **molecular shape** and **polarity**. Also **draw** the **shape** of each molecule.



7. The **shape** of a polyatomic ion can also be found using the **VSEPR** theory. Using the VSEPR theory determine the shape of the following polyatomic ions. Remember when drawing the **Lewis structure** for a polyatomic ion add or subtract sufficient valence electrons to account for the ion charge. (See 8.7 p60.) **(E)**



8. **Rank** the following groups of compounds in order of increasing molecular polarity. Give a brief statement that **justifies** your ranking.



**FIGURE 5** Molecular shape enables life on Earth!

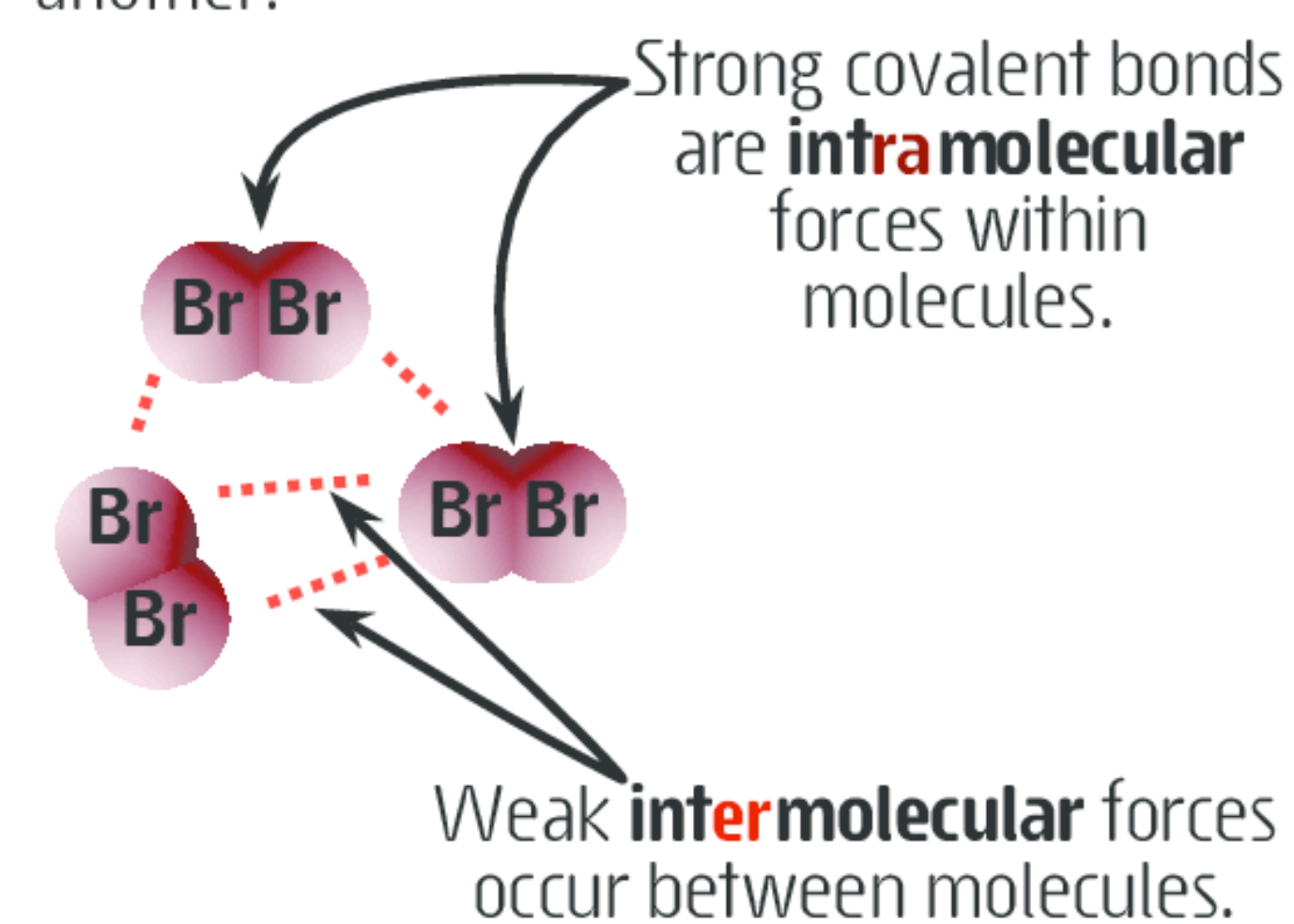


Molecular **shape** has an enormous impact on the chemistry of molecular substances. Water molecules for example have a **bent** shape rather than the linear shape common to many triatomic molecules (eg  $\text{CO}_2$  is linear). The bent shape allows water molecules to be **highly polar** and capable of **hydrogen bonding**. (See p131.) A direct consequence of this is its relatively high melting point and boiling point for a substance made of such small molecules. ( $0^\circ\text{C}$  and  $100^\circ\text{C}$  respectively.) Had water molecules been linear they would be non-polar, incapable of hydrogen bonding and water would certainly be a gas at temperatures well below  $-50^\circ\text{C}$ .

The fact that water molecules are bent and not linear means it has a reasonably high boiling point and consequently there is plenty of liquid water on planet Earth. Had water been a gas under Earth-like conditions, ie had a low boiling point, then liquid water most probably wouldn't exist on Earth. Amongst other things, this would have excluded the evolution of carbon based life forms as we know them. Clearly molecular shape can be of great significance!



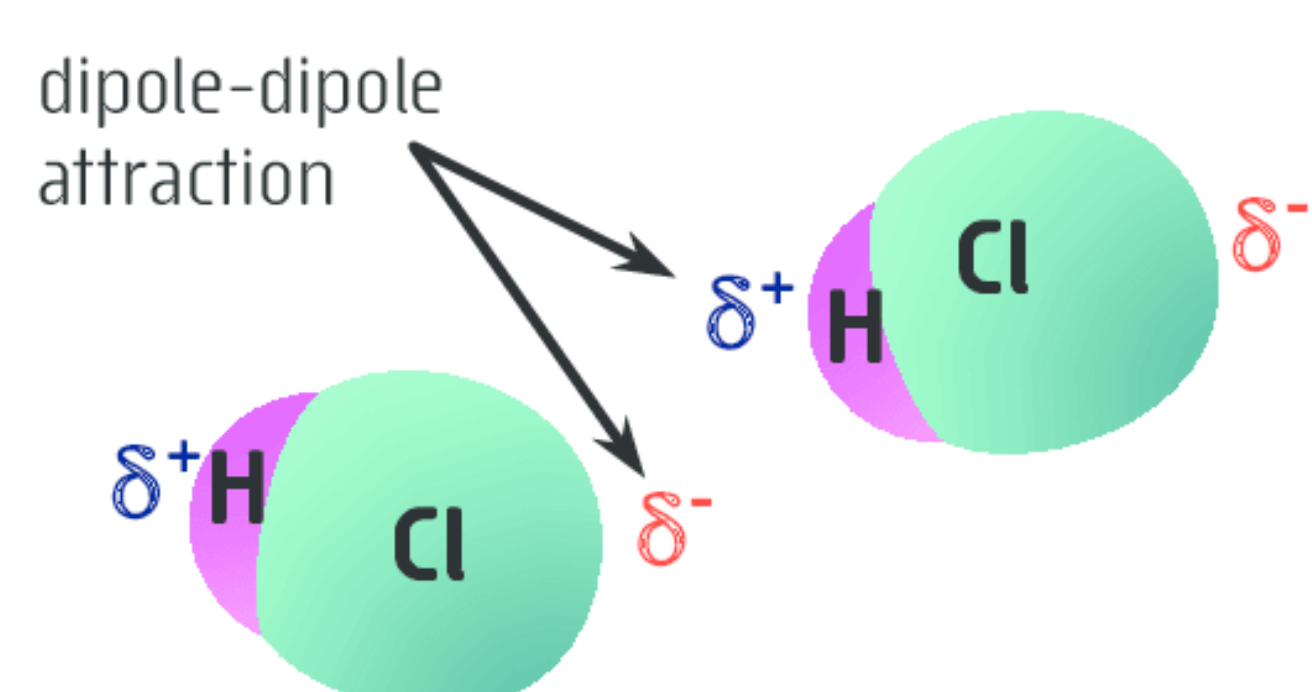
**FIGURE 6** Intermolecular forces are the weak forces of attraction **between** molecules that allow them to attract one another.



The three types of intermolecular forces are:

- **dispersion forces**
- **dipole-dipole forces**
- **hydrogen bonding.**

**FIGURE 7** Dipole-dipole attraction occurs between the oppositely charged ends of **polar molecules**.



**Some solvents** commonly found around the home include:

- **water** (very polar)
- **methylated spirits** (a moderately polar mixture of alcohols)
- **mineral turpentine** or turps (a non-polar mixture of hydrocarbons)
- **white spirit** (a non-polar mixture of hydrocarbons)

The choice of solvent will depend upon the polarity of the solute to be dissolved. Grimy stains like engine grease and oil (non-polar) are best dissolved with non-polar solvents like mineral turpentine or white spirit. Water would be a good solvent for acrylic paints which are mixtures of polar substances.

\* Since **molar mass** increases along with the number of molecular electrons it is often stated that dispersion forces increase with **molar mass** or **molecular size**.

## 15.4 Intramolecular forces and Intermolecular forces

Two distinct types of bonding are present in a molecular substance. The strongest of these are the **intramolecular forces**; these are the **covalent bonds** that keep atoms clustered together within the molecule. (See Fig 6.) Much weaker **intermolecular forces** between molecules keep them bonded to one another. These are the forces that are easily overcome when a molecular substance **melts**, **boils** or **evaporates**. The covalent bonds between atoms within the molecule are not affected during melting, boiling or evaporating. Only chemical changes affect these bonds.

Two types of intermolecular force are **dispersion** forces and **dipole-dipole** forces. These are sometimes referred to as van der Waals forces. A third type of intermolecular force is the **hydrogen bond**. The strength and type of intermolecular forces present in a substance depend upon the shape and size of its molecules and the elements it contains. This in turn greatly affects physical properties like melting point, boiling point and solubility.

Attempt Set 25 # 1, 2.

## 15.5 Intermolecular forces: Dipole-dipole forces

**Polar molecules** are able to attract one another due to the weak electrostatic attraction between their dipoles. (See Fig 7.) Such attractions are known as **dipole-dipole forces**. One effect of dipole-dipole forces is to **increase melting points and boiling points**. For this reason it can be seen that substances with polar molecules have slightly higher melting points and boiling points than other substances of similar molecular size that have non-polar molecules. (See Table 1.)

**TABLE 1** Polarity and its effect on melting point and boiling point

Substance	Molecular size (ie molar mass, g mol <sup>-1</sup> )	Molecular polarity (debye)	Melting point (°C)	Boiling point (°C)
<b>propane</b> (CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> )	44	0 (ie non-polar)	-188	-42
<b>methoxymethane</b> (CH <sub>3</sub> OCH <sub>3</sub> )	46	1.3	-139	-25
<b>ethanal</b> (CH <sub>3</sub> CHO)	44	2.7	-123	21
<b>acetonitrile</b> (CH <sub>3</sub> CN)	41	3.9 (most polar)	-45	82

The **solubility** of molecular substances in one another is also affected by the types of intermolecular forces present in those substances. (See 15.8.) Generally substances with dipole-dipole forces, ie polar ones, will be soluble in one another but not soluble in non-polar substances, ie ones that can't interact by dipole-dipole forces. This is why ethanal (polar) and water (polar) are quite soluble in one another but mineral turpentine (non-polar) isn't soluble in water. This solubility pattern where polar substances dissolve in other polar substances but don't dissolve in non-polar substances is often described as **like dissolves like**.

Another property of polar substances like water, is their ability to dissolve ionic solutes. This property is due to the attraction between the dipole of a polar molecule and an ion's charge. These attractive forces are known as **ion-dipole forces**, they are not a type of intermolecular force. (For a full description of ion-dipole forces, see 16.4 p140.)

Attempt Set 25 # 3.

## 15.6 Intermolecular forces: Dispersion forces

While **dispersion forces** occur in **all** molecular materials they are the only intermolecular forces of attraction present in **non-polar** substances like hydrocarbons and gases like N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>. These forces are typically weak for molecules with few electrons and show increasing strength for molecules with a greater number of electrons. This effect is clearly seen in the **non-polar**, alkane family of compounds where boiling point increases with increasing molar mass\*. (See border note.)

	<div> <div>—</div> <div>increasing molecular electrons (ie increasing molecular mass or size)</div> <div>→</div> </div>				
<b>compound</b>	methane, <b>CH<sub>4</sub></b>	ethane, <b>C<sub>2</sub>H<sub>6</sub></b>	propane, <b>C<sub>3</sub>H<sub>8</sub></b>	butane, <b>C<sub>4</sub>H<sub>10</sub></b>	pentane, <b>C<sub>5</sub>H<sub>12</sub></b>
<b>boiling point</b>	<b>-161.5 °C</b>	<b>-88.6 °C</b>	<b>-42.1 °C</b>	<b>-0.50 °C</b>	<b>36.1 °C</b>
	<div> <div>—</div> <div>increasing boiling points indicate increasing dispersion forces</div> <div>→</div> </div>				

Dispersion forces are also stronger in molecules whose shape allows maximum surface contact between molecules, ie linear in preference to branched or spherical shapes. Thus linear molecules will have stronger dispersion forces and hence higher melting points and boiling points than spherical or branched molecules of similar mass. (See Fig 8.)

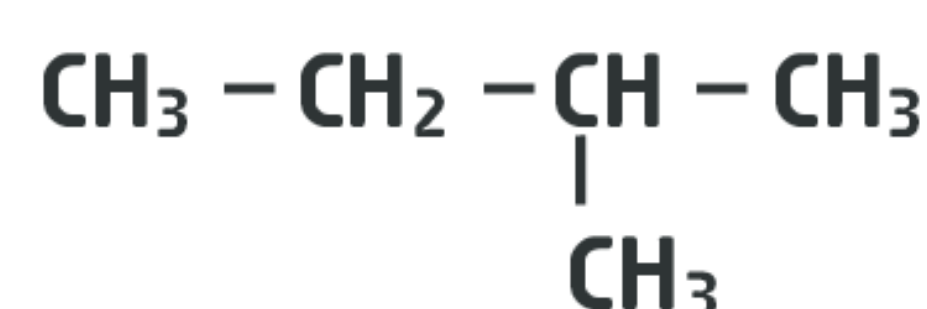


**C<sub>5</sub>H<sub>12</sub>** (pentane)



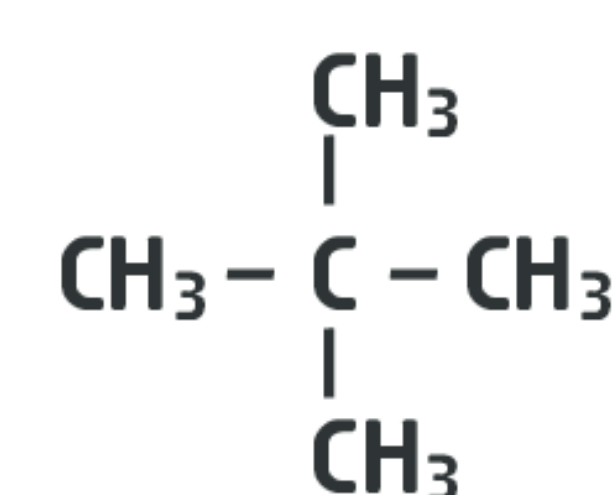
boiling point **36.1 °C**

**C<sub>5</sub>H<sub>12</sub>** (methylbutane)



boiling point **27.9 °C**

**C<sub>5</sub>H<sub>12</sub>** (dimethylpropane)



boiling point **9.5 °C**

**FIGURE 8** The three compounds at left, **pentane**, **methylbutane** and **dimethylpropane** all have the same molecular formula, **C<sub>5</sub>H<sub>12</sub>**, ie same size and number of electrons per molecule. Their differing strength of dispersion forces, as shown by their different boiling points, is due to their different shapes. This example shows how molecules with a linear shape have stronger dispersion forces than ones with a spherical or branched shape.

Dispersion forces arise when the random motion of electrons within a molecule produce short lived **temporary dipoles**. This can make otherwise non-polar molecules temporarily polar. (See Fig 9.) These polar molecules then cause nearby molecules to form similar temporary dipoles called **induced dipoles**. The molecule with the temporary dipole and the one with the induced dipole then experience weak electrostatic attraction known as **dispersion forces**. These attractive forces are in a state of rapid change as the temporary and induced dipoles constantly form, rapidly disappear and then reform elsewhere.

Attempt Set 25 # 4.

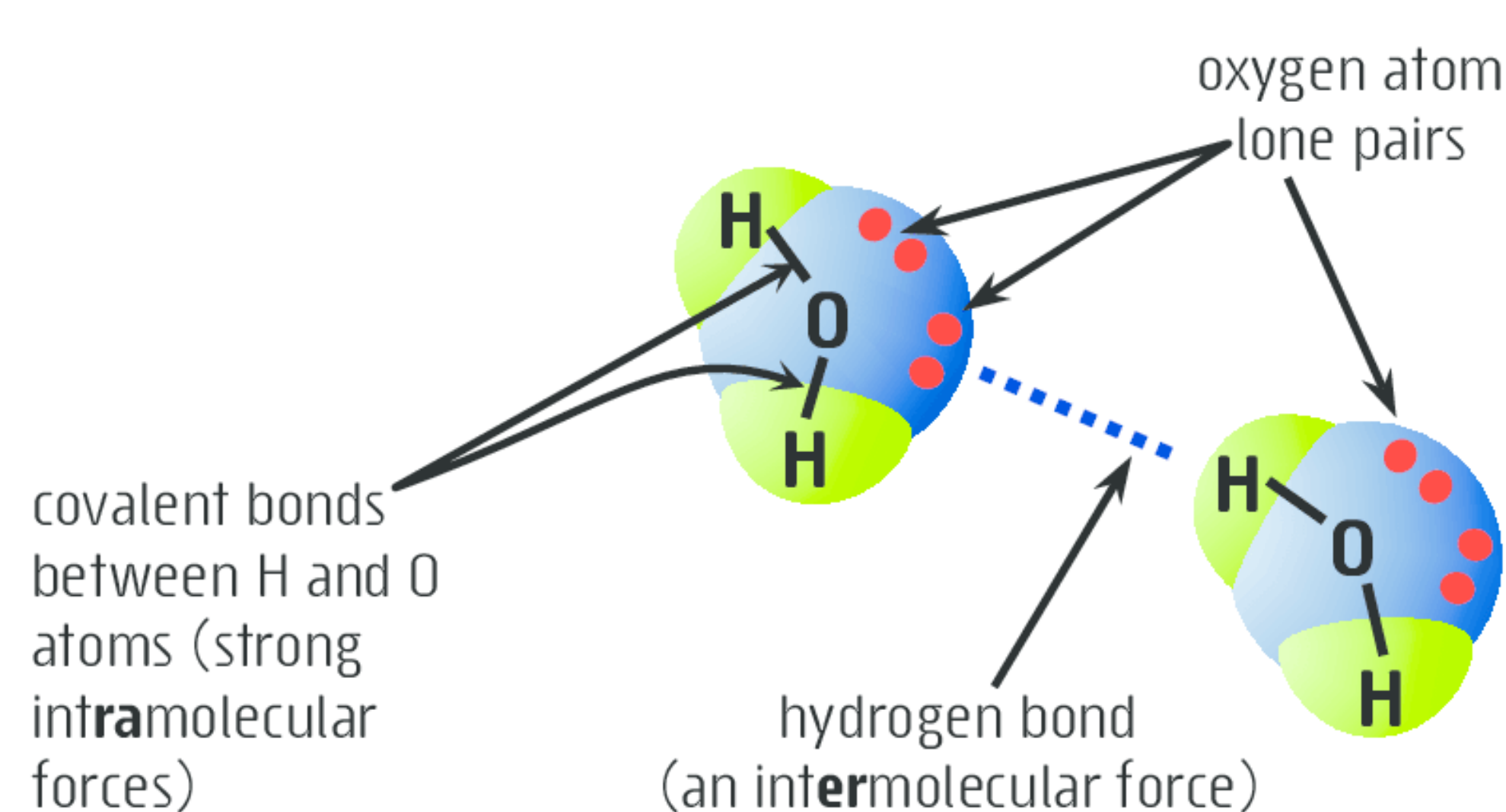
## 15.7 Intermolecular forces: Hydrogen bonding

Hydrogen bonds are **directional** intermolecular forces that can be as strong as 12% of the strength of a carbon to carbon covalent bond. These unique bonds only occur in molecules having an **H – F**, **H – O** or **H – N** arrangement of atoms. The hydrogen bond is due to the electrostatic attraction between a **lone pair** of electrons (negative) of a **F**, **O** or **N** atom and an **H atom** already covalently bonded to another **F**, **O** or **N** atom. (See Fig 10 and Fig 11.)

Hydrogen bonding is sometimes described as a form of **extreme dipole-dipole attraction** where the strong positive dipole of an H atom, ie one bonded to a **highly electronegative** F, O or N atom, is attracted to a strongly negative dipole of another F, O or N atom. The lone pair of electrons of the F, O or N atom and the H atom that form the hydrogen bond can be part of the same molecule or from different molecules. (See Fig 11.)

**Melting and boiling points** are much **higher** for substances that can hydrogen bond than for those of similar molecular size that cannot hydrogen bond. Solubility is also significantly affected by hydrogen bonding. Substances which experience hydrogen bonding between their molecules are **extremely soluble** in other substances which can also hydrogen bond. (See 15.8 below.)

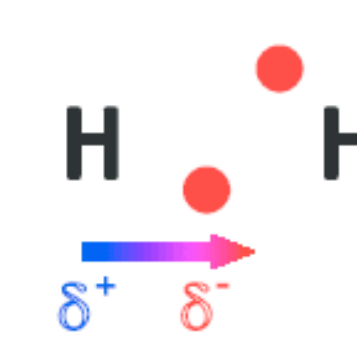
**FIGURE 11** Hydrogen bonding between two water molecules. A dotted line shows the hydrogen bond.



**FIGURE 9** Temporary dipole in a H<sub>2</sub> molecule



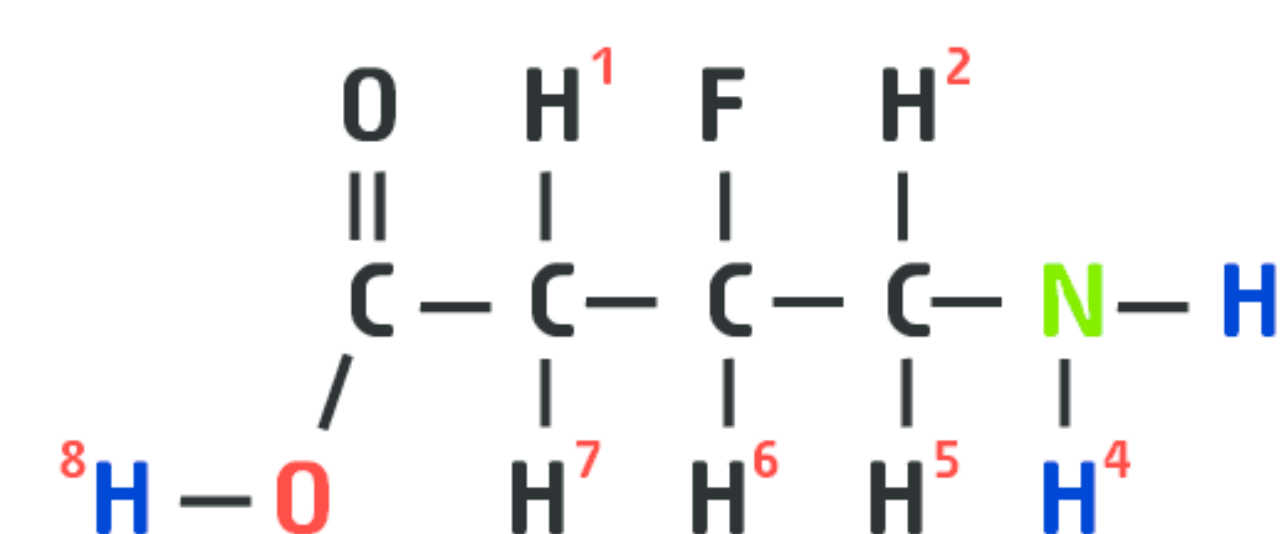
The H<sub>2</sub> molecule at left shows the **average** position of its two shared electrons. **No temporary dipole** is present.



The constant random movement of electrons in a H<sub>2</sub> molecule produces a constantly changing **temporary dipole**. The size and direction of this dipole depends upon the momentary random position of its two electrons. The dipole is shown with an arrow.



**FIGURE 10** Only certain hydrogen atoms are capable of **hydrogen bonding**. In this structure the hydrogen atoms labelled **3**, **4** and **8** are capable of hydrogen bonding while those labelled **1**, **2**, **5**, **6** and **7** are not capable of hydrogen bonding.



Attempt Set 25 # 5, 6, 7 and 8.

## 15.8 Intermolecular forces and physical properties

▪ **Changing phase:** For a molecular substance to **melt** or **boil** it must overcome, to some extent, the attraction between its molecules, ie its intermolecular forces. Heating a substance provides the energy needed to do this. Thus as the intermolecular forces within a substance increase in strength so too does its **melting point** and **boiling point**.

Since all molecular substances can interact by dispersion forces then as molecular mass (size/number of molecular electrons) increases there is a general increase in the melting and boiling points of molecular substances. This effect can be seen in any group of similar molecular compounds where molecular size varies. For example in the halogen group of elements melting and boiling points increase with molecular mass. (See Table 2.)

Substances that can also interact by dipole-dipole forces will have slightly higher melting and boiling points compared to other substances of similar molecular size that cannot interact this way. (See Table 3.)

**TABLE 3** Polarity and its effect on boiling point

Compound	Molecular formula	Molecular mass	Molecular polarity*	Boiling point
propane	C <sub>3</sub> H <sub>8</sub>	44 g mol <sup>-1</sup>	nil (0.0 D)	-42 °C
methoxymethane	CH <sub>3</sub> OCH <sub>3</sub>	46 g mol <sup>-1</sup>	low (1.3 D)	-25 °C
ethanal	CH <sub>3</sub> CHO	44 g mol <sup>-1</sup>	moderate (2.7 D)	21 °C

\* Molecular polarity is in debye units, D. Polarity increases with D.

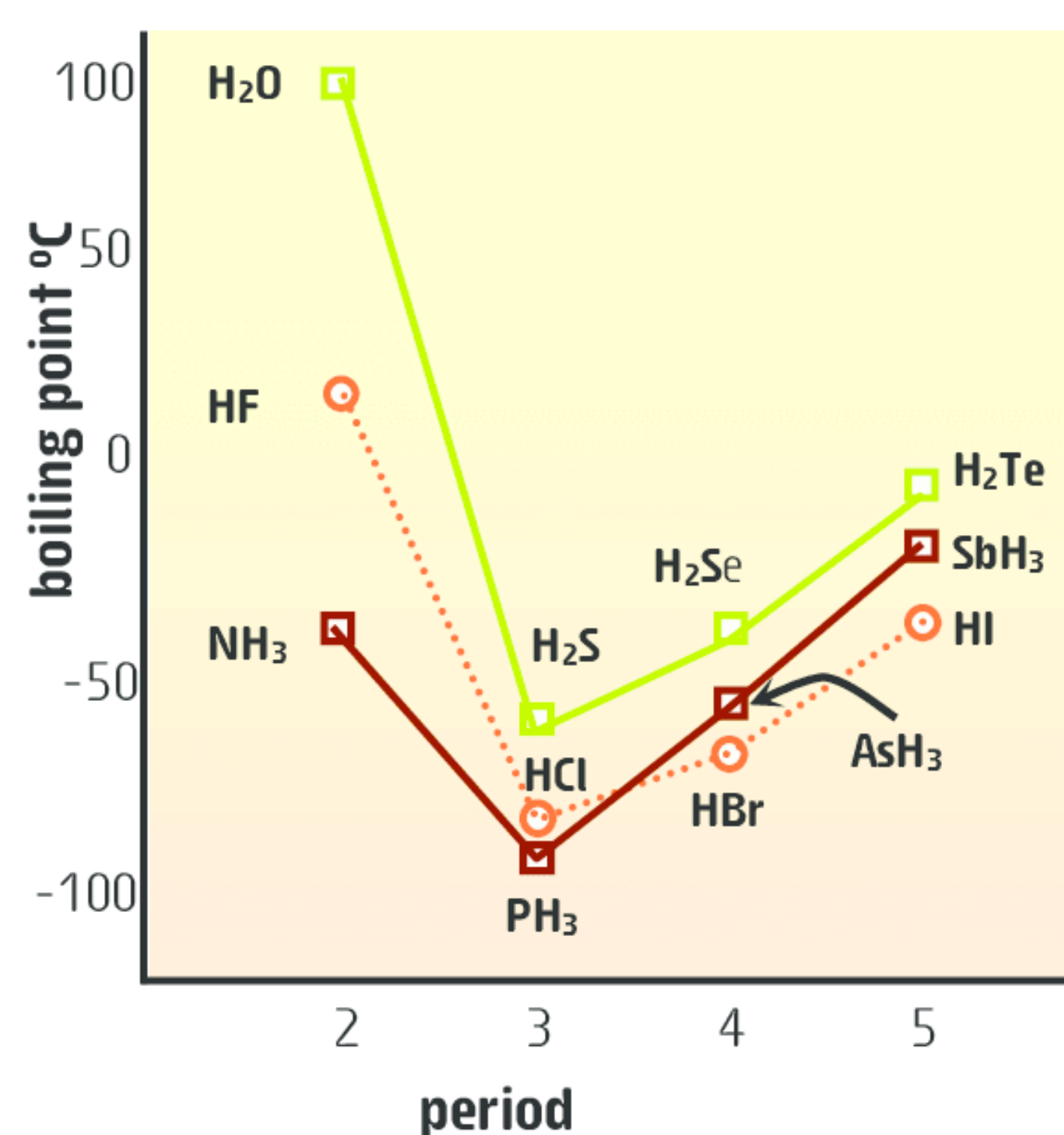
**TABLE 2** The melting points (**MP**) and boiling points (**BP**) of the **halogens** show a steady increase with increasing molecular mass (size/number of molecular electrons).

	Molar mass	MP (°C)	BP (°C)
<b>F<sub>2</sub></b>	38 g mol <sup>-1</sup>	-220	-188
<b>Cl<sub>2</sub></b>	71 g mol <sup>-1</sup>	-101	-35
<b>Br<sub>2</sub></b>	160 g mol <sup>-1</sup>	-7	59
<b>I<sub>2</sub></b>	254 g mol <sup>-1</sup>	114	184

Such data supports the idea that dispersion forces increase with increasing molar mass, ie increasing molecular size/number of molecular electrons.



**FIGURE 12** The **boiling points** of the hydrides of the elements from groups 15, 16, and 17 show the presence of hydrogen bonding in HF, H<sub>2</sub>O and NH<sub>3</sub>. In each case their boiling points are markedly higher than those of their closely related hydrides. Their higher boiling points are attributed to the presence of hydrogen bonding in these compounds.



A **vapour** is the gaseous phase of a material that would normally be a liquid or solid at room temperature and pressure, eg water vapour, sodium vapour and petrol vapour but oxygen gas or carbon dioxide gas.

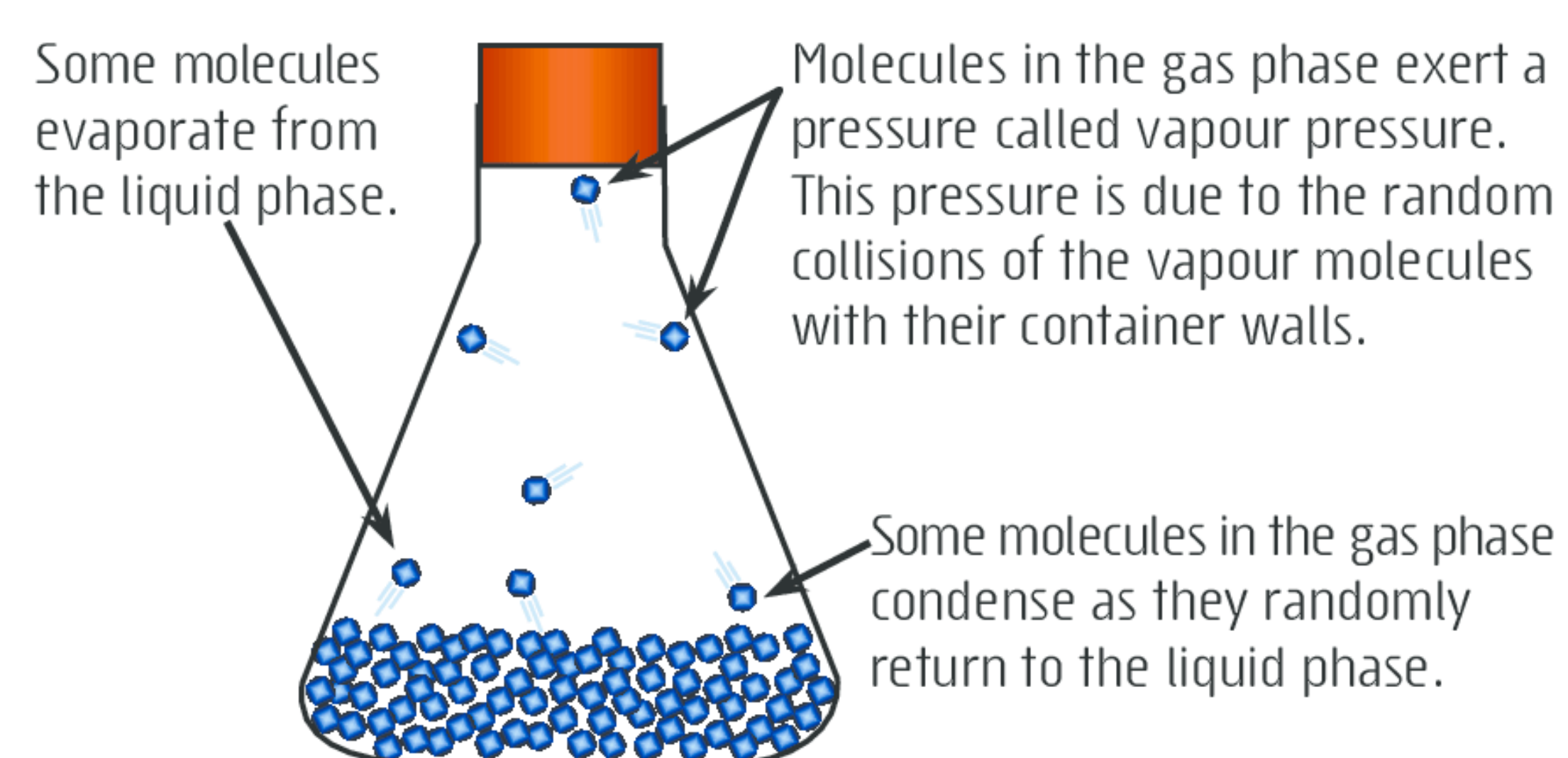
If **hydrogen bonding** is present within a molecular substance it will have higher **melting** and **boiling points** than other substances of similar molecular size that cannot hydrogen bond. This explains why water (H<sub>2</sub>O), hydrogen fluoride (HF) and ammonia (NH<sub>3</sub>) have significantly higher melting and boiling points than closely related compounds that don't hydrogen bond. (See Fig 12.) This effect is most pronounced in substances with small molecules.

▪ **Solubility:** A **solute** and **solvent** can only form a solution if the attractive forces acting between the solute molecules and solvent molecules are **comparable in strength** to the attractive forces acting within the pure solvent or pure solute. Generally, this happens for substances whose molecules attract by similar types of intermolecular forces. This means non-polar substances, ie ones that interact strongly by dispersion forces will tend to be soluble in other non-polar substances that also attract strongly by dispersion forces. However, these substances will not be soluble in polar substances whose molecules attract strongly by dipole-dipole forces or those that attract strongly by hydrogen bonding. This is why a non-polar mixture like petrol (a mixture of C<sub>5</sub>-C<sub>11</sub> hydrocarbons) is very soluble in non-polar kerosene (a mixture of C<sub>10</sub>-C<sub>15</sub> hydrocarbons) but essentially insoluble in water (a polar liquid). Similarly, hydrogen chloride, HCl (polar) is very soluble in water (polar) but essentially insoluble in petrol or kerosene (both non-polar).

In particular, compounds that attract strongly by **hydrogen bonding** are extremely soluble in other compounds that also attract strongly by **hydrogen bonding**. This explains why substances like sugar (C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>(OH)<sub>8</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH) and ammonia (NH<sub>3</sub>), which all interact strongly by hydrogen bonding, are extremely soluble in water which also interacts most strongly by hydrogen bonding.

▪ **Equilibrium vapour pressure:** Vapour pressure, is a measure of the tendency of a substance to **evaporate** and is measured in **kPa**. (See Fig 13.) When a substance evaporates its molecules must escape the intermolecular forces keeping it in the liquid phase. Thus weak intermolecular forces correspond to liquids that easily evaporate and have a high vapour pressure.

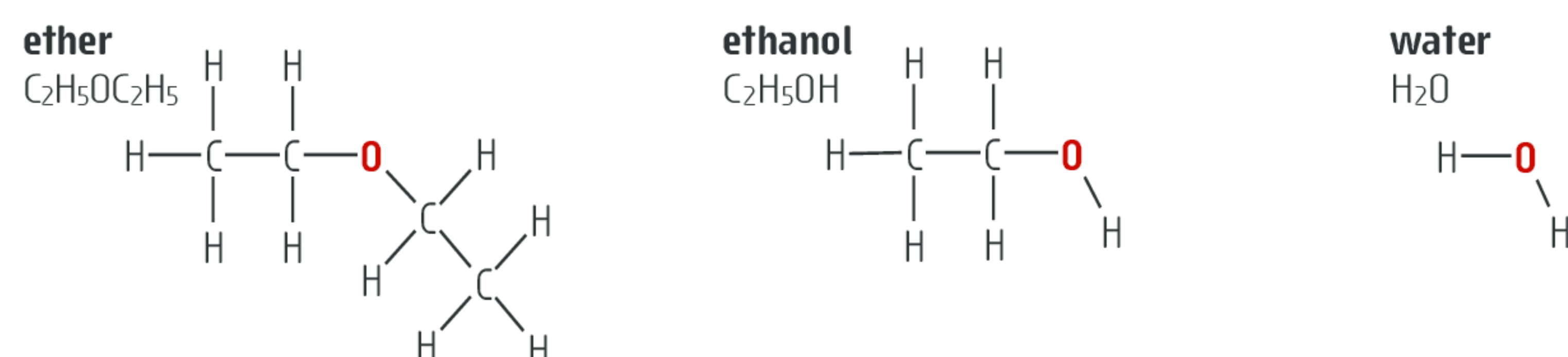
**FIGURE 13** If a liquid is kept in a sealed container then at some point the rate of evaporation of the liquid and the rate of condensation of the vapour become equal. At this point the pressure of the vapour reaches a steady value called the **equilibrium vapour pressure**. The greater the tendency for a liquid to evaporate, the higher its equilibrium vapour pressure will be.



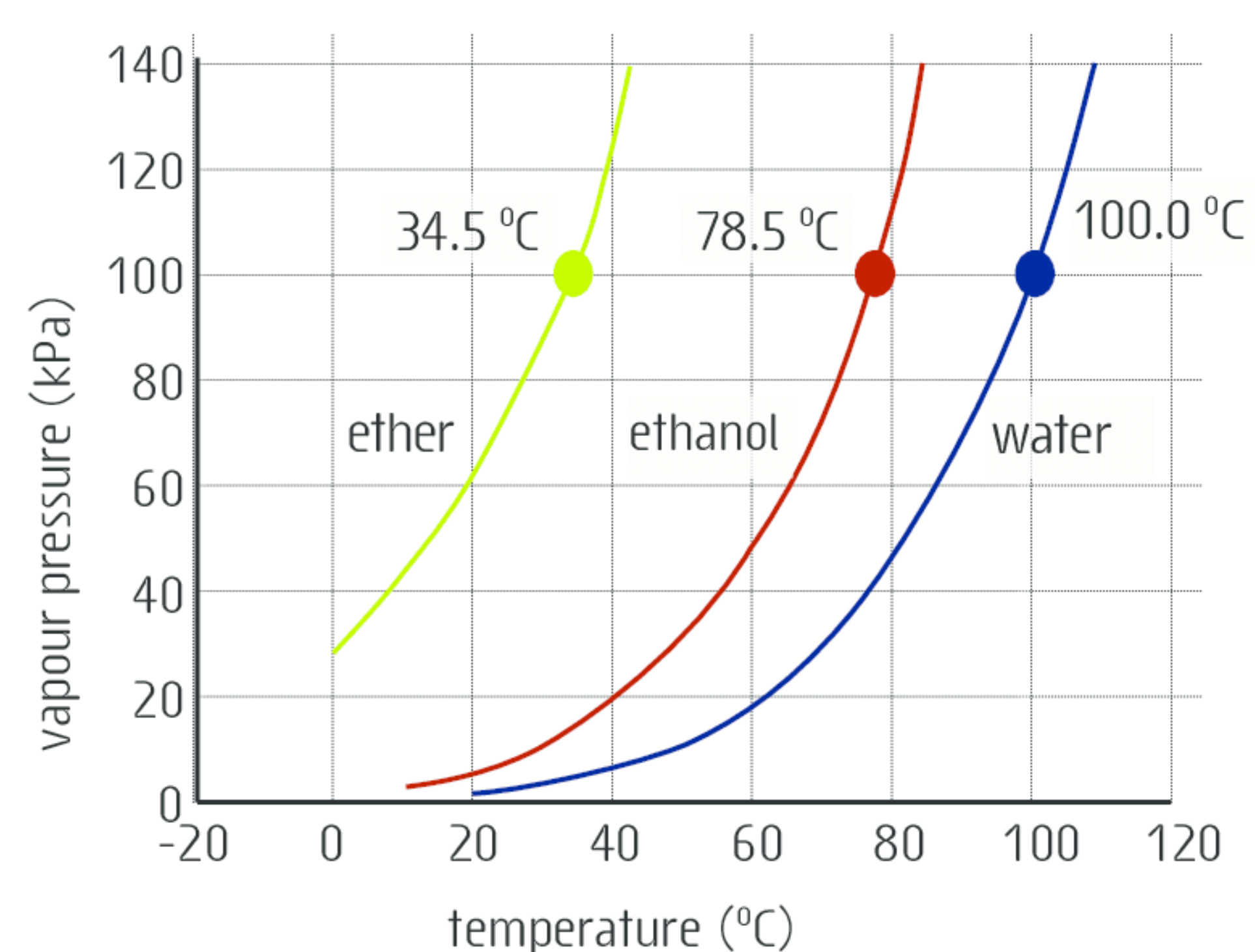
All substances show a greater tendency to evaporate with increasing temperature and so their vapour pressure also increases with temperature. (See Fig 14.) This is to be expected, as higher temperatures mean higher average molecular kinetic energies that better enable molecules to escape their intermolecular forces of attraction. It can also be seen in Fig 14 that the vapour pressure of different substances is not the same for the same temperature. Instead, for a given temperature, the substance with **weakest intermolecular forces**, ether, has the **highest vapour pressure** whilst water with the strongest intermolecular forces has the lowest vapour pressure.

**FIGURE 14** The **vapour pressure with temperature** graphs for **ether**, **ethanol** and **water** show the trend towards increasing vapour pressure with increasing temperature. However, for a given temperature the vapour pressure is highest where the intermolecular forces are lowest, ie **vapour pressure increases with weaker** intermolecular forces.

Although **ether** is polar and has the strongest dispersion forces, it has the weakest overall intermolecular forces. **Ethanol** has stronger intermolecular forces as it has up to two hydrogen bonds per molecule. Despite **water** having the weakest dispersion forces it is very polar and capable of having up to four hydrogen bonds per molecule. Thus, overall, water has the strongest intermolecular forces of the three and the lowest vapour pressure for a given temperature.



The **normal boiling point** of each liquid is marked on the graphs. This is the temperature at which the liquid has a vapour pressure equal to the normal atmospheric pressure, ie 101.3 kPa.



Attempt Set 25 # 9 to 13.



## 15.9 The unique properties of water

The **collective physical properties** of water are considered unique among molecular substances. Its unusual set of physical properties can be explained in terms of the **strong polarity** of its molecules and their extensive capacity for **hydrogen bonding**. Thus despite its small molecular size, (ie **weak dispersion forces**) water has a relatively high melting point and boiling point, 0 °C and 100 °C respectively. Similar sized molecular substances like methane (CH<sub>4</sub>) or hydrogen sulfide (H<sub>2</sub>S) for example are gases with very low melting and boiling points. Thus it is the ability of water molecules to form extensive hydrogen bonding with neighbouring water molecules that compensates for the weak dispersion forces and results in water having a relatively high melting point and boiling point.

Another significant property of water relates to its **density** in the **solid phase** (ice) being **lower** than its density in the **liquid** phase. **Most substances**, though not all, are denser in the solid phase. Under normal conditions water has a maximum density of **1.0 g mL<sup>-1</sup>** as a liquid at around 4 °C. When it freezes it undergoes a significant expansion and its density drops by about 8% to **0.918 g mL<sup>-1</sup>**. (See Fig 15.) The reduced density of the solid phase explains why ice floats on water. (See Fig 16.) Another effect of this is seen when lakes or rivers freeze they do so from the top down. Furthermore, the resulting surface ice acts as an insulating layer preventing the water beneath from completely freezing. This enables aquatic plants and animals to survive the freezing winter months.

This unusual property is due to the nature of the regular crystal lattice that forms when water freezes. In **ice** this lattice of molecules is arranged in such a way that allows each water molecule to form **four hydrogen bonds** with four neighbouring water molecules. (See Fig 16.) This arrangement **maximises hydrogen bonding** between water molecules however it takes up **more space** (is less dense) than the random arrangement of molecules in liquid water. As a result, water expands as it freezes and becomes less dense than liquid water.

**FIGURE 15** The force of expansion due to water freezing has caused this bottle to shatter. In nature this process helps to weather and fracture rock.

**FIGURE 16** Icebergs consist of pure solid water. They have a lower density than either pure water or sea water and so they float.



**Liquid water** has a **random** but **compact** arrangement of molecules that on average allows for fewer hydrogen bonds per molecule than the ice structure. It has a **higher density** because the same mass of water fits into a smaller volume. (For simplicity the presence of salt ions in this sea water has not been shown.)

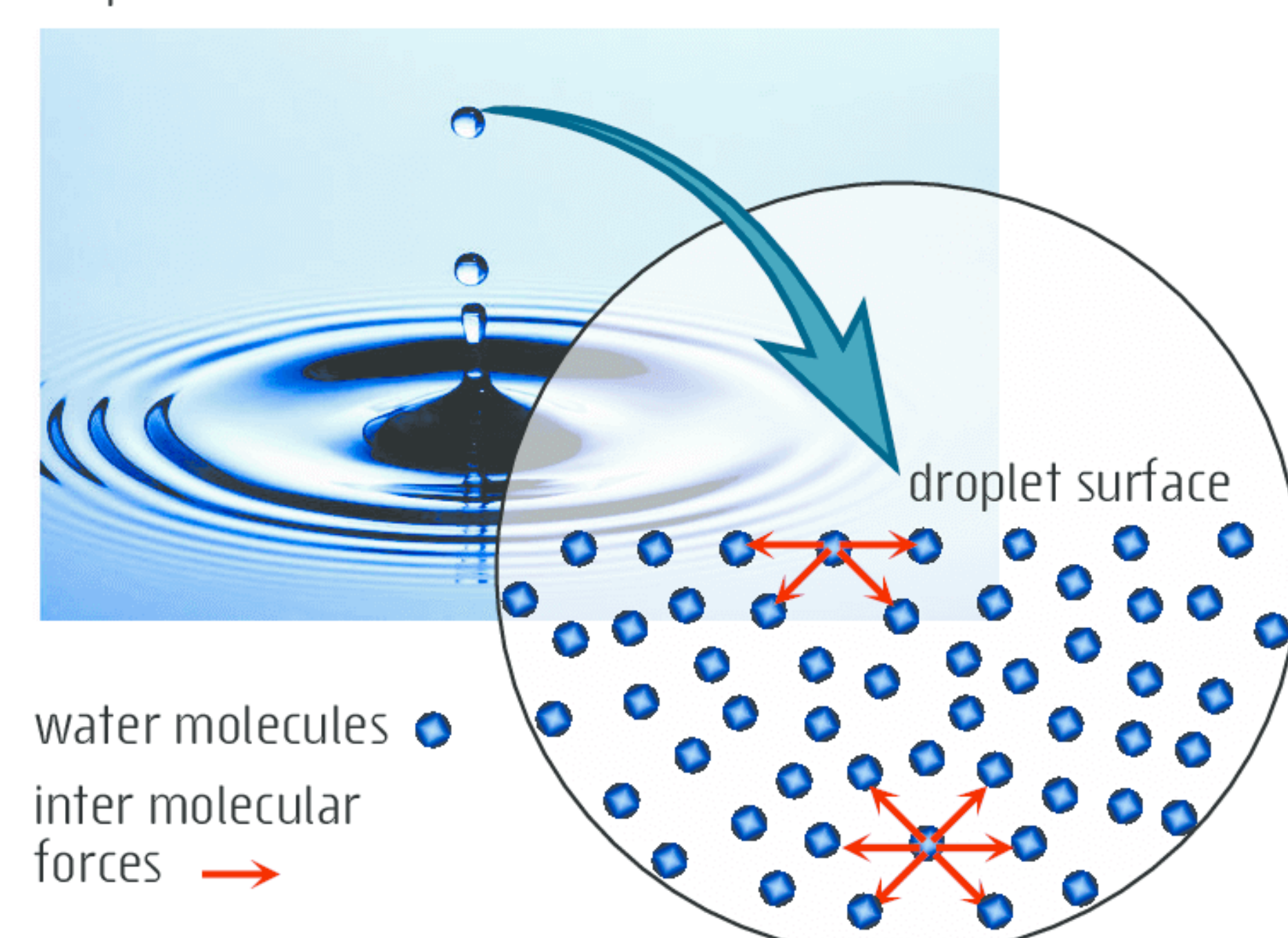
remember,  $\text{density} = \frac{\text{mass}}{\text{volume}}$

**Ice** has a highly **ordered arrangement** of water molecules that allows four hydrogen bonds per water molecule. Although these water molecules appear to be arranged in flat layers this is not the case. The lattice is more like that of diamond where each water molecule is at the centre of a **tetrahedral arrangement** of four water molecules (see above) to which it is hydrogen bonded.

Another significant property of water is its **high surface tension** which is amongst the highest known. Surface tension is shown by a liquid's tendency to resist any increase in its surface area. It gives water the appearance of having a stretchy surface skin that wants to contract. This is the property that causes water to form spherical droplets and allows certain insects to scamper across its surface without getting wet. (See Fig 22 p137.)

The high surface tension of water can be explained in terms of its **strong intermolecular forces**. At the water surface there is an imbalance of these forces causing surface molecules to be pulled inwards towards the bulk of the liquid. (See Fig 17.) As a consequence the surface is trying to contract and achieve a minimum area. This is why free falling or suspended drops of water try to achieve a spherical shape. This shape has the smallest possible surface to volume ratio. Of course the effects of gravity work against this causing suspended drops to become elongated.

**FIGURE 17** The spherical shape of water drops is a result of **surface tension**.



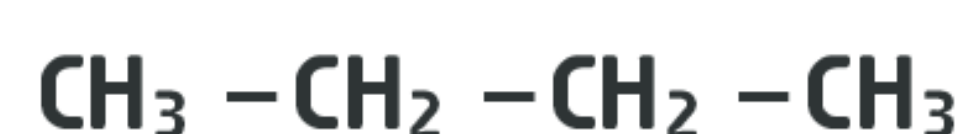
Complete Set 25.



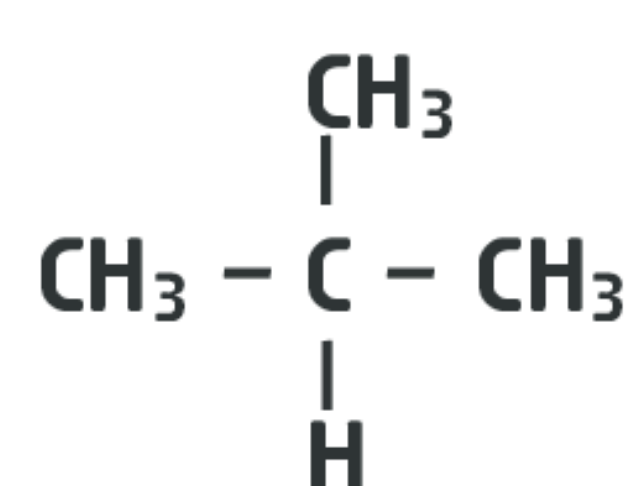
## Set 25 Intermolecular forces

- Name the type of bonding or forces of attraction involved in each of the following situations. Choose from **ionic bonds**, **covalent bonds**, **metallic bonds** or **intermolecular forces**. Also classify the bonds as **strong** or **weak**.
  - the bonding between the oxygen **atoms** (O) in an oxygen **molecule** (O<sub>2</sub>)
  - the bonding between neighbouring water **molecules** (H<sub>2</sub>O) in liquid water (H<sub>2</sub>O)
  - the bonding found in solid **sodium chloride** (NaCl)
  - the bonding between carbon **atoms** (C) in diamond (C)
  - the bonding that is overcome when **liquid** pentane (C<sub>5</sub>H<sub>12</sub>) **boils**
  - the bonding that is overcome when solid **sugar** (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) is heated to the point that a black residue of **carbon** (C) **remains**
  - the bonding that is overcome when molten iron is **vaporised**
  - the bonding that is overcome when the wax C<sub>22</sub>H<sub>46</sub> **melts** and then **vaporises**
- The two molecular compounds **galactose** and **glucose** are both solid sugars. Galactose has a melting point **167 °C** while glucose has a melting point of **146 °C**. What do the different melting points indicate about the relative strength of the **intermolecular forces** in galactose compared to those in glucose? **Explain**.
- Explain** the formation of **dipole-dipole forces** in molecular compounds using hydrogen sulfide as an example (H<sub>2</sub>S). You must include a sketch as part of your answer.
- All molecular substances can interact by **dispersion** forces.
  - Describe** the origin of these forces.
  - Each of the following substances interact only by dispersion forces. Refer to their boiling points and **state** which example from each pair has the higher dispersion forces. **Account** for the difference in strength of dispersion forces.
    - chlorine (Cl<sub>2</sub>) BP = -35 °C and nitrogen (N<sub>2</sub>) BP = -196 °C
    - ethane (C<sub>2</sub>H<sub>6</sub>) BP = -88.6 °C and methane (CH<sub>4</sub>) BP = -161.5 °C
    - butane (C<sub>4</sub>H<sub>10</sub>) BP = -0.5 °C and its isomer methylpropane [CH<sub>3</sub>CH(CH<sub>3</sub>)<sub>2</sub>] BP = -11.7 °C. (See Fig 18.)

**FIGURE 18** The two **isomeric structures** of butane (C<sub>4</sub>H<sub>10</sub>).



butane



methylpropane

### melting and boiling points

**weak**

**dipole-dipole**

**soluble**

**extremely soluble**

**covalent bonds**

**all**

**— OH**

**electrostatic**

**HF**

**insoluble**

**electrons**

**— NH**

**an F, O or N atom**

**liquid and solid**

**intermolecular forces**

**lone pair**

**molar mass**

- Complete** the following passage. Use the list of terms shown in the border.

The atoms within a molecule are strongly bonded by (a) \_\_\_\_\_. Forces that bond molecules to each other are generally (b) \_\_\_\_\_ forces known as (c) \_\_\_\_\_. The presence of intermolecular forces explains why molecular substances are able to form (d) \_\_\_\_\_ phases. The stronger these forces are, the higher a substance's (e) \_\_\_\_\_.

Dispersion forces occur in (f) \_\_\_\_\_ molecular substances and become stronger as the number of molecular (g) \_\_\_\_\_ increase. This means that as the molecular size increases, ie increasing (h) \_\_\_\_\_, so the melting and boiling points also increase.

Substances whose molecules are polar will also experience (i) \_\_\_\_\_ forces. These intermolecular forces are due to the weak (j) \_\_\_\_\_ attraction between the oppositely charged ends of the molecular dipoles.

Hydrogen bonds are a very specific type of intermolecular force that only occur in the compound (k) \_\_\_\_\_ or in other compounds whose molecules contain an (l) \_\_\_\_\_ or (m) \_\_\_\_\_ configuration of atoms. It involves strong electrostatic attraction between a hydrogen atom that is covalently bonded to (n) \_\_\_\_\_ and a (o) \_\_\_\_\_ of another O, F or N atom. Substances able to hydrogen bond have significantly higher melting and boiling points than other substances of similar molar mass that don't have hydrogen bonding ability.

*Continued over page.*



5. (continued) The nature of intermolecular forces and molecular polarity also has a significant effect on the solubility or miscibility of different substances. It is generally found that substances of similar polarity are <sup>(p)</sup> \_\_\_\_\_ in one another while substances of unlike polarity are <sup>(q)</sup> \_\_\_\_\_ in one another. Hydrogen bonding has a strong effect on solubility. If two substances can interact by hydrogen bonding they may be <sup>(r)</sup> \_\_\_\_\_ in one another.


6. The boiling point of **water** is **100 °C** while that of **hydrogen sulfide** is **-60 °C**. From this we can conclude that the intermolecular forces are much stronger in water than in hydrogen sulfide. Answer the following questions about these two substances.


- Name the types of intermolecular forces common to **both**  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .
- It can be said that the **dipole-dipole** forces in water are stronger than those in hydrogen sulfide. Explain why this should be so.
- In which of the two molecular substances are dispersion forces the **strongest**?
- The difference in boiling point for these two substances is not due to differences in dispersion forces. **Account** for the much higher boiling point of  $\text{H}_2\text{O}$ .
- Use a **diagram** to show the formation of **hydrogen bonds** in water.

7. Refer to the Lewis structures shown below and **determine** the types of **intermolecular forces** present in each of the substances.

a. carbon dioxide 

c. water 

b. phosphorous trifluoride 

d. methanal 

8. **Determine** the type of **intermolecular force(s)** present in each of the listed substances. You may need to draw their **Lewis structure** to determine the shape and polarity of these substances.

- |                         |                            |                           |                             |
|-------------------------|----------------------------|---------------------------|-----------------------------|
| a. $\text{Cl}_2$        | d. $\text{CH}_4$           | g. $\text{CF}_4$          | j. $\text{HCN}$             |
| b. $\text{H}_2\text{S}$ | e. $\text{NH}_3$           | h. $\text{CS}_2$          | k. $\text{CH}_3\text{COOH}$ |
| c. $\text{HF}$          | f. $\text{CH}_2\text{F}_2$ | i. $\text{CH}_3\text{OH}$ | l. $\text{H}_2\text{O}_2$   |

9. Choose the substance from each pair that you would expect to have the **higher boiling point**. **Justify** your answer.

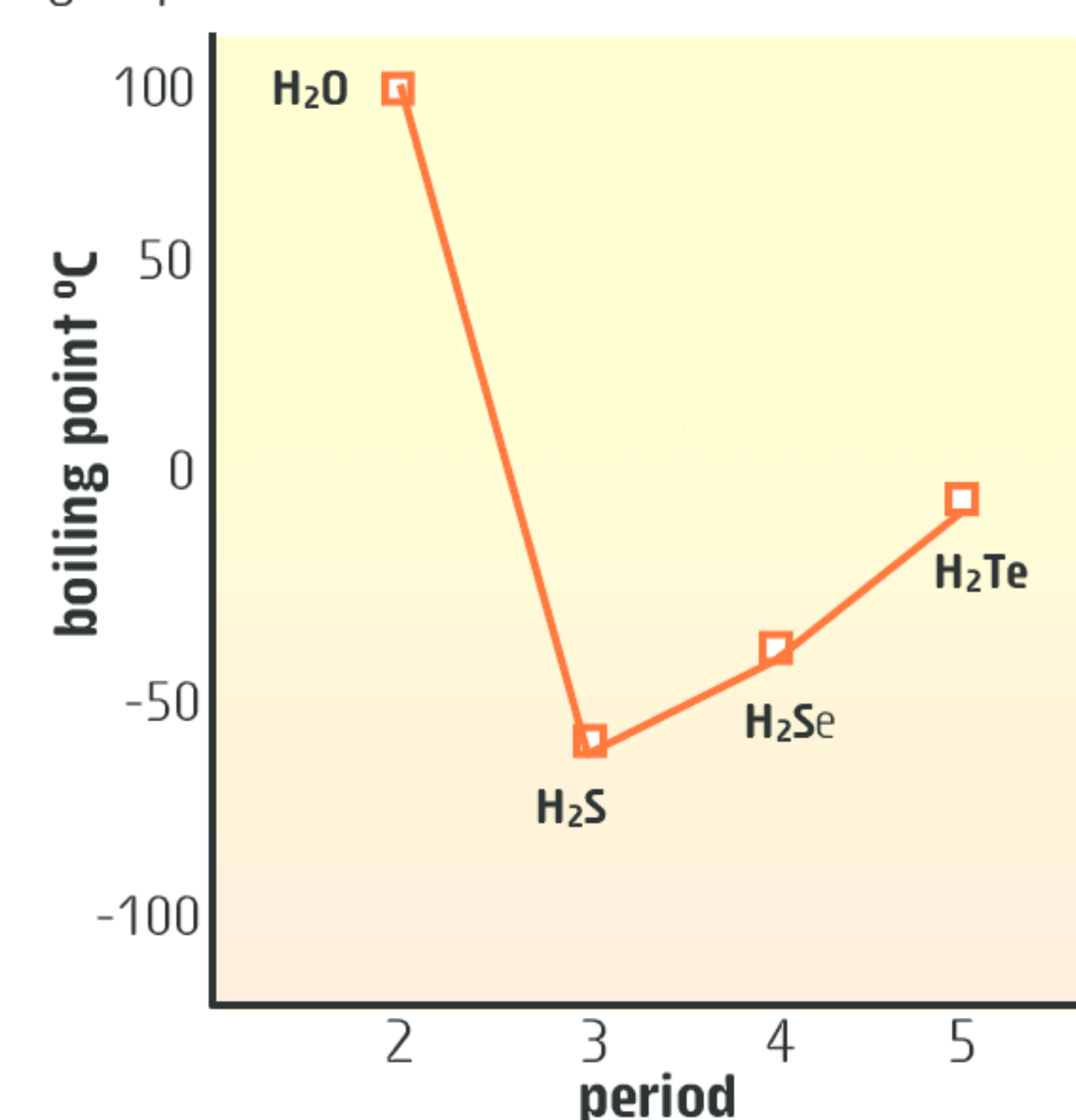
- fluorine ( $\text{F}_2$ ) and chlorine ( $\text{Cl}_2$ )
- methoxymethane ( $\text{CH}_3\text{OCH}_3$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ )
- methane ( $\text{CH}_4$ ) and butane ( $\text{C}_4\text{H}_{10}$ )

10. Water is a **liquid** at room temperature, which was a determining factor for the evolution of life on Earth. It has a freezing point of  $0\text{ °C}$  and a boiling point of  $100\text{ °C}$  (at normal atmospheric pressure). Similar compounds of other group 16 elements, like hydrogen sulfide ( **$\text{H}_2\text{S}$** ), hydrogen telluride ( **$\text{H}_2\text{Te}$** ) and hydrogen selenide ( **$\text{H}_2\text{Se}$** ) are all gases at normal laboratory conditions. (See Fig 19.) Discuss the **role** of **intermolecular forces** in affecting the **boiling point** of these compounds.

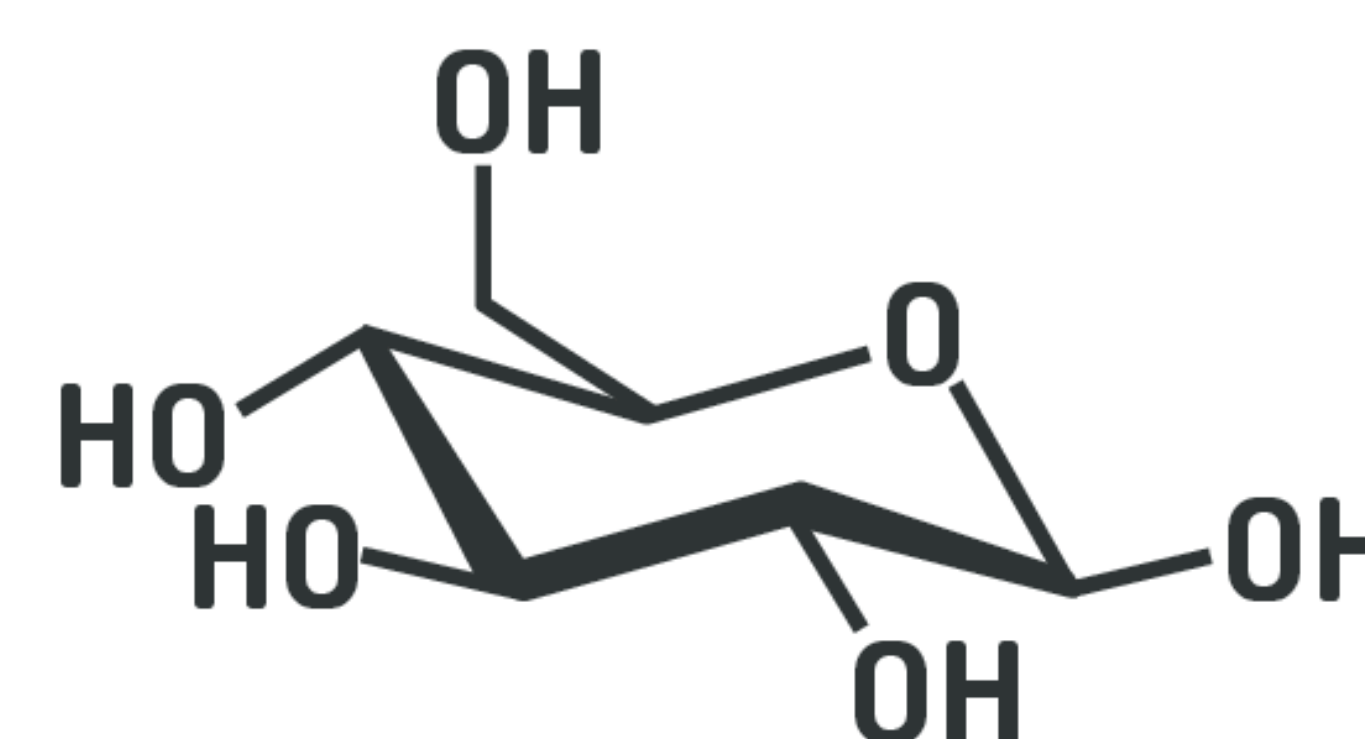
11. A student has a choice of two liquids: **water** ( $\text{H}_2\text{O}$ ) or **decane** ( $\text{C}_{10}\text{H}_{22}$ , a typical component found in the household solvent **mineral turpentine**) as a possible solvent for the listed substances below. Choose the **most suitable solvent** for each substance and **justify** your choice in terms of intermolecular forces and polarity.

- glycerol**,  $\text{CH}_2\text{OHCH}_2\text{OHCH}_2\text{OH}$
- petrol**, essentially  $\text{C}_8\text{H}_{18}$
- diesel** fuel, a mixture of hydrocarbons containing components like  $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$
- the monosaccharide **glucose**,  $\text{C}_6\text{H}_{12}\text{O}_6$  (See Fig 20.)

**FIGURE 19** The boiling points of the hydrides formed by the elements from group 16.

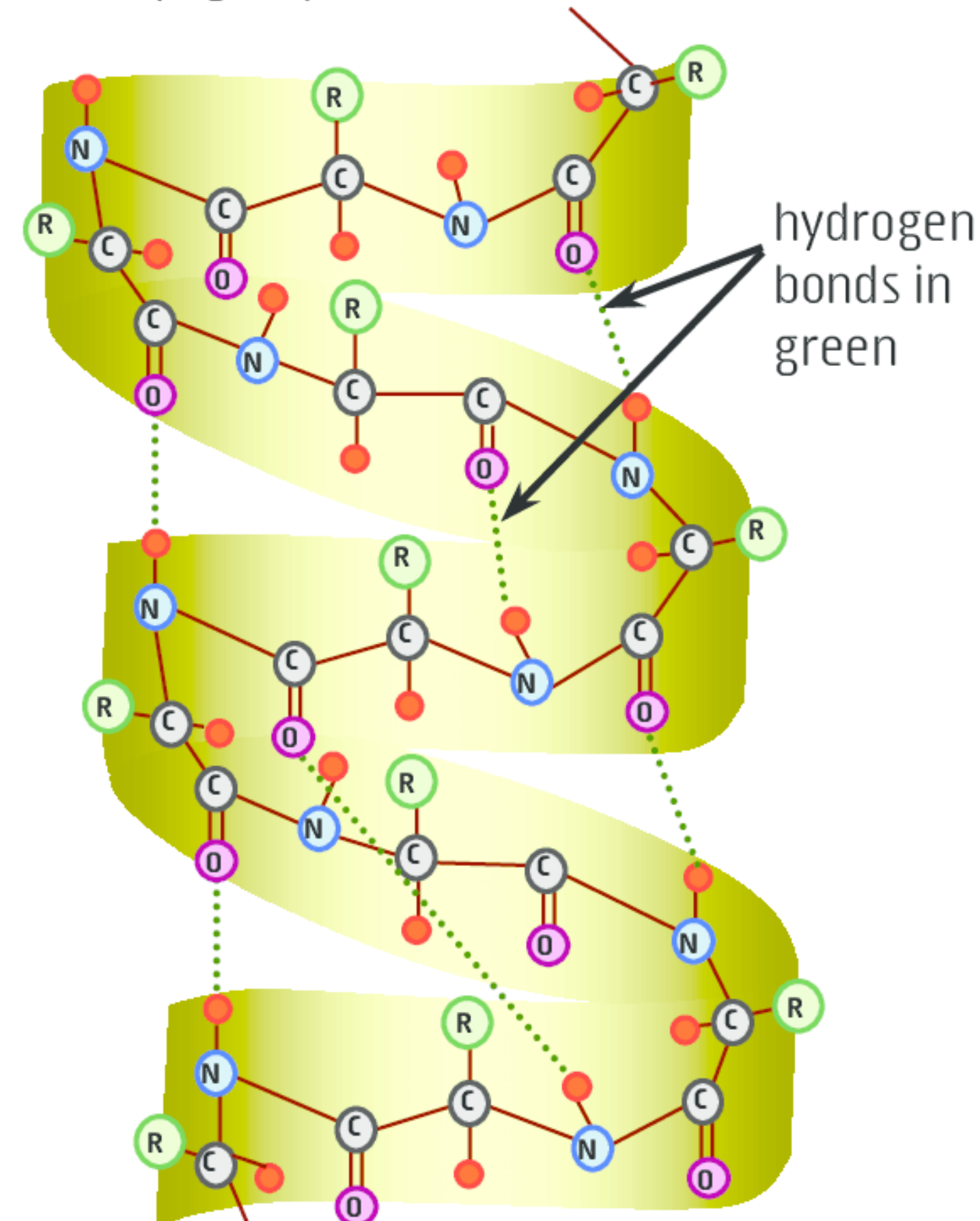


**FIGURE 20** This wire frame diagram shows the molecular structure of **glucose**. A carbon atom is present at each junction. Hydrogen atoms are assumed to fill any vacant positions.

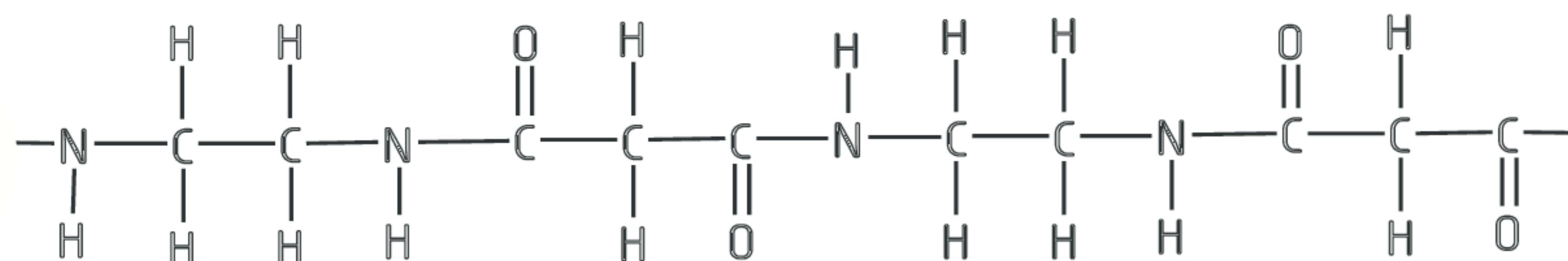




**FIGURE 21** A section of a **protein** molecule showing how hydrogen bonds form the  $\alpha$  **helical structure**. Hydrogen atoms are shown in red. 'R' is the general notation for an alkyl group, other atoms are labelled.



12. **Proteins** are one of the basic structural materials of which all living things are composed. An essential property of proteins is their ability to form **hydrogen bonds** between various parts of the molecule. Among other things this allows some proteins to form a regular spiral structure. Known as the  $\alpha$  **helical** form, this structure resembles a **right handed coiled spring**. (See Fig 21.) The following structure shows part of a protein molecule.



- Redraw this section of a protein molecule and **circle** the hydrogen atoms that are capable of hydrogen bonding. In your diagram show the lone pairs that **could** be involved in hydrogen bonding.
  - What is **unique** about the hydrogen atoms identified above that allows them to be involved in hydrogen bonding?
  - Determine from Figure 21 which lone pairs are **actually** involved in forming the hydrogen bonds responsible for the  $\alpha$  helical structure of a protein molecule.
13. With reference to **strength** and **types** of intermolecular forces account for the **difference** in the boiling points of the following pairs of compounds.
- methanol** ( $\text{CH}_3\text{OH}$ ), boiling point  $65^\circ\text{C}$  and **methane** ( $\text{CH}_4$ ), boiling point  $-162^\circ\text{C}$
  - methanol** ( $\text{CH}_3\text{OH}$ ), boiling point  $65^\circ\text{C}$  and **octane** ( $\text{C}_8\text{H}_{18}$ ), boiling point  $126^\circ\text{C}$
14. An ice cube placed into a glass of water will **float** on the surface. By comparison a cube of solid candle wax will **sink** if placed into a beaker of molten wax.
- Which of these two is considered '**normal**' behaviour for the solid phase of a substance, ie floating as with ice or sinking as with solid wax? Briefly **explain** your choice.
  - Explain** why solid ice has a **less dense** structure than liquid water.
15. The **solubility** of **alcohols** in water varies with the molar mass of the alcohol as shown here.

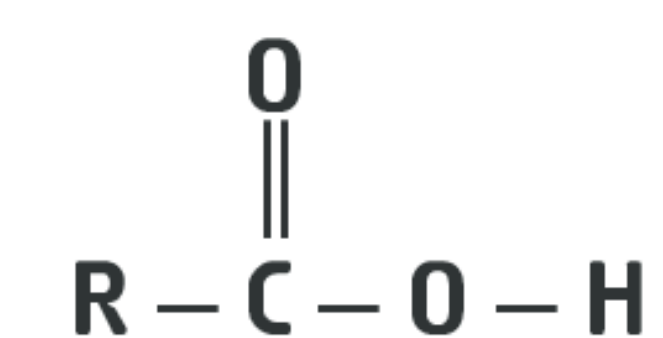
Alcohol	Molecular formula	Molar mass	Solubility in water g alcohol per 100 g of water
<b>methanol</b>	$\text{CH}_3\text{OH}$	32	infinitely soluble
<b>ethanol</b>	$\text{C}_2\text{H}_5\text{OH}$	46	infinitely soluble
<b>propan-1-ol</b>	$\text{C}_3\text{H}_7\text{OH}$	60	infinitely soluble
<b>butan-1-ol</b>	$\text{C}_4\text{H}_9\text{OH}$	74	8.1
<b>pentan-1-ol</b>	$\text{C}_5\text{H}_{11}\text{OH}$	88	2.6
<b>hexan-1-ol</b>	$\text{C}_6\text{H}_{13}\text{OH}$	102	0.59
<b>heptan-1-ol</b>	$\text{C}_7\text{H}_{15}\text{OH}$	116	0.093

- Suggest a **reason** why alcohols like methanol would be expected to be very soluble in solvents like water.
- How does the solubility of the listed alcohols vary with increasing **molar mass**?
- Suggest** an **explanation** for the trend you outlined in part (b) above.



16. Short chain carboxylic acids (see border note) like methanoic acid,  $\text{HCOOH}$  and ethanoic acid,  $\text{CH}_3\text{COOH}$  are infinitely soluble, ie **miscible** in water. Higher chain carboxylic acids like palmitic acid,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$  by comparison have a greasy feel and are not soluble in water. These longer chain carboxylic acids are known as fatty acids. Examine the structure of these short and long chain carboxylic acids, as shown at right and **account** for their **range of solubilities in water**.

All carboxylic acids have the general structure:



**R** represents either a single hydrogen atom or a chain of one or more carbon atoms. In methanoic acid, **R = H**, in ethanoic acid **R = CH<sub>3</sub>** and in palmitic acid **R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>**.

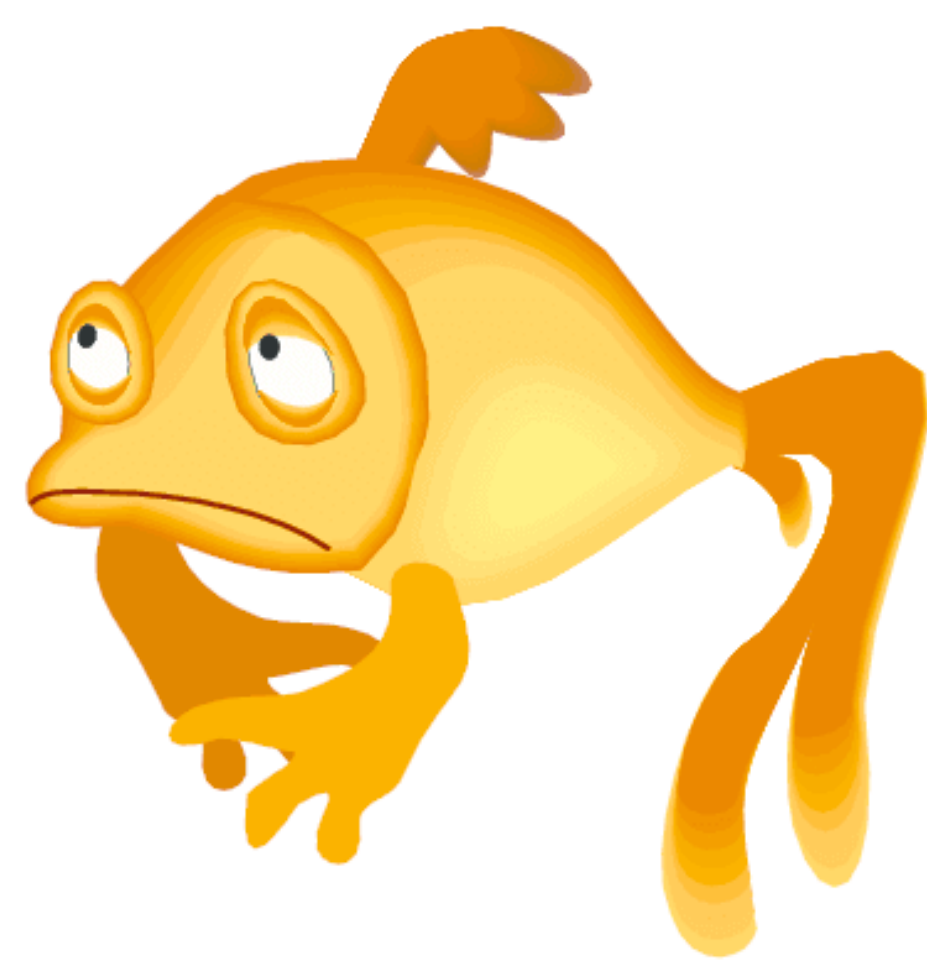
17. The spider shown in Fig 22 is able to walk on water without getting wet.
- What is the **name** of the property that allows the insect to do this?
  - Explain** in terms of intermolecular forces why liquids have a surface tension.
  - Overall, the intermolecular forces in benzene,  $\text{C}_6\text{H}_6$  are much less than in water. How would the surface tension of benzene **compare** to that of water? **Explain**.
  - Detergents improve the ability of water to wet a surface. How must this affect its surface tension?

FIGURE 22





# CHAPTER 16 | SOLUTIONS



Aquarium fish suffer stress when their tank water gets too warm. Being cold blooded animals, higher temperatures raise their metabolic rate which raises their oxygen demand. However, higher temperatures reduce the solubility of oxygen gas in water thus reducing its availability to the aquarium fish. (eg  $O_2$  solubility in fresh water is  $14.6 \text{ mg L}^{-1}$  at  $0^\circ\text{C}$  and  $6.5 \text{ mg L}^{-1}$  at  $40^\circ\text{C}$ )

A similar effect known as **thermal pollution** can be a problem in the wider marine environment. This can happen where water from rivers or lakes has been used as a coolant for electric power generation. Returning this warmed water back to the marine environment can result in thermal pollution of rivers and lakes. The higher water temperature reduces oxygen solubility thus placing stress on marine organisms. This effect of decreasing gas solubility with increasing temperature is true for all gases. By comparison, most solids (but not all) become more soluble with increasing temperature. (See Fig 2.)

At a given temperature:

- an **unsaturated** solution contains less solute than it is able to dissolve.
- a **saturated** solution contains as much solute as it can normally dissolve.
- a **supersaturated** solution contains more solute than it can normally dissolve.

Attempt Set 26 # 1 and 2.

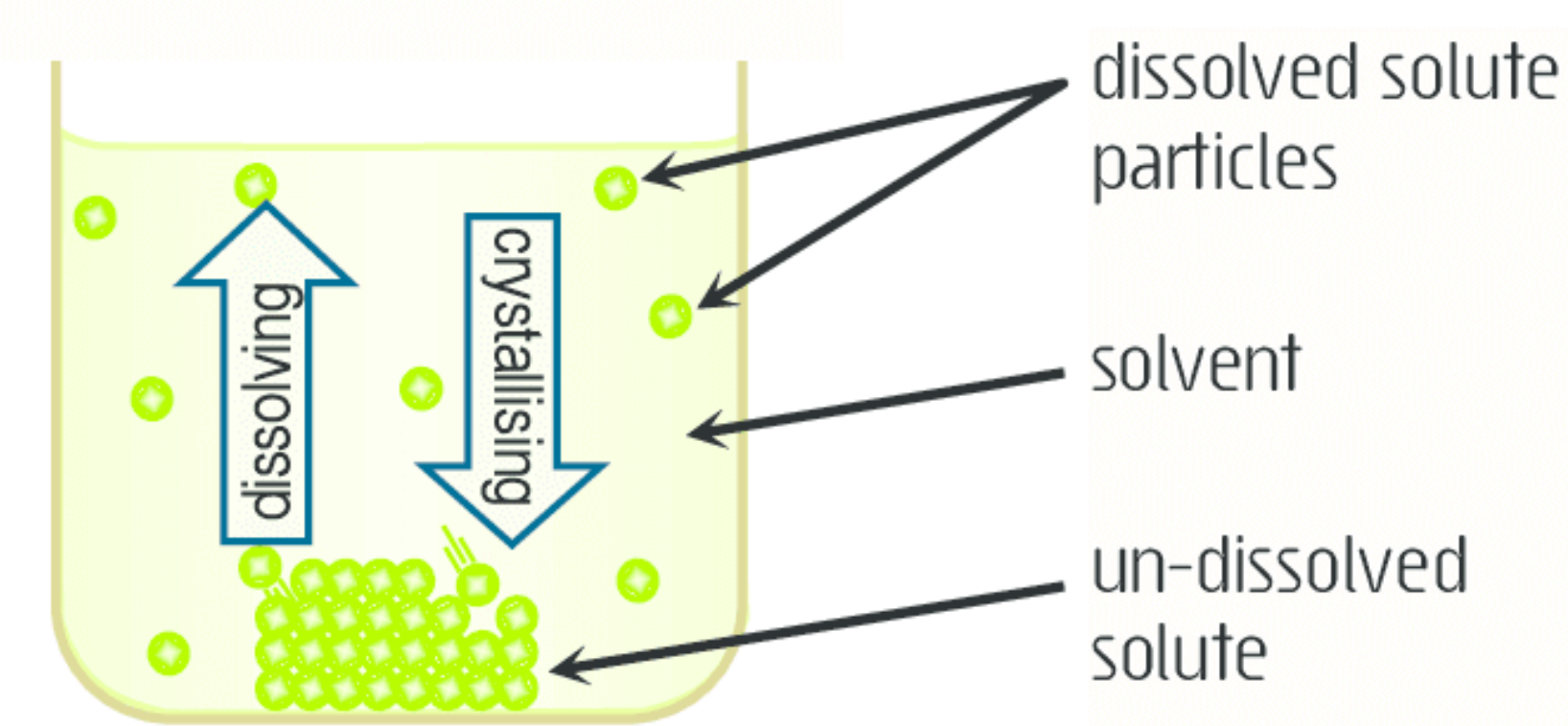
## Electrolyte strength and solubility

All ionic compounds are strong electrolytes despite their solubility. Thus sodium chloride, **NaCl** which is very **soluble** and silver chloride, **AgCl** which is considered **insoluble** are both **strong electrolytes**. This is true because whatever small amount of AgCl does dissolve (albeit very little) is entirely present as independent  $Ag^+(aq)$  and  $Cl^-(aq)$  ions.

## 16.1 Solutions and the dissolving process

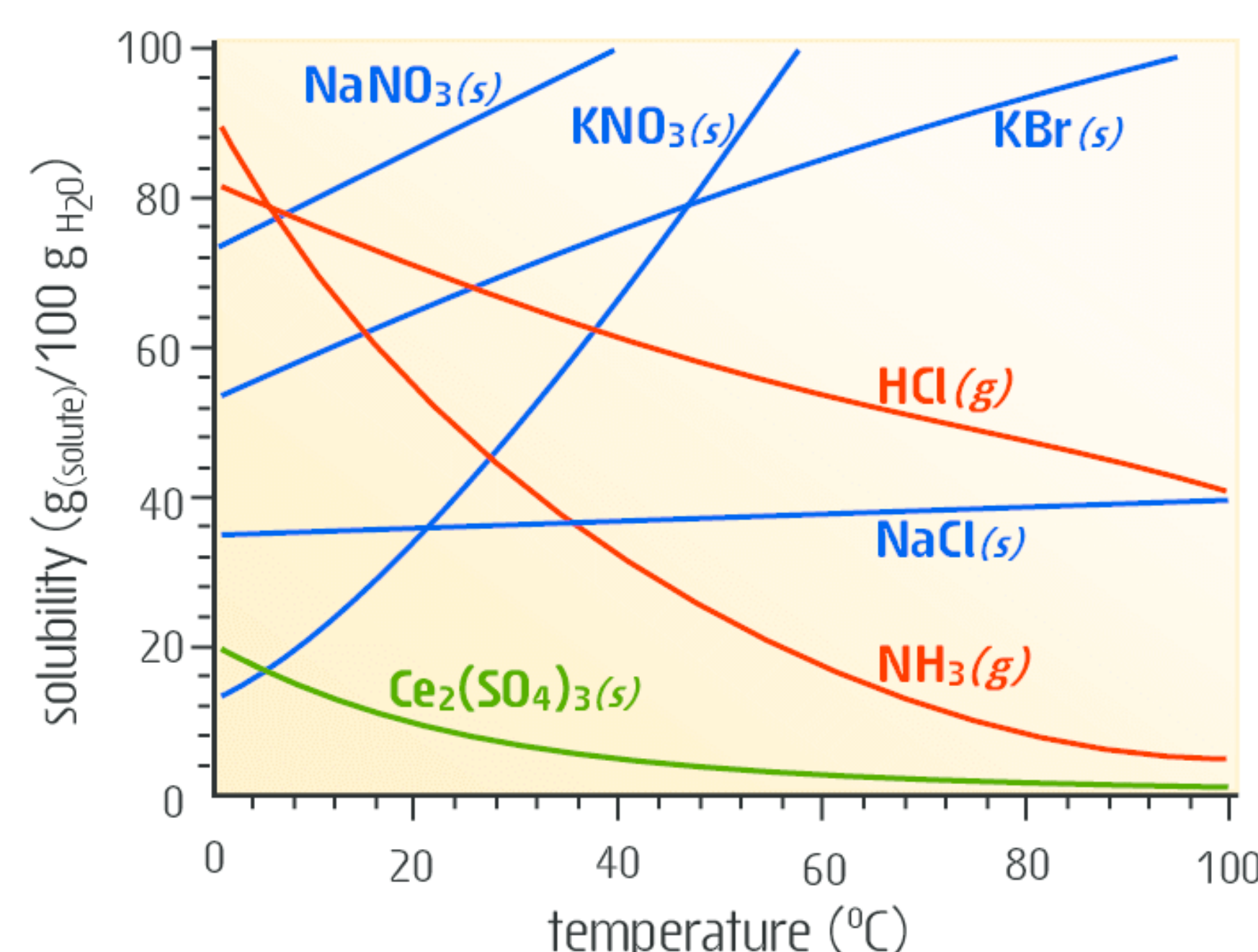
A solution is a mixture where the particles of a **solute** are homogeneously spread amongst the particles of a **solvent**, the major component of the mixture by mass. Solutions can be solid, eg alloys like brass and bronze, liquid such as sea water or gaseous, eg air. Here we will explore liquid solutions where the solvent is water. These are called **aqueous** solutions.

**FIGURE 1** The formation of an aqueous solution involves two opposing processes, dissolving and crystallising. As the solute dissolves the solution concentration increases. Crystallisation however, returns some of the dissolved solute to the solid form, thus reducing the solute concentration. When the speed of these two opposing processes is equal then the solute concentration is at a maximum and the solution is said to be **saturated**.



The **solubility** of a solute is often given as the mass that can dissolve in 100 grams of water, ie  $g_{(solute)} 100 g^{-1}_{(H_2O)}$ . Most solids are increasingly soluble with increasing temperature. Cerium(III) sulfate,  $Ce_2(SO_4)_3(s)$  is a notable exception which becomes less soluble with increasing temperature. Gases however, are always less soluble at higher temperatures. (See border note.)

**FIGURE 2** Graph of solubility in water with temperature for various substances. Most solids (blue) become more soluble with increasing temperature.  $Ce_2(SO_4)_3$  (green) is an exception to the rule. Gases by comparison (shown in red) all become less soluble as temperature rises.



A solute can continue to dissolve in water until its solution becomes **saturated**, ie contains as much dissolved solute as its solubility, at that temperature, will allow. Further solute may be added to a saturated solution but it will not dissolve. If however, further solute is added and it does dissolve then this shows the solution was **unsaturated**.

It is also possible to produce a **supersaturated** solution. Such a solution contains more dissolved solute than the solute's solubility at that temperature will normally allow. One way to do this is to produce a saturated solution at a higher temperature and then cautiously cool the solution, the cooler solution will be supersaturated. This however, is an unstable situation and soon the excess solute will begin to crystallise or precipitate from solution until the solution is no longer supersaturated but only saturated. (See border note.)

## 16.2 Solutes and ion formation (E)

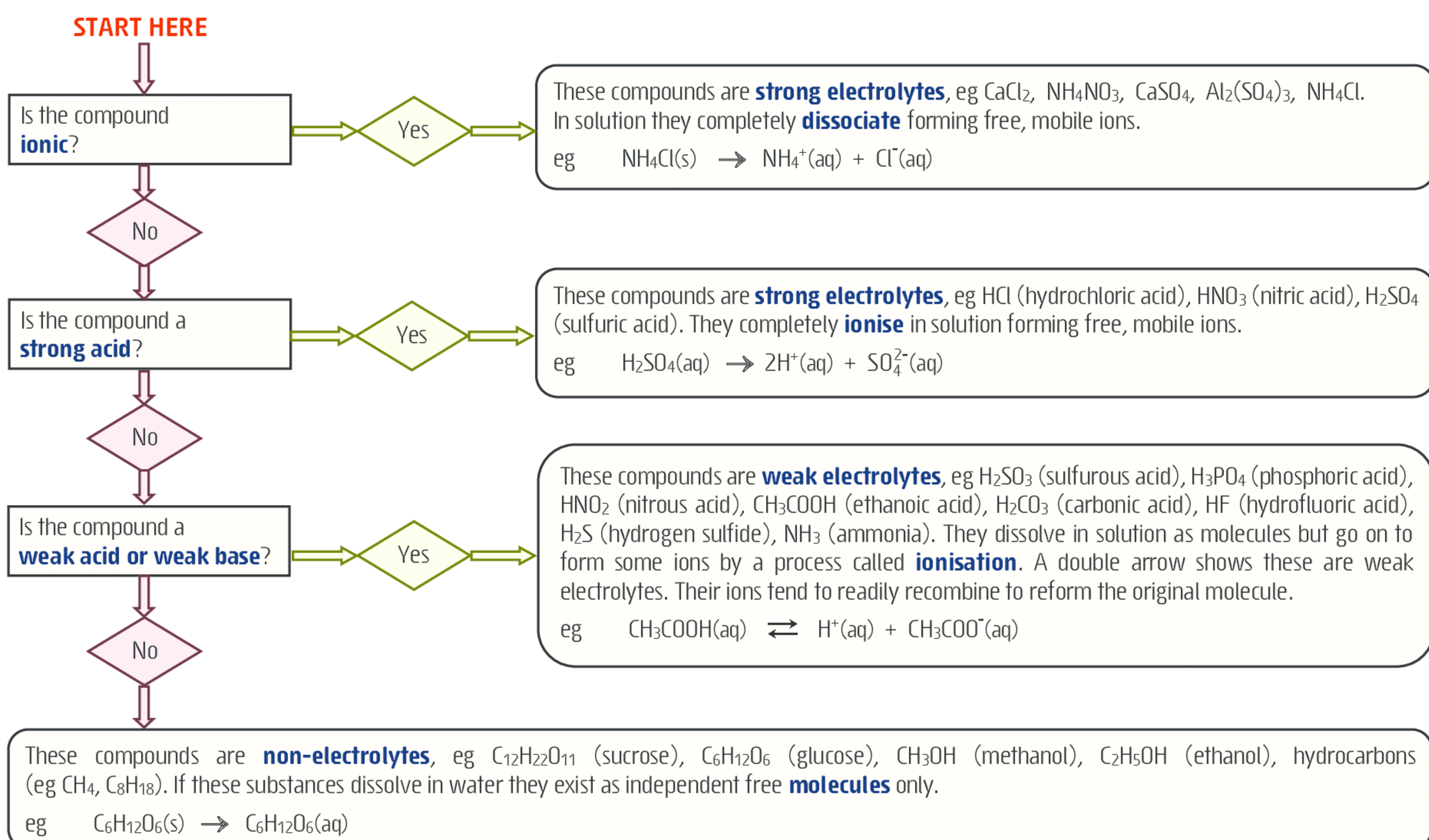
Some solutes dissolve in water producing molecules while others form ions. Aqueous solutes that produce ions when dissolved in water are classified as electrolytes as follows:

- **Strong electrolytes:** when these dissolve in water they are entirely present (or at least mostly) as independent mobile ions.
- **Weak electrolytes:** when these dissolve in water they are partly present as independent mobile ions (but mostly as molecules).
- **Non-electrolytes:** when these dissolve in water they do not produce ions. They are entirely present as molecules.

**All** ionic compounds are strong electrolytes, eg  $NaCl$ ,  $Ca(NO_3)_2$  and  $NH_4Br$ . Most covalent molecular substances, eg  $O_2$ ,  $I_2$ ,  $CS_2$  and  $CH_4$ , for example, are non-electrolytes. However, covalent molecular substances that are **strong acids**, eg  $HCl$ ,  $H_2SO_4$  and  $HNO_3$  are strong electrolytes while those that are **weak acids** or **bases** eg  $CH_3COOH$ ,  $H_2S$ ,  $H_2CO_3$  and  $H_2SO_3$  or  $NH_3$  are weak electrolytes. (See Fig 3.)



**FIGURE 3** Use the flow chart below to determine the type of electrolyte.



## 16.3 Equations of solvation

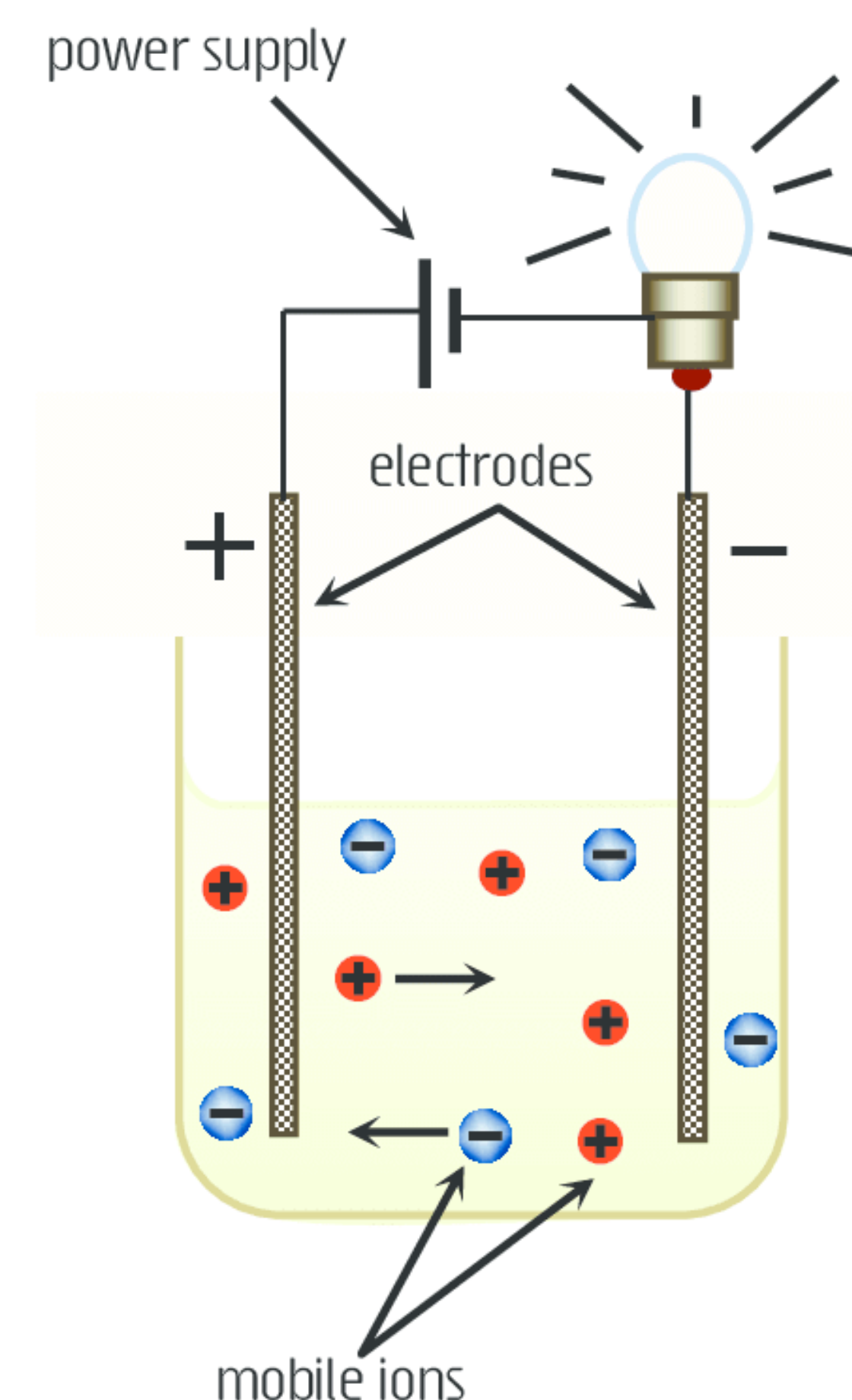
When an ionic electrolyte dissolves, the ions present within the ionic solid are released into water to form a solution of independent mobile ions. This process is termed **dissociation**. The formation of ions by a molecular electrolyte is a different process known as **ionisation**. During ionisation, molecules of the electrolyte (eg HCl, H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>) react with water to form ions not originally present within the substance. Both ionisation and dissociation result in a solution that contains independent mobile ions.

A **single arrow** (→) shows the ionisation or dissociation reaction goes to completion. This is the case for a strong electrolyte. Certain **molecular** substances such as CH<sub>3</sub>COOH, NH<sub>3</sub> or H<sub>2</sub>CO<sub>3</sub> (Fig 3) are weak electrolytes. Although these substances do ionise in aqueous solution the resulting ions tend to recombine to reform the original molecules. As such, only a small proportion of their molecules remain ionised when dissolved in water. For weak electrolytes like these a **double arrow** (⇌) is used to show the reaction does not go to completion, ie significant concentrations of ions and molecules are both present.

**EXAMPLE 1** Write equations showing how the following electrolytes dissolve in water to form ions.

Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> aluminium sulfate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s) → 2Al <sup>3+</sup> (aq) + 3SO <sub>4</sub> <sup>2-</sup> (aq) <b>dissociation</b>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> is ionic ∴ a strong electrolyte. A single arrow shows its dissociation goes to completion. The dissolved Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s) is present entirely as independent mobile Al <sup>3+</sup> (aq) and SO <sub>4</sub> <sup>2-</sup> (aq) ions.
HNO <sub>3</sub> nitric acid	HNO <sub>3</sub> (aq) → H <sup>+</sup> (aq) + NO <sub>3</sub> <sup>-</sup> (aq) <b>ionisation</b>	HNO <sub>3</sub> is a strong acid ∴ a strong electrolyte. Its ionisation goes to completion so the solution consists of independent mobile H <sup>+</sup> (aq) and NO <sub>3</sub> <sup>-</sup> (aq) ions. It contains very few, if any HNO <sub>3</sub> molecules.
CH <sub>3</sub> COOH ethanoic acid	CH <sub>3</sub> COOH(aq) ⇌ H <sup>+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq) <b>partial ionisation</b>	CH <sub>3</sub> COOH is a weak acid ∴ a weak electrolyte. Its ionisation is partial, so the solution contains mainly CH <sub>3</sub> COOH molecules with some H <sup>+</sup> (aq) and CH <sub>3</sub> COO <sup>-</sup> (aq) ions. A double arrow shows partial ionisation.

Although pure water is a non-conductor of electricity, aqueous solutions that contain a dissolved electrolyte will conduct. **Electrical conductivity** in a solution depends on the ability of positive ions to move freely towards the negative electrode while negative ions move freely towards the positive electrode. (See Fig 4.) Thus the greater the concentration of ions in a solution the greater is its ability to conduct a current. For this reason strong electrolytes always produce a more conducting solution than weak electrolytes of the same concentration. Non-electrolytes always produce non-conducting solutions.



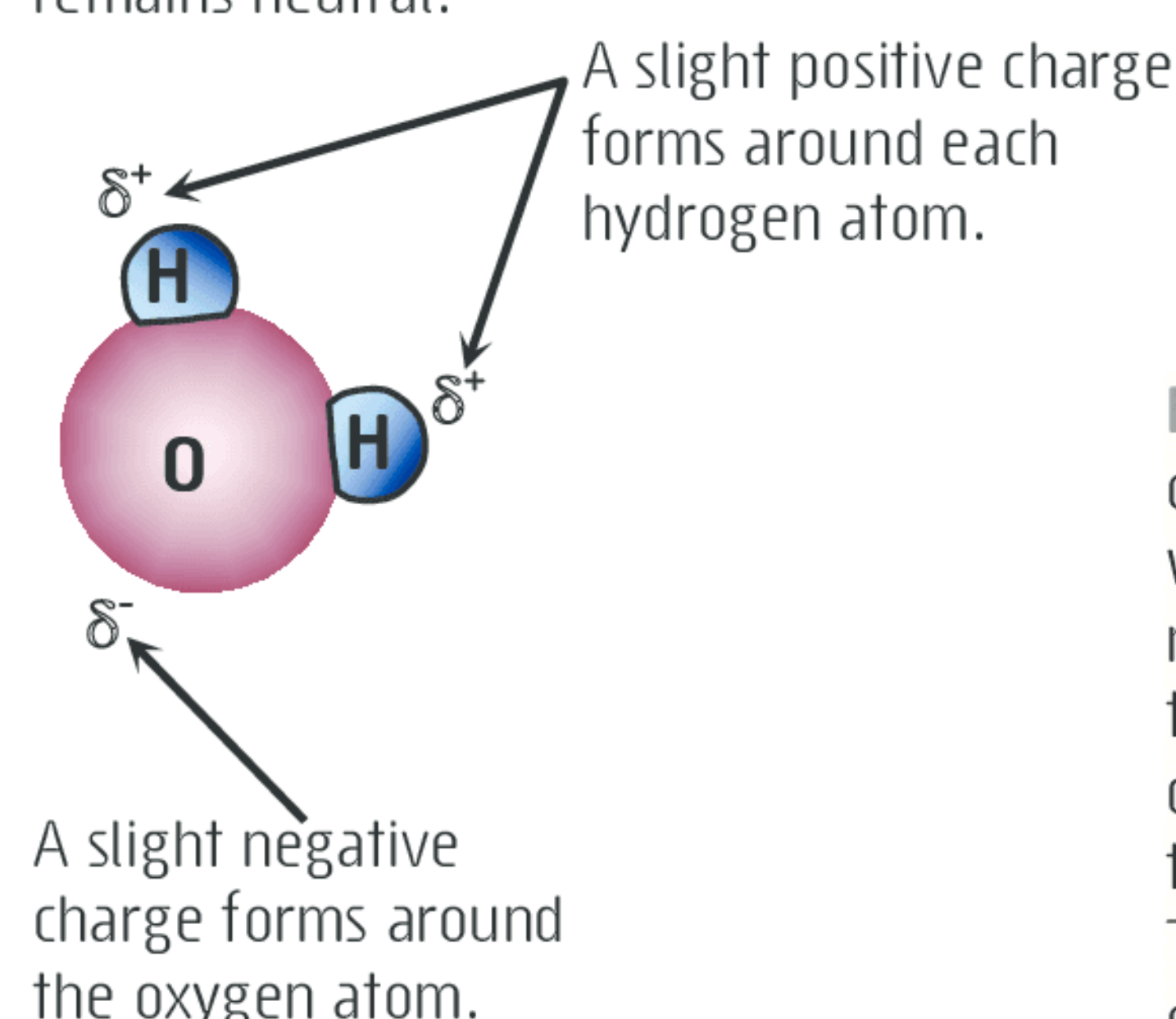
**FIGURE 4** Pure water is a non-conductor of electricity. When an electrolyte dissolves in water the resulting mobile ions allow the solution to conduct a current.

Conductivity involves positive ions moving towards the negative electrode and negative ions moving towards the positive electrode.

Attempt Set 26 # 3, 4 and 5.



**FIGURE 5** The **polar** nature of water is due to an uneven sharing of electrons within its molecules. The pair of electrons of the **O-H** bond are attracted more strongly to the more **electronegative O** atom. This causes both hydrogen atoms of the water molecule to have a **slight** ( $\ll 1$ ) positive charge ( $\delta^+$ ) while a slight ( $\ll 1$ ) negative charge ( $\delta^-$ ) develops around the oxygen atom. Molecules like this are said to have a **dipole**, ie a slightly positive ( $\delta^+$ ) and a slightly negative ( $\delta^-$ ) end, overall the molecule remains neutral.

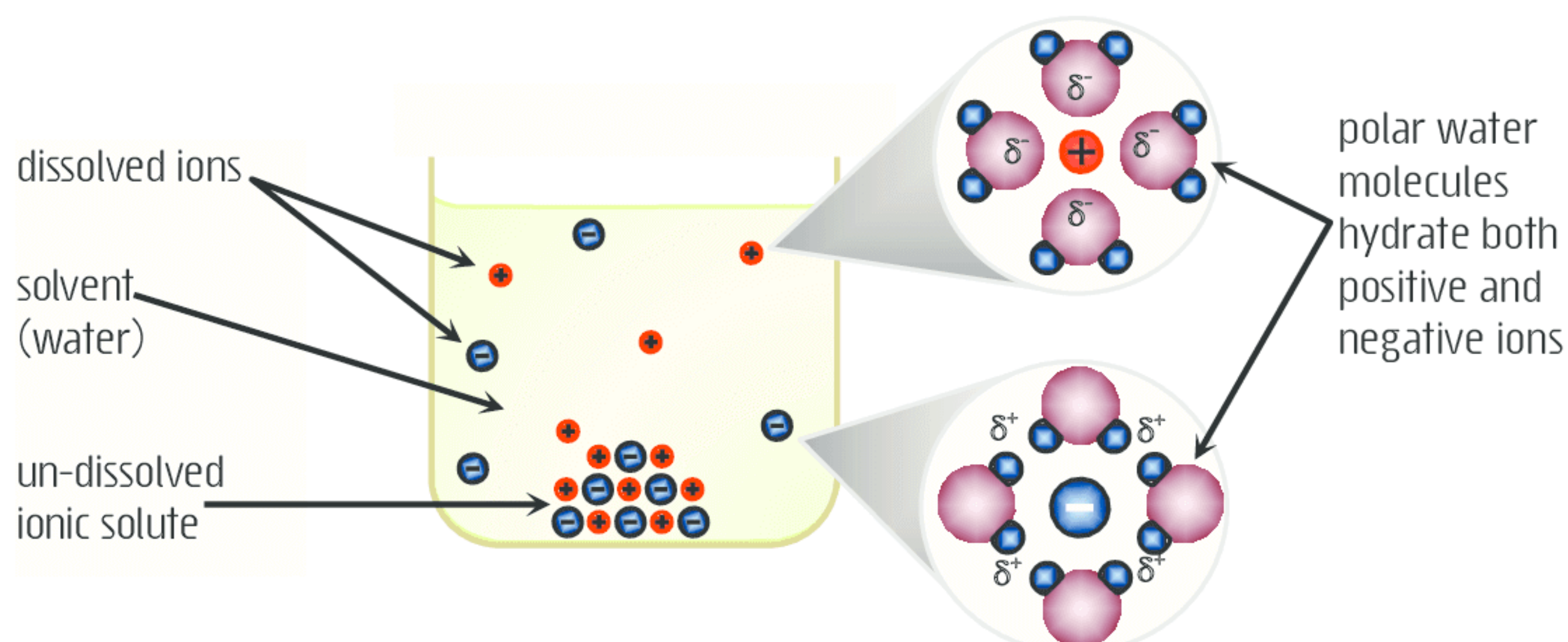


## 16.4 Ionic solubility and solvation

The solubility of ionic compounds depends largely on the **solvation** properties of polar solvents. Solvation involves the attraction of polar solvent molecules to both the positive and negative ions of an ionic solid. The highly polar nature of water molecules (Fig 5) allows water to be an excellent solvent for many ionic solutes.

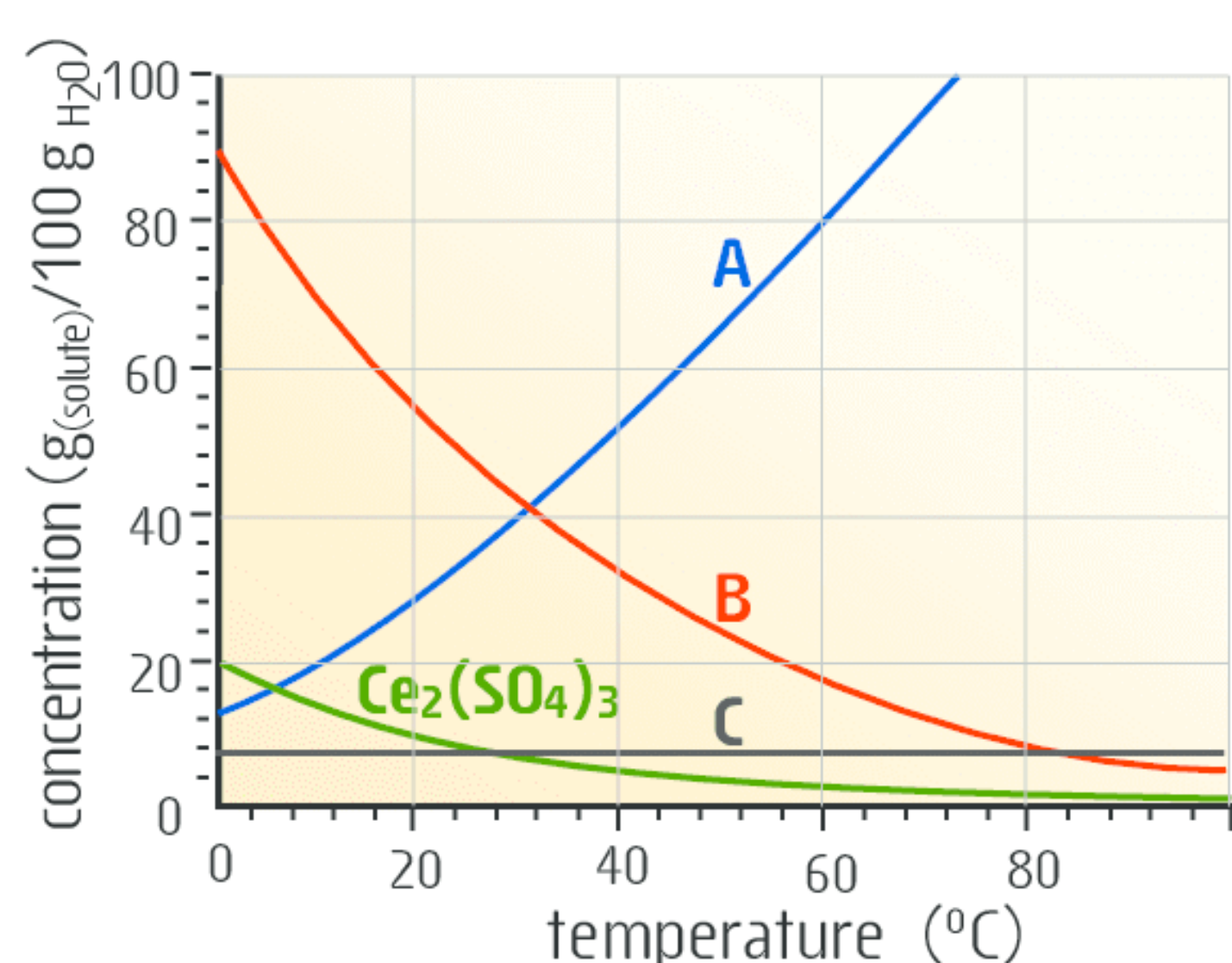
Solvation by water is known as **hydration**. It occurs because of the electrostatic forces of attraction, called **ion-dipole** forces, that form between an ion and the dipole of a water molecule. This involves the slightly positive ( $\delta^+$ ) hydrogen atoms in a water molecule being attracted to a negative ion while the slightly negative ( $\delta^-$ ) oxygen atom in the water molecule is attracted to a positive ion. These ion-dipole forces lead to hydration where each ion in solution is surrounded by several water molecules. The high solubility of many ionic solids in water is largely due to the ion-dipole forces overcoming the strong attractive forces between oppositely charged ions in the ionic solid. (See Fig 6.)

**FIGURE 6** When an ionic compound dissolves in water, the polar water molecules attract ions from the ionic lattice and disperse them evenly throughout the solution. This solution process relies on strong **ion-dipole forces** that lead to the ions being **hydrated**.



Complete Set 26.

## Set 26 Electrolytes in solution



**FIGURE 7** Graph of solubility in water with temperature for various substances, A, B, C and cerium sulfate.



**FIGURE 8** Solution **concentration** refers to the quantity of solute dissolved in a given quantity of solution. **Molarity (M or mol L<sup>-1</sup>)** is one way of expressing the concentration of a solute in solution. (See p145.)

This 0.1 mol L<sup>-1</sup> (0.1 mole per litre) copper sulfate solution contains 0.1 mole of copper sulfate dissolved in every one litre of solution.

- Give the **term(s)** that describes each of the following:
  - The two components that make up a solution.
  - The uniform way in which the components of a solution are mixed.
  - A solution of CaCl<sub>2</sub>(aq) that can dissolve more CaCl<sub>2</sub>(s).
  - A saturated solution of NaNO<sub>3</sub> that is carefully cooled from 80 °C to 45 °C.
  - The degree to which a solute can dissolve in water.
- The graph at left (Fig 7) shows the solubility of three hypothetical substances, **A**, **B** and **C** and the compound **cerium(III) sulfate**. The following questions refer to these graphs.
  - Which graph has a shape typical of the solubility curve for a gas? **Explain**.
  - What is **unusual** about the solubility curve for Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>?
  - A saturated solution of **A** is prepared at 40 °C using 100 g of water. What **minimum mass** of **A** is needed? What **happens** if this solution is now cooled to 20 °C? **Explain**.
- Use the flow chart in Fig 3 (p139) to decide if the listed compounds undergo dissociation or ionisation when dissolved in water. If ions are produced, write an appropriate **equation** to show this. If the substance dissolves without producing ions write NR (no reaction). Use a double arrow where appropriate.
 

a. sodium hydroxide solid (NaOH)	g. ammonium sulfate solid [(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ]
b. ethanoic acid liquid (CH <sub>3</sub> COOH)	h. hydrogen chloride gas (HCl)
c. copper(II) ethanoate solid [Cu(CH <sub>3</sub> COO) <sub>2</sub> ]	i. hydrogen sulfide gas (H <sub>2</sub> S)
d. ethanol liquid (C <sub>2</sub> H <sub>5</sub> OH)	j. chloroform liquid (CHCl <sub>3</sub> )
e. iron(III) chloride solid (FeCl <sub>3</sub> )	k. potassium dichromate solid
f. sucrose solid (C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> )	l. nitric acid liquid
- Choose from each of the following pairs of solutions the one having the highest electrical conductivity. **Justify** your choice. (See Fig 8 regarding concentration.) **(E)**
  - 1.0 mol L<sup>-1</sup> KCl(aq) or 0.1 mol L<sup>-1</sup> KCl(aq)
  - 1.0 mol L<sup>-1</sup> FeCl<sub>2</sub>(aq) or 1.0 mol L<sup>-1</sup> FeCl<sub>3</sub>(aq)
  - 1.0 mol L<sup>-1</sup> CH<sub>3</sub>COOH(aq) or 1.0 mol L<sup>-1</sup> HCl(aq)



5. Use your understanding of electrolytes and their properties to **account** for the following: **(E)**
- A solution made by dissolving hydrogen chloride gas in water contains very few HCl molecules, even though HCl(g) is composed entirely of molecules.
  - Both NaCl(s) and NaCl(aq) contain ions, yet NaCl(s) is a non-conductor of electricity while NaCl(aq) is a good electrical conductor.
  - Despite AgCl being a strong electrolyte, its solution can never contain a high concentration of Ag<sup>+</sup>(aq) and Cl<sup>-</sup>(aq) ions.
  - A solution of Cu(NO<sub>3</sub>)<sub>2</sub> contains no particles of formula Cu(NO<sub>3</sub>)<sub>2</sub>(aq).

6. The following passage describes the formation of an ionic solution of sodium chloride by mixing NaCl(s) and H<sub>2</sub>O(l). Complete the passage by selecting the correct terms from the ones listed. Note, some of these terms are distractors and will not be used.

When NaCl(s) is added to water, the salt (a) \_\_\_\_\_ forming a random mixture of ions in water. The ability of NaCl(s) to form an (b) \_\_\_\_\_ solution is due to the (c) \_\_\_\_\_ nature of water molecules.

Polar molecules are ones that have an uneven distribution of (d) \_\_\_\_\_. This causes part of the molecule to have a slight positive charge while elsewhere the molecule has a (e) \_\_\_\_\_. The strong polarity of water molecules allows both sodium ions and chloride ions to become (f) \_\_\_\_\_ attracted to water molecules. This results in the formation of (g) \_\_\_\_\_ ions where each ion is strongly attracted by (h) \_\_\_\_\_ forces to several water molecules. The dissolving and hydration of NaCl(s) in water can be represented by the (i) \_\_\_\_\_ equation as shown here: NaCl(s) → (j) \_\_\_\_\_ + \_\_\_\_\_.

**electrostatically**

**Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)**

**ionisation**

**aqueous**

**ion-dipole**

**electrons**

**hydrated**

**dipolar**

**slight negative charge (δ<sup>-</sup>)**

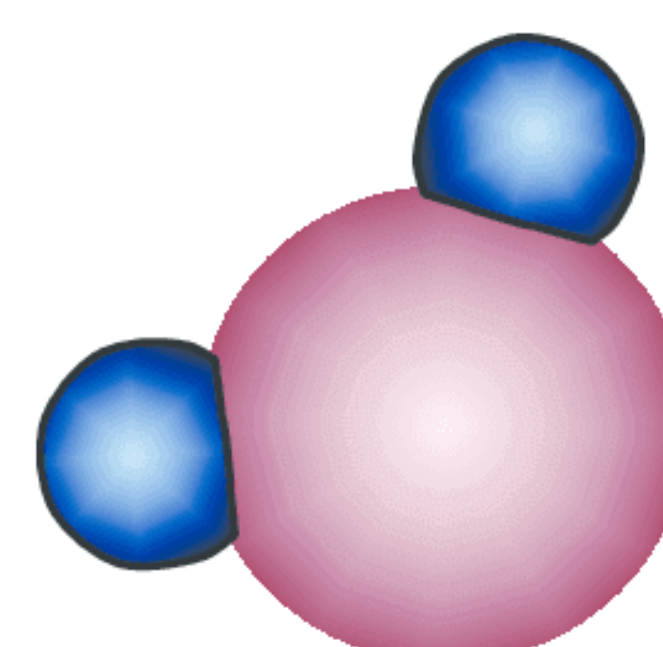
**dissolves**

**polar**

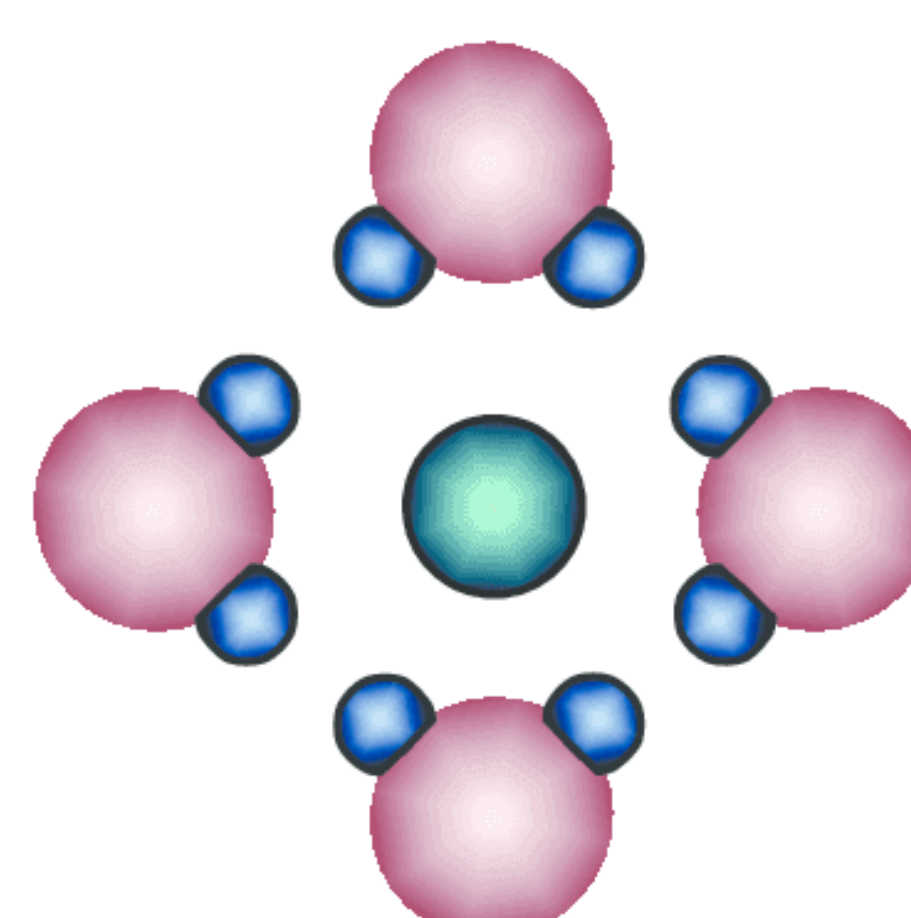
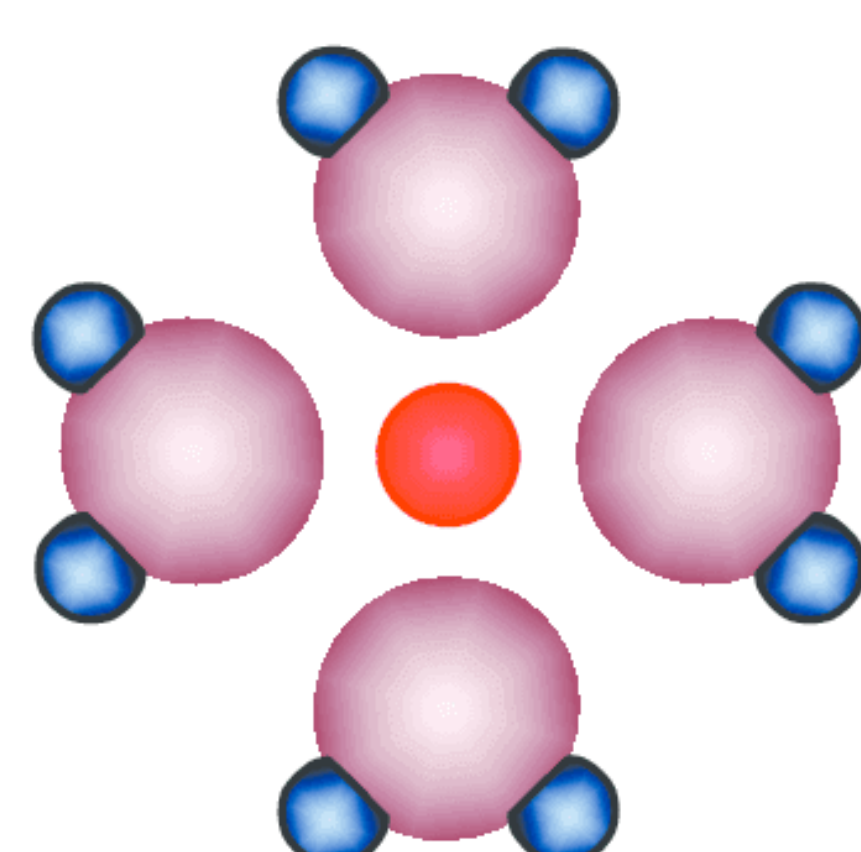
**dissociation**

7. Water is said to be a highly polar solvent. Its ability to dissolve many ionic compounds is due largely to its polarity which causes ions in water to become hydrated. (See border note.)

- a. **Complete** the partially drawn water molecule by labelling the:
- hydrogen atoms
  - oxygen atom
  - slightly positive regions (δ<sup>+</sup>)
  - slightly negative region (δ<sup>-</sup>).



- b. With reference to your labelled diagram in 7(a), **describe** what is meant by the statement, 'Water molecules are polar.'
- c. **Complete** the partially drawn sketch of a hydrated bromide ion and a hydrated potassium ion. On the sketch label water molecules, Br<sup>-</sup>, K<sup>+</sup>, δ<sup>+</sup> and δ<sup>-</sup>.



8. Common table salt (NaCl) is very soluble in water (36 g per 100 g of water) yet only slightly soluble in methanol, CH<sub>3</sub>OH(l) (1.4 g per 100 g of methanol) and insoluble in hexane, C<sub>6</sub>H<sub>14</sub>(l).
- Account** for the high solubility of salt in water. You should include a sketch and refer to ion-dipole forces in your answer.
  - From the data provided, what relationship exists between the solubility of NaCl in a solvent and the solvent's polarity? Is this trend to be expected? **Explain**.

**Water** is such an effective solvent for ionic solutes that it is difficult to find sources of it that do not contain dissolved salts. Around 97.2% of the Earth's water is found in the ocean and this contains 3.5% by mass dissolved salts. The **ions** of greatest concentration in **sea water** are:

Cl <sup>-</sup> (aq).....	0.55 mol L <sup>-1</sup>
Na <sup>+</sup> (aq).....	0.47 mol L <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup> (aq).....	0.028 mol L <sup>-1</sup>
Mg <sup>2+</sup> (aq).....	0.054 mol L <sup>-1</sup>
Ca <sup>2+</sup> (aq).....	0.010 mol L <sup>-1</sup>
K <sup>+</sup> (aq).....	0.010 mol L <sup>-1</sup>



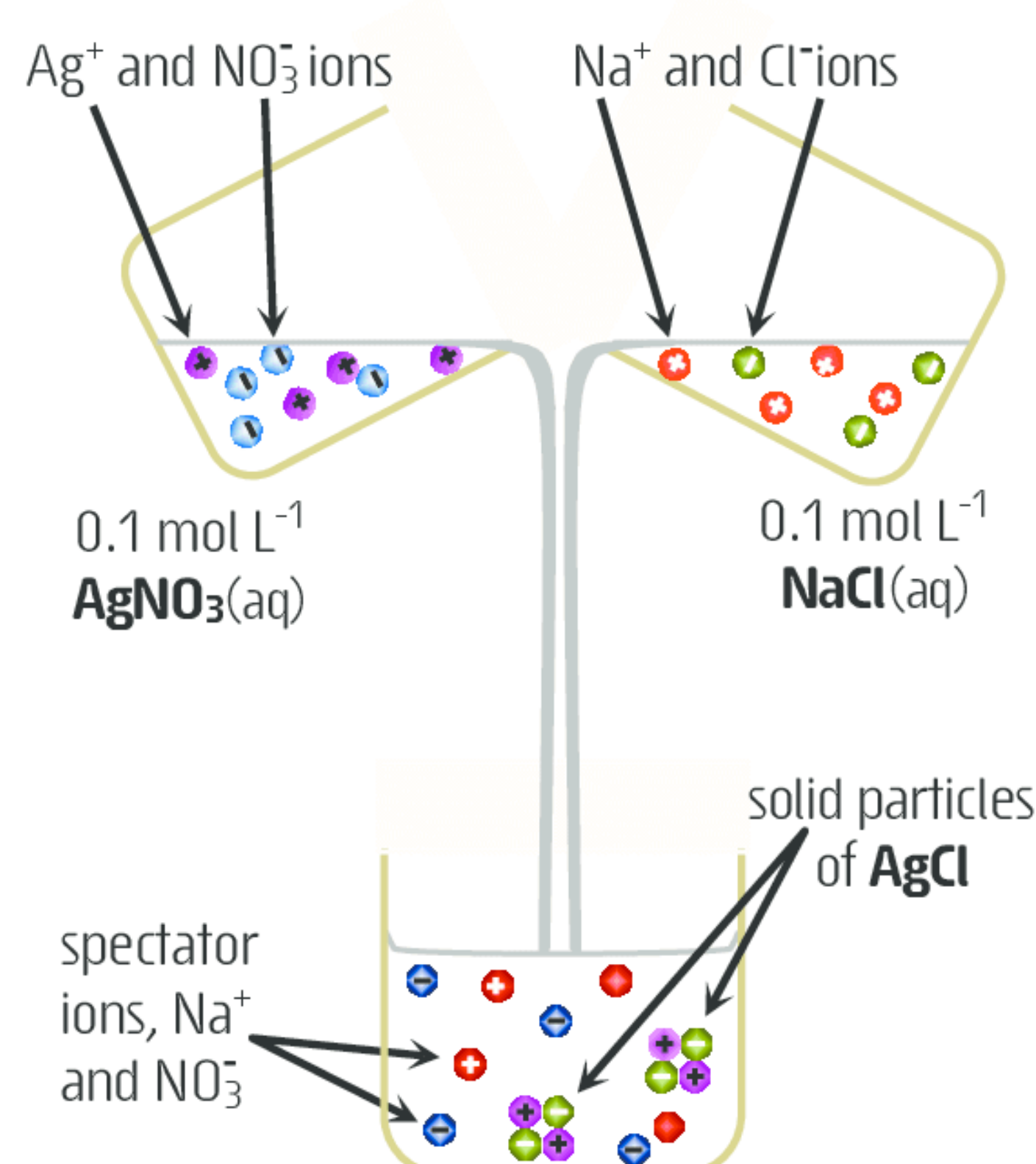
Sea water also contains some other very important dissolved substances like **oxygen** and **carbon dioxide**. In water CO<sub>2</sub> dissolves to produce HCO<sub>3</sub><sup>-</sup>(aq) and CO<sub>3</sub><sup>2-</sup>(aq) ions. These ions are extremely important to marine organisms like mussels, oysters, clams, corals and various microorganisms. These creatures form shells and bones by the precipitation of CaCO<sub>3</sub>(s) from dissolved Ca<sup>2+</sup>(aq) and HCO<sub>3</sub><sup>-</sup>(aq).



**Soluble:** More than 0.10 mol of it can dissolve in 1 L of solution.

**Slightly soluble:** Between 0.10 and 0.01 mol of it can dissolve in 1 L of solution.

**Insoluble:** Less than 0.010 mol of it can dissolve in 1 L of solution.



**FIGURE 9** Mixing  $0.1 \text{ mol L}^{-1} \text{ NaCl(aq)}$  and  $0.1 \text{ mol L}^{-1} \text{ AgNO}_3\text{(aq)}$  produces a solution that is super saturated with  $\text{Ag}^+\text{(aq)}$  and  $\text{Cl}^-\text{(aq)}$  ions. This happens as  $\text{AgCl(s)}$  has a very low solubility. As a result, insoluble  $\text{AgCl(s)}$  immediately precipitates and causes the mixture to go cloudy white. Precipitation continues until the mixture is no longer super saturated with  $\text{Ag}^+\text{(aq)}$  and  $\text{Cl}^-\text{(aq)}$ .

Attempt Set 27 # 2, 3, 4 and 5.

**FIGURE 10** Mixing a few drops of  $0.1 \text{ mol L}^{-1} \text{ NaI(aq)}$  and  $0.1 \text{ mol L}^{-1} \text{ Pb(NO}_3)_2\text{(aq)}$  produces a bright yellow precipitate of  $\text{PbI}_2\text{(s)}$ . This reaction can be used to verify the presence of  $\text{Pb}^{2+}\text{(aq)}$  in solution.



## 16.5 Precipitation reactions

A precipitation reaction occurs when an insoluble solid forms within a previously clear solution. One way this can happen with ionic solutes is when two solutions containing different ions are combined and mixed. If any pair of ions in the mixture of two solutions can form an insoluble compound (see solubility rules Table p249) then the insoluble compound will 'come out' of solution, rapidly forming a **precipitate**. (See Fig 9 and 10.)

During a precipitation reaction the precipitate is in the form of a **suspension**. This consists of many tiny particles of solid that initially remain spread throughout the mixture. This suspension causes the reaction mixture to go cloudy in appearance. Over time the suspended particles will settle out to the bottom of the reaction vessel.

**EXAMPLE 2** Solutions of  $\text{Pb(NO}_3)_2\text{(aq)}$  and  $\text{NaI(aq)}$  are combined and mixed. Will a precipitate form? If so, give its formula. All solution concentrations are  $1 \text{ mol L}^{-1}$ . (See Fig 10.)

Identify and list all ions present in the combined mixture of two solutions.

Ions present in the mixture are:

**$\text{Pb}^{2+}\text{(aq)}$**  and  **$\text{NO}_3^-\text{(aq)}$**  [from  $\text{Pb(NO}_3)_2\text{(aq)}$ ]

**$\text{Na}^+\text{(aq)}$**  and  **$\text{I}^-\text{(aq)}$**  [from  $\text{NaI(aq)}$ ]

Write the formula for possible precipitates by combining pairs of oppositely charged ions.

Possible precipitates are:

**$\text{PbI}_2$**  and  **$\text{NaNO}_3$**

Refer to the solubility rules (Table p249) and determine the solubility of these substances.

$\text{PbI}_2$  is **insoluble**

$\text{NaNO}_3$  is **soluble**

Any insoluble or slightly soluble compound can be expected to form a precipitate.

$\therefore$  a precipitate of  **$\text{PbI}_2\text{(s)}$**  (bright yellow) will form.

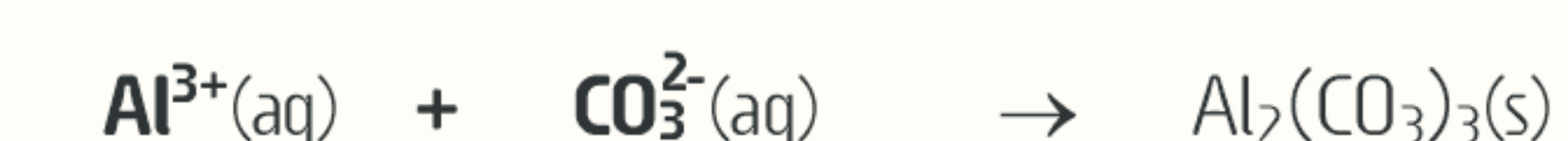
Attempt Set 27 # 1.

**EXAMPLE 3** Write a net ionic equation for the precipitation of  $\text{Al}_2(\text{CO}_3)_3$  from a mixture of  $\text{AlCl}_3\text{(aq)}$  and  $\text{Na}_2\text{CO}_3\text{(aq)}$ .

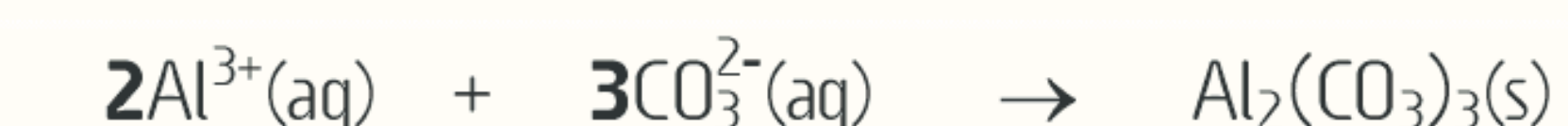
Write the precipitate formula on the product side of the equation.



On the reactant side write the ions that form the precipitate.



Balance the equation.



## 16.6 Using precipitation to distinguish compounds

Precipitation reactions can sometimes be used to verify the presence of a particular ion in solution. If a solution is thought to contain lead ions,  $\text{Pb}^{2+}\text{(aq)}$  for example then the addition of some sodium iodide solution,  $\text{NaI(aq)}$  would substantiate this by producing a bright yellow precipitate. (See Fig 10.) This idea can sometimes be used to distinguish between two or more soluble compounds. Using this example, the white solid lead nitrate,  $\text{Pb(NO}_3)_2\text{(s)}$  can be distinguished from the white solid calcium nitrate,  $\text{Ca(NO}_3)_2\text{(s)}$ . To do this each solid is first dissolved in distilled water in two separate test tubes. A few drops of sodium iodide solution,  $\text{NaI(aq)}$  are then added to each solution. The  $\text{Pb(NO}_3)_2\text{(aq)}$  will be distinguished as it produces a bright yellow precipitate while the  $\text{Ca(NO}_3)_2\text{(aq)}$  will remain a clear colourless solution.

This technique only works if the substances to be distinguished contain at least one ion with a different pattern of solubility. For this reason it is not possible to use precipitation to distinguish solutions like  $\text{NaNO}_3\text{(aq)}$  and  $\text{KNO}_3\text{(aq)}$ . Although these solutions contain different cations, ie  $\text{Na}^+\text{(aq)}$  and  $\text{K}^+\text{(aq)}$ , these cations have the same pattern of solubility.

**EXAMPLE 4** Describe how you could use a chemical test based on precipitation to distinguish between the two aqueous solutions **barium chloride** [ $\text{BaCl}_2\text{(aq)}$ ] and **barium iodide** [ $\text{BaI}_2\text{(aq)}$ ]. Indicate the observations you would expect and the inferences you could make.

List the ions present in each solution.

Ions present:  **$\text{BaCl}_2\text{(aq)}$**  contains  **$\text{Ba}^{2+}\text{(aq)}$**  and  **$\text{Cl}^-\text{(aq)}$**

**$\text{BaI}_2\text{(aq)}$**  contains  **$\text{Ba}^{2+}\text{(aq)}$**  and  **$\text{I}^-\text{(aq)}$**

Using solubility rules identify any different pattern of solubility for the ions present.

The same cation,  **$\text{Ba}^{2+}\text{(aq)}$**  is present in each of the unknown solutions so this can't be used to distinguish them. The two anions however, do have a different pattern of solubility with  **$\text{Ag}^+\text{(aq)}$** . Chloride,  **$\text{Cl}^-\text{(aq)}$**  produces a white precipitate,  **$\text{AgCl(s)}$**  while  **$\text{I}^-\text{(aq)}$**  produces a pale yellow precipitate,  **$\text{AgI(s)}$** .

Based on this, choose a suitable test reagent.

The test reagent needs to be an aqueous solution of  **$\text{Ag}^+\text{(aq)}$** . As all nitrates are soluble use a solution of  **$\text{AgNO}_3\text{(aq)}$**  as the test reagent.

Conduct the test and identify the unknowns from your observations.

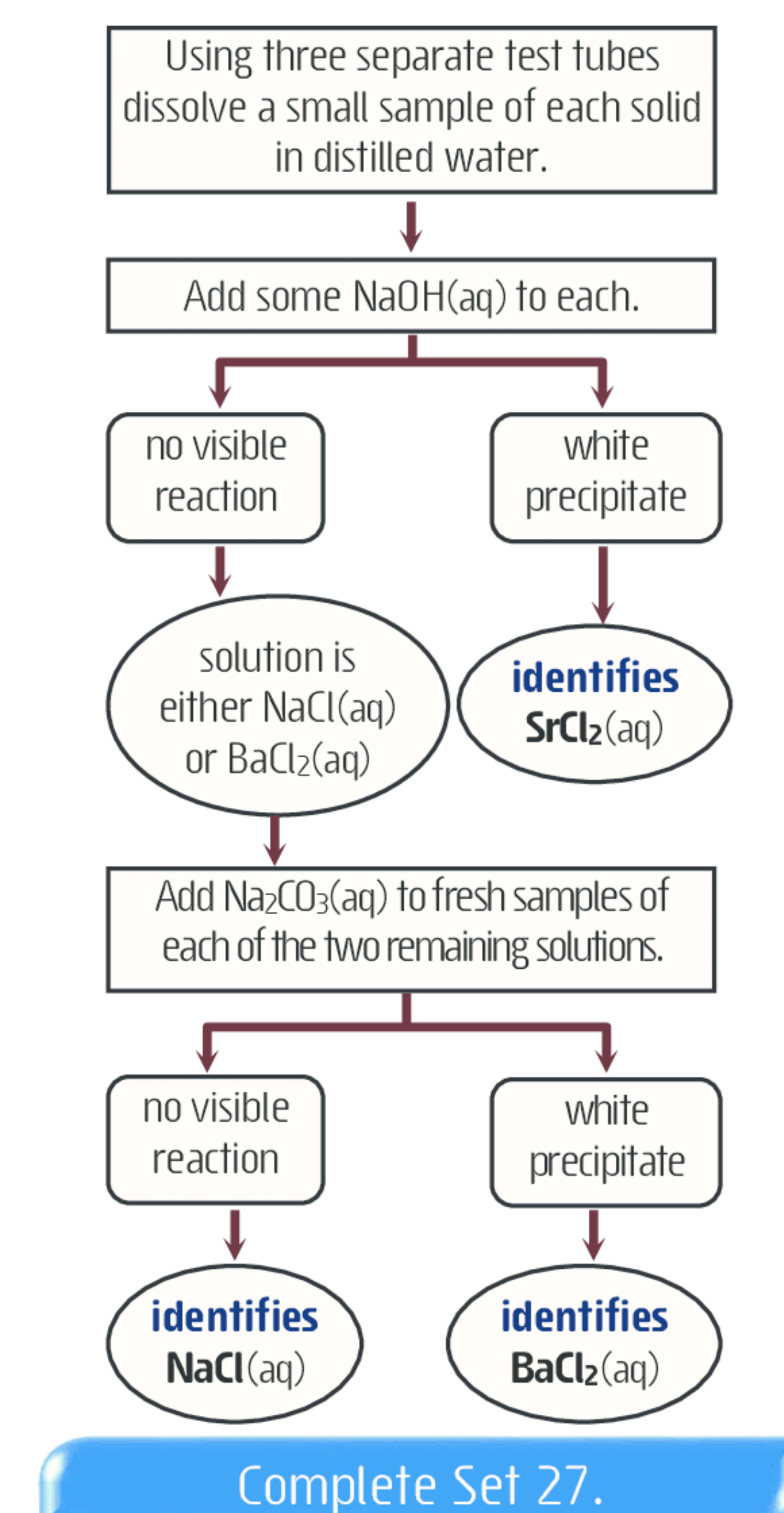
Place samples of the unknown solutions into two separate test tubes. Add a few drops of the test reagent  $\text{AgNO}_3\text{(aq)}$  to each. The solution producing a **white precipitate** must be  $\text{BaCl}_2\text{(aq)}$ . The **creamy yellow precipitate** identifies  $\text{BaI}_2\text{(aq)}$ .



**EXAMPLE 5** Describe a procedure using precipitation that distinguishes the three white solids, **barium chloride** [BaCl<sub>2</sub>(s)], **strontium chloride** [SrCl<sub>2</sub>(s)] and **sodium chloride** [NaCl(s)]. Indicate any observations you would expect and the inferences you could make. (See Fig 11.)

Using three separate test tubes dissolve the solids in distilled water.	Each of the substances is a white soluble solid so expect three clear colourless solutions to be formed. (These are the unknown solutions to be tested.)
List the ions present in each of the unknown solutions.	The ions present are: BaCl <sub>2</sub> (aq) contains <b>Ba<sup>2+</sup></b> (aq) and <b>Cl<sup>-</sup></b> (aq) SrCl <sub>2</sub> (aq) contains <b>Sr<sup>2+</sup></b> (aq) and <b>Cl<sup>-</sup></b> (aq) NaCl(aq) contains <b>Na<sup>+</sup></b> (aq) and <b>Cl<sup>-</sup></b> (aq)
Identify any solubility differences for the ions present.	The same anion, Cl <sup>-</sup> (aq) is present in each of the unknown solutions so this can't be used to distinguish them. Of the cations, Sr <sup>2+</sup> (aq) produces a white precipitate with <b>OH<sup>-</sup></b> (aq) while the other two cations, Na <sup>+</sup> (aq) and Ba <sup>2+</sup> (aq) would give no reaction.
Based on this, choose a suitable test reagent.	The test reagent needs to be an aqueous solution of <b>OH<sup>-</sup></b> (aq). As all sodium compounds are soluble use a solution of <b>NaOH</b> (aq) as the test reagent.
Conduct the test and identify one of the three unknowns.	Add a few drops of the test reagent NaOH(aq) to each of the three unknown solutions. The one that produces a <b>white precipitate</b> is the SrCl <sub>2</sub> (aq) solution. The other two solutions produce no reaction.
Repeat Step 3 for the remaining two unknowns.	The same anion, Cl <sup>-</sup> (aq) is present in each of the two remaining unknown solutions so this can't be used to distinguish them. Of the cations, Ba <sup>2+</sup> (aq) produces a white precipitate with CO <sub>3</sub> <sup>2-</sup> (aq), PO <sub>4</sub> <sup>3-</sup> (aq) or SO <sub>4</sub> <sup>2-</sup> (aq) while Na <sup>+</sup> (aq) gives no reaction.
Based on this, choose a suitable test reagent.	Use an aqueous solution of CO <sub>3</sub> <sup>2-</sup> (aq), PO <sub>4</sub> <sup>3-</sup> (aq) or SO <sub>4</sub> <sup>2-</sup> (aq) as the test reagent. All sodium salts are soluble so use a solution of Na <sub>2</sub> CO <sub>3</sub> (aq), Na <sub>3</sub> PO <sub>4</sub> (aq) or Na <sub>2</sub> SO <sub>4</sub> (aq) as the test reagent.
Conduct the test and identify the remaining two unknowns.	Add a few drops of the test reagent, eg Na <sub>2</sub> CO <sub>3</sub> (aq) to fresh samples of the two remaining unknown solutions. The one that produces a <b>white precipitate</b> is the BaCl <sub>2</sub> (aq) solution. The solution showing no reaction is NaCl(aq).

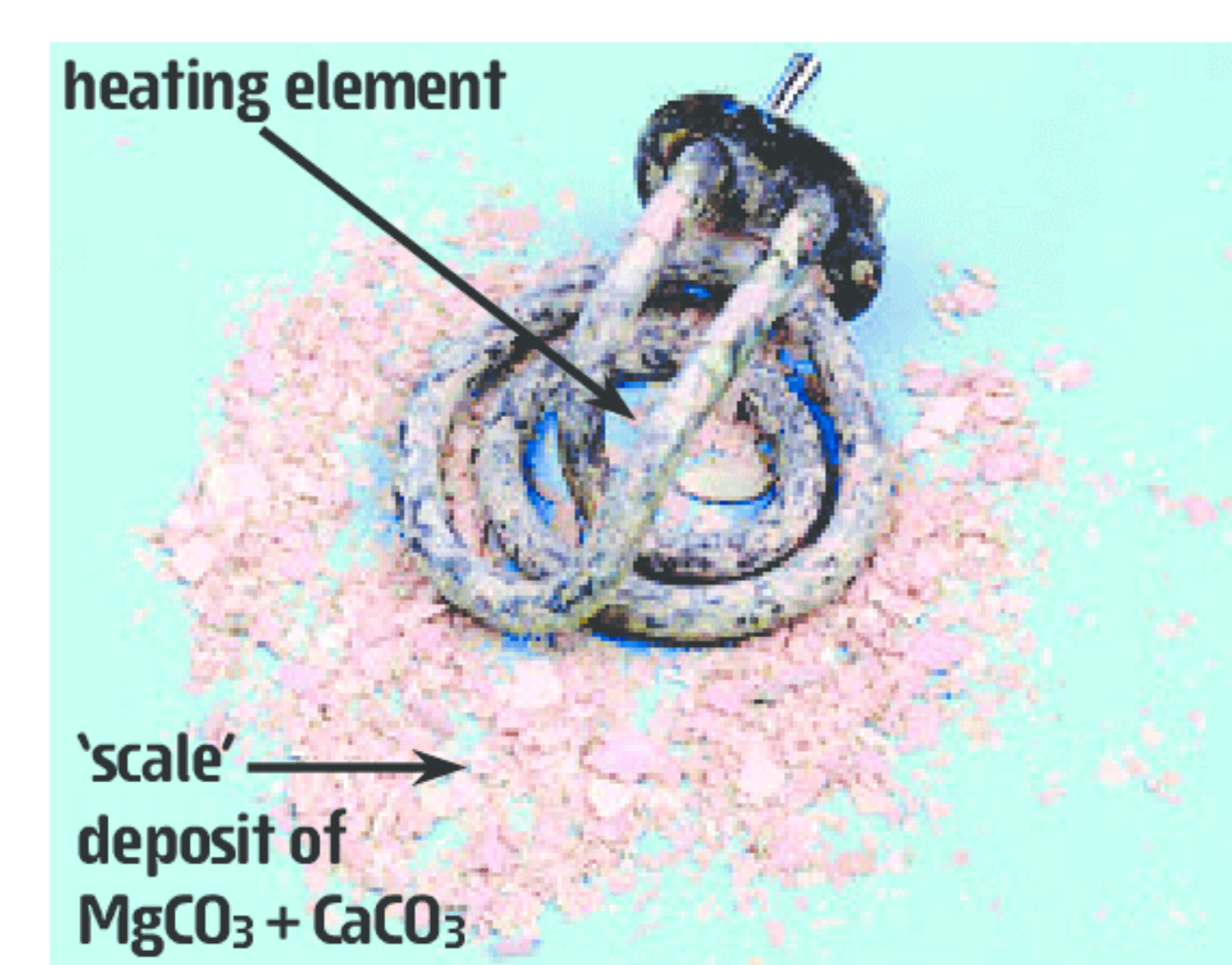
**FIGURE 11** This flow diagram shows how the three solids **BaCl<sub>2</sub>**, **SrCl<sub>2</sub>** and **NaCl** can be identified and distinguished from each other by a series of precipitation reactions.



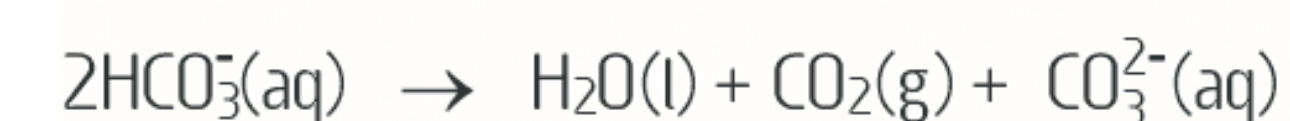
## Set 27 Precipitation reactions

- Alicia and Lara carried out several experiments in which they mixed two different 0.1 mol L<sup>-1</sup> solutions in test tubes and looked to see if a precipitate formed. The solutions they mixed are listed below. In which experiments do you think they will observe a precipitate? If a precipitate is expected, give its **formula** and **colour**.
  - Zn(NO<sub>3</sub>)<sub>2</sub>(aq) and Na<sub>2</sub>CO<sub>3</sub>(aq)
  - FeCl<sub>2</sub>(aq) and KOH(aq)
  - (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>(aq) and MgCl<sub>2</sub>(aq)
  - sodium chloride solution and lead II nitrate solution
  - calcium nitrate solution and sodium sulfate solution
  - barium chloride solution and potassium sulfate solution
- Write a **net ionic equation** for the precipitation of each the following compounds.
  - AgBr
  - Zn(OH)<sub>2</sub>
  - Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>
  - Boiler scale (Fig12) a mixture of MgCO<sub>3</sub> and CaCO<sub>3</sub>
- Gavin and Michael perform the following series of experiments. In which cases do you expect they will observe a precipitation reaction? Where a reaction occurs write a **net ionic equation** to show this and give an **expected observation**.
  - A Na<sub>2</sub>CO<sub>3</sub> solution is mixed with a CaCl<sub>2</sub> solution.
  - KBr(aq) and NaOH(aq) are mixed.
  - A NaCl solution is mixed with a AgNO<sub>3</sub> solution.
  - CaCl<sub>2</sub>(aq) and Ba(OH)<sub>2</sub>(aq) are mixed.
  - A few drops of NaOH solution is added to excess CrCl<sub>3</sub> solution.
  - Some copper nitrate solution is added to a sodium hydroxide solution.
  - A tin(II) chloride solution is combined with a sodium carbonate solution.
  - Cobalt(II) chloride and sodium hydroxide solutions are mixed.
  - Zinc chloride and lead nitrate solutions are combined.
  - Some sodium sulfate solution is added to a calcium chloride solution.
  - Sodium iodide solution and magnesium nitrate solution are combined.
  - Limited potassium hydroxide is added to excess aluminium chloride solution.

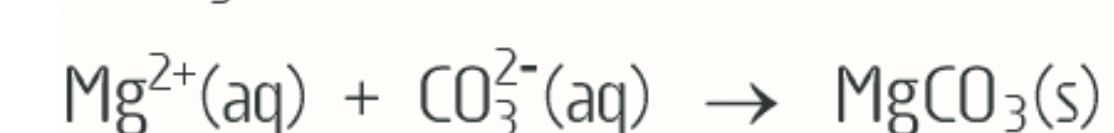
**Solubility rules** and the **colours** of ions and common precipitates can be found in the appendix section on p247 and p249 respectively.



**FIGURE 12** An undesirable precipitation reaction can sometimes occur in kettles and water boilers. This happens if boiled water contains dissolved impurities such as Ca(HCO<sub>3</sub>)<sub>2</sub> or Mg(HCO<sub>3</sub>)<sub>2</sub>. These soluble compounds are often present where water has passed through or over limestone. Water containing these dissolved minerals is termed **temporary hard water**. Heating these solutions decomposes the HCO<sub>3</sub><sup>-</sup> ion.



The formation of carbonate ions, CO<sub>3</sub><sup>2-</sup> then results in the precipitation of insoluble MgCO<sub>3</sub> or CaCO<sub>3</sub>.

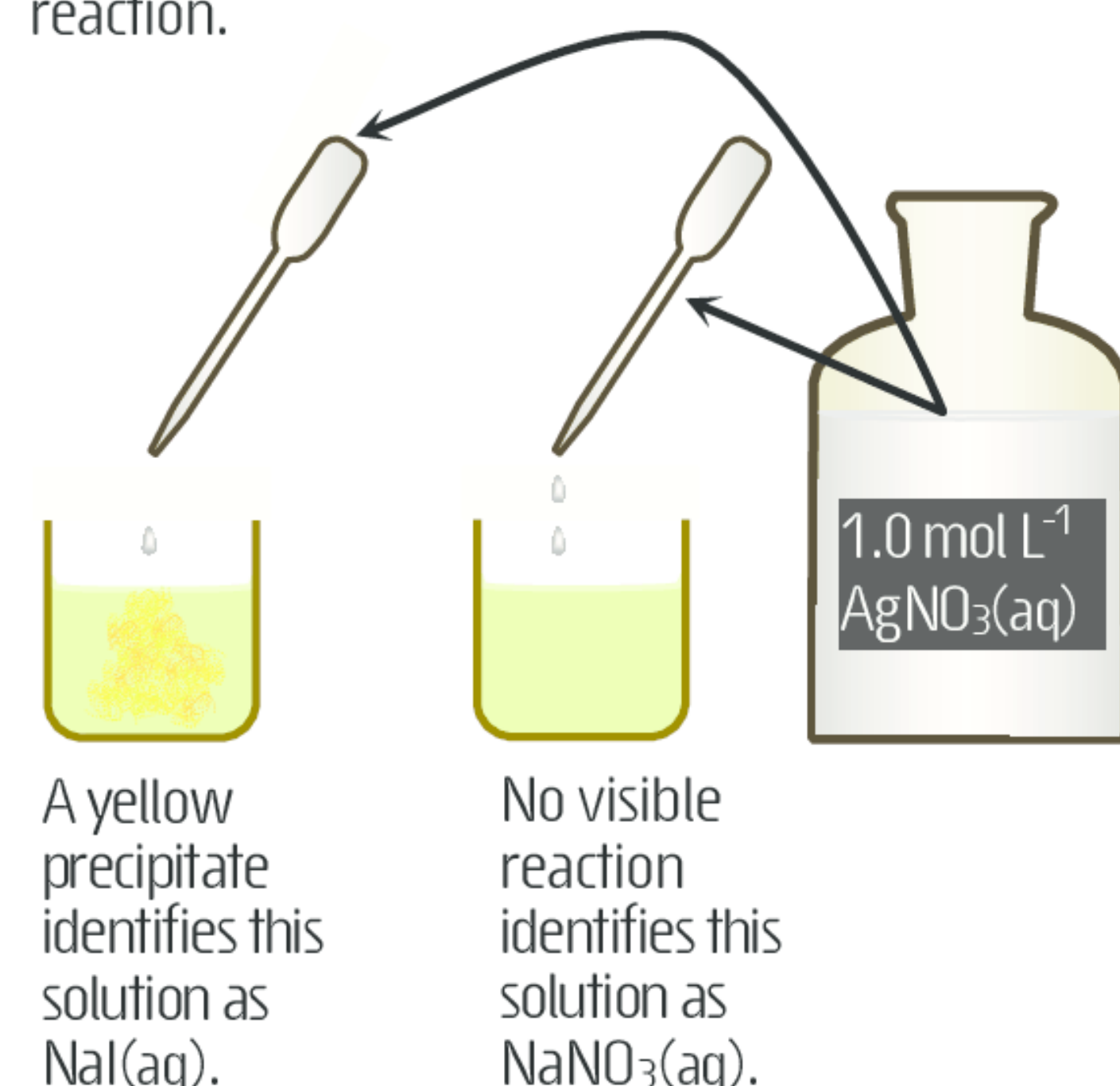


These precipitates form a deposit called **'boiler scale'** on the surface of the heating element. This reduces heating efficiency and may actually lead to the boiler pipes becoming blocked with boiler scale.

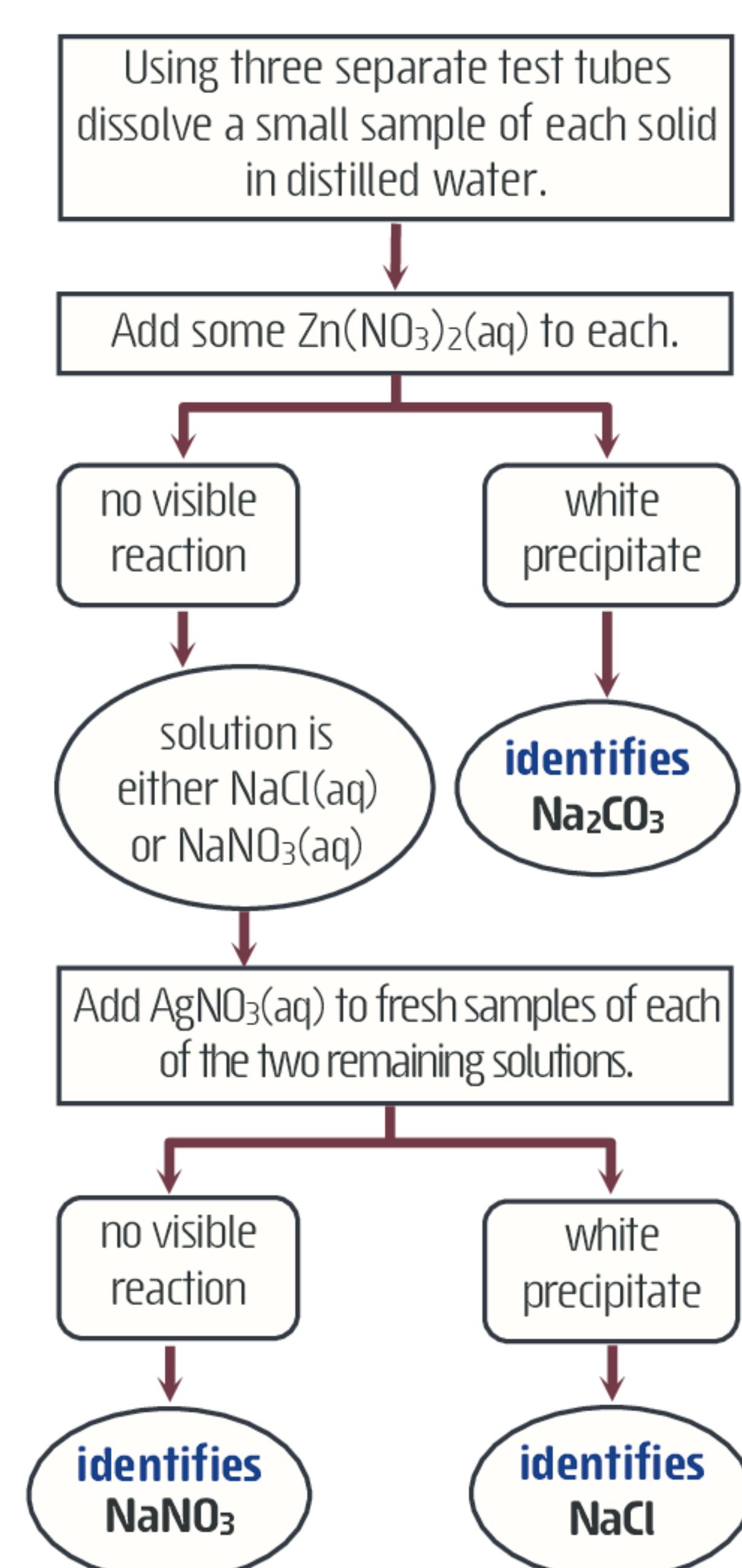
Industrial boilers, such as those in power stations, must use distilled water to avoid the problem of scale formation.



**FIGURE 13** A precipitation reaction can sometimes be used to identify solutions. For example, if a few drops of silver nitrate solution are added to the clear colourless solutions of NaI(aq) and NaNO<sub>3</sub>(aq) then NaI(aq) is identified as it produces a yellow precipitate [AgI(s)], while NaNO<sub>3</sub>(aq) has no reaction.



**FIGURE 14** This flow diagram shows how the three solids NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> can be identified and distinguished from each other by a series of precipitation reactions.



4. In a series of experiments the following observations were made. Unfortunately the student recording these results didn't record which combination of reagents produced each result. The reagents and observations are listed below. What is the most likely combination of reagents responsible for each observation? **Name two reagents** from this list that could have produced each observed result and write the **formula for the precipitate**. See the appendix section for the colours of common ions and compounds.

<b>CoCl<sub>2</sub>(aq)</b>	<b>CuSO<sub>4</sub>(aq)</b>	<b>Pb(NO<sub>3</sub>)<sub>2</sub>(aq)</b>	<b>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(aq)</b>
<b>FeCl<sub>3</sub>(aq)</b>	<b>Na<sub>2</sub>CO<sub>3</sub>(aq)</b>	<b>MgI<sub>2</sub>(aq)</b>	<b>FeSO<sub>4</sub>(aq)</b>

- A brown precipitate formed when a pale brown solution was mixed with a colourless solution.
  - A white precipitate was produced from two clear colourless solutions.
  - A colourless and a pale green solution were mixed and turned cloudy as a pale green precipitate formed.
  - A clear blue solution and a colourless solution were mixed and produced a green precipitate.
  - A bright yellow precipitate was formed from two clear colourless solutions.
  - A pink solution and a clear colourless solution were mixed and formed a red precipitate.
5. Insoluble ionic compounds can be made in the laboratory by a precipitation process. For example, ZnCO<sub>3</sub>(s) can be made by mixing Zn(NO<sub>3</sub>)<sub>2</sub>(aq) with Na<sub>2</sub>CO<sub>3</sub>(aq) then filtering, washing and drying the resulting precipitate. **Name** suitable solutions that when mixed together would precipitate the following compounds.

a. CoCO<sub>3</sub>      b. Ni(OH)<sub>2</sub>      c. Cr(OH)<sub>3</sub>      d. BaSO<sub>4</sub>

6. It is sometimes possible to distinguish between a pair of solutions by using a precipitation reaction. For example, if a few drops of silver nitrate solution are added to the clear colourless solutions of NaI(aq) and NaNO<sub>3</sub>(aq) then NaI(aq) is identified as it produces a yellow precipitate (AgI(s) forms), while NaNO<sub>3</sub>(aq) has no reaction. (See Fig 13.)

The two solutions **NaOH(aq)** and **Na<sub>2</sub>CO<sub>3</sub>(aq)** are both clear and colourless. These solutions contain the same cation, Na<sup>+</sup>(aq), but have different anions. Is it possible to tell these two apart by adding a few drops of one of the following reagents? **Explain**.

**NaNO<sub>3</sub>(aq)**      **Ca(NO<sub>3</sub>)<sub>2</sub>(aq)**      **Fe(NO<sub>3</sub>)<sub>2</sub>(aq)**      **Ba(NO<sub>3</sub>)<sub>2</sub>(aq)**

7. **Explain** how a precipitation reaction can be used to distinguish the solutions of Mg(NO<sub>3</sub>)<sub>2</sub>(aq) and Pb(NO<sub>3</sub>)<sub>2</sub>(aq).

8. Consider the pairs of substances (a) to (d). Is it possible to tell these apart by adding a few drops of one of the following reagents?

**NaBr(aq)**      **Na<sub>2</sub>CO<sub>3</sub>(aq)**      **MgSO<sub>4</sub>(aq)**      **Pb(NO<sub>3</sub>)<sub>2</sub>(aq)**

If so, **state** which **reagent** should be used and what **observation** would be noted.

- Pb(NO<sub>3</sub>)<sub>2</sub>(aq) and Ca(NO<sub>3</sub>)<sub>2</sub>(aq)
  - AgNO<sub>3</sub>(aq) and Ca(NO<sub>3</sub>)<sub>2</sub>(aq)
  - Na<sub>2</sub>CO<sub>3</sub>(aq) and K<sub>2</sub>CO<sub>3</sub>(aq)
  - Fe(NO<sub>3</sub>)<sub>2</sub>(aq) and Fe(NO<sub>3</sub>)<sub>3</sub>(aq)
9. **Describe** how a precipitation reaction can be used to distinguish the two **solids** KCl(s) and KI(s).

10. Using precipitation reactions and reagents of your choosing, show how to distinguish each substance in the following groups of three compounds. You will need to **explain** your process in written form or by using a flow diagram. (See Fig 14.) Remember, to perform a precipitation reaction, the test substances must be in solution. Equations are **not** needed.

- KOH(s), K<sub>2</sub>SO<sub>4</sub>(s) and KCl(s)
- NaCl(s), NaI(s) and Na<sub>2</sub>CO<sub>3</sub>(s)
- MgCl<sub>2</sub>(s), CaCl<sub>2</sub>(s) and BaCl<sub>2</sub>(s)



## 16.7 Solution concentration

While the concentration of a solute in a solution can be expressed using a variety of units (Table 1) it is usually expressed as a ratio of solute to solution:

$$\text{Concentration} \propto \frac{\text{quantity of solute}}{\text{quantity of solution}}$$

Note: 'Solution' includes both solute and solvent.

When expressing the concentration of a solute, the units chosen will depend on the situation. In a laboratory situation, moles per litre ( $\text{mol L}^{-1}$  or M) would be preferred, parts per million (ppm) would be appropriate for solutes of very low concentration and % by mass or grams per litre ( $\text{g L}^{-1}$ ) might be useful for everyday packaging information. (See Fig 15.)

TABLE 1 Equations for calculating solution concentration

Concentration	Equation	Explanation
<b>moles per litre</b> (molarity) $\text{mol L}^{-1}$	$c = \frac{n}{V}$	<b>c</b> is the concentration of solute in moles per litre ( $\text{mol L}^{-1}$ ) <b>n</b> is the amount of solute in moles (mol) <b>V</b> is the volume of solution (solvent + solute) in litres (L)
<b>grams per litre</b> $\text{g L}^{-1}$	$c_{\text{g L}^{-1}} = \frac{m}{V}$	<b>c<sub>g L<sup>-1</sup></sub></b> is the concentration of solute in grams per litre ( $\text{g L}^{-1}$ ) <b>m</b> is the mass of solute in grams (g) <b>V</b> is the volume of solution (solvent + solute) in litres (L)
<b>parts per million</b> (by mass) ppm	$c_{\text{ppm}} = \frac{m_s \times 10^6}{m_t}$	<b>c<sub>ppm</sub></b> is the concentration of solute in parts per million by mass (ppm) <b>m<sub>s</sub></b> is the mass of solute in grams (g) <b>m<sub>t</sub></b> is the mass of solution (solvent + solute) in grams (g)

**EXAMPLE 6** A solution of sodium carbonate was prepared by dissolving 4.35 g of  $\text{Na}_2\text{CO}_3$  in a small amount of water. Then using a volumetric flask (Fig 16), the solution volume was made up to 250.0 mL. The final solution has a total mass of 252.4 g. Determine the concentration of this solution in:

- a.  $\text{mol L}^{-1}$       b.  $\text{g L}^{-1}$       c. ppm.

**a. moles per litre**

$$n(\text{Na}_2\text{CO}_3) = \frac{m}{M} = \frac{4.35}{105.99} = \mathbf{0.0410 \text{ mol}}$$
 Find the moles of solute from its given mass.

$$c(\text{Na}_2\text{CO}_3) = \frac{n}{V} = \frac{0.0410}{0.2500} = \mathbf{0.164 \text{ mol L}^{-1}}$$
 Find the solute concentration in  $\text{mol L}^{-1}$  by using the solution volume (0.2500 L) and the moles of solute (0.0410 mol).

**b. grams per litre**

$$c(\text{Na}_2\text{CO}_3) = \frac{m}{V} = \frac{4.35}{0.2500} = \mathbf{17.4 \text{ g L}^{-1}}$$
 Using the volume of solution (0.2500 L) and mass of solute (4.35 g) find the solute concentration in  $\text{g L}^{-1}$ .

**c. parts per million**

$$c(\text{Na}_2\text{CO}_3) = \frac{m_s \times 10^6}{m_t} = \frac{4.35 \times 10^6}{252.4} = \mathbf{17200 \text{ ppm}}$$
 Using the mass of solution (252.4 g) and the mass of solute (4.35 g) find the solute concentration in parts per million.

Attempt Set 28 # 1 to 9.

## 16.8 Ion concentration in strong electrolyte solutions

Strong electrolytes are those solutes that when dissolved in water, are completely in the form of independent ions. All ionic compounds and the strong acids, typically including sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ) and hydrochloric acid ( $\text{HCl}$ ) are strong electrolytes. The concentration of each ion from a strong electrolyte equals the electrolyte concentration, multiplied by the ion's subscript from the solute's chemical formula. (See border note.)

**EXAMPLE 7** What is the concentration of all of the ions in the following two solutions?

- a.  $3.1 \text{ mol L}^{-1} \text{Al}_2(\text{SO}_4)_3(\text{aq})$   
b.  $0.80 \text{ mol L}^{-1} (\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2(\text{aq})$

a.  $c[\text{Al}^{3+}(\text{aq})] = 2 \times c[\text{Al}_2(\text{SO}_4)_3] = 2 \times 3.1 = \mathbf{6.2 \text{ mol L}^{-1}}$   
 $c[\text{SO}_4^{2-}(\text{aq})] = 3 \times c[\text{Al}_2(\text{SO}_4)_3] = 3 \times 3.1 = \mathbf{9.3 \text{ mol L}^{-1}}$

As  $\text{Al}^{3+}$  has a subscript of 2 and  $\text{SO}_4^{2-}$  has a subscript of 3.

b.  $c[\text{NH}_4^+(\text{aq})] = 2 \times c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2] = 2 \times 0.80 = \mathbf{1.6 \text{ mol L}^{-1}}$   
 $c[\text{Fe}^{2+}(\text{aq})] = 1 \times c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2] = 1 \times 0.80 = \mathbf{0.80 \text{ mol L}^{-1}}$   
 $c[\text{SO}_4^{2-}(\text{aq})] = 2 \times c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2] = 2 \times 0.80 = \mathbf{1.6 \text{ mol L}^{-1}}$

Since  $\text{NH}_4^+$  has a subscript of 2,  $\text{Fe}^{2+}$  has a subscript of 1 and  $\text{SO}_4^{2-}$  has a subscript of 2.



FIGURE 15 Many household products have their active ingredients listed as a percentage by mass. **Methylated spirits** for example typically contains **94%** ethanol, **5%** methanol and **1%** petroleum oil by mass.

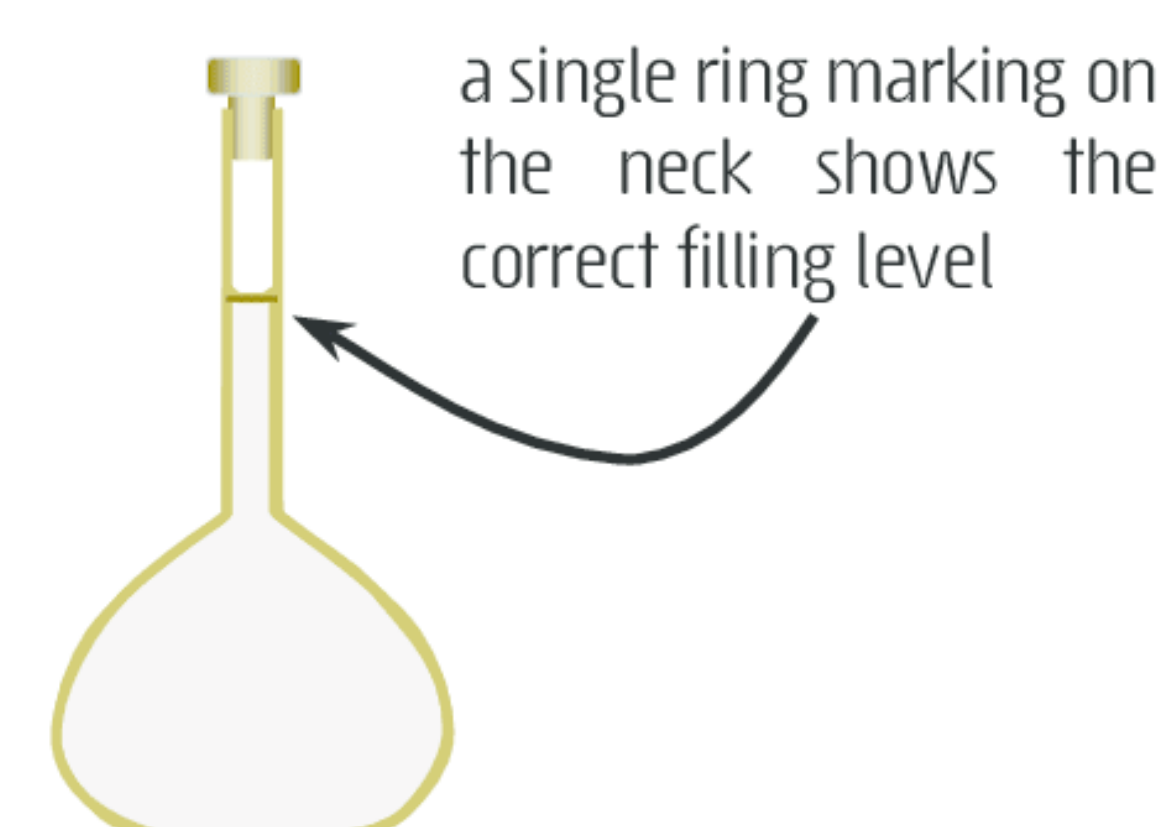
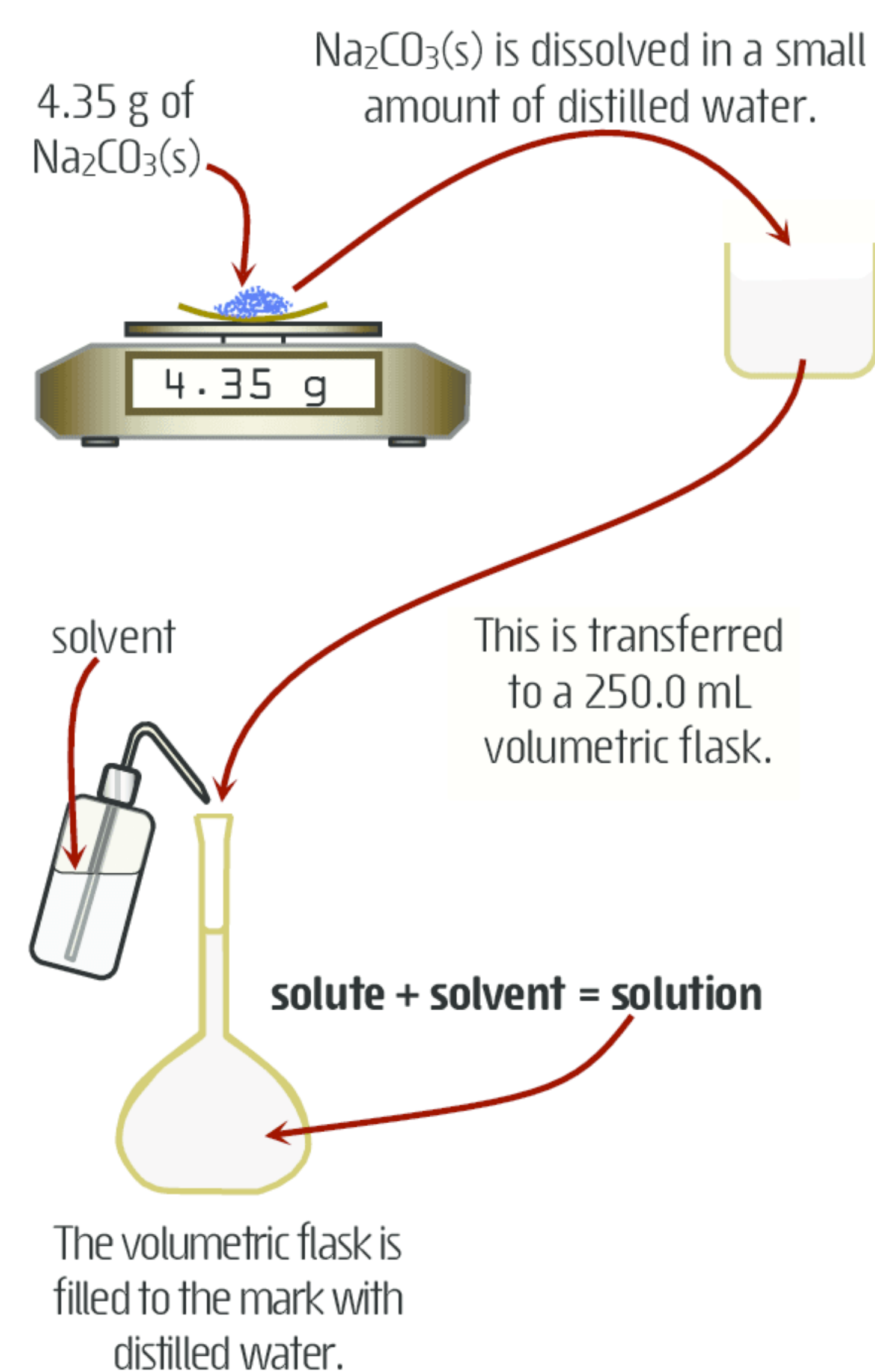
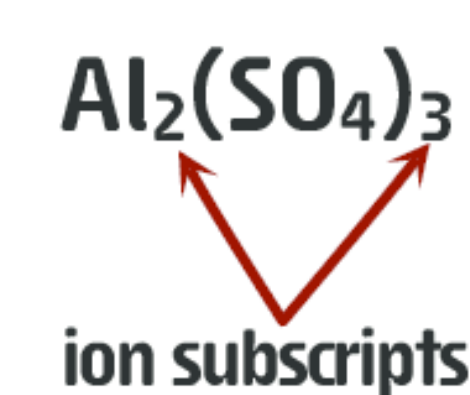


FIGURE 16 A **volumetric flask** is a piece of laboratory glassware used for preparing solutions of a precise concentration. The flask measures a specific volume such as 100.00 mL, 250.00 mL and so on. When filled to the correct volume, the bottom of the meniscus is aligned with a single ring graduation mark on the neck of the flask.

Here a **primary standard solution** of  $\text{Na}_2\text{CO}_3$ , ie a solution of an accurately known concentration is being prepared using a volumetric flask.



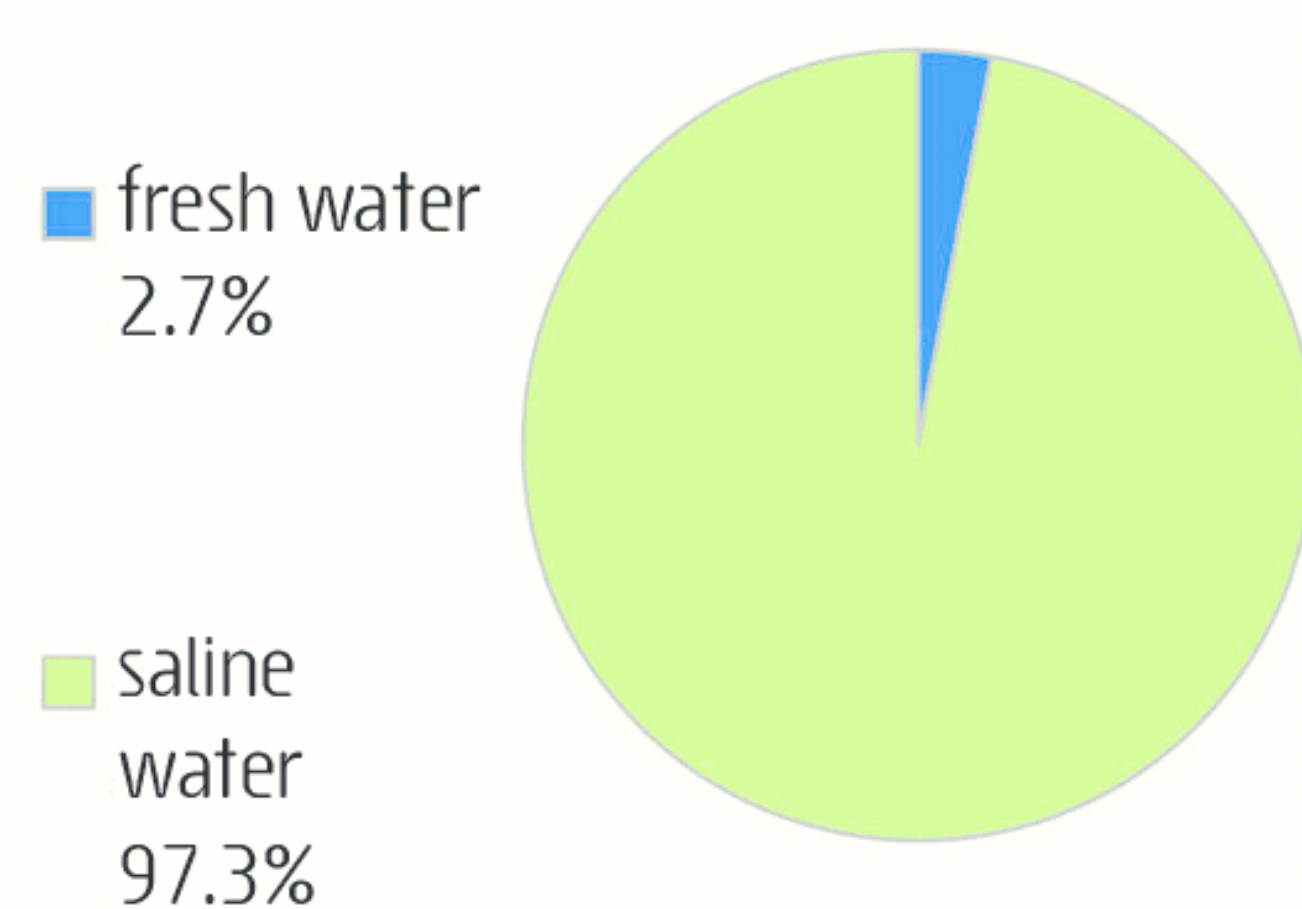
The two ions in aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3$  are the aluminium ion,  $\text{Al}^{3+}$  and the sulfate ion,  $\text{SO}_4^{2-}$ . Their subscripts are **2** and **3** respectively.



Attempt Set 28 # 10 and 11.



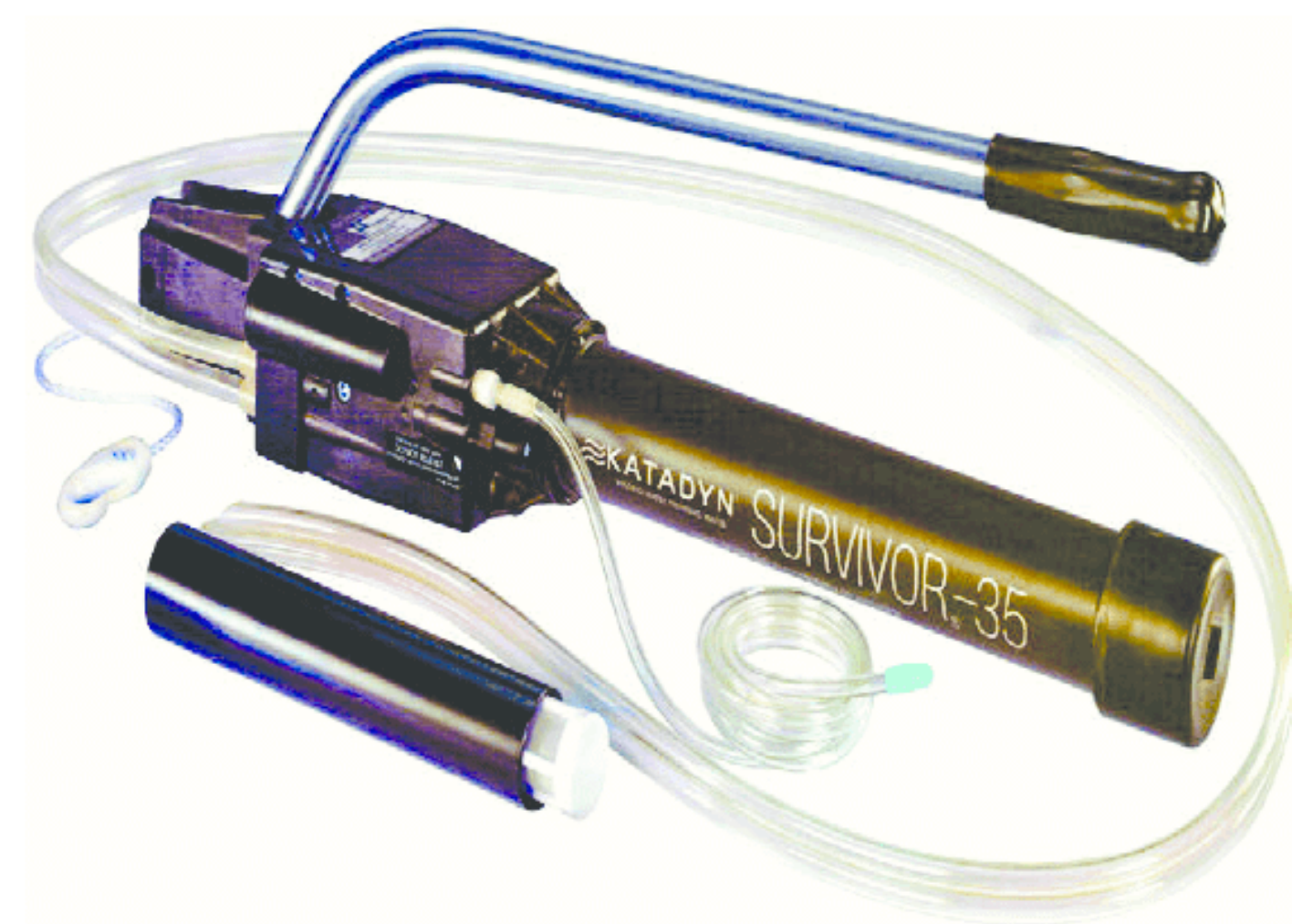
FIGURE 17 Water on the Earth's surface.



Of all the water on Earth **97.3%** is **saline** with 97.2% of it in the ocean. Only **2.7%** occurs as **fresh water**. Most of this (68%) is tied up in the polar ice caps and glaciers with only **0.6 %** of the total available as fresh water in rivers, lakes, swamps or groundwater.

Attempt Set 28 # 12 and 13.

FIGURE 18 Hand held and operated **reverse osmosis** desalination units like this are suitable for producing potable water in a wide variety of situations. Note the lever handle used to pump and apply the pressure needed to initiate reverse osmosis. Image courtesy of Katadyn Products Inc.



## 16.9 Need a drink?

On average, water makes up around 55–78% of a person's body mass, though this varies with gender, age and body weight. In our bodies, water plays a vital role as a solvent for metabolic processes, for transporting nutrients and is essential for the excretion of cellular waste from our body. Evaporation of water from our skin also helps regulate body temperature. It is said we can go a few weeks without food but only days without water.

Although water is the most abundant compound on the Earth's surface finding some to drink is not so easy. (See Fig 17.) Most of the water around us is not suitable for drinking or cooking, as it contains dissolved salts which would dehydrate us or dissolved substances like organic compounds or heavy metals which may be toxic to our organs or carcinogenic (cancer causing). Even freshwater supplies may not be potable if they contain suspended matter such as clay particles or microorganisms (pathogens) that can cause diseases like cholera or dysentery.

A good understanding of chemical principles and methods of analysis are vital in designing and maintaining water treatment facilities for the production of water that is safe to drink and cook with. Water like this is known as **potable water**. Potable water should be clear, colourless, odourless, contain no pathogens or toxic substances and be pleasant to taste. In Australia the National Health and Medical Research Council (**NHMRC**) provides guidelines for water quality management. While there is no specific limit on the maximum allowable total dissolved solids (**TDS**) in drinking water, the NHMRC recommends 'for good palatability TDS in drinking water should not exceed  $600 \text{ mg L}^{-1}$ '. Such dissolved substances are typically in the form of various non-toxic ions, eg  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SiO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$  or non-toxic dissolved organic matter.

Depending upon the source of water chosen it must be treated differently to make it potable. The traditional source of water in Western Australia has been rivers and dams. Water from these sources typically only required disinfection and fluoridation. However, due to increased demand and changing rainfall patterns, groundwater has become most significant and more recently drinking water is being sourced from the Indian Ocean. Water from these sources requires more intensive treatment to make it potable.

Perth, including the South West, the Goldfields and Agricultural regions share a supply system known as the **Integrated Water Supply System (IWSS)**. In 2012–2013 the IWSS provided approximately 285 billion litres of fresh, clean drinking water to more than 1.9 million people. The mix of water sources for that year was: 40% groundwater, 27% seawater desalination from Kwinana plus a second major desalination plant at Binningup and surface water provided 33%. The proportion of desalinated water has now increased to well above 40% as the second stage of the 'Southern Seawater Desalination Plant' (Binningup plant) is now fully commissioned.

### 16.10 Potable water from seawater

The most abundant water source on Earth is sea water. Its high salinity, typically greater than  $35,000 \text{ mg L}^{-1}$  TDS, make it unsuitable for drinking, washing or agriculture. Two approaches used to produce potable water from sea water are **distillation** and **reverse osmosis**. (See Fig 18.) The principle of sea water distillation is the same as that applied in the laboratory (p26). Water, a volatile solvent, is evaporated from sea water, that contains salt, a non-volatile solute. The resulting water vapour is condensed to produce distilled water free of any dissolved salts. Usually the evaporation is carried out in several stages at progressively lower pressure, called multi-stage flash distillation, so that less energy is needed in the evaporation process. Also by using a heat exchange process the heat released from the condensation of water vapour is transferred to incoming cold sea water. This increases energy efficiency by recycling some of the heat used in the evaporation process. Despite this, the greatest disadvantage of distillation is its high energy demand.

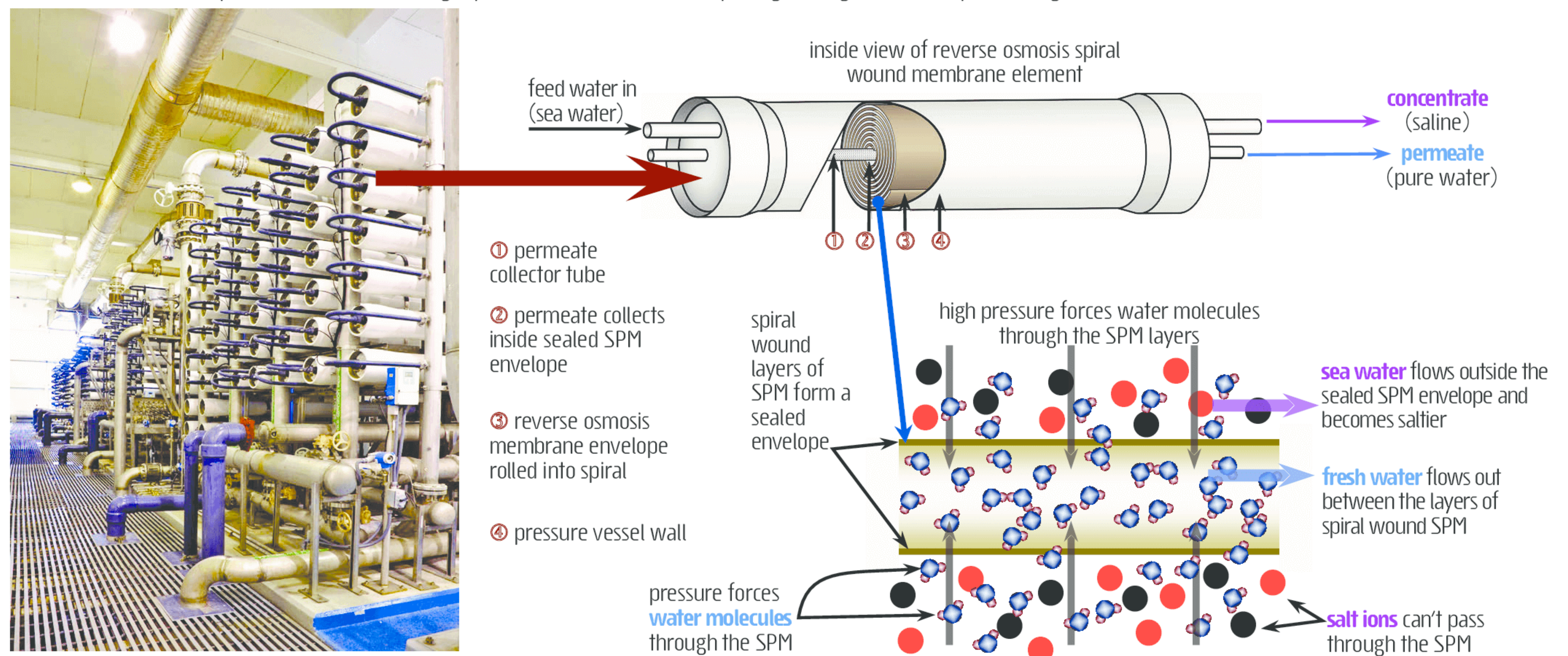
Another approach to obtaining fresh water from sea water involves a natural process, called osmosis, that plants use to draw water from the soil into their roots. The cell membrane of plant root cells acts like a **semi permeable membrane (SPM)** that allows water molecules to pass through but not larger molecules or salt ions. **Osmosis** is the natural tendency of water to diffuse through a SPM from a solution of low salt concentration to one of a higher salt concentration until the salt concentration on both sides of the SPM is the same. Thus plant root hair cells are able to absorb water through their cells SPM because the salt concentration inside the cells is maintained at a higher level than in the surrounding fresh water. As a result pure water is drawn into the cell's saltier interior by osmosis. If plants are watered with salty water they wilt because osmosis causes water to flow out of their root cells into the saltier surrounding water.



Commercial **reverse osmosis (RO)** units use high pressure to force water through a synthetic semi permeable membrane (**SPM**) in the opposite direction to which water would naturally flow. In this process pressure is applied to salty water (eg sea water), called the feed water, that flows on one side an SPM. This pressure causes water to flow out of the salty feed water and through the SPM to produce pure water. During RO the feed water becomes saltier as around 45% or more of the water content is removed. The resulting fresh water is called the **permeate**. (See border note.) Ions, larger organic molecules, cellular organisms and viruses do pass through the SPM.

**Permeate** is the term for a substance that diffuses through a semi permeable membrane. By comparison, **filtrate** is the term for a substance that passes through the microscopic pores of a filter paper during filtration.

**FIGURE 19** The picture below shows a bank of cylindrical **reverse osmosis pressure vessels (PVs)** in a typical desalination plant. Each PV contains several spiral wound membrane elements (SWMEs) connected end on end down the length of the PV tube. Within each SWME fresh water, called permeate is separated from salty feed water (sea water). The SWME consists of several layers of material including a semi permeable membrane (SPM) in the form of a **rolled sealed envelope** plus various channel spacer layers that allow feed water (salty) and permeate water (fresh) to flow between the space on either side of the SPM. **High pressure** forces water molecules through the SPM and into the SPM envelope. Salt ions and other larger particles such as viruses and pathogenic organisms can't pass through the membrane.



In Western Australia, reverse osmosis (RO) is used to produce fresh water at both the Kwinana and Binningup desalination plants. At both plants permeate water (fresh water) is collected then treated for **disinfection** with chlorine as well as being **fluoridated** before storage or addition to the IWSS. Also, as the water produced by RO is essentially deionised water (distilled water) it is necessary to add some salts for both taste and health reasons. This is done by adding both carbon dioxide gas and lime (CaO) and results in a suitable pH as well as a total dissolved salt level of around 200 mg L<sup>-1</sup>.

Although **energy consumption** is a significant issue in all desalination processes, the technology of reverse osmosis, especially the design of the membranes themselves, have greatly improved in the last decade resulting in significantly reduced power needs. Pressure exchange technology further enhances the energy efficiency of RO. This technology is used to transfer the residual high pressure of outgoing salty wastewater to incoming sea water. Reclaiming pressure this way can reduce overall RO plant energy requirements by 50-60%.

Typically reverse osmosis requires around a third the energy input of the most efficient thermal distillation plants. Also, for reasons of **sustainability** and **reduced greenhouse gas emissions** the Water Corporation (of WA) has offset the energy requirements of the Southern Seawater Desalination Plant by purchasing the entire energy output (≈65 MW) of two purpose built renewable energy farms near Geraldton.

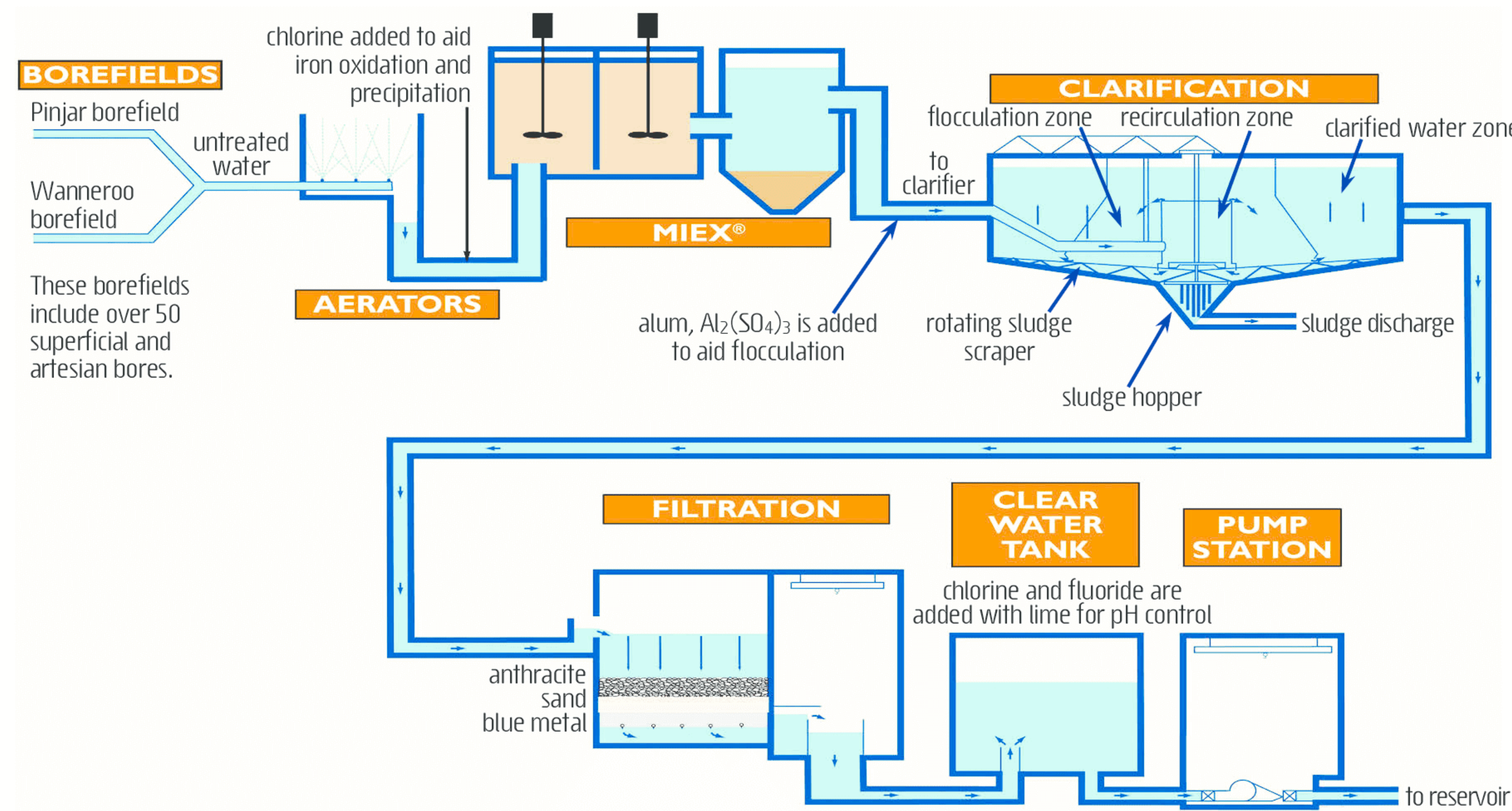
Attempt Set 28 # 14 and 15.

## 16.11 Groundwater treatment

Groundwater currently supplies about 40% of the needs for the IWSS which supplies Perth, the South West, the Goldfields and Agricultural regions. At present around 180 bores are used to draw water from the Yarragadee and Leederville aquifers. Most of these bores are located in Perth's northern suburbs. Groundwater is treated at six groundwater treatment plants to remove contaminants that may include finely suspended solids as well as various dissolved substances like manganese, iron, hydrogen sulfide, carbon dioxide and organic compounds.



**FIGURE 20** The **Wanneroo groundwater treatment plant** features an Australian developed **MIEX®1** Resin process (magnetised ion exchange) that prevents an intermittent 'swampy' odour occurring in treated groundwater supplied to Perth's northern suburbs. Unlike conventional ion exchange, the MIEX®1 resin more effectively removes dissolved organic compounds from drinking water, the source of the odour and taste concerns. Image courtesy of the Water Corporation of WA.



**FIGURE 21 Fluoride** is a naturally occurring ion found in many water sources. Its concentration may vary from less than 0.1 mg L<sup>-1</sup> in surface waters through to greater than 1.5 mg L<sup>-1</sup> in some groundwater sources. Health authorities have long recognised that fluoride levels of up to 1.5 mg L<sup>-1</sup> reduce tooth cavity rates by strengthening tooth enamel. This occurs as fluoride changes the mineral in tooth enamel from **hydroxyapatite**, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH(s) into **fluorapatite**, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F(s), a more acid resistant mineral.



To maximise the public health benefit from fluoridation the fluoride concentration in drinking water supplies in Western Australia is maintained between **0.6–1.0 mg L<sup>-1</sup>**. To confirm acceptable fluoridation, water supplies are sampled and tested at least weekly.

It is also known that constant exposure to higher fluoride levels (greater than 1.5 mg L<sup>-1</sup>) may lead to **dental fluorosis**, an aesthetic mottling of tooth enamel. Very high fluoride exposure can lead to a skeletal problem called skeletal fluorosis.

With this in mind water fluoridation is supported by the World Health Organisation, the Australian Dental Association, the Australian Medical Association and the National Health Medical and Research Council.

Some of the typical processes involved in groundwater treatment include:

- **Aeration:** Groundwater often contains dissolved gases like carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). These increase the acidity of water while H<sub>2</sub>S also gives water a bad odour. Spraying groundwater into the air helps to expel these gases and increase the concentration of dissolved oxygen. The extra dissolved oxygen, along with some added chlorine, oxidise and remove any dissolved organic compounds that may be present. The added Cl<sub>2</sub>(aq) and O<sub>2</sub>(aq) also reduce the solubility of dissolved iron and manganese. This assists in their later removal by clarification and filtration. While neither iron or manganese are toxic, manganese compounds cause water to have a black colouration and iron compounds give water a brown appearance. Both cause staining of clothing and other surfaces.
- **Clarification:** This occurs after aeration and involves the removal of fine particles that may be suspended in the groundwater. Such particles will not normally settle out and their presence causes water to be turbid (unclear) and coloured. Clarification is achieved in a large settling tank where alum, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and lime, CaO are added while stirring. Alum is a coagulant or flocculating agent. It causes fine suspended particles to clump together and quickly settle out. Clarified water is then drawn off the top of the settling tanks.
- **Sand filtration:** Clarified groundwater may still be coloured and contain fine suspended particles. To remove these the water is passed through filter beds of granulated anthracite (coal with up to 98% carbon) and coarse sand. Anthracite is very effective at adsorbing organic materials that otherwise cause water to be coloured.
- **Disinfection:** Despite clarification and filtration, harmful pathogenic bacteria and viruses may be present. Chlorination or chloramination is used to destroy these. The latter involves the use of chlorine in conjunction with ammonia to produce a longer lasting disinfectant. This is particularly relevant to the Goldfields and Agricultural Water Supply Scheme where disinfection is required across an extensive and long network of pipes. Sufficient chlorine is added to ensure its concentration stays slightly above 1 ppm at the consumer outlet.
- **Fluoridation:** The presence of fluoride ions in drinking water is known to reduce tooth cavity rates by strengthening tooth enamel. (See Fig 21.) To maximise the public health benefit from fluoridation the fluoride concentration in drinking water supplies in Western Australia are maintained between 0.6–1.0 mg L<sup>-1</sup> (0.85 mg L<sup>-1</sup> is considered ideal). A maximum dose rate of 1 mg L<sup>-1</sup> is prescribed in the 'Fluoridation of Public Water Supplies Act' which is managed by the Department of Health. Fluoridation involves adjusting the natural fluoride concentration often present in groundwater to between 0.6 mg L<sup>-1</sup> and 1.0 mg L<sup>-1</sup> by adding fluorosilicic acid, (H<sub>2</sub>SiF<sub>6</sub>). In WA this is obtained as a by-product of phosphate fertiliser manufacture. These levels are regularly monitored at each of the individual treatment plants. (See border note.)



▪ **pH:** Australian guidelines specify an aesthetic pH range of 6.5 to 8.5. pH correction is achieved by the addition of lime,  $\text{CaO}$  (for increasing pH) or by dissolving carbon dioxide gas,  $\text{CO}_2$  (lowers pH). Stronger acids and bases such as sulfuric acid or sodium hydroxide may also be used for this purpose.

In some areas groundwater may require further treatment. At the Neerabup Water Treatment Plant in WA the water has been identified as quite '**hard**', meaning it will not easily lather with soap. Hard water is not a health hazard but can lead to the build up of mineral deposits, called scale (essentially a  $\text{CaCO}_3$  deposit, see Fig 12 p143), in kettles, hot water pipes and fittings. Hardness in water is due to the presence of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions and can occur when groundwater is drawn from areas rich in calcium or magnesium minerals. The problem has been addressed at the Neerabup Water Treatment Plant by using a crystallisation process that rapidly precipitates  $\text{Ca}^{2+}$  ions as calcium carbonate onto seed crystals of calcite ( $\text{CaCO}_3$ ).

## 16.12 Water monitoring

As well as managing the water treatment process chemists play an important role in monitoring water quality. The Water Corporation of WA for example, in conjunction with the Department of Health, manage water quality consistent with Australian guidelines as specified by the National Health and Medical Research Council (NHMRC).

This involves extensive regular testing of water quality for a number of properties including **pH**, **total dissolved solids**, **turbidity**, **bacterial** and **viral pathogens** plus a range of potentially toxic metal ions, loosely called **heavy metals**, including, Sb, Cd, Cr, Cu, Al, Pb, Ni, Zn, As, Ba, Be, B, Hg, Mo, Se, Ag and U, as well as a variety of hydrocarbons, pesticides, nitrates ( $\text{NO}_3^-$ ), cyanides ( $\text{CN}^-$ ) and iodides ( $\text{I}^-$ ). In 2011-2012 the Water Corporation in WA took more than 65,000 water samples and produced in excess of 275,000 individual analyses on these samples.

**Arsenic** monitoring is particularly important for bores in the Gwelup region (11 km north of Perth) where very high concentrations of arsenic, iron and aluminium have recently been identified in near surface water. A study of **domestic garden bores** in the Gwelup area in 2004 identified 50 bores with  $\text{pH} < 5.5$ . Of these bores, dissolved iron was recorded at concentrations up to  $1300 \text{ mg L}^{-1}$ , aluminium up to  $290 \text{ mg L}^{-1}$ , and arsenic up to  $0.8 \text{ mg L}^{-1}$ . While there is no health guideline for iron or aluminium, for arsenic this represents a concentration eighty times the NHMRC guideline of  $0.01 \text{ mg L}^{-1}$ . Other tests on water from purpose drilled bores in the area have since recorded arsenic concentrations of up to  $7.3 \text{ mg L}^{-1}$  at shallow depths near the water table. It is **important to note** that water used for public consumption is drawn from much deeper levels in the Gnangara Mound where such contamination has not been recorded. It is important however, to regularly monitor groundwater for the presence of such potential contaminants. (See Fig 22.)

Complete Set 28.

### Set 28 Solution concentration and drinking water

1. What is the **concentration** in  $\text{mol L}^{-1}$  of each solute in the following solutions?
  - a. a 2.40 L solution of  $\text{NaOH(aq)}$  containing 1.41 mol of  $\text{NaOH}$
  - b. a 561 mL sample of vinegar solution containing 0.71 mol of  $\text{CH}_3\text{COOH}$
2. What is the **molarity** (concentration in  $\text{mol L}^{-1}$ ) of the solutes in the following solutions?
  - a. 16.2 g of  $\text{CuSO}_4$  dissolved in 1.94 L of solution
  - b. 139 mg of  $\text{NaCl}$  dissolved in 0.494 L of solution
  - c. 11.77 L of solution containing 129 g of iron(III) sulfate-9-water ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ )

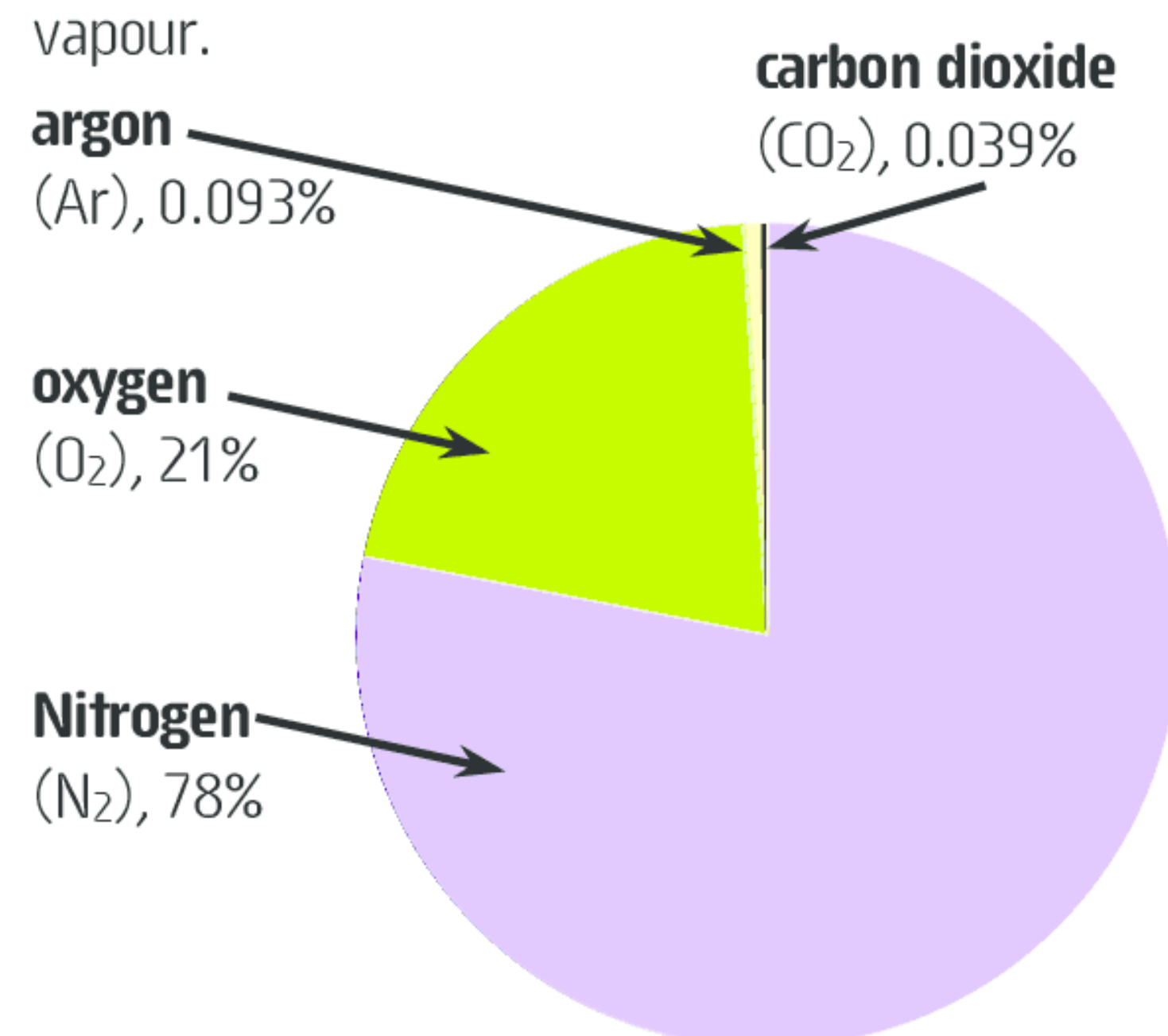


**FIGURE 22** Wells like this **shallow tube well** became a very important water source in Bangladesh from the late twentieth century. This followed an extensive shallow tube well drinking water program intended to provide villagers a bacteria free water supply for drinking washing and agriculture. Unfortunately authorities did not test for **arsenic** in the groundwater and it is now known that many of these shallow wells are heavily contaminated with naturally occurring arsenic. Similar problems are known to occur in many parts of **Southeast Asia**, where similar hydrology results in high concentrations of arsenic in near surface groundwater.

Some effects the villagers suffer as a result of exposure to arsenic in their drinking water include skin rashes and thickening, nausea, diarrhoea and vomiting, partial paralysis, numbness in hands and feet and blindness. Longer term exposure is associated with a variety of cancers such as lung, kidney, liver, prostate, bladder and skin cancer.



**FIGURE 23** The **Earth's atmosphere** is a gaseous solution, ie a homogeneous mixture of gases. The two major components are oxygen and nitrogen with variable amounts of water vapour.



#### How much oxygen is there in your bedroom?

A typical bedroom has the internal dimensions of 3.0 m x 3.0 m x 2.4 m, giving it an internal volume of around 22 m<sup>3</sup>. This space would contain around 22000 L of air (1 m<sup>3</sup> = 1000L) consisting of around:

- 20 kg of  $\text{N}_2(\text{g})$
- 6.0 kg of  $\text{O}_2(\text{g})$
- 0.340 kg of  $\text{Ar}(\text{g})$
- 0.013 kg of  $\text{CO}_2(\text{g})$ .

**FIGURE 24** These one ounce **gold ingots** (one troy ounce  $\approx$  31.1 g) are currently valued at A\$1512 each (<http://goldprice.org> at 6/01/2016). The amount of gold shown here would be present in a volume of seawater equal to over thirty five olympic sized swimming pools!



3. **Calculate** the concentration in **g L<sup>-1</sup>** for the solute in each of following solutions.
  - a. a 375 mL soda water solution containing 1.90 g of dissolved carbon dioxide ( $\text{CO}_2$ )
  - b. a 375 mL soft drink containing 112 g of dissolved sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ).
4. What **mass** of solute is contained in each of the following solutions?
  - a. 15 L of 1.5 mol L<sup>-1</sup>  $\text{Ca}(\text{NO}_3)_2(\text{aq})$
  - b.  $7.50 \times 10^2$  mL of 4.59 mol L<sup>-1</sup>  $\text{Na}_2\text{CO}_3(\text{aq})$
5. Determine the **concentration** in **ppm** for each of the following solutions.
  - a. A sodium carbonate solution with a total volume of 4.375 L containing 122.0 g of  $\text{Na}_2\text{CO}_3$ . The total mass of this solution is 4.460 kg.
  - b. A 562 g sample of tap water that on evaporation was found to have contained 0.75 g total dissolved solids.
6. Georgina's mum buys an orange cordial concentrate that contains 2.5 mol L<sup>-1</sup> sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). On average Georgina uses 35 mL of the cordial concentrate to make herself a glass of refreshing cordial drink. What **mass** of **sugar** is in Georgina's drink and thus determine the number of **heaped teaspoons** of sugar it contains? Assume a heaped teaspoon contains around 6 g of sugar.
7. Air is a gaseous solution (see Fig 23) as it contains a homogeneous mixture of several different gases. A 16.6 L sample of dry air contains 16.2 g of  $\text{N}_2$ , 4.97 g of  $\text{O}_2$ , 0.275 g of  $\text{Ar}$  and 0.0102 g of  $\text{CO}_2$  gas.
  - a. **Determine** the concentration of oxygen ( $\text{O}_2$ ) and carbon dioxide ( $\text{CO}_2$ ) in air in **g L<sup>-1</sup>**.
  - b. What **volume** of air contains 1.0 kg of oxygen?
  - c. What is the **concentration** of carbon dioxide gas in air in **ppm** by **mass**?
8. The sanitation of most household swimming pools is achieved by adding calcium hypochlorite  $\text{Ca}(\text{ClO})_2$ . This chlorine compound is a strong oxidising agent that kills bacteria and helps to maintain a sanitary swimming pool. A particular swimming pool contains 81 kL of water and requires a  $\text{Ca}(\text{ClO})_2$  concentration of  $5.3 \times 10^{-6}$  mol L<sup>-1</sup>. What **mass** of  $\text{Ca}(\text{ClO})_2(\text{s})$  should be added to the pool to achieve the required chlorination level? You may assume the pool water originally contained no calcium hypochlorite.
9. Gold (Fig 24) is one of the more unexpected elements to be found in sea water. Its estimated concentration in sea water is  $1.4 \times 10^{-3}$  ppm. Given the world's oceans have a mass of  $1.4 \times 10^{21}$  kg determine the total **mass of gold** dissolved in the Earth's oceans.
10. **State** the concentration of all of the ions in each of the following solutions. You may use your calculator though **no working** is required.
  - a. 4.5 mol L<sup>-1</sup>  $\text{HCl}$
  - b. 1.4 mol L<sup>-1</sup>  $\text{Ca}(\text{NO}_3)_2$
  - c. 0.75 mol L<sup>-1</sup>  $\text{Cr}_2(\text{SO}_4)_3$
11. A saturated solution of aluminium sulfate contains 22.5 g of  $\text{Al}_2(\text{SO}_4)_3$  dissolved in a litre of solution. Determine the **concentration** in mol L<sup>-1</sup> of the aluminium and sulfate ions in this solution.
12. Water is a most essential compound for life, industry and agriculture. It is also the most abundant compound on the Earth's surface yet very little of it is suitable for direct use. **Account** for the lack of directly potable water.
13. What is meant by **TDS** as it applies to drinking water and why isn't there a specific upper limit on TDS?



14. An increasing amount of the potable water used in Western Australia is now being sourced from the ocean. A major part of the treatment process used for producing potable water from sea water involves reverse osmosis (RO). Plants use a similar process called osmosis when absorbing water from the soil. They do this by absorbing water into their root hair cells through semi permeable cellular membranes.
- What is meant by **potable** water?
  - Suggest** why an increasing amount of water in WA is being sourced from the ocean.
  - A semi permeable membrane is vital in both osmosis and RO. What is a semi permeable membrane and how is it involved in enabling plants to absorb water from the soil?
  - How is RO in an industrial desalination plant similar but different to the osmosis process that enables plants to absorb water from the soil?
15. Desalination plants are said to be high energy users and thus there are issues of sustainability when sourcing water by this process. Consider the following.
- Most of the energy involved in desalination by RO involves the use of pressure and an SPM to separate various salt ions from water molecules. **Why** should energy be needed to separate ions like  $\text{Na}^+$  from  $\text{H}_2\text{O}$  molecules? **Explain** in terms of chemical bonding.
  - Desalination by distillation is said to use much more energy than RO. Consider the extra physical process (other than the separation of ions from water) involved in desalination by distillation and thus **explain** why more energy is involved in desalination by distillation.
16. The presence of fluoride ions,  $\text{F}^-(\text{aq})$  in domestic water supplies (fluoridation) at a concentration of up to 1 ppm is known to be beneficial to dental health by preventing tooth decay. In practice a satisfactory range of fluoride concentration is 0.6 to 1.0 ppm. Some water authorities in Australia maintain fluoride concentration in public water supplies by the addition of compounds like sodium fluorosilicate or sodium fluoride.
- What **mass** of fluoride ion,  $\text{F}^-(\text{aq})$  must be present in 45000 L of tap water ( $\approx$  volume of a backyard swimming pool) to give it a fluoride,  $\text{F}^-(\text{aq})$  concentration of 1.0 ppm? You may assume 1.0 L of tap water has a mass of 1.00 kg.
  - Determine the **mass** of **sodium fluoride**, NaF that must be added to the 45 000 L of tap water in part (a).
  - An NaF(aq) solution of concentration 2.0 ppm ( $4.8 \times 10^{-5} \text{ mol L}^{-1}$ ) has a  $\text{F}^-(\text{aq})$  ion concentration of around 0.90 ppm ( $4.8 \times 10^{-5} \text{ mol L}^{-1}$ ). As you would expect, the molar concentrations of NaF(aq) and  $\text{F}^-(\text{aq})$  in this solution are the same, ie both are  $4.8 \times 10^{-5} \text{ mol L}^{-1}$ . However, the concentration in ppm of NaF(aq) and  $\text{F}^-(\text{aq})$  are not the same, ie 2.0 ppm and 0.90 ppm respectively. **Account** for the difference.
  - An alternative method of fluoridation involves adding a saturated solution of sodium fluoride (NaF) to drinking water. What is the **concentration** of **fluoride ions** ( $\text{F}^-$ ) in **ppm** for a saturated sodium fluoride solution containing 4.1 g of NaF in every 100 g of solution?
17. In 2012-2013 the Water Corporation of WA provided an average of  $9.79 \times 10^8$  L of water per day throughout WA. As a final final step in their routine treatment of drinking water chlorine is added and maintained within the reticulated supply at around 1 ppm.
- Why** is chlorine added to drinking water as described?
  - What** total **mass** of chlorine,  $\text{Cl}_2$  would need to be added daily to produce an initial 1.0 ppm  $\text{Cl}_2$  concentration? Remember 1.0 L of water has a mass of 1.0 kg.
  - In order to maintain a minimum 1 ppm chlorine level throughout the reticulated system more  $\text{Cl}_2$  than calculated above needs to be added. **Suggest** why.



# CHAPTER 17 | ACIDS AND BASES

The distinctive properties of acids make them useful food additives. Vinegar, for example, contains the active ingredient **ethanoic acid** (CH<sub>3</sub>COOH). It gives **vinegar** its unique odour and sharp taste. As well as being an excellent flavour enhancer vinegar solutions are also used in pickling (a type of food preserving) as ethanoic acid inhibits and kills bacteria.



**Citric acid** (H<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>), obtained from lemons and limes is another common food acid. It gives foods a sharp sour taste. Many cola style beverages contain **phosphoric acid** (H<sub>3</sub>PO<sub>4</sub>) for an enhanced tangy taste.

**Salts** are formed when one or more of the acidic hydrogen atoms from an acid have been replaced by a metal ion(s).

**acid ..... some of its salts**  
**HCl**..... NaCl, KCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>  
**HNO<sub>3</sub>** ..... NaNO<sub>3</sub>, AgNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>  
**H<sub>2</sub>SO<sub>4</sub>**..... KHSO<sub>4</sub>, BaSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
The formula for the salts of organic acids, such as ethanoic acid (CH<sub>3</sub>COOH) can be written with the positive metal ion at the end or the start of the formula.  
eg sodium ethanoate:  
**NaCH<sub>3</sub>COO** or **CH<sub>3</sub>COONa**

The reaction of an acid with a carbonate or hydrogen carbonate can be thought of as a **two stage** process. Initially this reaction produces the unstable compound carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and a salt. Carbonic acid then rapidly **decomposes** forming **H<sub>2</sub>O** and **CO<sub>2</sub>**, ie H<sub>2</sub>CO<sub>3</sub> = H<sub>2</sub>O + CO<sub>2</sub>. Thus carbonic acid does not appear in the final overall equation.



**Sulfur dioxide** is a poisonous colourless gas with a pungent choking odour.

## 17.1 Chemical and physical properties of acids and bases

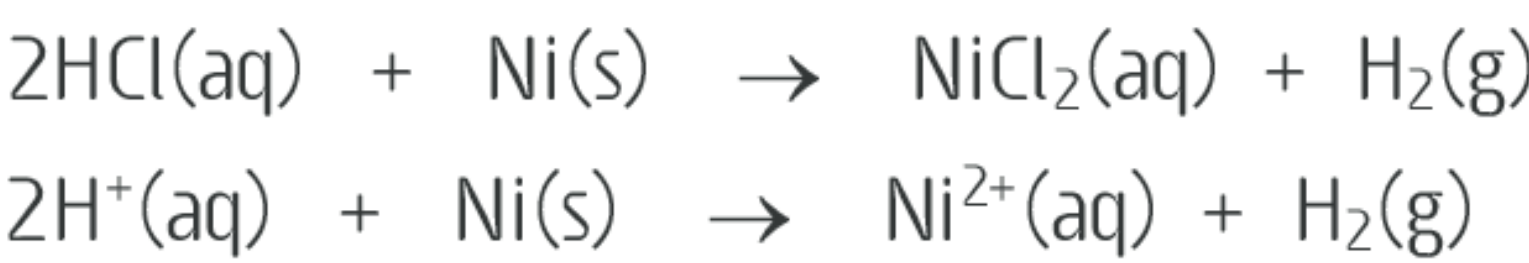
Acids and bases are two distinct groups of compounds that are well known for their unique set of chemical and physical properties. **Acidic solutions** typically conduct an electric current, will turn blue litmus red and have a sour taste. Similarly **basic solutions** also conduct an electric current, however these solutions will turn red litmus blue, have a bitter taste and a slippery soapy feel.

Some of the **chemical properties** of acidic and basic solutions are illustrated below. These are summarised with a general word equation and an example showing a chemical equation and a **net ionic equation** (see 6.3 p44-5) for the property.

- **Acidic** solutions dissolve most **metals** (Pb, Sn, Ni, Co, Cd, Fe, Cr, Zn, Mn, Al, Mg, Na, Ca, Sr, Ba, K, Li), forming a salt (see border note) and hydrogen gas. The metals Au, Pt, Ag and Cu are unaffected by dilute acids.

ACID	+	METAL	→	SALT	+	H <sub>2</sub> (g)
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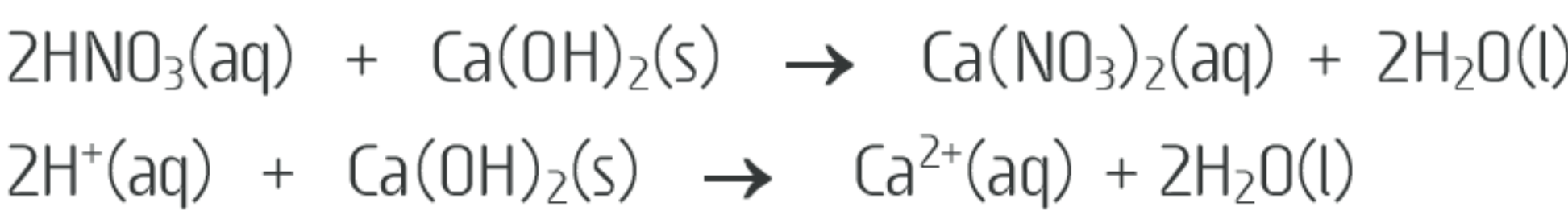
Example: Some hydrochloric acid solution is poured onto a strip of nickel metal.



- **Acidic** solutions react with **metal hydroxides** producing a salt and water.

ACID	+	METAL HYDROXIDE	→	SALT	+	H <sub>2</sub> O
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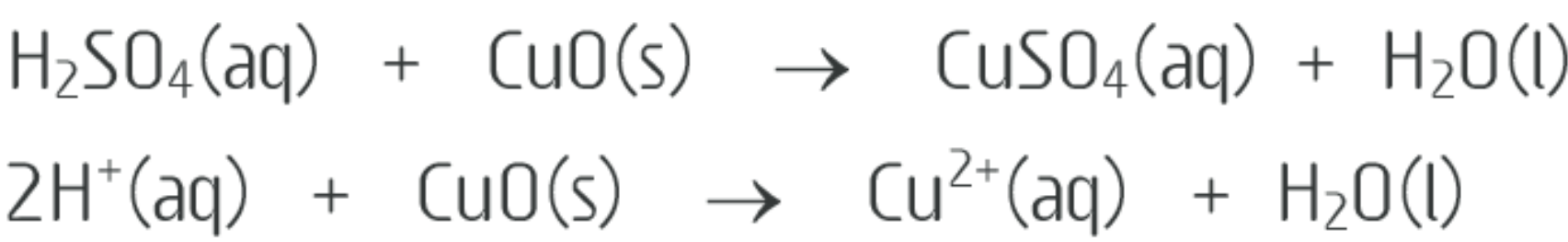
Example: A solution of nitric acid is poured onto some calcium hydroxide solid.



- **Acidic** solutions react with **metal oxides** producing a salt and water. (Note the similarity to the reaction between acids and metal hydroxides.)

ACID	+	METAL OXIDE	→	SALT	+	H <sub>2</sub> O
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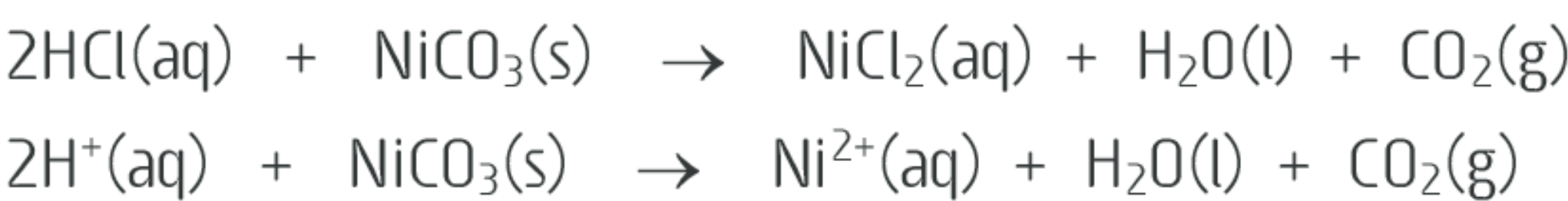
Example: A sulfuric acid solution is added to solid copper(II) oxide.



- **Acidic** solutions react with **carbonate compounds** producing a salt, water and carbon dioxide gas.

ACID	+	CARBONATE	→	SALT	+	H <sub>2</sub> O	+	CO <sub>2</sub> (g)
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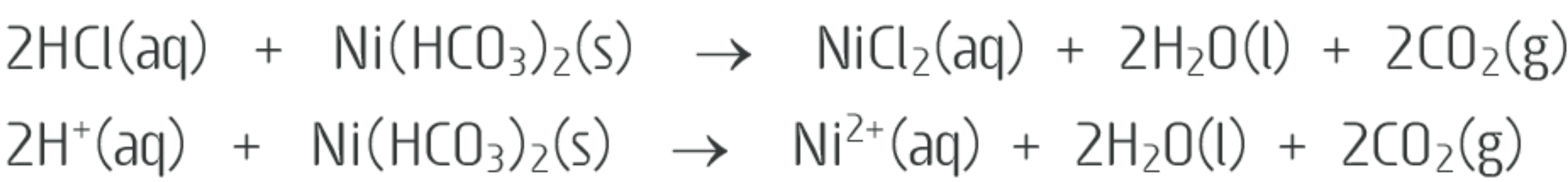
Example: Hydrochloric acid solution is added to solid nickel carbonate.



- **Acidic** solutions react with **hydrogencarbonate compounds** producing a salt, water and carbon dioxide gas.

ACID	+	HYDROGENCARBONATE	→	SALT	+	H <sub>2</sub> O	+	CO <sub>2</sub> (g)
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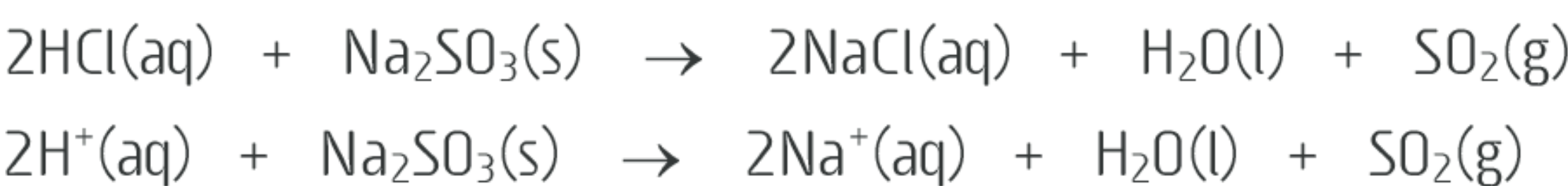
Example: Hydrochloric acid solution is added to solid nickel hydrogencarbonate.



- **Acidic** solutions react with **metal sulfites** producing a salt, water and sulfur dioxide. (Note the similarity to the acid/carbonate reaction.) **(E)**

ACID	+	METAL SULFITE	→	SALT	+	H <sub>2</sub> O	+	SO <sub>2</sub> (g)
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Example: Hydrochloric acid solution and sodium sulfite powder are mixed.





- Basic solutions react with **ammonium salts** producing a salt, water and ammonia gas.



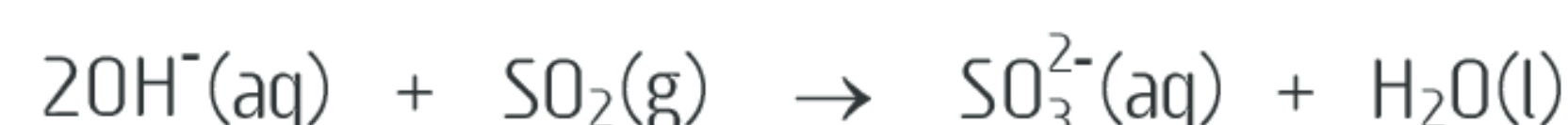
Example: A potassium hydroxide solution is mixed with an ammonium chloride solution.



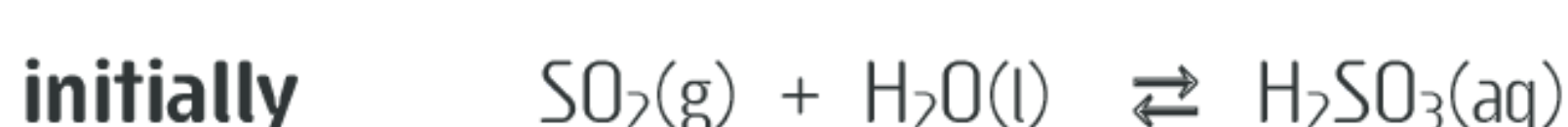
- Basic solutions react with **non-metal oxides** producing a salt and water. These reactions are best understood by visualising the acid that forms when the oxide dissolves in water. (See margin notes at right.) **(E)**



Example: Sulfur dioxide gas is bubbled through a potassium hydroxide solution.



Reactions like the one above are better visualised as a two part process. First the non-metal oxide dissolves in water to form an acid solution. The resulting acid is then neutralised by the base, see below.



The margin notes at right show what acid(s) to expect from some common non-metal oxides.



**Ammonia** is a toxic colourless gas that has a characteristic irritating pungent odour.

Non-metal oxide	Acid formed in water
CO <sub>2</sub> ..... carbon dioxide	H <sub>2</sub> CO <sub>3</sub> ..... carbonic acid
SO <sub>2</sub> ..... sulfur dioxide	H <sub>2</sub> SO <sub>3</sub> ..... sulfurous acid
SO <sub>3</sub> ..... sulfur trioxide	H <sub>2</sub> SO <sub>4</sub> ..... sulfuric acid
NO <sub>2</sub> ..... nitrogen dioxide	HNO <sub>3</sub> and HNO <sub>2</sub> ..... nitric and nitrous acid
P <sub>4</sub> O <sub>10</sub> ..... phosphorous (v) oxide	H <sub>3</sub> PO <sub>4</sub> ..... phosphoric acid

Complete Set 29.

## Set 29 Acid-base properties and reactions

- A student conducted several tests on the solutions A to H. The solutions may contain a concentrated strong acid, a concentrated strong base or a neutral salt. From the results obtained, determine whether the solutions are **acidic**, **basic** or **neutral** or if the test was **inconclusive**. Briefly justify your answer.

### Solution Test results

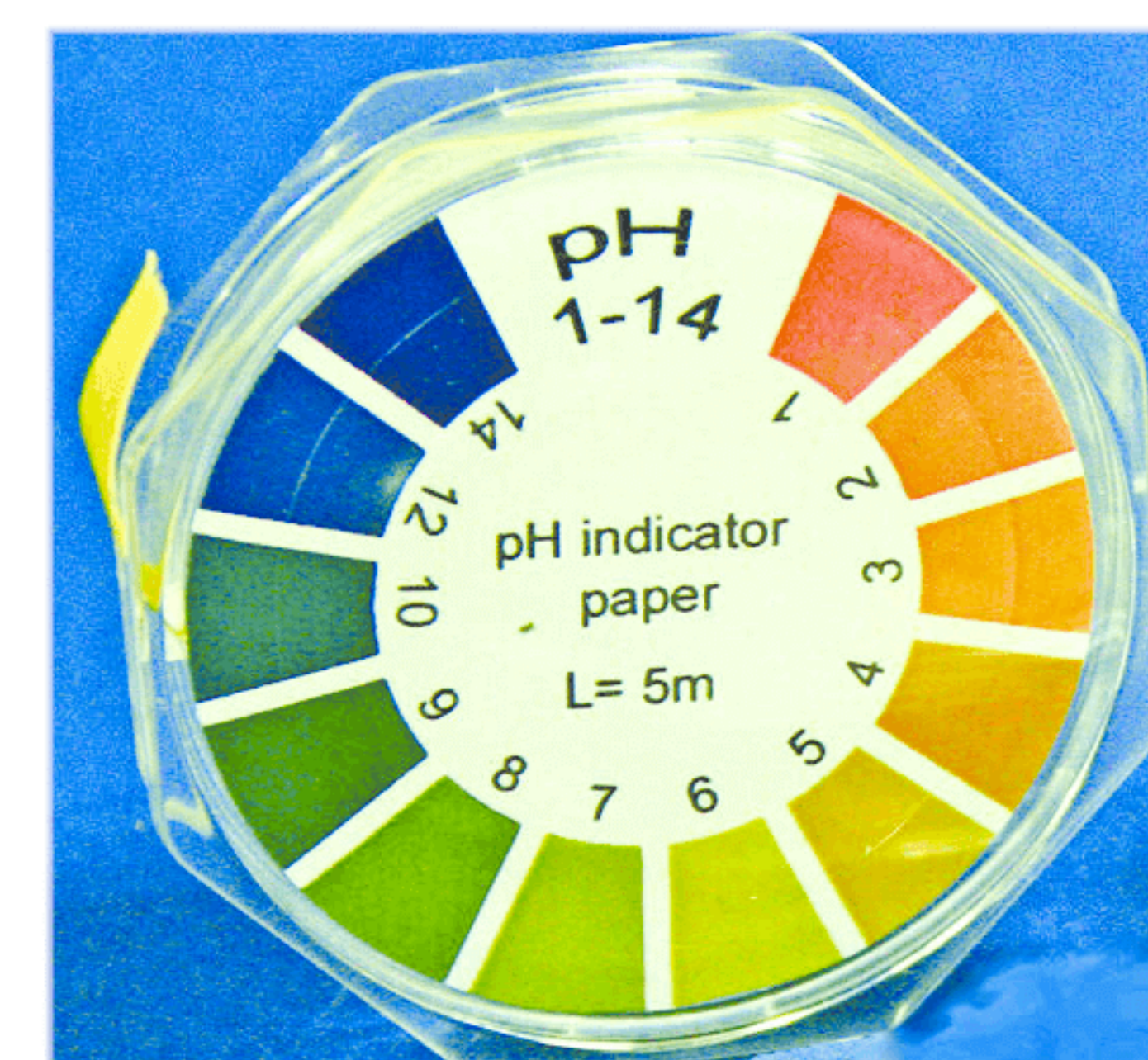
- |          |  |
|----------|--|
| <b>A</b> | This solution was tested with blue litmus. The litmus turned red.  |
| <b>B</b> | This solution did not change the colour of blue or red litmus.   |
| <b>C</b> | Rapid fizzing occurred when a strip of magnesium was added. The colourless gas formed was found to be hydrogen gas.                          |
| <b>D</b> | The solution was found to be a good electrical conductor and didn't change the colour of a piece of blue litmus.                             |
| <b>E</b> | The solution has a pH of 1 (see p156) and showed no reaction with a strip of copper metal.   |
| <b>F</b> | This solution showed no reaction with powdered sodium carbonate. A piece of red litmus added to a fresh sample of the solution remained red. |
| <b>G</b> | When solid ammonium chloride was added to this solution it produced a strong pungent odour.  |
| <b>H</b> | Universal indicator paper turns green in this solution. (See Fig 1.)   |

- Predict the **reaction products** (no equation needed) when the following pairs of reagents are combined. Write **molecular formula** for the **products** formed and indicate their phase, ie **(s)**, **(l)**, **(g)** or **(aq)**.

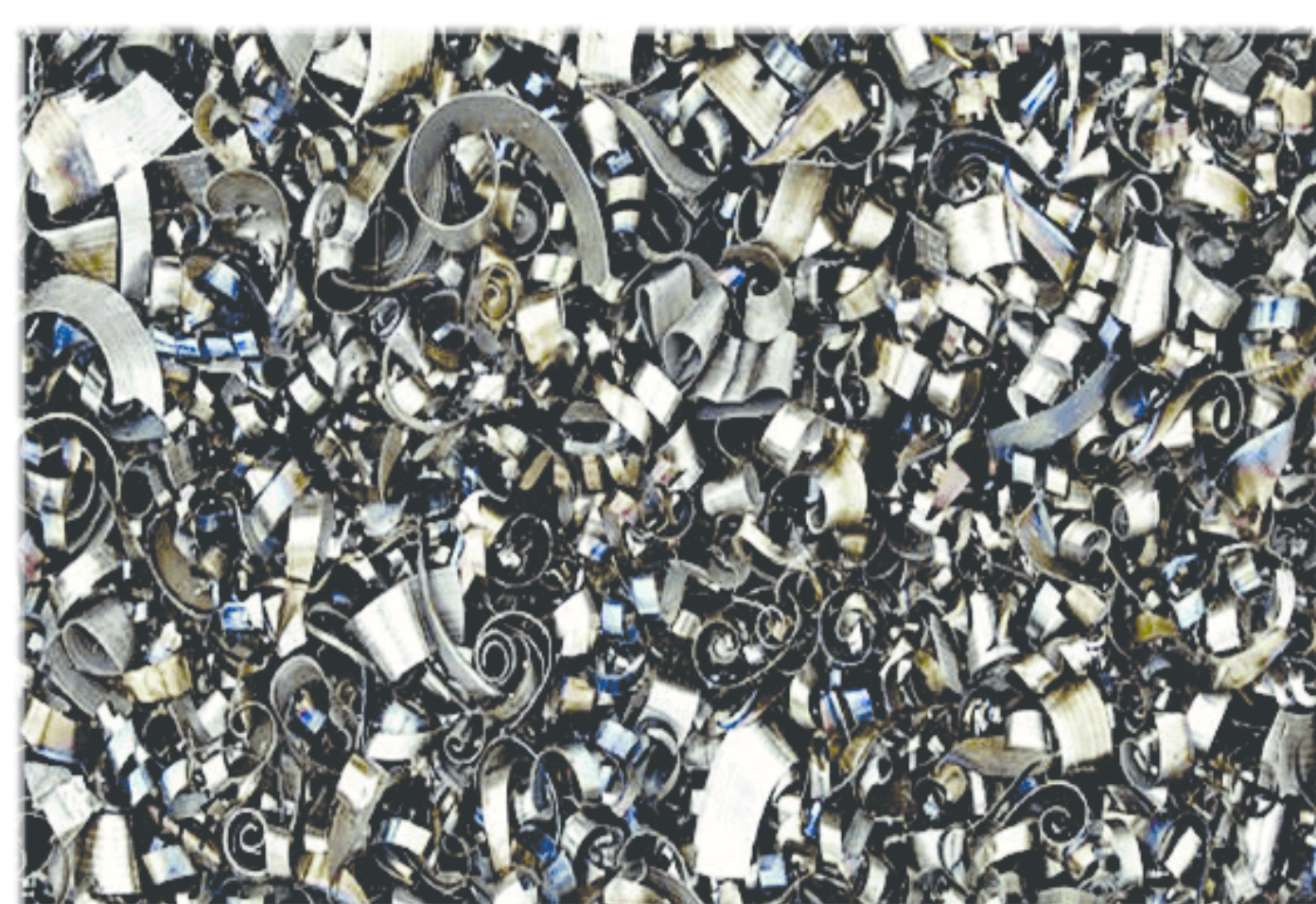
- |   |  |
|---|--|
| a. H <sub>2</sub> SO <sub>4</sub> (aq) and MgCO <sub>3</sub> (s)                  | f. H <sub>2</sub> SO <sub>4</sub> (aq) and Zn(s)               |
| b. HCl(aq) and Ca(s)  | g. HCl(aq) and CaO(s)  |
| c. HNO <sub>3</sub> (aq) and Na <sub>2</sub> CO <sub>3</sub> (s)                  | h. NH <sub>4</sub> Cl(aq) and NaOH(aq)                         |
| d. H <sub>2</sub> SO <sub>4</sub> (aq) and Zn(HCO <sub>3</sub> ) <sub>2</sub> (s) | i. SO <sub>3</sub> (g) and Ba(OH) <sub>2</sub> (aq) <b>(E)</b> |
| e. CH <sub>3</sub> COOH(aq) and Mg(OH) <sub>2</sub> (s)                           | j. CO <sub>2</sub> (g) and NaOH(aq) <b>(E)</b>                 |

**FIGURE 1 Universal indicator** is a mixture of several indicators that produce a range of colours which gradually change with a solution's pH.

Indicators may be used in solution form or can be impregnated into paper strips. This photograph shows a roll of **pH indicator paper** with its pH colour chart.

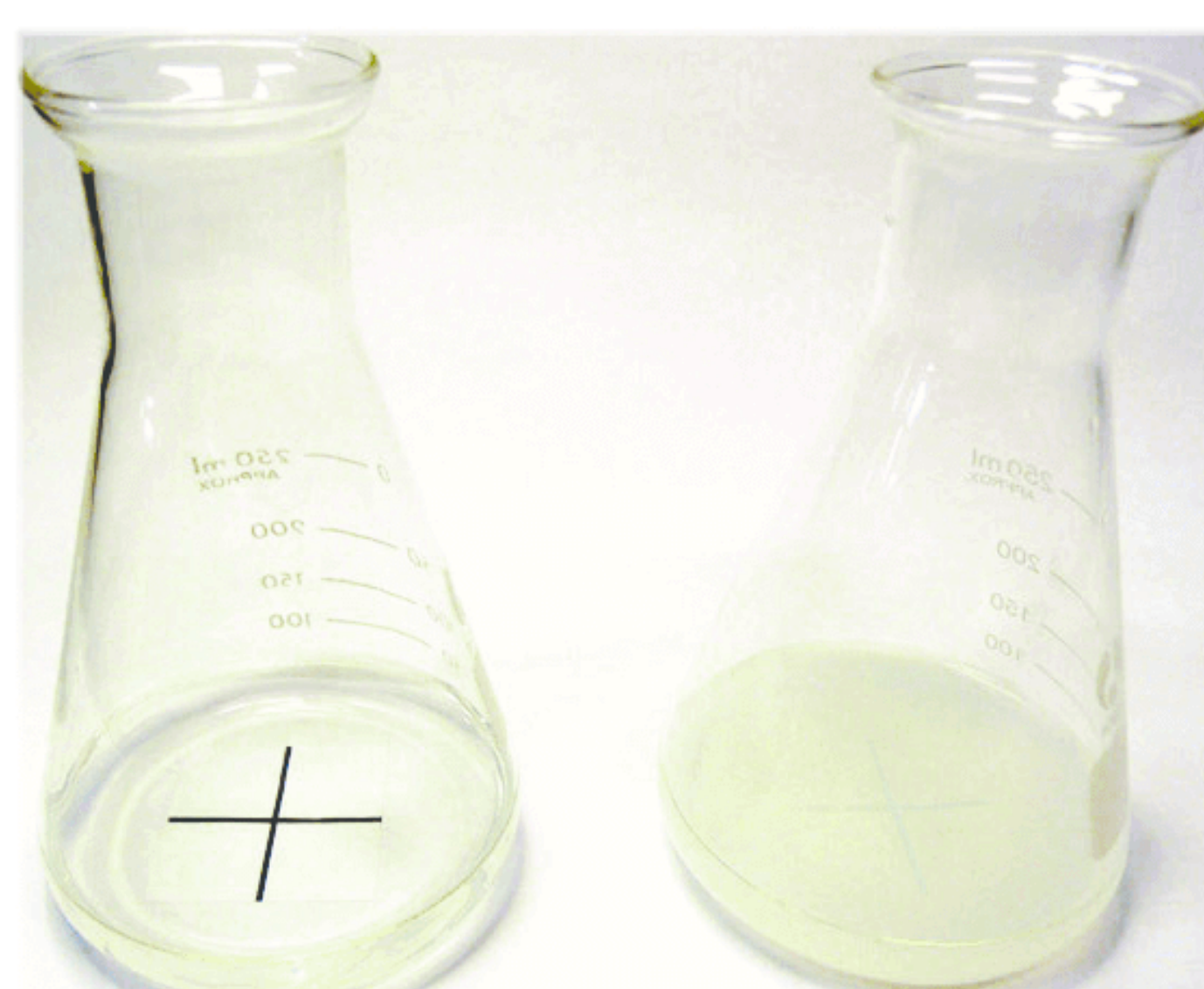






**FIGURE 2** Turnings are small metal shavings. They have a high surface area that promotes a more rapid reaction rate.

\*See Chapter 6 to review writing net ionic equations.



**FIGURE 3** The cloudy mixture on the right consists of a **suspension** of fine particles of solid sulfur spread throughout (suspended in) a liquid phase. By comparison the contents of the flask on the left is clear as it does not contain the **sulfur** suspension. Notice how the black cross is not clearly visible through the suspension.

3. Write a **balanced chemical equation** (not ionic) for the chemical reaction that takes place when each of the following pairs of reagents is combined.
  - a.  $\text{HNO}_3(\text{aq})$  and  $\text{Al}_2(\text{CO}_3)_3(\text{s})$
  - b.  $\text{HCl}(\text{aq})$  and  $\text{Fe}(\text{OH})_3(\text{s})$
  - c.  $\text{HNO}_3(\text{aq})$  and  $\text{BaO}(\text{s})$
  - d.  $\text{NH}_4\text{Cl}(\text{aq})$  and  $\text{KOH}(\text{aq})$
  - e.  $\text{HCl}(\text{aq})$  and  $\text{Fe}(\text{s})$
  - f. ethanoic acid solution and solid zinc carbonate
  - g. sulfuric acid solution and solid aluminium **turnings** (See Fig 2.)
  - h. phosphoric acid solution and solid barium hydroxide
  - i. carbon dioxide gas and powdered barium hydroxide **(E)**
  - j. sulfur trioxide gas and sodium hydroxide solution **(E)**
  - k. potassium sulfite solution and hydrochloric acid solution **(E)**
  - l. sulfur dioxide gas and sodium hydroxide solution **(E)**

4. A chemical change will happen in some of the following situations. If a reaction is expected write a balanced **net ionic equation\*** for the reaction and give an **observation** that could be expected for the reaction. Where no reaction occurs write NR.
  - a. Powdered  $\text{CuCO}_3$  is added to a  $\text{HNO}_3$  solution [ie  $\text{H}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$ ].
  - b. Solid copper(II) oxide is added to a nitric acid solution.
  - c. Powdered  $\text{Mg}(\text{OH})_2$  is added to a concentrated  $\text{NaOH}$  solution.
  - d. Granulated  $\text{Zn}$  is added to a  $\text{HCl}$  solution.
  - e. An ethanoic acid solution is added to solid magnesium carbonate.
  - f. A sulfuric acid solution is added to a copper(II) hydroxide **suspension**. (See Fig 3.)
  - g. A hydrochloric acid solution is added to an aluminium hydroxide suspension.
  - h. Magnesium ribbon is added to an ethanoic acid solution.
  - i. Ammonium chloride solution is added to potassium hydroxide solution.
  - j. Copper turnings are added to a hydrochloric acid solution.
  - k. Carbon dioxide gas is bubbled through a sodium hydroxide solution. **(E)**
  - l.  $\text{SO}_2$  gas is bubbled through a  $\text{KOH}$  solution. **(E)**
  - m. A  $\text{Na}_2\text{SO}_3$  solution is added to a  $\text{HCl}$  solution. **(E)**

5. William and Natalie carried out several chemical tests on the following substances:

**$\text{CuO}(\text{s})$**

**$\text{Ca}(\text{OH})_2(\text{s})$**

**$\text{Cr}_2(\text{CO}_3)_3(\text{s})$**

**$\text{NH}_4\text{Cl}(\text{s})$**

**$\text{MgCO}_3(\text{s})$**

They treated these substances with different reagents as outlined below. Using their observations, determine which of the above substances is being tested in each case. Support your answer with a **brief explanation**.

**Test (i)**

A nitric acid solution was added to one of the above substances. It was observed to dissolve and produce a clear blue solution.

**Test (ii)**

A solution of sodium hydroxide was added to a sample of this substance, however it did not dissolve or show any reaction. Another sample of the same substance when added to an hydrochloric acid solution dissolved to produce a clear colourless solution. No other changes were noted.



**Test (iii)**

This substance readily dissolved in excess hydrochloric acid solution, yielding a clear green solution.

**Test (iv)**

This substance was added to excess hydrochloric acid resulting in a clear colourless solution and a colourless gas being evolved.

**Test (v)**

This compound dissolved in water and nitric acid to give a clear colourless solution and no other change. With sodium hydroxide solution it produced a strongly pungent odour.

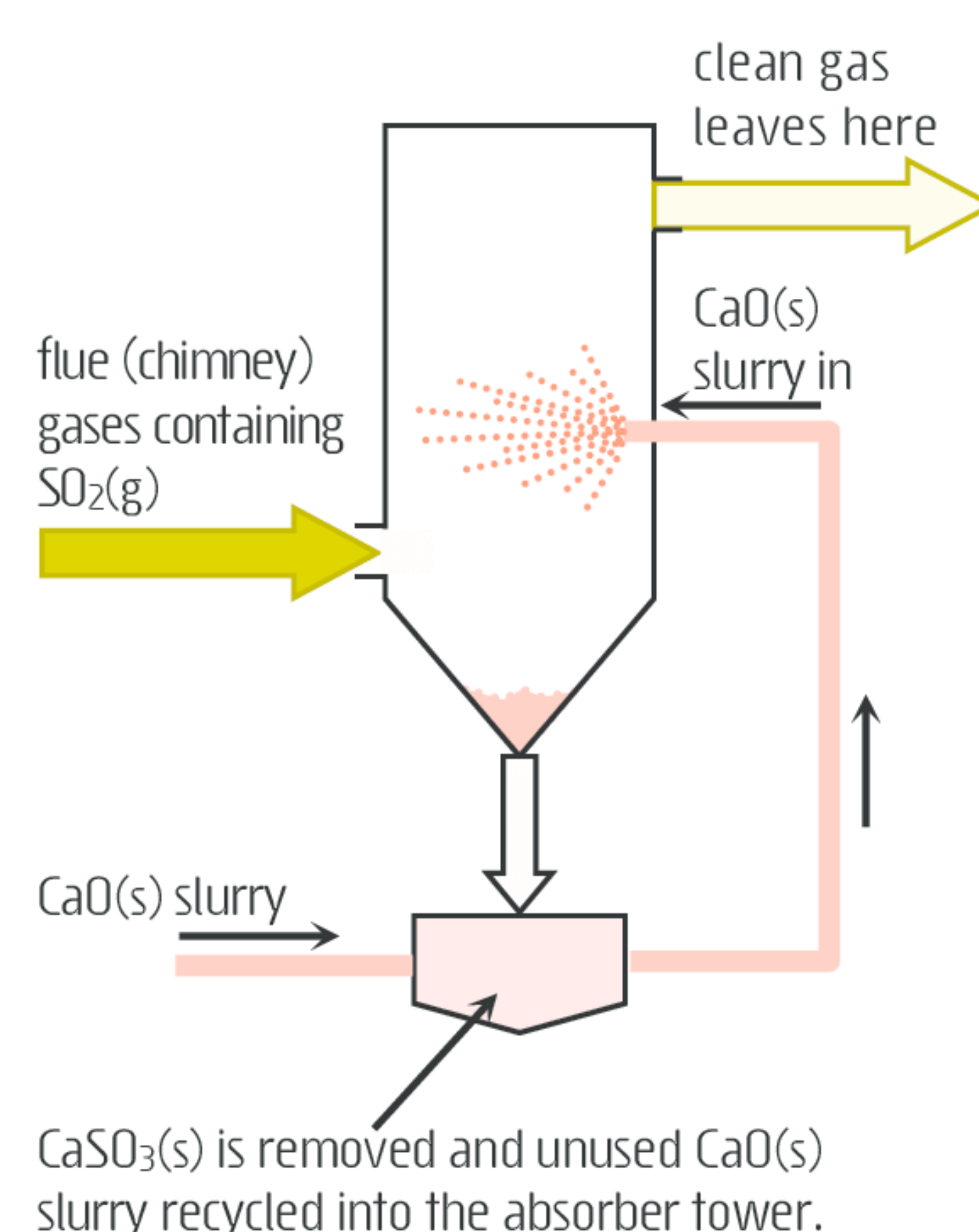
6. Craig and Nicole are presented with several groups of unlabelled substances. While they know what substances are in each group they aren't told which is which. Their objective is to identify each substance in the group. To do this Craig and Nicole must use a **chemical test** using any **acid** or **base** solution normally found in the laboratory. Describe how they could achieve their objective. Clearly note what they would do and the **observations** expected along with the **conclusions** they could make.
- Zn(s) and Ag(s)
  - Mg(s) and Fe(s)
  - $\text{CuCO}_3(\text{s})$  and  $\text{Cu}(\text{OH})_2(\text{s})$
  - solid samples of ammonium chloride, calcium chloride and zinc carbonate

7. The effect known as **acid rain** is a result of sulfur oxides and nitrogen oxides like  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{NO}_2$  present in the atmosphere. Although these gases are normally found in the atmosphere (eg from volcanoes, biological decay and forest fires) their concentration has increased greatly with industrialisation. In particular, the burning of fossil fuels that contain sulfur accounts for about 75-80% of all atmospheric sulfur oxides.

One method that is being used successfully to eliminate  $\text{SO}_2$  emissions from coal fired power stations involves passing the flue gases through a '**wet scrubber**'. (See Fig 4.) Here flue gases mix with a limestone or **lime slurry**. Sulfur oxides in the flue gases react with the active component in the slurry,  $\text{CaCO}_3$  or  $\text{CaO}$  producing a solid precipitate. This method removes 95%-98% of the  $\text{SO}_2$  pollutants originally present in the flue gases of coal fired power stations. **(E)**

- Write an equation(s) to show how  $\text{SO}_2(\text{g})$  reacts with  $\text{CaO}$  in a 'wet scrubber'.
- How would acid rain containing sulfur trioxide affect metal structures like those made of iron? Explain with the aid of an equation(s).
- The weathering of marble statues and limestone buildings is greatly accelerated by excessive exposure to acid rain. Using equations explain how the presence of oxides of nitrogen, like  $\text{NO}_2$ , can cause the deterioration of limestone and marble structures. (Remember,  $\text{CaCO}_3$  is the major component of both limestone and marble.)

**FIGURE 4** A **wet scrubber** can be used to remove sulfur dioxide from power station flue (chimney) gas. One type of wet scrubber uses a fine spray of calcium oxide (lime) slurry to absorb  $\text{SO}_2(\text{g})$ . The slurry is a mixture of water and fine particles of solid  $\text{CaO}$ . The small  $\text{CaO}$  particle size and fine spray ensure good contact between  $\text{SO}_2(\text{g})$  and  $\text{CaO}(\text{s})$ . This helps to promote a fast reaction rate where  $\text{CaSO}_3(\text{s})$  is the product.









## 17.4 Strong and weak acids and bases

Although all acids have similar chemical properties they do not express them equally. Their rates of reaction under similar conditions, for example, are not the same. Some acids, such as hydrochloric and sulphuric acid are said to be **strong acids** and always produce a more vigorous reaction for the same conditions, than do **weak acids** like ethanoic acid or phosphoric acid. (See Fig 8.)

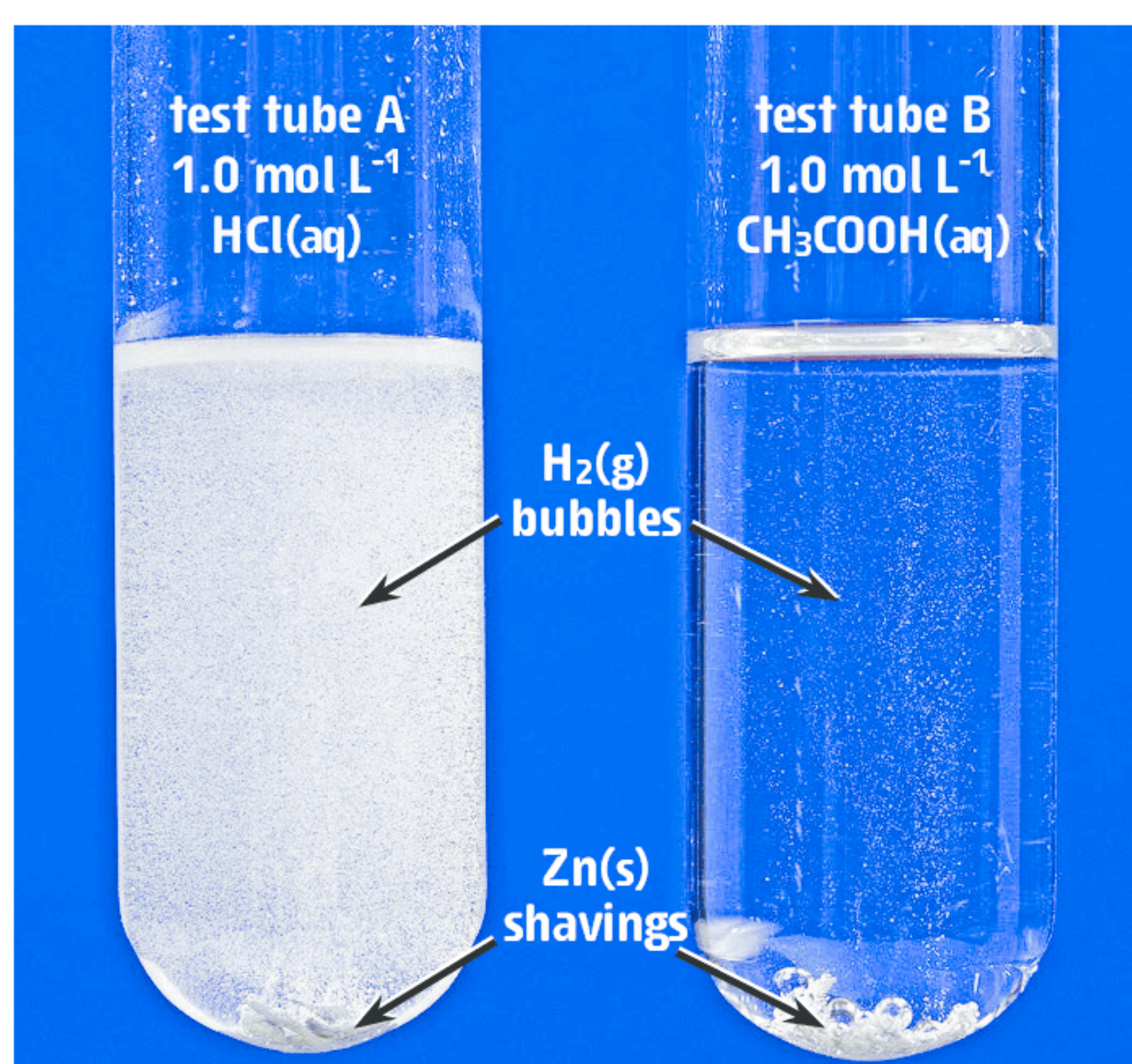
**FIGURE 8** In each of these test tubes small **zinc** shavings are reacting with hydrogen ions from two different  $1.0 \text{ mol L}^{-1}$  acid solutions.



Note the small bubbles, these are due to the formation of hydrogen gas.

Although both test tubes contain an acid with the **same**  $1.0 \text{ mol L}^{-1}$  **concentration**, the rate of formation of hydrogen gas is greater in test tube **A** than in test tube **B**. The difference occurs as test tube A contains a **strong acid**, hydrochloric acid, while test tube B contains a **weak acid**, ethanoic acid.

As stronger acids are more fully **ionised** they produce higher concentrations of hydrogen ions (for the same acid concentration) and hence give a more vigorous reaction.



The Arrhenius theory explains acid strength in terms of degree of ionisation. It states strong acids dissolve in water to undergo **complete ionisation**. Thus all of the dissolved acid converts into ions. A single arrow ( $\rightarrow$ ) in the ionisation equation shows this. By comparison, Arrhenius identifies a weak acid as one that undergoes **partial ionisation**, ie remaining mostly in the form of unionised molecules. Double arrows ( $\rightleftharpoons$ ) show the partial nature of this reaction. Thus, according to Arrhenius, for the same concentration, a strong acid will always produce a higher  $\text{H}^+(\text{aq})$  concentration due to its more complete ionisation and hence show stronger acidic properties than a weak acid. (See Example 1 and Table 1.)

**EXAMPLE 1** Write ionisation equations for the strong acid  $\text{HNO}_3$  and the weak acid  $\text{CH}_3\text{COOH}$  (ethanoic acid). Describe the significance of acid strength on the ionisation of these two acids.

$\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$   
 $\text{HNO}_3$  is a strong acid so use a **single** arrow.

$\text{HNO}_3$  is a strong acid (Table 1) so it undergoes **complete ionisation** (single arrow) to produce  $\text{H}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$  ions. Very few (if any)  $\text{HNO}_3$  molecules will remain in the solution.

$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$   
 $\text{CH}_3\text{COOH}$  is a weak acid so use a **double** arrow.

$\text{CH}_3\text{COOH}$  is a weak acid (Table 1) so it only **partially ionises** in water (double arrow). It produces some  $\text{H}^+(\text{aq})$  and  $\text{CH}_3\text{COO}^-(\text{aq})$  ions but remains mostly in the form of  $\text{CH}_3\text{COOH}$  molecules.

**TABLE 1** Strength of some acids and bases

### Strong acids

hydrochloric acid ..... **HCl**  
 sulfuric acid..... **$\text{H}_2\text{SO}_4$**   
 nitric acid ..... **$\text{HNO}_3$**

### Weak acids

sulfurous acid..... **$\text{H}_2\text{SO}_3$**   
 phosphoric acid..... **$\text{H}_3\text{PO}_4$**   
 hydrofluoric acid.....**HF**  
 ethanoic acid..... **$\text{CH}_3\text{COOH}$**   
 carbonic acid ..... **$\text{H}_2\text{CO}_3$**   
 ammonium salts .....eg  **$\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$**

### Strong bases

**oxides** of group 1 .....eg  **$\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$**   
 and group 2 metals...eg  **$\text{MgO}$ ,  $\text{CaO}$ ,  $\text{BaO}$**   
**hydroxides** of group 1 eg  **$\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$**   
 and group 2 metals .....eg  **$\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$**

### Weak bases

metal phosphates .....eg  **$\text{Na}_3\text{PO}_4$ ,  $\text{K}_3\text{PO}_4$**   
 metal carbonates .....eg  **$\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$**   
 metal hydrogen- .....eg  **$\text{NaHCO}_3$ ,  $\text{KHCO}_3$**   
 carbonates  **$\text{Ca}(\text{HCO}_3)_2$**   
 ammonia.....ie  **$\text{NH}_3$  or  $\text{NH}_4\text{OH}$**

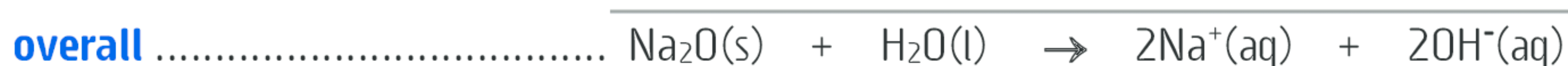
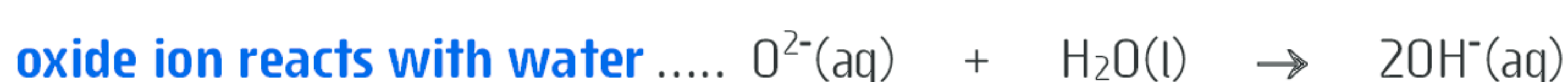
Attempt Set 30 # 3 and 4.

## 17.5 Acid-base properties of metal and non-metal oxides (E)

Many **non-metal oxides** are **acidic**. This is not immediately apparent from the Arrhenius theory. However, non-metal oxides like  $\text{CO}_2$  and  $\text{SO}_3$  combine with water to form acids. (See border note.) The resulting acids then ionise to form hydrogen ions and an acidic solution.



Many **metallic oxides** like  $\text{Na}_2\text{O}$  or  $\text{CaO}$  are basic in nature. This also is not immediately obvious from the Arrhenius theory. When these metallic oxides dissolve in water they **dissociate** releasing positive metal ions and oxide ions  $\text{O}^{2-}(\text{aq})$ . The oxide ion then rapidly combines with water to produce hydroxide ions  $\text{OH}^-(\text{aq})$ . Thus when dissolved in water a metal oxide converts into a basic solution of the corresponding **metal hydroxide**.



Even many **insoluble** metallic oxides, eg  $\text{CaO}$  and  $\text{MgO}$ , will absorb water to produce an hydroxide as shown here.



Non-metal oxide	Acid formed in water
$\text{CO}_2$ ..... carbon dioxide	<b><math>\text{H}_2\text{CO}_3</math></b> carbonic acid
$\text{SO}_2$ ..... sulfur dioxide	<b><math>\text{H}_2\text{SO}_3</math></b> sulfurous acid
$\text{SO}_3$ ..... sulfur trioxide	<b><math>\text{H}_2\text{SO}_4</math></b> sulfuric acid
$\text{NO}_2$ ..... nitrogen dioxide	<b><math>\text{HNO}_3</math> and <math>\text{HNO}_2</math></b> nitric and nitrous acid
$\text{P}_4\text{O}_{10}$ ..... phosphorous (v) oxide	<b><math>\text{H}_3\text{PO}_4</math></b> phosphoric acid

Complete Set 30.



## Set 30 Understanding acids and bases

FIGURE 9 Universal indicator pH colour chart.



Universal indicator colours may vary slightly due to specific manufacturer formulations. Typical universal indicator colours are; pH 0–3 (red), pH 4–6 (orange-yellow), pH 7 (green), pH 8–10 (blue), pH 11–14 (purple).

**Careful!** Don't confuse strong and weak with concentrated and dilute.

**Concentrated** and **dilute** refer to the ratio of solute to solution. A dilute acid has a low ratio of acid to solution, eg  $0.1 \text{ mol L}^{-1} \text{ HCl(aq)}$ , a concentrated acid has a high ratio of acid to solution, eg  $6.0 \text{ mol L}^{-1} \text{ HCl(aq)}$ .

**Strong** and **weak** refer to the degree to which an acid or base produces ions when dissolved in water. A strong acid, eg  $\text{HCl(aq)}$ , completely separates into ions when in solution. Weak acids, eg  $\text{H}_2\text{CO}_3\text{(aq)}$ , only partially ionise into ions and are mostly present as molecules when dissolved in water.

ionises

blue

red

hydroxide ions

hydrogen ions

$\text{Na}_2\text{CO}_3$

$\text{NaOH}$

$\text{H}_2\text{CO}_3$

$\text{HNO}_3$

reactive metals

dissociate

greater

pungent

sour

fully ionise

1. A student tested several solutions, A to E, by adding a few drops of **universal indicator solution** to each. She obtained the following results.

solution	A	B	C	D	E
indicator colour	orange	blue	green	red	purple
pH (estimate)					

- Estimate the pH range of each solution and complete the table above. (See Fig 9.)
  - From these solutions choose the one(s) that fit the following descriptions.
    - The most acidic solution.
    - Any neutral solution(s).
    - Any solution(s) that will turn blue litmus red.
    - The solution with the highest hydrogen ion concentration.
    - Any solution(s) with the same hydrogen ion and hydroxide ion concentration.
    - Those solutions with basic properties.
2. Each of the substances listed here dissolve in water and change its pH. Do they produce acidic or basic solutions? Write **equations** and use the **Arrhenius** theory to support your answer. (See Table 1.)
    - $\text{HCl(g)}$
    - $\text{HF(g)}$
    - $\text{NaOH(s)}$
    - $\text{CH}_3\text{COOH(aq)}$
    - $\text{Ba(OH)}_2\text{(s)}$
  3. Give an **answer** and a brief **explanation** for each of the following questions. (See border note.)
    - Which of these solutions has the highest hydrogen ion concentration:  $1.0 \text{ mol L}^{-1} \text{ HNO}_3\text{(aq)}$  or  $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{COOH(aq)}$  ?
    - Which solution is most basic:  $1.0 \text{ mol L}^{-1} \text{ NH}_3\text{(aq)}$  or  $1.0 \text{ mol L}^{-1} \text{ NaOH(aq)}$  ?
    - Which solution is most acidic:  $1.0 \text{ mol L}^{-1} \text{ HCl(aq)}$  or  $0.10 \text{ mol L}^{-1} \text{ HCl(aq)}$  ?
    - Which solution has the lowest pH:  $1.0 \text{ mol L}^{-1} \text{ HCl(aq)}$  or  $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4\text{(aq)}$  ?
    - Which solution gives the most vigorous reaction with calcium carbonate granules:  $1.0 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4\text{(aq)}$  or  $1.0 \text{ mol L}^{-1} \text{ HNO}_3\text{(aq)}$  ?
  4. Use the list of terms given (at left) to complete the following passage.  
 Acidic solutions are those that taste (a) \_\_\_\_\_, liberate hydrogen gas with (b) \_\_\_\_\_ and turn blue litmus red. A solution is said to be basic if it turns (c) \_\_\_\_\_ litmus (d) \_\_\_\_\_ and produces a (e) \_\_\_\_\_ odour with ammonium salts. The properties of acidic solutions are attributed to the presence of (f) \_\_\_\_\_. Basic solutions owe their properties to the presence of (g) \_\_\_\_\_.  
 The **Arrhenius** theory can explain the acidic and basic nature of various substances. According to the Arrhenius theory an acid is a substance that (h) \_\_\_\_\_ in water releasing hydrogen ions into solution. Strong acids like (i) \_\_\_\_\_ and  $\text{HCl}$  (j) \_\_\_\_\_ producing (k) \_\_\_\_\_ hydrogen ion concentrations than do weak acids like  $\text{CH}_3\text{COOH}$  or (l) \_\_\_\_\_. Bases are understood to be substances like (m) \_\_\_\_\_ that contain hydroxide ions. These (n) \_\_\_\_\_ when dissolved in water releasing hydroxide ions into solution. The Arrhenius model can not explain the basic properties of substances like (o) \_\_\_\_\_ or  $\text{NH}_3$  as although these produce basic solutions they clearly do not contain hydroxide ions.
  5. Classify the following oxides as producing acidic or basic solutions when added to water. **(E)**
    - $\text{SO}_3\text{(g)}$
    - $\text{NO}_2\text{(g)}$
    - $\text{Na}_2\text{O(s)}$
    - $\text{BaO(s)}$
    - $\text{P}_4\text{O}_{10}\text{(s)}$
  6. The two oxides  $\text{K}_2\text{O}$  and  $\text{SO}_2$  are both soluble in water. Write equations showing how each of these substances dissolves in water and cause its pH to change. **(E)**



7. The unique properties of acids and bases find application in many everyday situations. Consider the following examples and answer the associated questions.
- Vinegar (see border note) is used as a food additive for its sharp sour taste and characteristic pungent odour. It also inhibits bacterial growth due to its low pH. The active ingredient in vinegar is ethanoic acid ( $\text{CH}_3\text{COOH}$ ).
    - Write a **Arrhenius** equation showing how ethanoic acid produces hydrogen ions in an aqueous vinegar solution.
    - What is the effect of ethanoic acid on the **pH** of the vinegar? **Explain**.
    - Household vinegar contains around 6% ethanoic acid and is quite safe to consume. This is equivalent to an approximately  $1 \text{ mol L}^{-1}$  ethanoic acid solution. A  $1 \text{ mol L}^{-1}$  sulfuric acid solution, however, would not be safe to use as a food acid. **Account** for this difference.
  - Household ammonia based cleaners can contain as much as 10% ammonia by mass. This is equivalent to  $\approx 6 \text{ mol L}^{-1} \text{NH}_3(\text{aq})$ . These solutions are excellent floor cleaners as they have the ability to dissolve greasy substances. The active ingredient in these cleaners is ammonia ( $\text{NH}_3$ ). The basic nature of the ammonia solution and its ability to clean greasy surfaces is a result of the following reaction of ammonia with water.



A  $6 \text{ mol L}^{-1}$  solution of sodium hydroxide (see Fig 10) is also basic and has grease dissolving properties. Why is it not advisable to use such a solution for cleaning floors in the home? **Explain**.

8. Chloe has a problem with some recently laid bathroom tiles. It seems the tiler made quite a mess leaving patches of white tile grout stuck to the floor tile surface. Chloe would like an easy way of washing the grout off without lots of scraping. However as the major ingredient in grout is insoluble calcium oxide ( $\text{CaO}$ ) she is not having much success. She has a few items around the house at her disposal which she thinks might be of help. These are listed here. Discuss the suitability of each of these items for the purpose of removing the unwanted grout. You should also consider safety aspects of each substance.

**baking soda** (mainly solid  $\text{NaHCO}_3$ )

**drain cleaner** (essentially pure  $\text{NaOH}$  solid)

**spirits of salts** (contains concentrated  $\text{HCl}$ )

**vinegar** (contains  $\approx 5\% \text{CH}_3\text{COOH}$ )

9. **Soil pH** is an important consideration in agriculture. It can greatly affect the availability of plant nutrients present in the soil. Although the ideal soil pH varies with plant species, a pH of between 6 and 7.5 will suit most plant types. In order to maintain optimum crop yields, farmers monitor and control their soil pH. Substances like **agricultural lime** and **ammonium nitrate** can be used to do this.
- Agricultural lime can be added to acidic soils to adjust its pH. The major component of agricultural lime is  $\text{CaCO}_3(\text{s})$  with varying amounts of  $\text{CaO}(\text{s})$ ,  $\text{MgCO}_3(\text{s})$  and  $\text{MgO}(\text{s})$  also present. How do these substances react with acid [ $\text{H}^+(\text{aq})$ ] present in the soil and how does this alter soil pH? Use suitable equations to support your answer.
  - In terms of neutralisation, explain how using the nitrogen based **fertiliser** ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) would affect soils with a high pH? Explain with the aid of an equation. (See reactions of ammonium salts p153.)

10. Acids like  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  are said to be **polyprotic**. Polyprotic acids contain more than one acidic hydrogen atom and can release these into solution in a successive manner. (See border note at right.) Write **three separate equations** to represent the first, second and third ionisation (releasing of a hydrogen ion) of the triprotic acid, phosphoric acid. Your first equation should show the formation of  $\text{H}_2\text{PO}_4^-$  from  $\text{H}_3\text{PO}_4$ . The second equation should show the formation of  $\text{HPO}_4^{2-}$  from  $\text{H}_2\text{PO}_4^-$  and so on. Use double or single arrows for each equation as appropriate. **(E)**

A **vinegar** solution contains the active ingredient **ethanoic acid** ( $\approx 6\%$  by mass). Such a solution can be safely used as a food acid or around the home to remove scale deposit, such as  $\text{MgCO}_3$  or  $\text{CaCO}_3$  from inside a kettle.



**FIGURE 10 Sodium hydroxide**,  $\text{NaOH}$ ; also known as **caustic soda** or **lye**, is the most important of the strong bases. It is used in the manufacture of soaps, rayon, paper, alumina refining and in petroleum refining. Its ability to saponify fats and oils (convert into soap) contributes to its use around the home as a drain cleaner and oven cleaner.

Pure  $\text{NaOH}$  is a white solid that is very soluble in water. Care should be taken when preparing solutions of  $\text{NaOH}$  as it produces a considerable amount of heat as it dissolves. Always use **safety glasses** when handling sodium hydroxide or its solutions. If skin contact occurs wash off with plenty of water. Contact with eyes is more serious and can cause long term damage. If eye contact does occur immediately flush with plenty of water. Continue for at least ten minutes and call for immediate medical help.

Acids like  $\text{HCl}$  and  $\text{HNO}_3$  are **monoprotic**. This means one mole of acid can produce one mole of  $\text{H}^+$  ions when neutralised with a strong base like  $\text{NaOH}$ .

**Diprotic** acids like  $\text{H}_2\text{SO}_4$  produce two  $\text{H}^+$  ions for each molecule of acid. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a **triprotic** acid that can ultimately produce three moles of  $\text{H}^+$  ions when reacting with a strong base like  $\text{NaOH}$ .



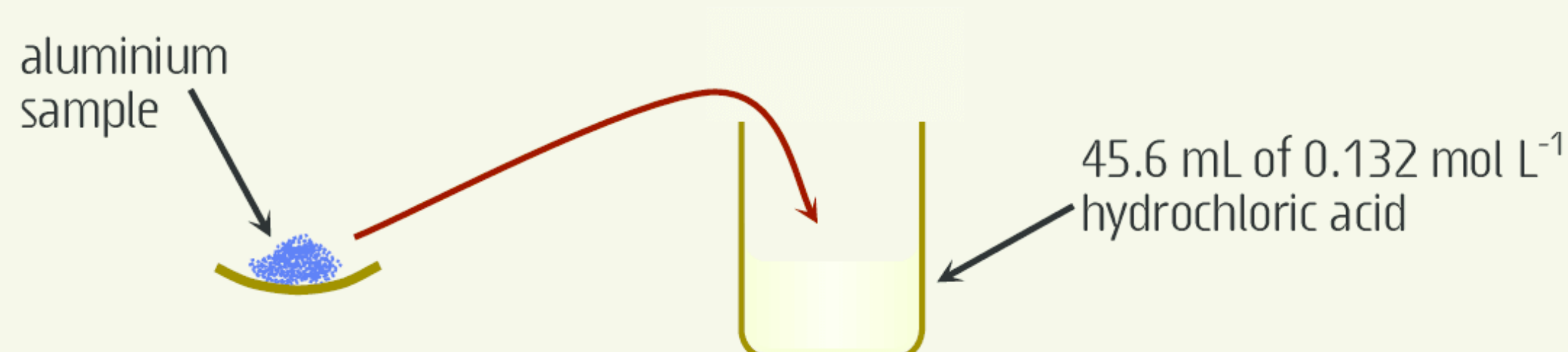
# CHAPTER 18 | MORE ON STOICHIOMETRY

## 18.1 Stoichiometry involving solutions

**Remember**, when using  $n = cV$ :  
 $c$  is concentration ( $\text{mol L}^{-1}$ )  
 $n$  is moles of solute ( $\text{mol}$ )  
 $V$  is the solution volume ( $\text{L}$ ).

Chemical procedures often involve reactions where one or more of the reagents are in the **solution phase**. Quantities of these reagents are measured in terms of the volume and concentration of solution. The solution concentration relationship,  $n = cV$  allows the molar amount of these reagents to be found and then stoichiometrically related to other substances in the reaction. (See Example 1.)

**EXAMPLE 1** What mass of aluminium can be dissolved by 45.6 mL of  $0.132 \text{ mol L}^{-1}$  hydrochloric acid?



Write an equation for the change described.

$$n(\text{HCl}) = cV = 0.132 \times 45.6 \times 10^{-3} = 6.02 \times 10^{-3} \text{ mol}$$

Use the concentration equation to find the  $n(\text{HCl})$ . Volume must be in L, ie  $45.6 \text{ mL} = 45.6 \times 10^{-3} \text{ L}$ .

$$n(\text{Al}) = \frac{2}{6} \times n(\text{HCl}) = \frac{2}{6} \times 6.02 \times 10^{-3} = 2.01 \times 10^{-3} \text{ mol}$$

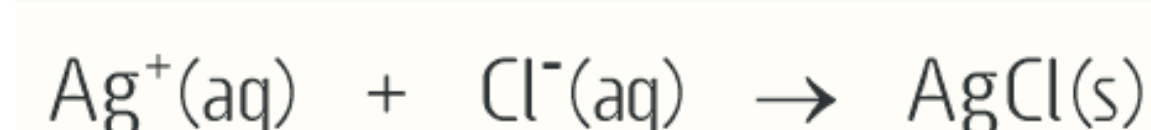
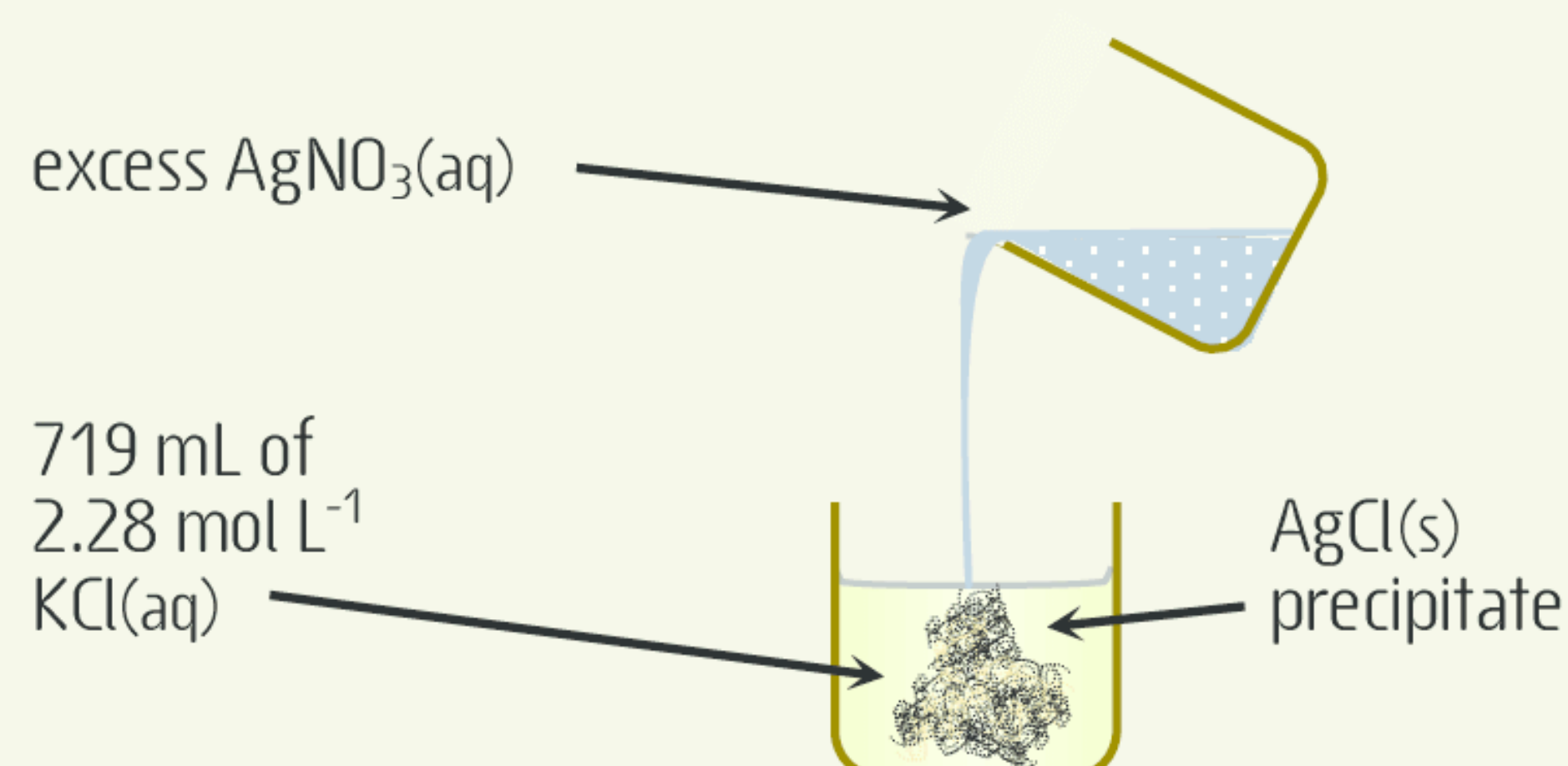
The coefficient of Al is 2, while that of HCl is 6, thus the molar amount of Al in the reaction is  $(2/6)$  that of HCl.

$$m(\text{Al}) = n \times M = 2.01 \times 10^{-3} \times 26.98 = 5.41 \times 10^{-2} \text{ g Al (3SF)}$$

Convert the moles of Al to an equivalent mass.

Attempt Set 31 # 1.

**EXAMPLE 2** Determine the mass of silver chloride that can be precipitated when excess silver nitrate solution is added to 719 mL of  $2.28 \text{ mol L}^{-1}$  potassium chloride solution.



Write an equation for the change described.

$$n(\text{KCl}) = cV = 2.28 \times 0.719 = 1.64 \text{ mol}$$

Volume must be in L, ie  $719 \text{ mL} = 0.719 \text{ L}$ .

$$n(\text{Cl}^-) = n(\text{KCl}) = 1.64 \text{ mol}$$

The chloride ion subscript in KCl is 1, thus one mole of KCl contains 1 mole of  $\text{Cl}^-$ .

$$n(\text{AgCl}) = n(\text{Cl}^-) = 1.64 \text{ mol}$$

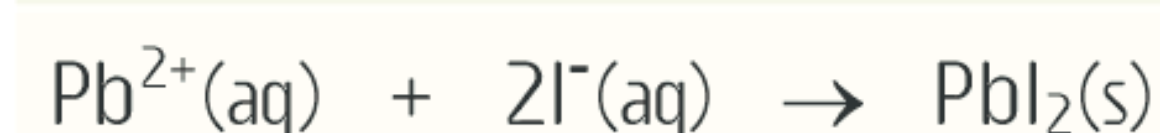
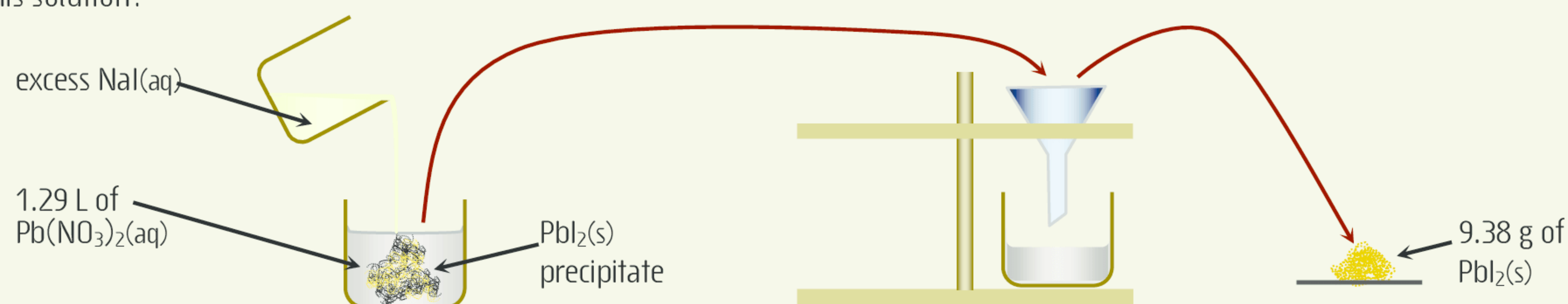
Both AgCl and  $\text{Cl}^-$  have a coefficient of 1 in the equation.

$$m(\text{AgCl}) = nM = 1.64 \times 143.35 = 235 \text{ g AgCl (3SF)}$$

Convert the moles of AgCl to an equivalent mass.

Attempt Set 31 # 2.

**EXAMPLE 3** The analysis of a lead nitrate solution [ $\text{Pb}(\text{NO}_3)_2\text{(aq)}$ ] involved adding excess sodium iodide solution [ $\text{NaI(aq)}$ ] to 1.29 L of the lead nitrate solution. The resulting precipitate of  $\text{PbI}_2\text{(s)}$  was filtered, washed and dried and found to have a mass of 9.38 g. What was the **concentration of lead nitrate** in this solution?



Write an equation for the change described.

$$n(\text{PbI}_2) = \frac{m}{M} = \frac{9.38}{461.0} = 2.03 \times 10^{-2} \text{ mol}$$

Convert the mass of  $\text{PbI}_2$  to an equivalent molar amount.

$$n(\text{Pb}^{2+}) = n(\text{PbI}_2) = 2.03 \times 10^{-2} \text{ mol}$$

Both  $\text{PbI}_2$  and  $\text{Pb}^{2+}$  have a coefficient of 1 in the equation.

$$n[\text{Pb}(\text{NO}_3)_2] = n(\text{Pb}^{2+}) = 2.03 \times 10^{-2} \text{ mol}$$

The lead ion subscript in  $\text{Pb}(\text{NO}_3)_2$  is 1.

$$c[\text{Pb}(\text{NO}_3)_2] = \frac{n}{V} = \frac{2.03 \times 10^{-2}}{1.29} = 1.58 \times 10^{-2} \text{ mol L}^{-1} \text{ (3SF)}$$

The moles of  $\text{Pb}(\text{NO}_3)_2$  and its solution volume can now be used to determine the solution concentration.

Attempt Set 31 # 3.



**EXAMPLE 4** In a laboratory investigation, Mario added excess sodium carbonate [ $\text{Na}_2\text{CO}_3$ ] to 25.0 mL of **sulfuric acid solution** [ $\text{H}_2\text{SO}_4(\text{aq})$ ]. He found the reaction produced 47.2 mL of carbon dioxide gas [ $\text{CO}_2(\text{g})$ ] measured at STP. What was the **concentration** of sulfuric acid used in the experiment?



$$n(\text{CO}_2) = \frac{V_{(\text{STP})}}{22.71} = \frac{47.2 \times 10^{-3}}{22.71} = 2.08 \times 10^{-3} \text{ mol}$$

$$n(\text{H}_2\text{SO}_4) = n(\text{CO}_2) = 2.08 \times 10^{-3} \text{ mol}$$

$$c(\text{H}_2\text{SO}_4) = \frac{n}{V} = \frac{2.08 \times 10^{-3}}{25.0 \times 10^{-3}} = \mathbf{8.31 \times 10^{-2} \text{ mol L}^{-1}} \quad (3\text{SF})$$

Write an equation for the reaction between sulfuric acid and sodium carbonate.

Find the moles of  $\text{CO}_2$  using the molar volume of gases relationship, ie  $n_{(\text{gas})} = V_{(\text{STP})} \div 22.71$ . Gas volume must be in litres (ie 47.2 mL =  $47.2 \times 10^{-3}$  L) measured at STP.

Both  $\text{H}_2\text{SO}_4$  and  $\text{CO}_2$  have a coefficient of 1 in the above equation.

Use the concentration relationship to determine the concentration of sulfuric acid. Solution volume must be in litres, ie 25.0 mL =  $25.0 \times 10^{-3}$  L.

Complete Set 31 and Set 32.

## Set 31 Stoichiometry involving solutions

- What **mass** of magnesium ribbon (**Mg**) will dissolve in 25.5 mL of  $6.60 \text{ mol L}^{-1}$   $\text{HCl}(\text{aq})$ ?
- A chemical investigation involves the precipitation of  $\text{PbI}_2(\text{s})$  by the reaction of 65.5 mL of  $0.750 \text{ mol L}^{-1}$   $\text{Pb}(\text{NO}_3)_2(\text{aq})$  with excess sodium iodide solution. What **mass** of **lead iodide** can be expected to form?
- A tap water sample (Fig 1) is analysed for its chloride ion concentration by adding excess  $\text{AgNO}_3(\text{aq})$  to precipitate the chloride ion as  $\text{AgCl}(\text{s})$ . An analysis of this type used 125 mL of tap water and produced 1.38 g of  $\text{AgCl}(\text{s})$  precipitate.
  - Using this information, find the **concentration** of **chloride ions** in the tap water.
  - Assuming the chloride ions in tap water are due solely to dissolved  $\text{NaCl}$ , calculate the **sodium chloride** concentration in **mol L<sup>-1</sup>** and **g L<sup>-1</sup>** for the tap water sample.
- In a laboratory exercise Joanne and Verena prepared hydrogen gas by the reaction of zinc with hydrochloric acid. What minimum **volume** of  $2.5 \text{ mol L}^{-1}$   $\text{HCl}(\text{aq})$  should be used if they need to produce at least 1.5 L of  $\text{H}_2(\text{g})$  measured at STP?
- The predominant anions in sea water are  $\text{Cl}^-(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$ . Two chemistry students, Matthew and Michelle have designed an experiment to determine the concentration of these ions in sea water. They first added excess  $\text{Ba}(\text{NO}_3)_2(\text{aq})$  to 325 mL of sea water causing the precipitation of  $\text{BaSO}_4(\text{s})$ . Michelle filtered, washed and dried the  $\text{BaSO}_4(\text{s})$  precipitate and found it had a mass of 2.65 g. To the filtrate Matthew added excess  $\text{AgNO}_3(\text{aq})$  precipitating the chloride ion in the sea water as  $\text{AgCl}(\text{s})$  and 23.3 g of  $\text{AgCl}(\text{s})$  was obtained. Using their data, find the **concentration** of  $\text{Cl}^-(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$  in the sea water sample. Express your answer in **mol L<sup>-1</sup>** and **g L<sup>-1</sup>**.
- Ariell wanted to find out the concentration of the active ingredient ethanoic acid in some homemade vinegar her mum had made. To do this she measured 20.00 mL of the vinegar and added  $0.1520 \text{ mol L}^{-1}$   $\text{KOH}$  solution to it. She used 15.19 mL of  $\text{KOH}(\text{aq})$  to completely neutralise the ethanoic acid in her mum's vinegar. Using this information find the **concentration** of **ethanoic acid** ( $\text{CH}_3\text{COOH}$ ) in the vinegar sample.
- Milk of magnesia, a suspension of  $\text{Mg}(\text{OH})_2(\text{s})$  in water, is used to treat indigestion caused by excess stomach acid. (See Fig 2.) One spoonful, equivalent to 880 mg of  $\text{Mg}(\text{OH})_2(\text{s})$  is usually sufficient for this purpose. Assume a person's stomach contained 450 mL of hydrochloric acid [ $\text{HCl}(\text{aq})$ ] with a concentration of  $0.075 \text{ mol L}^{-1}$ . What is the **concentration** of **HCl** after taking one spoonful of milk of magnesia?
- What **mass** of  $\text{BaSO}_4(\text{s})$  can be expected when 1.12 L of  $0.0569 \text{ mol L}^{-1}$   $\text{Ba}(\text{OH})_2(\text{aq})$  is combined with excess  $\text{K}_2\text{SO}_4(\text{aq})$ ?
- Chlorine gas can be produced in the laboratory by the reaction of hydrochloric acid and manganese(IV) oxide (manganese dioxide).
 
$$\text{MnO}_2(\text{s}) + 4\text{HCl}(\text{aq}) \rightarrow \text{MnCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{Cl}_2(\text{g})$$

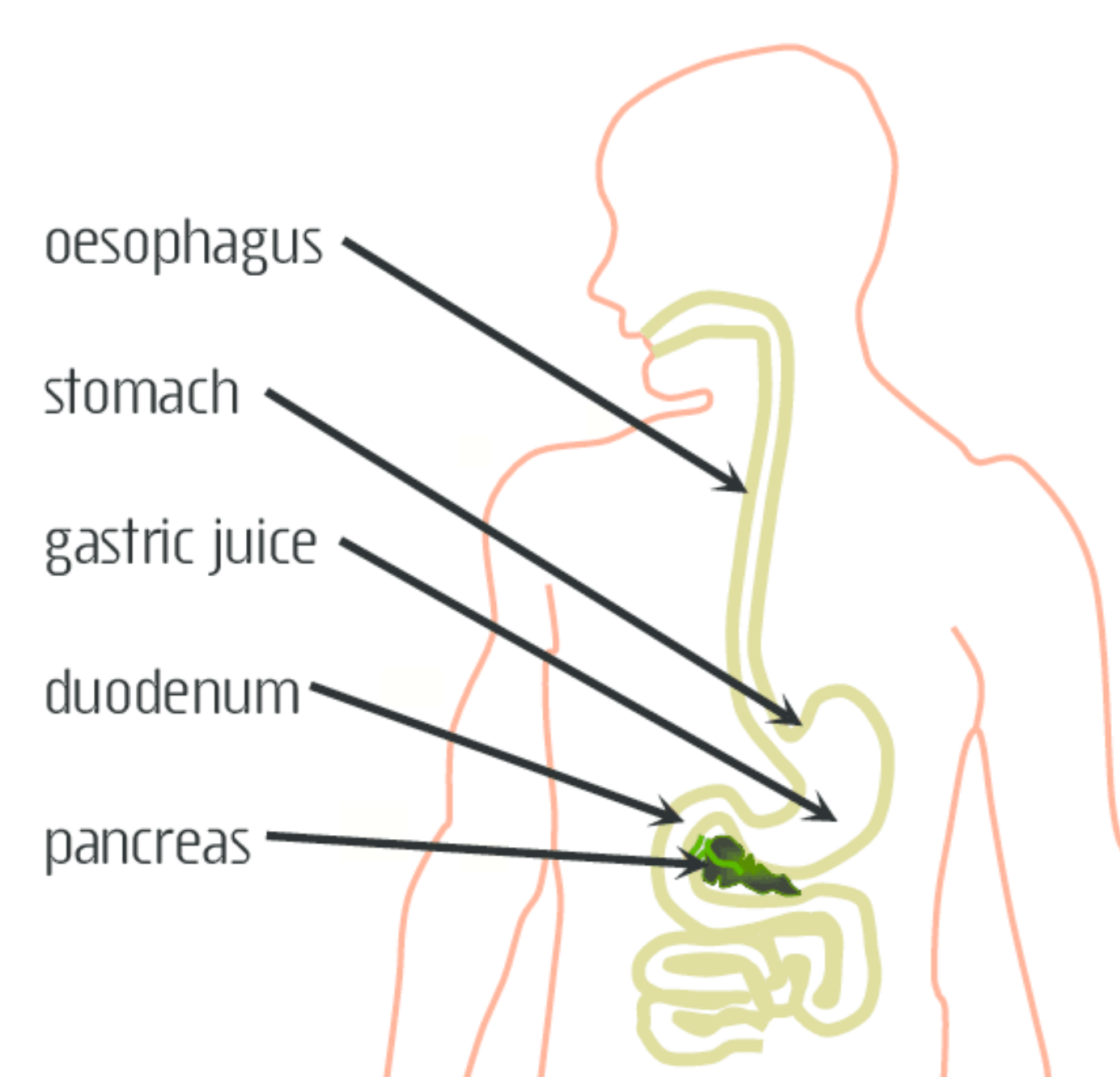
What maximum **volume** of **chlorine gas** can be produced from the reaction of 25 mL of  $1.5 \text{ mol L}^{-1}$   $\text{HCl}(\text{aq})$  with excess  $\text{MnO}_2(\text{s})$ ? Assume STP conditions apply.



**FIGURE 1** In major reticulated Australian water supplies the total dissolved solids (TDS) can range from below  $100 \text{ mg L}^{-1}$  to more than  $750 \text{ mg L}^{-1}$ . Water with low TDS can taste flat, while water with high TDS tastes salty and causes scaling in pipes, fittings and household appliances. The 2011 Australian Drinking Water Guidelines provide guidance in the palatability of drinking water according to TDS concentration:

- 0 to  $600 \text{ mg L}^{-1}$  is considered good.
- 600 to  $900 \text{ mg L}^{-1}$  is fair.
- 900 to  $1200 \text{ mg L}^{-1}$  is poor.
- Greater than  $1200 \text{ mg L}^{-1}$  is unacceptable.

Precisely what level of TDS an individual water supply system decides to accept depends upon community acceptance, available water resources, and the cost and practicality of changing the natural TDS levels.



**FIGURE 2** Gastric fluids in the human stomach are produced by parietal cells in the stomach wall. These fluids contain **hydrochloric acid** with a pH of around 1 to 2.

Hydrochloric acid assists with the digestion of proteins. It also inhibits the growth of microorganisms thus helping to prevent infection inside the stomach.

As the partly digested contents of the stomach pass into the duodenum they are neutralised by the action of sodium bicarbonate secreted from the pancreas.

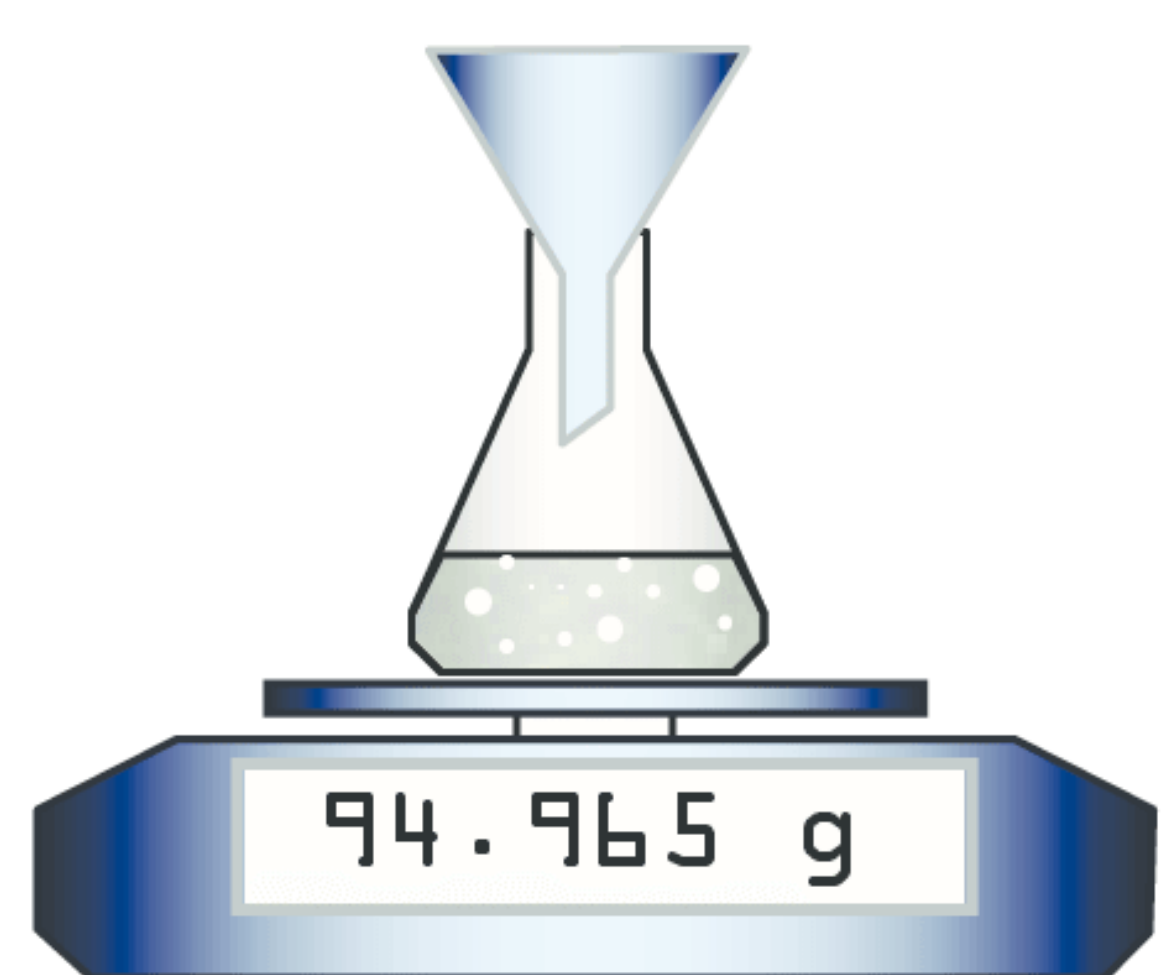
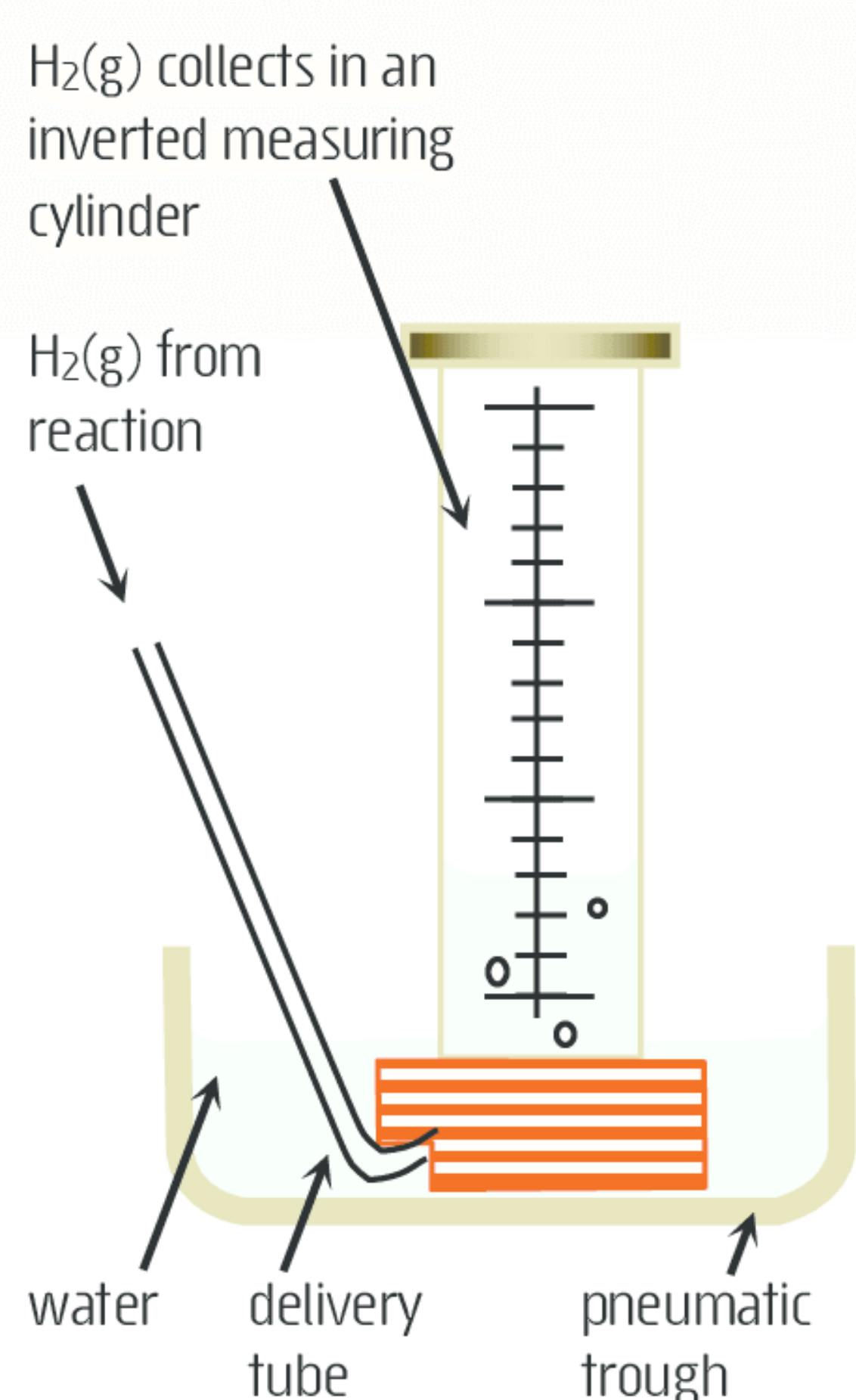


Acids like **HCl** and **HNO<sub>3</sub>** are **monoprotic**. This means one mole of acid can produce one mole of H<sup>+</sup> ions when neutralised with a strong base like NaOH.

**Diprotic** acids like **H<sub>2</sub>SO<sub>4</sub>** produce two H<sup>+</sup> ions for each molecule of acid. Phosphoric acid, **H<sub>3</sub>PO<sub>4</sub>** is a **triprotic** acid.

**FIGURE 3** Gases with very low solubility in water, like hydrogen, can be collected by the **downward displacement of water**. The volume of gas collected is easily found by using an inverted measuring cylinder.

The temperature of a gas collected this way will be similar to room temperature and its pressure will be room pressure when the water level inside the cylinder matches the water level inside the pneumatic trough.



**FIGURE 4** Hydrogen gas has a very low solubility in aqueous solution. So as the gas H<sub>2</sub> is formed it escapes from the reaction mixture. The loss of mass in the reaction mixture can be assumed to be equal to the mass of H<sub>2</sub> produced. Using a conical flask with a filter funnel in the mouth of the flask helps reduce loss of liquid by spattering from the reaction vessel. H<sub>2</sub> can still escape through the opening in the filter funnel.

10. A student investigation involved separating by filtration and crystallisation a sample of a crystalline compound from some plant tissue and then identifying it. A litmus test showed the solution of the compound to be quite acidic. To identify the compound the student carefully weighed a 465.2 mg sample of it and dissolved this in about 20 mL of water. Exactly 25.74 mL of 0.1578 mol L<sup>-1</sup> KOH solution was needed to neutralise this solution.

- How can litmus be used to identify the acidic nature of the unknown compound?
- Assuming the acid is **monoprotic** (see border note) and complete neutralisation occurs, determine the **molar mass** of the acid. [Hint: Let the acid formula be HX. Thus the anion of this acid must be X<sup>-</sup> and the salt formula will be KX. Now a balanced equation can be written and the stoichiometric mole ratio found.]
- How would your answer to (b) change if the acid was found to be **diprotic**?

## Set 32 Reviewing stoichiometry

- A 13.5 g sample of brass, an alloy of copper and zinc was tested for its zinc content. To do this the sample was finely powdered and allowed to dissolve in excess hydrochloric acid until no further reaction occurred. Copper present in the alloy is unaffected as it does not react with the acid. The reaction with zinc produces hydrogen gas which was collected by the downward displacement of water as shown in Fig 3. The collected gas occupied a volume of 2.28 L. Its STP volume was determined to be 2.07 L.
  - Write a balanced **equation** for the reaction between hydrochloric acid and zinc.
  - Why is the STP volume of hydrogen lower than the actual volume of gas collected?
  - Determine the **mass** of **zinc** that was present in the 13.5 g sample of brass.
  - What **hazards** are associated with producing and collecting hydrogen gas?
- Bubbling **ammonia** gas into a **sulfuric acid** solution produces the fertiliser ammonium sulfate.
  - Write a **balanced equation** for the reaction of ammonia (NH<sub>3</sub>) and pure sulfuric acid, H<sub>2</sub>SO<sub>4</sub>(l) to produce ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>].
  - What **mass** of H<sub>2</sub>SO<sub>4</sub> is needed to form 1.00 tonne of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> fertiliser?
  - Determine the **volume** of ammonia gas used if it is measured at STP.
- Gemma and her partners conducted an investigation into the reaction between **magnesium** and **hydrochloric acid**. They carefully measured the mass of a conical flask assembly containing a solution of hydrochloric acid. (See Fig 4.) To this they added a weighed piece of magnesium and allowed the hydrogen that formed to escape. They designed their reaction vessel (flask + filter funnel) so that only the gas hydrogen escaped from the flask and no droplets of solution were lost. The flask with its contents was reweighed after the reaction was complete. They recorded the following data:
 

initial mass of flask assembly + HCl(aq) + Mg(s) ..... 94.965 g

final mass of flask assembly + HCl(aq) + Mg(s) after reaction ..... 94.816 g

  - Write a **balanced equation** for the reaction between hydrochloric acid and magnesium.
  - Why is the mass of the flask assembly + HCl solution + Mg after reaction less than before the reaction?
  - What **mass** of hydrogen was formed in the reaction?
  - By a suitable calculation, determine the **mass** of **magnesium** that reacted.
  - In this investigation Gemma and her group chose to use a balance capable of measuring **milligram** amounts. How would their results have been affected if they used a balance only capable of measuring **tenths** of a gram? **Explain**.
  - What **hazards** are posed by the use of 6.0 mol L<sup>-1</sup> hydrochloric acid and consequently what precautions should the students take in conducting this investigation?
- Ethyne** (commonly known as acetylene) can be produced in the laboratory from the reaction of calcium carbide (CaC<sub>2</sub>) with water. A sample of ethyne was produced this way by mixing 2.10 g of CaC<sub>2</sub> with excess water. What **STP volume** of ethyne can be expected from this reaction mixture?





5. **Limestone** is an important building material used for constructing walls for houses and for retaining purposes. It consists of sand grains, essentially  $\text{SiO}_2(\text{s})$  bound together by the mineral calcium carbonate,  $\text{CaCO}_3(\text{s})$ . A student interested in the percentage of  $\text{CaCO}_3$  in a limestone sample conducted an analysis of it. He measured a 3.59 g sample of the limestone and added it to excess  $4.0 \text{ mol L}^{-1}$  hydrochloric acid. The resulting carbon dioxide gas was collected and found to have an STP volume of 549 mL.
- Write an **equation** for the reaction between hydrochloric acid and calcium carbonate.
  - Calculate the **mass** of  $\text{CaCO}_3$  that was present in the 3.59 g sample of the limestone.
  - What mass of sand ( $\text{SiO}_2$ ) was present in the limestone sample?
6. **Lime** ( $\text{CaO}$ ) is an important material in the building industry. It is used as wall plaster and is an important component of many types of cement. The major use of lime in Western Australia is in alumina refining, gold extraction, in mineral sands processing and is also used for raising the pH of drinking water. Lime is obtained by heating and decomposing calcium carbonate found in high grade limestone deposits and certain types of marine shell deposits.

Edward and Lee are investigating a sample of **marine shells** as a potential economic source of calcium carbonate for lime manufacture. To determine the percentage of calcium carbonate in the shells, some of the shells are crushed, weighed and treated with hydrochloric acid. The acid dissolves  $\text{CaCO}_3$  in the shells producing carbon dioxide gas. The reaction for dissolving the calcium carbonate is shown here.



The acid and shell mixture is gently heated ensuring the reaction is complete and all of the carbon dioxide is driven off from the mixture. The resulting  $\text{CO}_2$  gas is bubbled into a potassium hydroxide ( $\text{KOH}$ ) solution where it is absorbed forming **potassium carbonate** and causing an **increase in mass** of the potassium hydroxide solution. Their data is shown:

mass of crushed shells .....	8.765 g
mass of conical flask + $\text{KOH}$ solution .....	98.019 g
mass of conical flask + $\text{KOH}$ solution + absorbed $\text{CO}_2(\text{g})$ .....	100.857 g

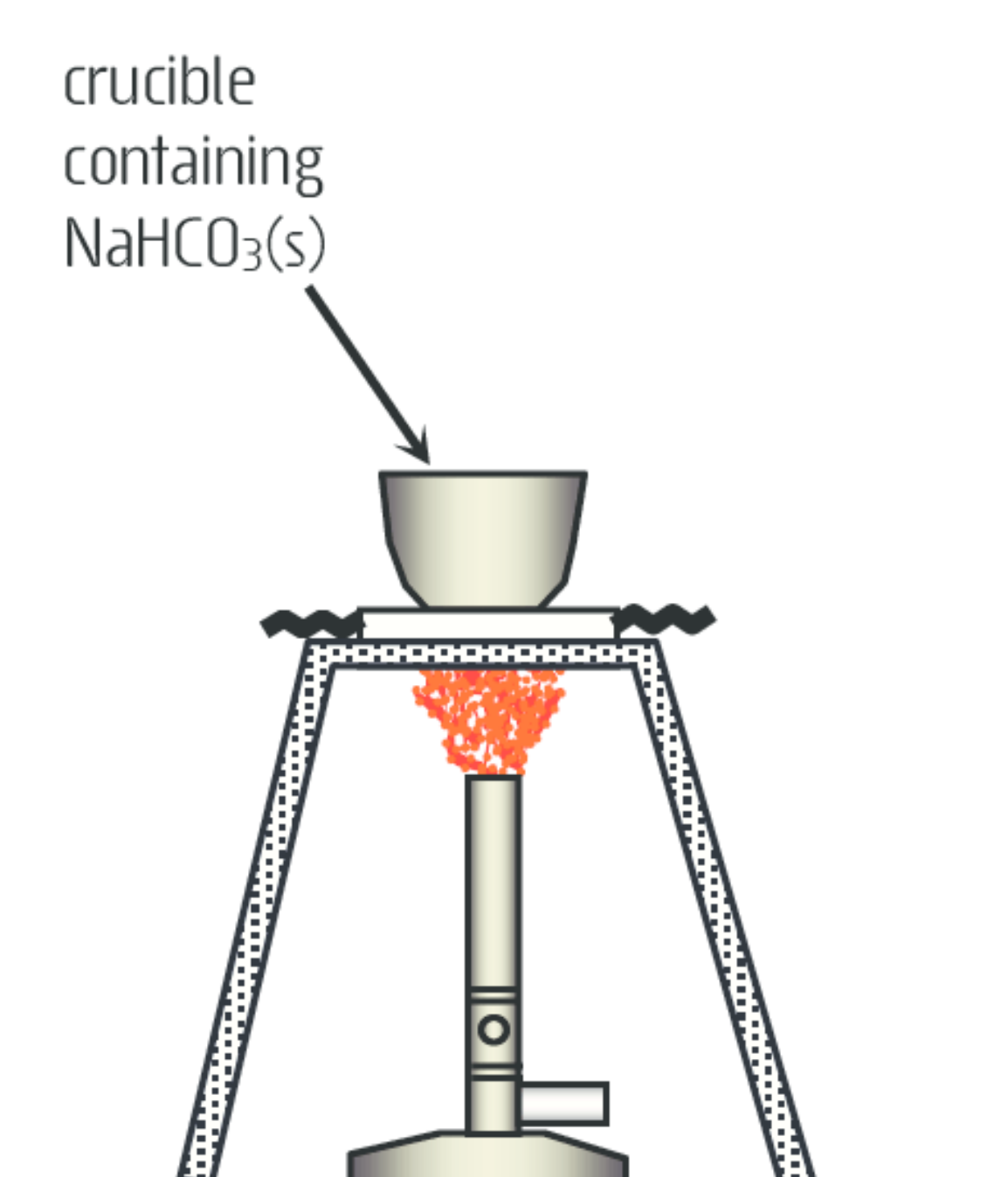
- What **mass** of  $\text{CO}_2$  gas was absorbed into the  $\text{KOH}$  solution and hence what mass of carbon dioxide was liberated from the reaction of the shells with the  $\text{HCl}$  solution?
  - Determine the **mass** of  $\text{CaCO}_3$  in the shell sample.
  - What is the **percentage** by mass of  $\text{CaCO}_3$  in this shell sample? **See border note. (E)**
  - Edward and Lee could have chosen to collect and measure the volume of carbon dioxide gas formed from the reaction using the downward displacement of water technique. (See Fig 3 p159.) They decided not to use this technique as Lee had learnt that carbon dioxide gas is slightly soluble in water. Had they chosen to use this technique **how** would their calculated result for the %  $\text{CaCO}_3$  in the shells have been affected? Would this have been a **random** or **systematic** error? **Explain.**
7. A Chemistry class investigated the ratio between the **moles of  $\text{NaHCO}_3$  used** and **moles of  $\text{Na}_2\text{CO}_3$  produced** when solid sodium hydrogencarbonate,  $\text{NaHCO}_3(\text{s})$  is decomposed. To do this each group heated a carefully weighed sample of  $\text{NaHCO}_3(\text{s})$  and weighed the decomposed product,  $\text{Na}_2\text{CO}_3(\text{s})$ . (See Fig 5.) A summary of the class results and two incomplete columns are shown.

mass of $\text{NaHCO}_3(\text{s})$ decomposed	mass of $\text{Na}_2\text{CO}_3(\text{s})$ produced	moles of $\text{NaHCO}_3$ decomposed	moles of $\text{Na}_2\text{CO}_3$ produced
2.56	1.62		
3.80	2.38		
4.11	3.13		
6.34	3.94		
7.07	4.46		

- Determine the moles of each compound,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  involved in the reaction for each trial. Enter this into the last two columns of the above table.
- Using a suitable scale plot a line graph for  $n(\text{NaHCO}_3)$  (**y-axis**) against  $n(\text{Na}_2\text{CO}_3)$  (**x-axis**).
- Determine the gradient of your graph.
- What does your answer to (c) indicate about the **ratio** of the **coefficients** for  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  in the balanced equation for the decomposition of  $\text{NaHCO}_3$ ?
- One of the data points is clearly in **error**. What type of error is this? **Explain.**

To find the percentage of a component in a mixture:

$$\% \text{ component} = \frac{\text{m}(\text{component}) \times 100}{\text{m}(\text{mixture with component})}$$



**FIGURE 5** As  $\text{NaHCO}_3(\text{s})$  is heated it decomposes forming  $\text{Na}_2\text{CO}_3(\text{s})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}_2(\text{g})$ . These gases escape from the crucible leaving only  $\text{Na}_2\text{CO}_3(\text{s})$  in the crucible after heating is complete. Thus the mass of  $\text{Na}_2\text{CO}_3(\text{s})$  formed in the reaction equals the mass of the crucible after heating minus the mass of the empty crucible.

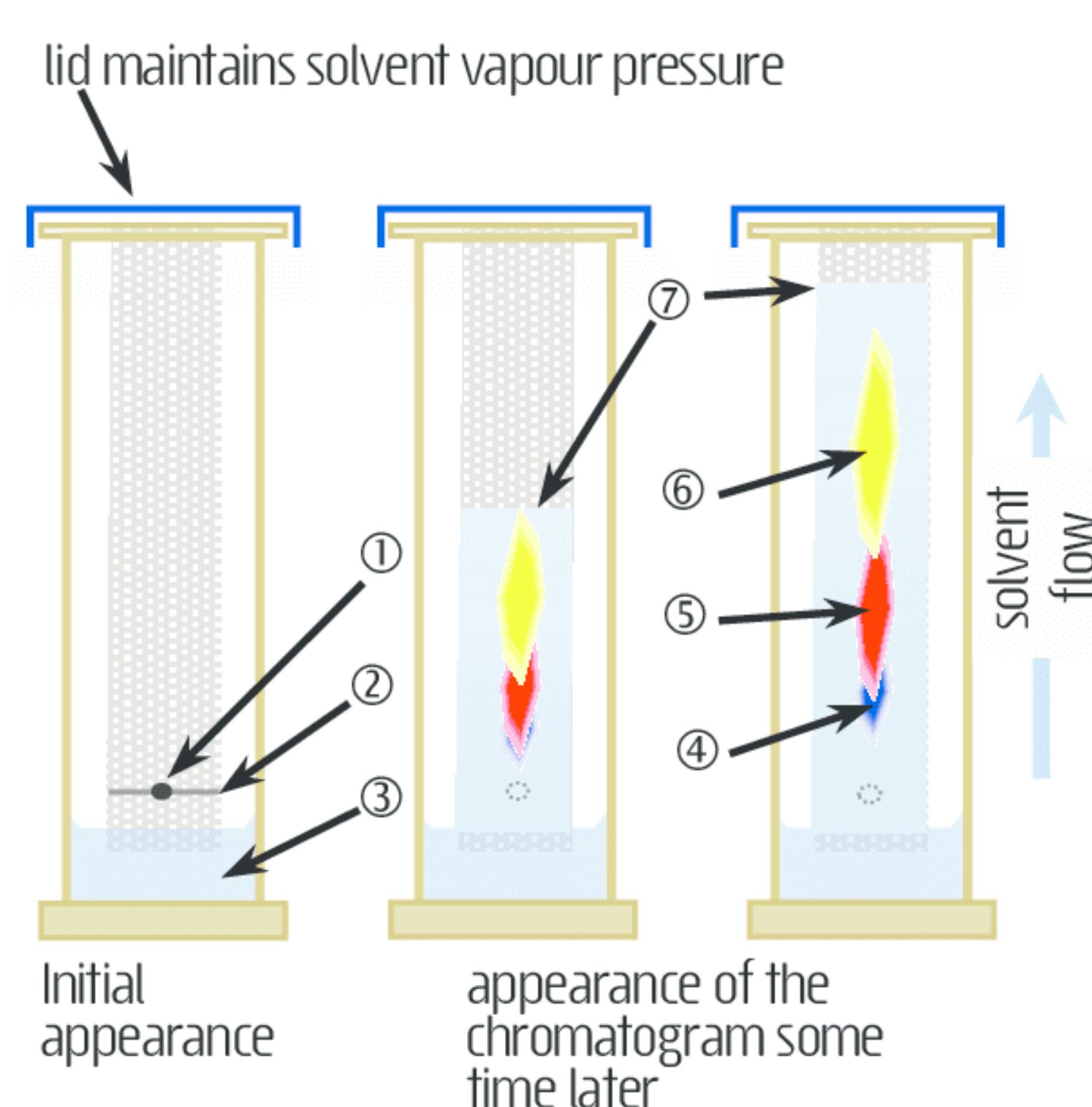


# CHAPTER 19 | CHROMATOGRAPHY



**FIGURE 1** This researcher is using **gas chromatography** to analyse samples of wine to determine the aromatic characteristics of different grapes and their suitability for use in winemaking.

**Adsorption** is the binding of molecules to a surface, ie molecules become **adsorbed** when they adhere or stick to a surface.



**FIGURE 2** Paper chromatography for a sample of food dye. A small sample of the dye, ① is placed on a pencil line, ② at the base of a strip of chromatography paper. The chosen solvent, ③ soaks up through the paper chromatography strip by capillary action. Over time the various components of the dye, ④, ⑤ and ⑥, begin to separate according to their polarity.

Note the solvent front, ⑦ advances more quickly than any of the components in the mixture. An important measure of a component's tendency to move with the mobile phase is its **retardation factor,  $R_f$** . (Also known as the **retention factor**.) In paper chromatography  $R_f$  is defined as:

$$R_f = \frac{\text{distance moved by solute}}{\text{distance moved by solvent}}$$

If measured under identical conditions  $R_f$  can be used to identify the components in a mixture.

Attempt Set 33 # 1 and 2.

## 19.1 Chromatography: An introduction

Chromatography is one of the most widely used laboratory techniques for the **separation** and **identification** of the substances in a mixture. Moreover, chromatography is a very useful technique for finding the **concentration** of each substance in a mixture. Instrumental chromatographs can analyse very small samples, microlitre quantities ( $1 \times 10^{-6}$  L) are sufficient. They can also detect picogram amounts ( $1 \times 10^{-12}$  g) in these samples.

Not surprisingly applications are found in many areas of research and industry including the petroleum industry, in microbiology, in environmental science such as for air monitoring, in the food and beverage industry for quality control and in the analysis of contaminants like pesticides. In the pharmaceutical industry they are used to measure the purity and composition of drug samples and in forensic investigations to monitor the illegal use of performance enhancing substances in sport.

Chromatographic applications in research and industry typically involve the use of complex instrumental chromatographs like the **gas liquid chromatograph (GC or GLC)** or **high performance liquid chromatograph (HPLC)**. The principles of chromatography however, are most easily seen in the simpler techniques of **paper chromatography**, **thin-layer chromatography (TLC)** and **column chromatography**. In these examples a moving liquid phase flows over a stationary solid phase. **Separation** of individual components from a mixture relies on their differing solubility (due to differing intermolecular forces) in the moving liquid phase compared to their tendency to **adsorb** (see border note) to the stationary solid phase. Substances that tend to stay dissolved in the moving liquid phase become separated from those that tend to adsorb (adhere) onto the stationary solid phase.

## 19.2 Paper chromatography (E)

In paper chromatography a small amount of the mixture to be separated is dissolved in a suitable solvent. A drop or two of this mixture is carefully spotted along a pencil line drawn at one end of a strip of chromatography paper, the **stationary phase**. (More specifically, the stationary phase consists of **water molecules** bound to the cellulose fibres of the chromatography paper.) The prepared paper strip is dipped into a suitable solvent in a sealed container. By capillary action, the solvent, ie the **mobile phase**, soaks up into the chromatography paper and moves through the spotted mixture carrying its various components at different speeds up along the chromatography strip. (See Fig 2.)

The resulting separation of components is due to their differing polarity. Very polar components will have a strong tendency to **adsorb** onto the chromatography paper (also polar in nature). These progress slowly up the chromatography strip. Components with a greater tendency to remain **dissolved** in the mobile phase, a solvent of variable polarity, progress quickly up the paper strip. In this way the individual pure substances within a mixture become separated and concentrated at different distances along the paper chromatography strip.

This technique is easily seen if the various components are coloured. The position or presence of colourless components can still be identified by exposing the dried paper strip to a suitable indicator. This is a reagent that reacts to produce a coloured product. A **ninhydrin** ( $C_9H_6O_4$ ) spray for example is an excellent way to show the presence of any suspected amino acids or amine compounds present on the chromatogram. Ninhydrin reacts with these compounds to give a striking purple colour. In a similar way forensic scientists use ninhydrin to 'develop' (make visible) latent fingerprints as it reacts with the amino acid lysine present in the fingerprint. Other reagents such as **iodine vapour** are also suitable as indicators. **Ultra violet light** may also be used to help detect the presence of separated components that are otherwise invisible.



## 19.3 Column chromatography (E)

Column chromatography was the original method of chromatography developed by the Russian-Italian botanist, **Mikhail Tswett**. (See Fig 4.) Tswett used this technique for the separation of coloured pigments (chlorophylls and carotenoids) from plant extracts. (See Fig 3.)

Column chromatography uses a glass tube packed with small beads of silica gel ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) as the **stationary phase**. The vertical glass tube is filled with a suitable solvent, the **mobile phase** and a small volume of mixture to be separated is added to the top of the column. Opening a tap located at the bottom of the tube allows solvent to flow down through the tube and out the tap end. Solvent is continually dripped into the top of the chromatography column to match the rate at which it leaves the bottom of the column. Over time the components of the mixture are seen to move down the column eventually forming separate bands due to their different tendency to **adsorb** to the stationary phase or remain **dissolved** in the mobile phase. By changing the collecting vessel at the bottom of the column it is possible to separately collect the components of the mixture as they exit the bottom of the column.

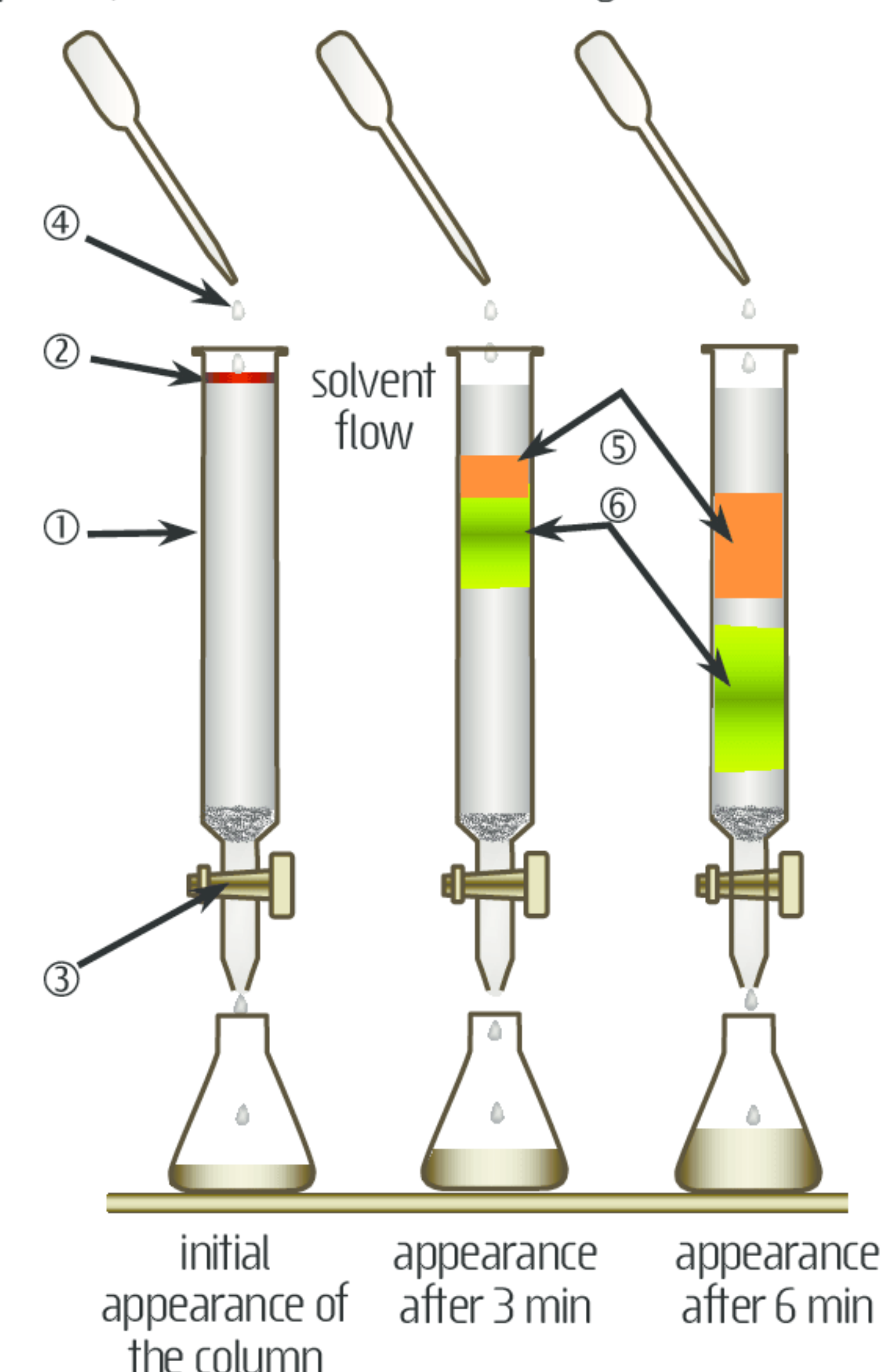


**FIGURE 4** The invention of chromatography is attributed to the Russian-Italian botanist, **Mikhail Tswett** (1872-1919). His technique was first outlined in a scientific paper in 1905 and then again as 'chromatography' in 1906.

Tswett was experimenting with techniques for isolating the various pigments (chlorophylls and carotenoids) present in plant extracts. His technique involved adding a solution of the pigment mixture to the top of a glass column packed with about 3-4 cm of finely powdered calcium carbonate, the stationary phase.

Tswett used solvents like petroleum ether, a  $\text{C}_5$ - $\text{C}_6$  hydrocarbon mixture, as the mobile phase to flush the pigment mixture through the column. As the mixture passed down the column it separated into a series of coloured bands. Each band consisted of a single pigment that had separated from the mixture. These coloured bands are said to have inspired the name Tswett chose for this separation technique, 'chromatography' after 'chroma' and 'graphe', which are Greek words meaning 'colour' and 'to write'.

**Figure 3** The column in **column chromatography** consists of a glass tube, ① filled with an appropriate solvent (the mobile phase) and packed with small beads of alumina or silica gel (the stationary phase). A small sample of solution containing the mixture, ② is placed at the top of the column. Opening a tap at the base of the column, ③ allows the mixture and solvent to flow downwards and out of the column. Fresh solvent is continually added to the column, ④. Over time the various components of the mixture, ⑤ and ⑥, begin to separate depending upon their tendency to stay dissolved in the solvent versus their tendency to adsorb onto the stationary phase, ie the alumina or silica gel.



## 19.4 Thin-layer chromatography

Thin-layer chromatography (TLC) is similar to paper chromatography. However, instead of using paper it uses a thin glass plate coated with either finely powdered alumina,  $\text{Al}_2\text{O}_3$  or silica,  $\text{SiO}_2$  (both have a polar nature) as the stationary phase. The mobile phase is a solvent chosen for its ability to dissolve and separate the components in the mixture. As most components analysed by TLC are molecular in nature their **polarity** will affect their **solubility** in the chosen solvent. Selecting a suitable solvent (or mixture of solvents), ie one that gives a good separation, involves trying a variety of solvents with progressively increasing polarity and noting which works best. Alkanes like hexane for example, are suitable as non-polar solvents while esters (eg ethyl acetate), ketones (eg acetone) and alcohols like ethanol are progressively more polar.

As with paper chromatography the solvent or mobile phase moves up by capillary action through the stationary phase (ie the polar alumina or silica gel layer) carrying the various components of the mixture at different rates depending upon their polarity. This results in the various pure components of the mixture separating out along the silica gel coated glass slide. The separations produced with TLC are sharper and better defined than those from paper chromatography. As such TLC is more reliable when attempting to separate and identify the components of a mixture.

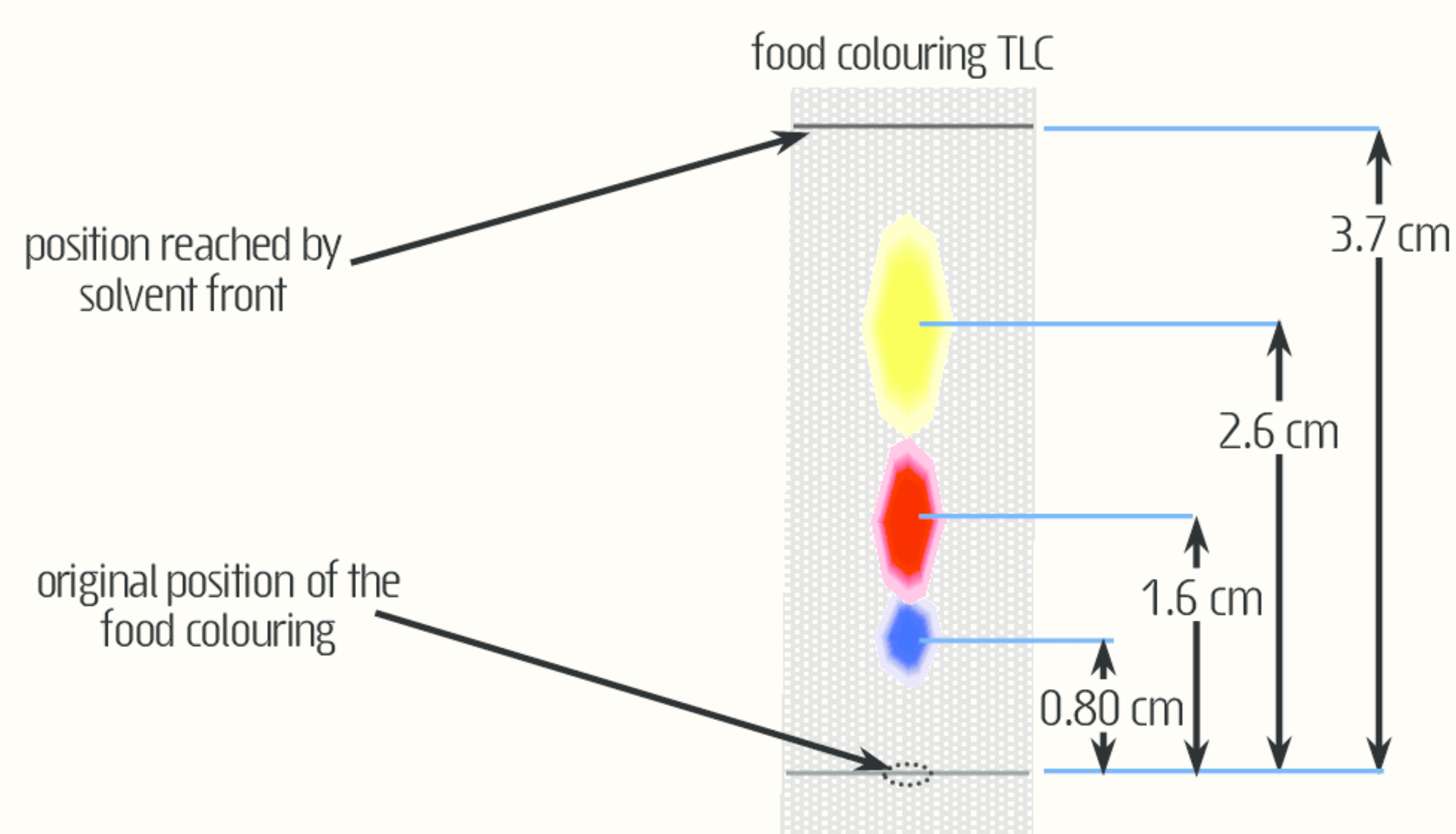
Substances on a TLC or paper chromatogram are identified by their **retardation factor**,  $R_f$ . (See Example 1.) The greater a substance's  $R_f$  the faster it progresses as the chromatogram develops. The maximum value is 1.00. This equates to a substance that moves at the same rate as the solvent phase. An  $R_f$  of zero means the substance does not move at all. In TLC or paper chromatography,  $R_f$  is found by comparing the distance moved by the substance (or solute) compared to the distance moved by the solvent. (See border note.) The  $R_f$  of a given substance is not a constant but depends upon the nature of the stationary and mobile phases and temperature of the run. For this reason a TLC of the different pure substances thought to be present in the mixture need to be produced under identical conditions in order to determine comparative  $R_f$  values.

To find the **retardation factor**, also known as the **retention factor**, of a substance from a paper chromatogram or TLC:

$$R_f = \frac{\text{distance moved by substance (solute)}}{\text{distance moved by solvent}}$$



**EXAMPLE 1** A food colouring used in cake decorating is thought to have been accidentally contaminated with an incorrect blue dye not suitable as a food grade dye. In order to determine the safety of the batch of food colouring a technician performs a TLC on a sample of it using a 1% salt solution as the mobile phase. The suspect blue dye was also analysed in the same way and its retardation factor determined to be 0.32. Analyse the TLC chromatogram of the food colouring and determine if there is any evidence of contamination with the blue dye.



$$R_f = \frac{\text{distance moved by solute}}{\text{distance moved by solvent}}$$

$$R_f(\text{yellow dye}) = \frac{2.6 \text{ cm}}{3.7 \text{ cm}} = 0.70$$

$$R_f(\text{red dye}) = \frac{1.6 \text{ cm}}{3.7 \text{ cm}} = 0.43$$

$$R_f(\text{blue dye}) = \frac{0.80 \text{ cm}}{3.7 \text{ cm}} = 0.22$$

**Answer:** The blue dye in the food colouring has an  $R_f$  of 0.22. None of the other component dyes present in the food colouring have an  $R_f$  close to the contaminant  $R_f$  of 0.32. Hence there is no evidence of contamination with the incorrect blue dye.

TLC has the advantage of being a simple and inexpensive technique for confirming the purity of a compound. It is ideal for separating ink components, plant extracts and is used with the manufacture and design of dyes. There are TLC screening tests for most drugs of abuse, including opioids, amphetamines, barbiturates, cocaine and marijuana. Although TLC is suitable for screening urine samples it is prone to false positives. If TLC gives a positive result a confirmatory test is used. Gas chromatography used in conjunction with mass spectrometry is the generally accepted method for the confirmed identification of drugs of abuse. (See Fig 11 p170.)

Attempt Set 33 # 3 and 4.

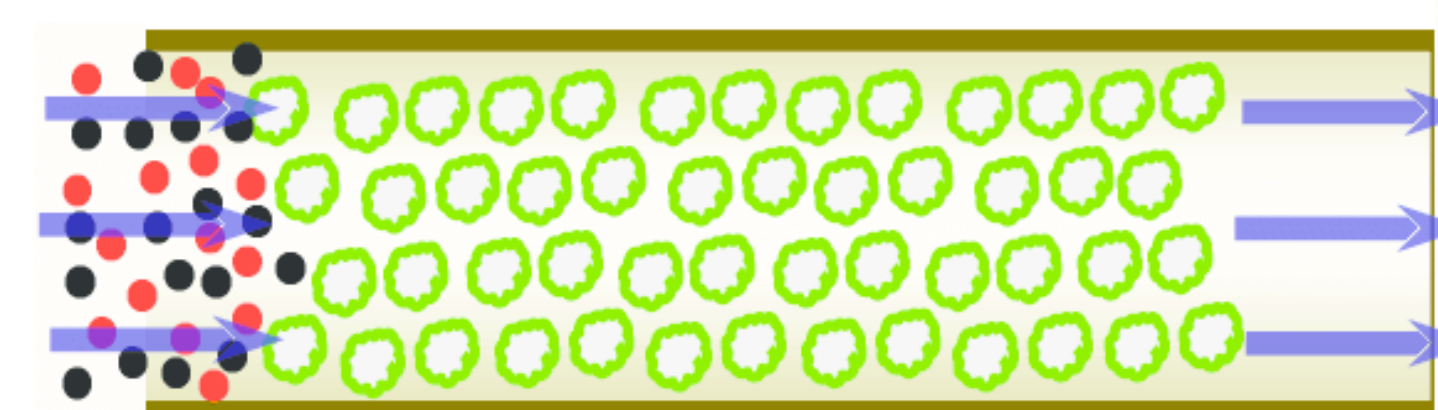
**FIGURE 5** Section of a **gas chromatography column** (not to scale) showing the inert  $\text{SiO}_2$  particles coated with a high boiling point non-volatile liquid. A mobile gas phase such as helium flushes the vaporised mixture of gases (**black** and **red**) through the column.

As the mixture of gases moves through the column they become separated depending upon their tendency to remain in the stationary liquid phase (coating the  $\text{SiO}_2$  particles) or to stay in the mobile gas phase. In this example the black molecules have the higher **retention time** as they have a lower volatility and/or interact more strongly with the liquid stationary phase.

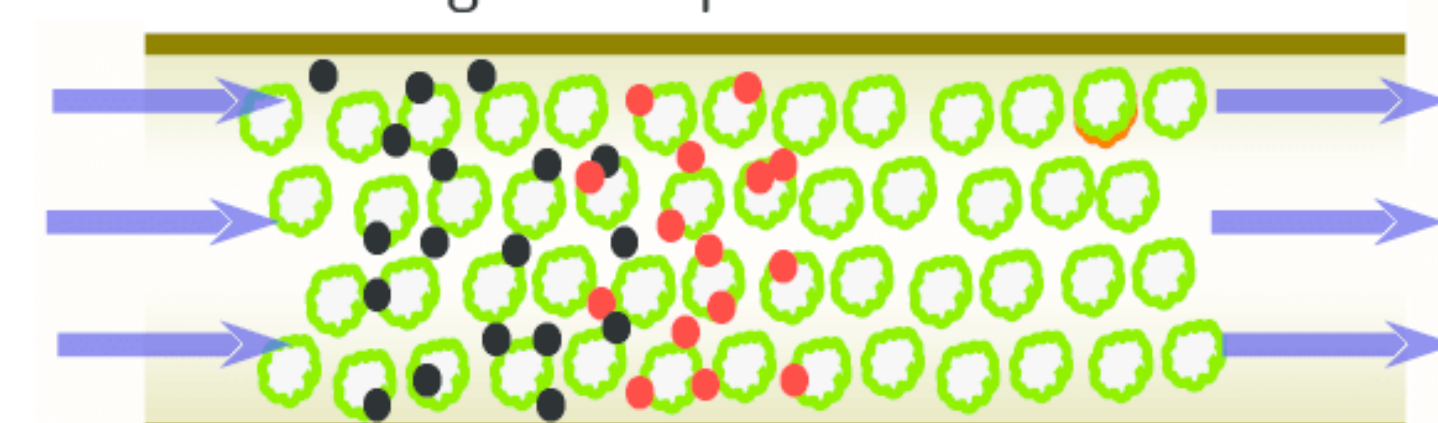
**Key:**

- direction of carrier gas flow
- $\text{SiO}_2$  particles
- liquid stationary phase coating on  $\text{SiO}_2$
- vaporised mixture of molecules

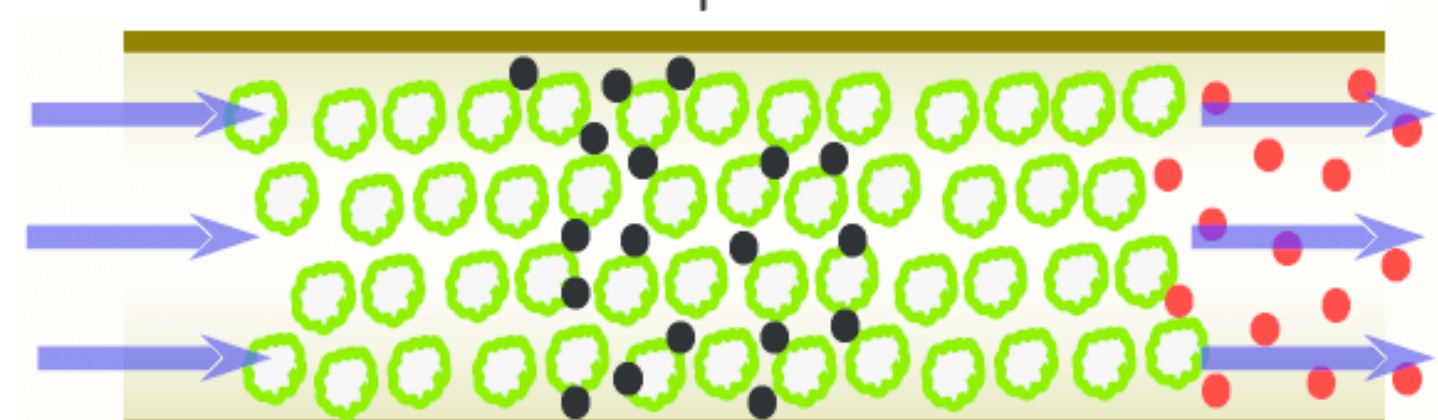
Gas mixture is introduced into the column.



The mixture begins to separate.



The mixture has been separated.



## 19.5 Instrumental chromatography

The techniques of chromatography that find application in research and industry typically involve the use of instruments such as the **gas chromatograph (GC)**, also known as a gas liquid chromatograph, **GLC** or **high performance liquid chromatograph (HPLC)**. The separation principles applied in these instruments are similar to those for the simpler (less expensive) techniques of TLC and column chromatography. Separation of individual components, called **analytes**, from the mixture relies on their differing distribution between a moving phase and a stationary phase.

## 19.6 Gas chromatography

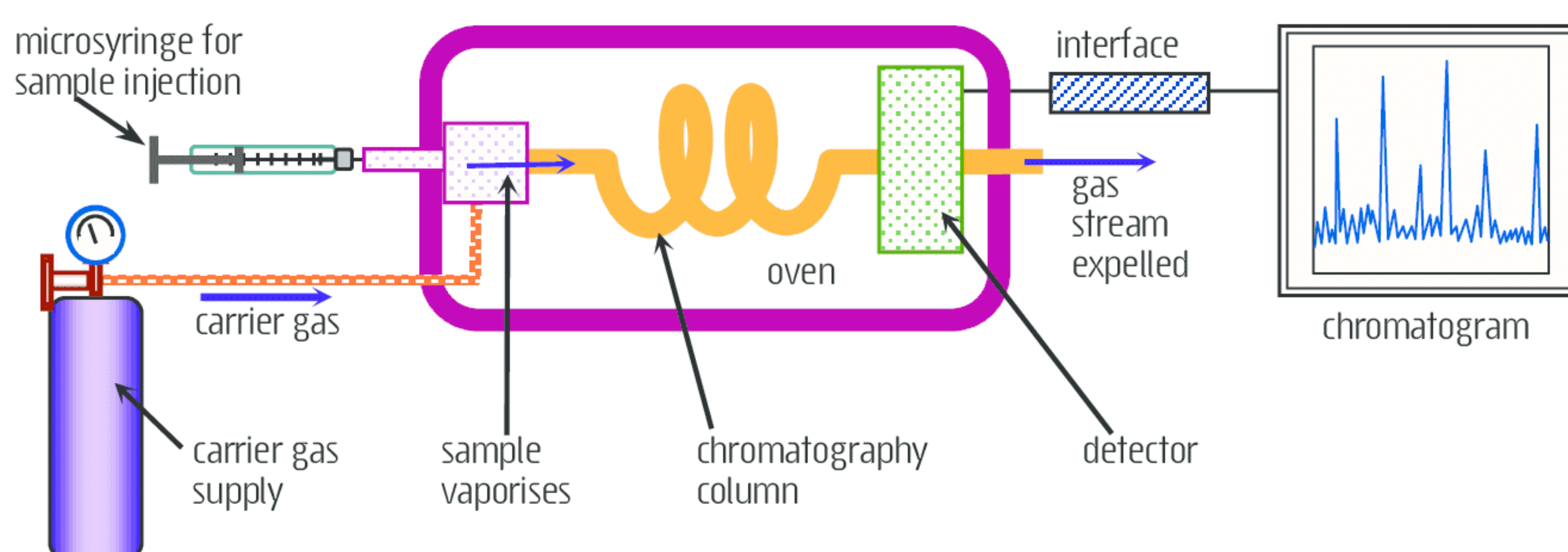
Gas Chromatography (**GC**) is ideal for **identifying** individual substances and their **concentrations** in a variety of complex mixtures. GC uses a mobile phase consisting of a chemically **inert carrier gas** like helium or nitrogen rather than the liquid mobile phase used in TLC. The stationary phase is a **high boiling point non-volatile viscous liquid** that is **coated** (adsorbed) onto solid particles such as silica ( $\text{SiO}_2$ ). These liquid coated particles are packed within a long stainless steel column. Most packed GC columns have an internal diameter of 2–5 mm and are typically 1.5–10 m in length. For this reason it is convenient to wind the column into a coil. Some columns, known as capillary columns, have a hollow interior with the non-volatile liquid coated onto the inside of the column. These may be a few tenths of a millimetre in diameter and much longer than the packed columns, some are up to a 100 m in length. (See Fig 9.)

The **liquid mixture** to be analysed by GC is introduced into the carrier gas stream by injecting through a silicon rubber seal using a microsyringe. (See Fig 6.) The high temperature of the injecting chamber (up to 250 °C) vaporises the sample which then flows along with the carrier gas stream into the chromatography column. The column is situated inside an oven and is maintained at a suitable temperature that produces a good separation of the components in the mixture.

Various **analytes** in the mixture have differing tendencies to remain in either the stationary liquid phase or in the carrier gas stream. This essentially depends upon the analyte's **volatility** (tendency to evaporate). Analytes with a high volatility have a greater tendency to remain in the mobile gas phase. These quickly exit the column and hence will have a low **retention time**. (See Fig 5.)



As a result of the differing retention times, individual analytes in the mixture emerge separately from the end of the chromatography column. Here they are analysed as they pass through a detector. Detector signals are digitally recorded and can be displayed on screen or printed as a paper chart called a **chromatogram**. (See Fig 7.) The chromatogram has numerous peaks. (See Fig 8.) Each peak indicates the presence and concentration of a particular analyte in the mixture.

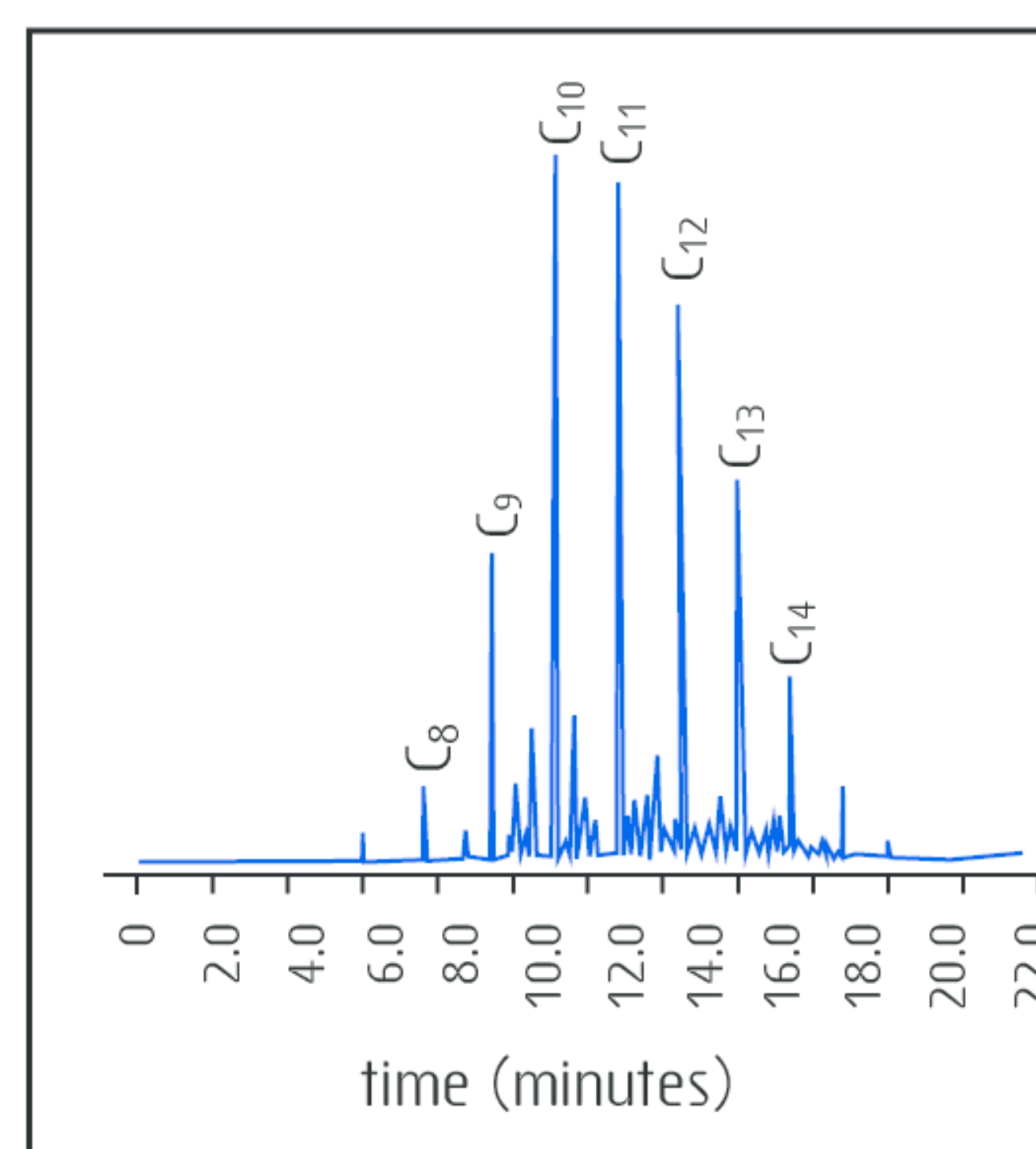


**FIGURE 7 Operation of a gas chromatograph** (above)

A sample is injected via a silicon rubber seal in the injection port (A). The vaporised sample is carried by the carrier gas through the chromatography column (B). Various analytes in the sample travel at different rates through the column and become separated. A detector (C) signals the presence of the analytes as they emerge from the column. The detector signal is processed and displayed on screen or printed as an intensity versus retention time **chromatogram**.

**FIGURE 8 Chromatogram of kerosene** (right)

Notice there are several major peaks. Each peak represents a different compound in the mixture that is kerosene. The retention time of these compounds depends upon their **volatility** which is closely related to their **boiling point**. This in turn depends upon the molecule's **molar mass** or number of carbon (C) atoms. The C number for each peak is shown. The height and area of each peak is proportional to that compound's concentration in the kerosene sample.



**Retention time** is an important characteristic of each analyte in the mixture. This primarily depends upon the analyte's **boiling point/volatility**. Low boiling point analytes, ie those with weak intermolecular forces, have a high volatility and tend to remain in the carrier gas. These exit the column sooner and thus have a lower retention time than higher boiling point analytes. The chromatogram of kerosene (Fig 8) clearly shows this as the different analytes exit the column in order of increasing molar mass (lowest first) which is also the order of increasing intermolecular forces (dispersion forces). Retention time also depends upon the column **temperature**. As temperature increases so the retention time of all analytes will decrease. As an example, a 10 °C increase in column temperature will usually halve the retention time. Sometimes the column temperature is programmed to slowly increase over time. This can help elute less volatile analytes which may otherwise be very slow to exit the column.

The **flame ionization detector** (FID) is a commonly used detector that signals the presence of an analyte in the carrier gas exiting the chromatography column. While the FID does not actually identify the analyte it does give its retention time which can be used to identify it. Another important detector used in conjunction with the GC is the **mass spectrometer** (MS). This instrument is a stand-alone analytical tool that can positively identify a great variety of compounds. (See 1.11 p9.) For this reason GC coupled with MS finds great application in forensic analysis such as for the detection of performance enhancing or banned substances in blood or urine samples. Portable GCMS systems are also available and these can be taken into the field for direct analysis of forensic or environmental samples.

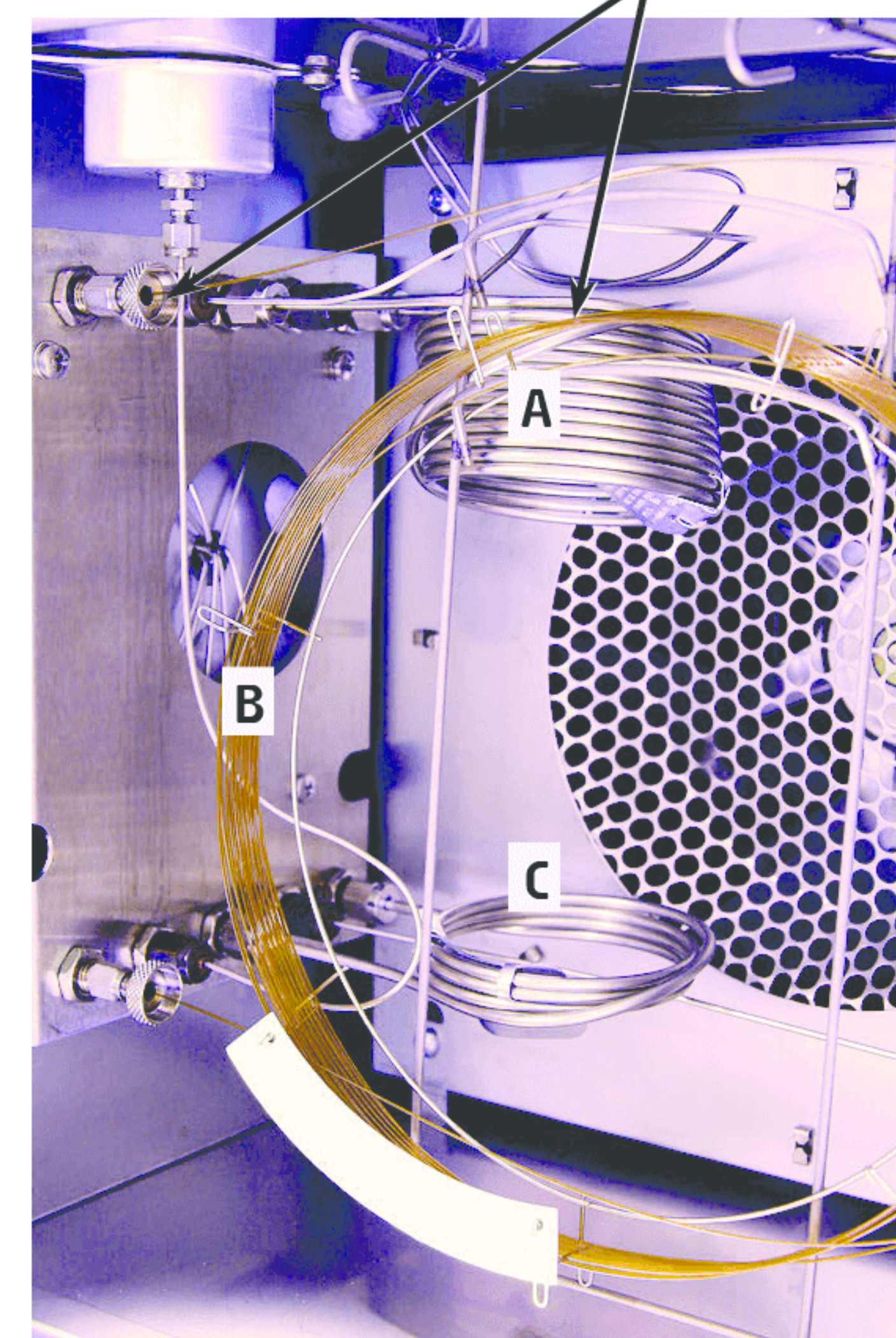
## 19.7 Identifying analytes from retention time

The **peaks** in a chromatogram are characterised by their **height**, **area**, and **retention time**. These peak features can be used to **identify** an analyte and determine its **concentration** in the mixture. To identify the presence of a suspected analyte, a chromatogram of that pure compound is produced using the same column, carrier gas, gas flow rate and temperature. Comparing the retention time of the pure analyte to that of the analytes in the mixture indicates its presence in the mixture. (See Example 2.)

**FIGURE 6** A forensic chemist injecting a sample into a gas chromatograph via its injector port.



inside view showing coiled chromatography columns and injection ports



**FIGURE 9** Inside a gas chromatograph oven. Several different chromatography columns can be seen. Column A and C are **packed columns** while column B is a **capillary column**. Notice how the columns are coiled so that they conveniently fit inside the oven.

Attempt Set 33 # 5.

Some terms frequently used in instrumental chromatography:

**Eluent:** The solvent or mobile phase.

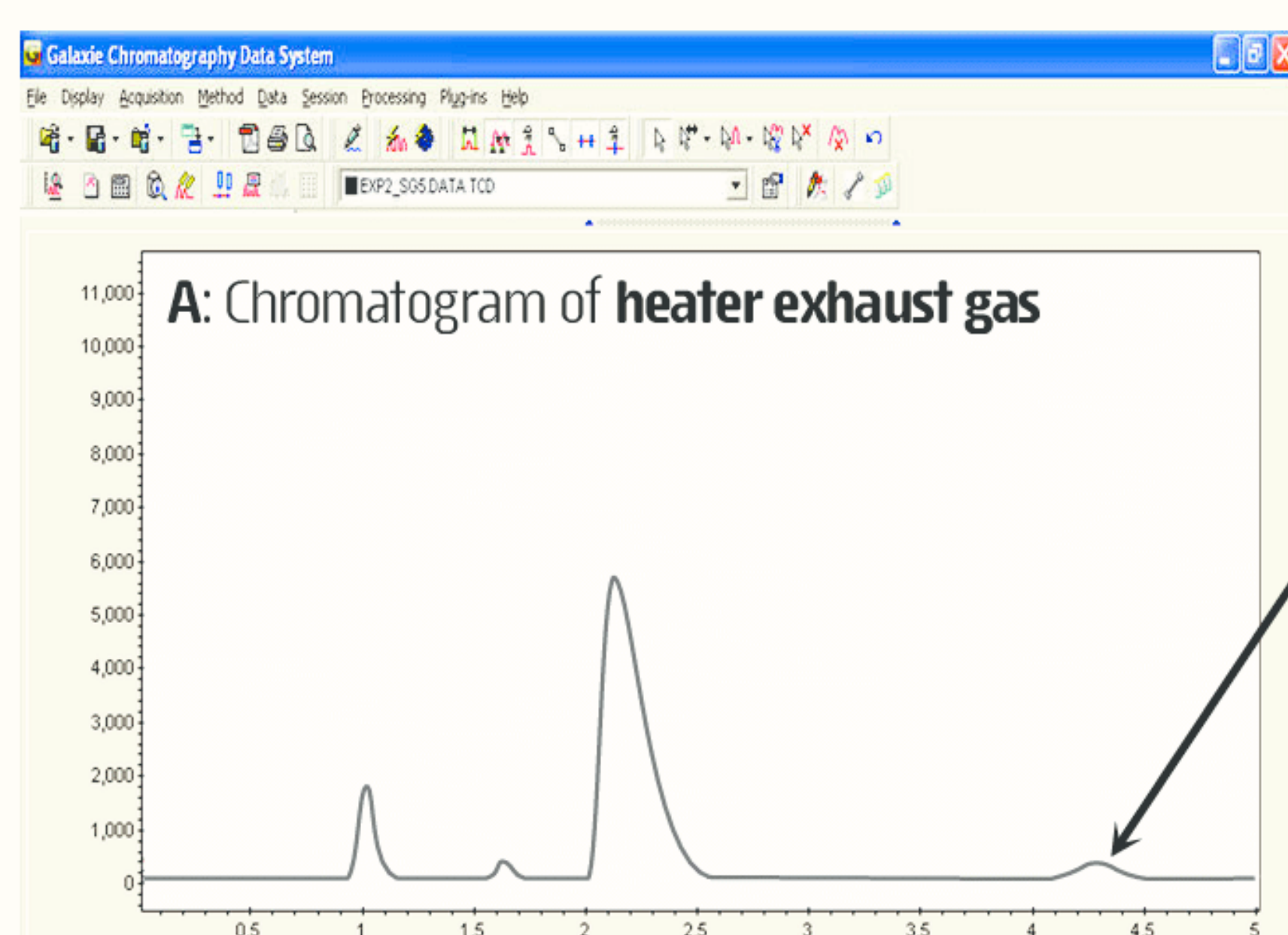
**Analyte:** The substance being analysed or separated.

**Retention time:** The time between injecting a sample and detecting the analyte.

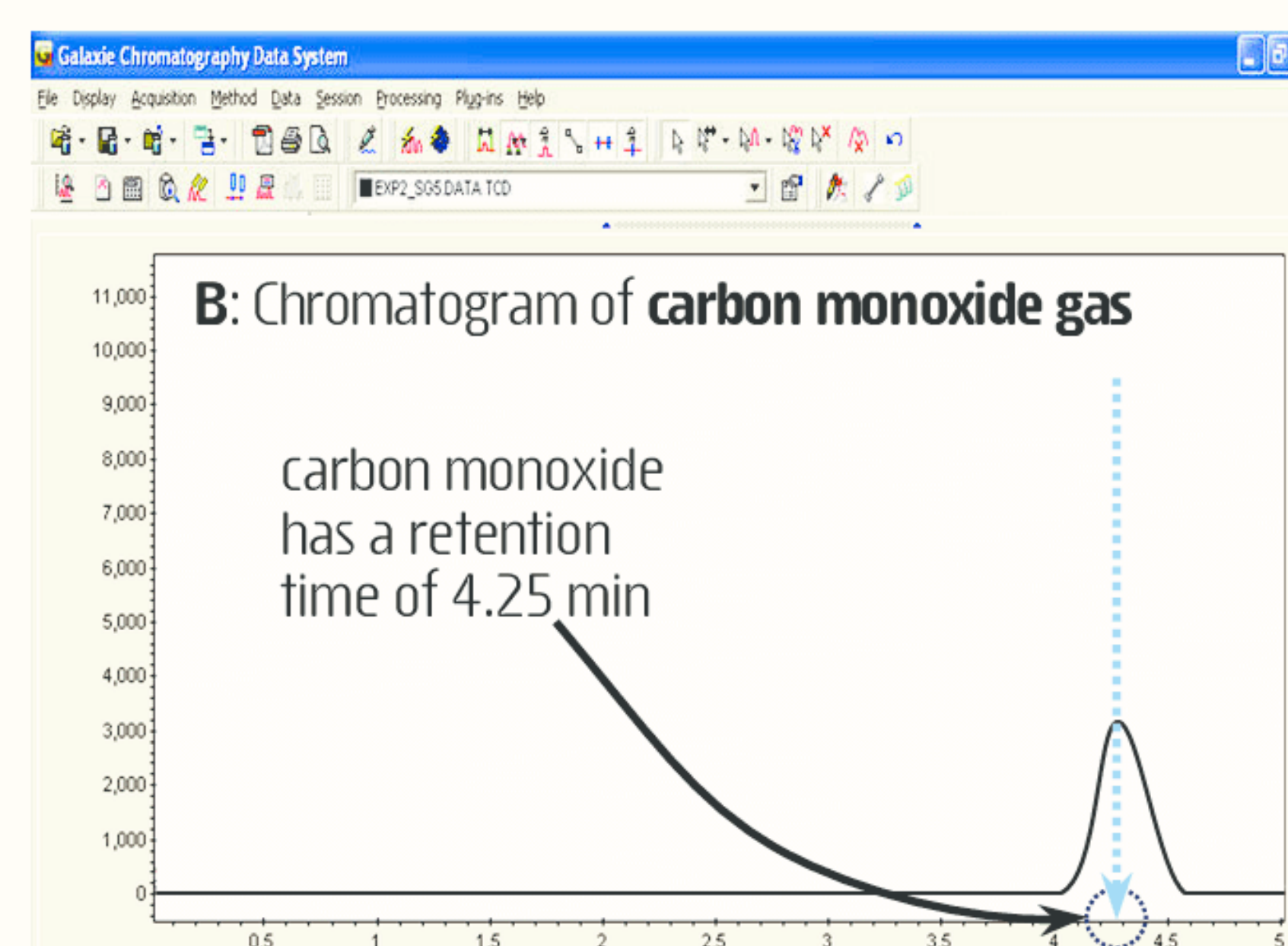


**EXAMPLE 2** When operating correctly, un-flued (no chimney) gas room heaters must **not** produce **carbon monoxide gas**. If the gas heater is operating poorly it may produce some carbon monoxide gas due to **incomplete combustion**. This situation is dangerous as CO(g) is colourless, odourless and **toxic**. Breathing air, even with a low concentration of CO(g) for an extended period can lead to loss of consciousness and possibly death.

**Chromatogram A** (below left) is of a sample of exhaust gas from a small un-flued (no chimney) domestic gas heater. **Chromatogram B** is of pure **carbon monoxide**. Compare the **retention times** of the gases from chromatogram A with that for carbon monoxide (chromatogram B) and determine if the gas heater is operating correctly.



Note the small peak of retention time 4.25 min.



**Answer:** Chromatogram B, (pure carbon monoxide) shows CO has a retention time of **4.25 min** for this column and conditions. A peak, although much smaller, of the same retention time also occurs in chromatogram A for the gas heater exhaust gas. This suggests the gas heater is producing some CO(g) albeit at a lower concentration (lower peak).

Attempt Set 33 # 6.

The height and area of a chromatogram peak can also be used to determine the **concentration** of an analyte in the mixture. To do this the chromatograph must be calibrated with a set of standards of known concentration. (See 19.9 p169).

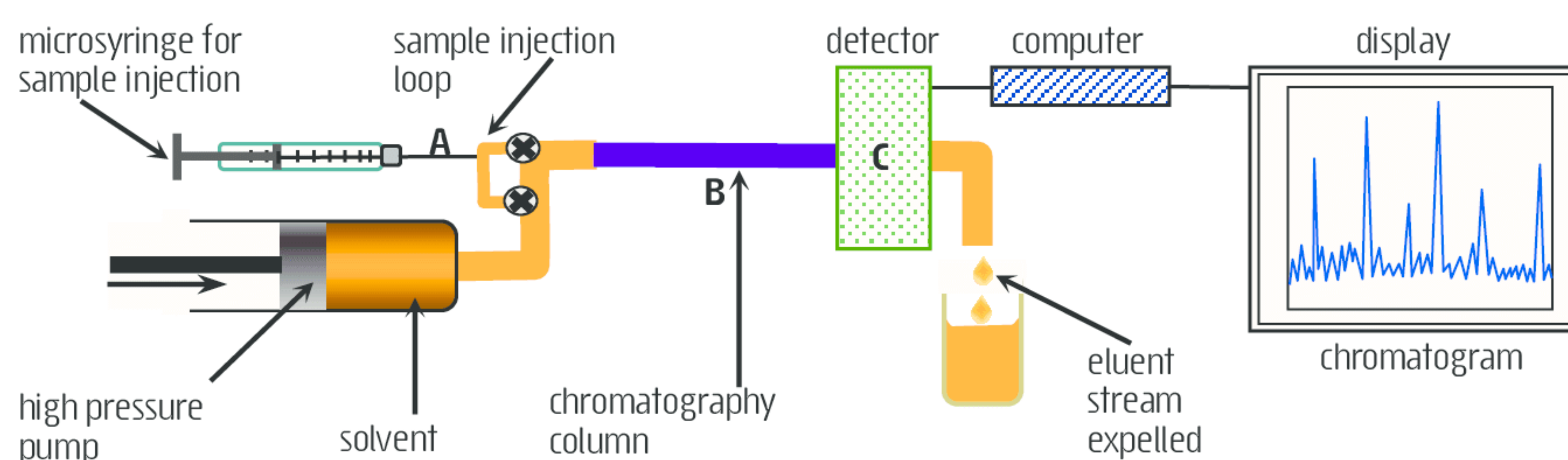
## 19.8 High performance liquid chromatography

While GC is ideal for the analysis of molecular mixtures that can be vaporised, it is unsuitable for compounds that decompose when heated or do not easily vaporise. Typically compounds with a molar mass greater than  $300 \text{ g mol}^{-1}$  cannot be analysed by GC. These compounds can be analysed using an important variation of GC known as 'high performance (high pressure) liquid chromatography' (**HPLC**). HPLC operates at room temperature with the analyte mixture present as a liquid or solution. Instead of the mobile inert gas phase used in gas chromatography HPLC uses a liquid solvent as the mobile phase. The stationary phase consists of a tightly packed column of fine particles such as  $\text{SiO}_2(\text{s})$ . Most packed HPLC columns are shorter than GC columns with a 3-5 mm diameter and 10 – 30 cm length.

The small particle size of the stationary phase in HPLC is important as it presents a large surface area that allows a greater interaction with the analytes in the mobile phase. This results in a more efficient separation. However, this also has the effect of greatly reducing the flow rate of the solvent and mixture through the column. Using a high pressure pump increases the flow rate by forcing the solvent mixture through the column, hence the 'high pressure' in the name HPLC.

**FIGURE 10 Operation of an HPLC**

The sample is injected via an injection loop (A) into a high pressure column of solvent. The sample passes through the chromatography column (B) where the various analytes in the sample travel at different rates through the column and become separated. A detector (C) signals the presence of any analytes as they emerge from the column. The detector signal is processed and is displayed on screen as a chromatogram along with a table of data showing retention times, peak height and area.



In HPLC, **polarity** is a major variable affecting the retention time of an analyte. In **normal phase HPLC** the surface of the stationary solid phase is polar, for example  $\text{SiO}_2$ . The mobile phase is a non-polar solvent like hexane. This configuration of polarities causes polar analytes to have a greater retention time as they have a greater tendency to adsorb onto the polar stationary phase rather than dissolve in the non-polar mobile liquid phase. As a result the higher the polarity of an analyte the greater will be its retention time and the longer it takes to travel through the column. In **reverse phase HPLC** the stationary phase is non-polar while the mobile phase is polar. In this more commonly used configuration the most polar analyte elutes from the column first.



The **relative polarity** of the stationary and mobile phase can be altered in order to achieve a suitable separation of the components of the mixture. Sometimes the composition and hence polarity of the mobile phase is programmed to slowly change over time so that analytes which are initially strongly adsorbed eventually become released and flow with the mobile phase.

An **ultra violet light detector** is often used with HPLC to identify the presence of analytes in the eluent (the solution exiting the column). These detectors rely on the **absorbance** of UV light that occurs when an analyte is present in the eluent. The resulting chromatograms can be used to detect the presence and concentration of analytes as shown below in Example 3.

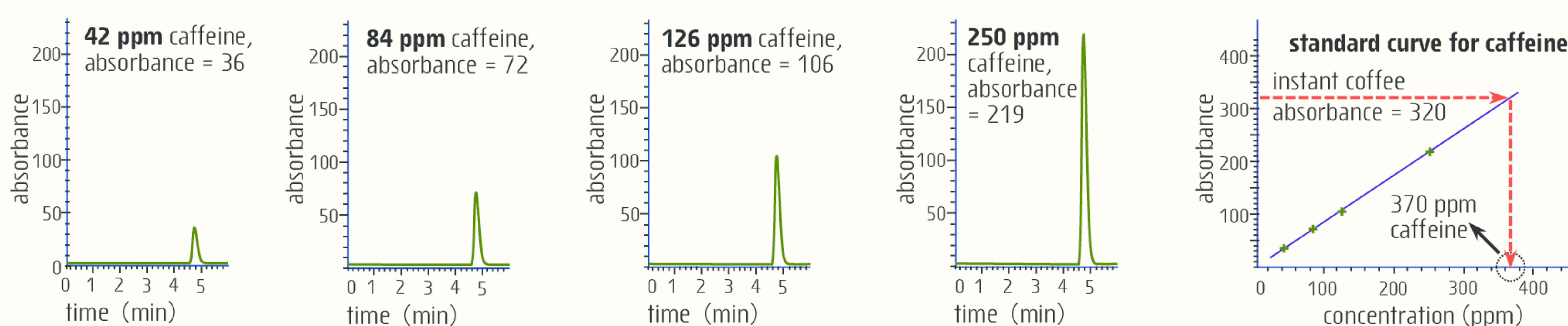
## 19.9 Concentration analysis from the HPLC chromatograph

To determine the **concentration** of an analyte in a mixture the chromatograph must first be **calibrated** for the specific analyte. To do this a set of solutions of known concentration, ie **standards**, are prepared and analysed using the chromatograph. A graph or **standard curve** of **peak height** (eg absorbance) or **peak area** versus **concentration** is then produced from this data. Using the same chromatograph and column conditions the unknown mixture is now analysed. These results are then applied to the standard curve to determine the concentration of the unknown. Typically, computer algorithms directly analyse a detector's output signal and compare the unknown mixture with the standards to directly find the unknown's concentration. Similar techniques are used with GC chromatographs.

**EXAMPLE 3** Caffeine is a stimulant present in chocolate and many beverages. HPLC can be used to determine the concentration of caffeine in such foods and drinks. To do this the HPLC must first be calibrated by injecting a set of standard solutions of known caffeine concentration. The resulting data is graphed to obtain a standard curve. This curve is then used to find the concentration of caffeine in an unknown sample.

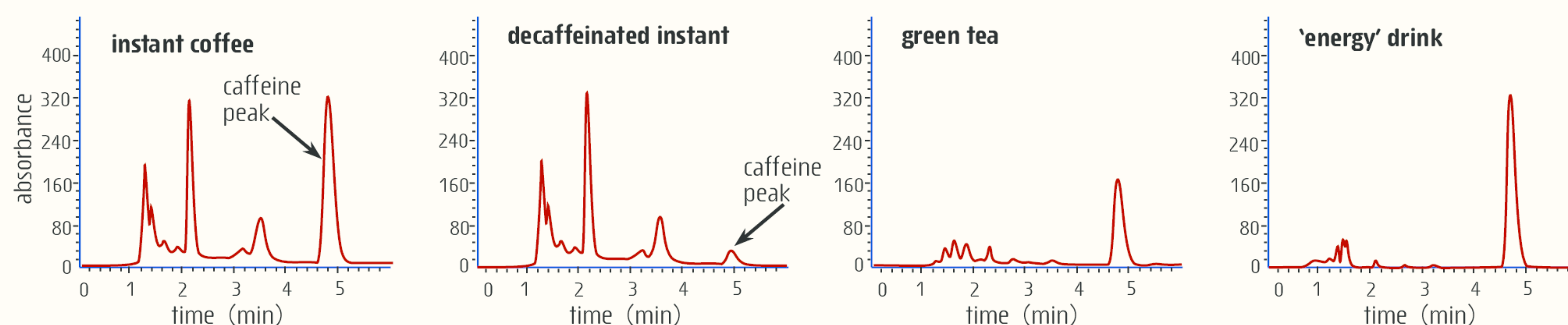
- Refer to the caffeine chromatograms shown below to produce a standard caffeine curve.
- Use this curve to determine the caffeine concentration in each of the beverages?

a. Data from the individual caffeine curves (below) has been used to construct the **standard curve for caffeine**, below right.



- b. The standard chromatograms (above) show the retention time for caffeine is 4.8 min. All of the beverage chromatograms below show some degree of absorbance at 4.8 min showing they all contain some caffeine, even the 'decaffeinated' instant coffee. Other substances in the beverage samples produce their own characteristic peaks as seen in the various chromatograms. The caffeine peak heights and the caffeine standard curve are used to find the caffeine concentration in each beverage.

**Instant coffee:** Absorbance = 320, ie 370 ppm caffeine. **Decaffeinated instant coffee:** Absorbance = 32, ie 40 ppm caffeine. **Green tea:** Absorbance = 165, ie 190 ppm caffeine. **'Energy' drink:** Absorbance = 327, ie 375 ppm caffeine.



Attempt Set 33 # 7 and 8.

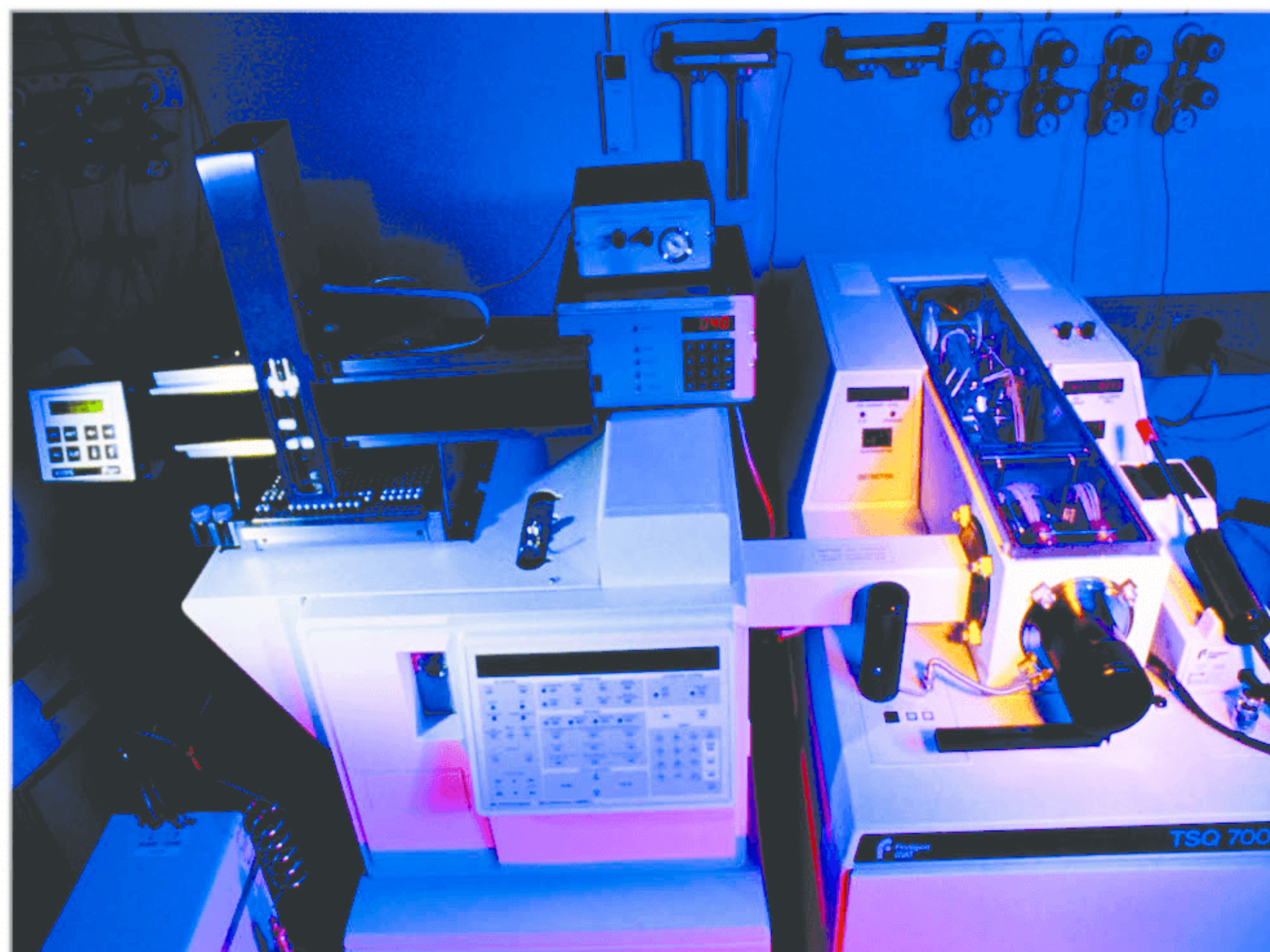
## 19.10 Applications of GC and HPLC instrumental analysis

Both HPLC and GC are ideal for analysing the **composition** and **concentration** of individual compounds in complex mixtures. They are very reliable, efficient and relatively quick analytical techniques requiring only minute samples. HPLC and GC can also be used as non-destructive separation techniques allowing isolated compounds to be collected for further analyses.

GC analysis however, requires compounds to be in a gas or vapour state and hence is limited to substances that are gases or vaporise without decomposing when heated. Typically this means molecular compounds of molar mass  $<300 \text{ g mol}^{-1}$ . Compounds of higher molar mass typically decompose before vaporising. HPLC has the advantage of being able to analyse these compounds as vaporisation is not involved.



For example, **GC** can be used to analyse the alcohol content of wines or blood alcohol (as alcohols are readily volatile) but directly analysing the sugar composition of fruit juices would be problematic as sugars like fructose and sucrose, for example, decompose rather than vaporise when heated. HPLC would be more appropriate for analysing sugar content as sugars can be prepared as solutions and do not need to be vaporised for HPLC analysis.



**FIGURE 11 Forensic drug detection apparatus**

A gas chromatograph (centre) connected to a mass spectrometer (right) in a forensic laboratory. This equipment is sensitive enough to detect picogram quantities of illegal drugs in the hair of a suspect, weeks after any drugs were taken.

A sample injection robot (top left) transfers samples from small vials to the GC. Here the samples are vaporised then separated within the chromatography column according to their molar mass. The attached mass spectrometer detects, identifies and determines the concentration of individual substances as they elute from the chromatography column.

Considering these limitations, some general applications of **gas chromatography** include:

- Environmental monitoring of pollutants in air, water and soil.
- Detecting the presence of dangerous gases such as methane or carbon monoxide in underground mines.
- Forensic analysis of crime scene residues such as blood, fibre or accelerant residues.
- Testing for illegal or banned drugs such as amphetamines, analgesics and anabolic steroids in athletes' or mine workers' urine samples.
- Analysis of petroleum and petroleum refined products.
- Scientific research involving concentration and composition analysis of various mixtures.

**HPLC** has application in similar areas to GC providing the analytes are soluble in a suitable solvent and their polarity allows separation. Some applications include:

- Quality control and analysis of fats and oils, vitamins, sugars, caffeine, antioxidants and suspected contaminants such as pesticides in the food and beverage industry.
- Drug analysis and quality control in the development and manufacture of pharmaceuticals.
- Analysis of amino acids, peptides, proteins and pharmaceuticals in biochemical research.

At the Australian Minerals Research Centre in WA, CSIRO is using HPLC in research to help find alternative extraction techniques for gold ore processing. These techniques may be more environmentally sustainable and allow the industry to continue in areas not currently possible. The Chemistry Centre WA uses HPLC extensively for forensic analysis, water testing (to monitor nitrates which are thought to affect pregnancy) and the analysis of illicit drugs in blood and urine samples.

Complete Set 33.

## Set 33 Chromatography

**GC**

**paper**

**identify**

**stationary solid**

**adsorbed onto**

**HPLC**

**concentration**

**TLC**

**food and beverage**

**dissolve in**

**pure substances**

**sensitive**

**picogram**

**microlitre**

**mobile liquid**

**blood and urine**

1. Use the list of terms to **complete** the following passage about **chromatography**.

Chromatography is an analytical technique used for separating the individual (a) \_\_\_\_\_ in a mixture. It can be used to (b) \_\_\_\_\_ the individual substances as well as determine their (c) \_\_\_\_\_ in the mixture. Some simple and inexpensive techniques of chromatography include (d) \_\_\_\_\_ chromatography and (e) \_\_\_\_\_. In these techniques the mixture to be separated is added onto the (f) \_\_\_\_\_ phase. A (g) \_\_\_\_\_ phase then flows over the stationary solid phase carrying the components of the mixture along the length of the stationary phase. Components in the mixture become separated according to their tendency to (h) \_\_\_\_\_ the mobile liquid phase or remain (i) \_\_\_\_\_ the stationary solid phase.

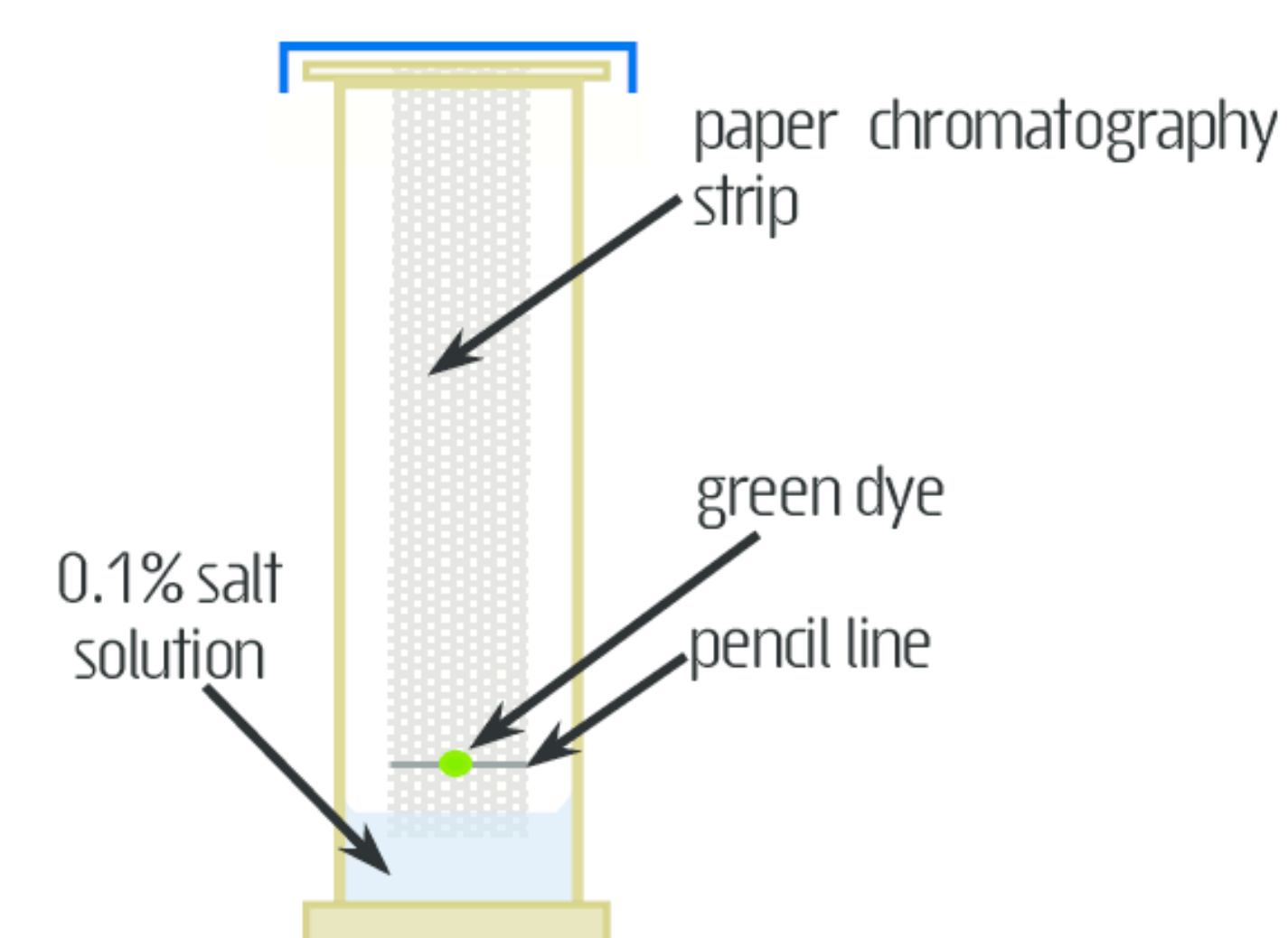
Instrumental methods of chromatography include (j) \_\_\_\_\_ and (k) \_\_\_\_\_. These techniques are extremely (l) \_\_\_\_\_ being able to analyse samples as small as (m) \_\_\_\_\_ quantities and able to detect (n) \_\_\_\_\_ amounts in these samples. Chromatographs find wide application in research and industry such as in the (o) \_\_\_\_\_ industry for quality control and the analysis of contaminants like pesticides. They are an essential tool in the forensic analysis of (p) \_\_\_\_\_ samples for monitoring the use of illegal performance enhancing substances in sport.



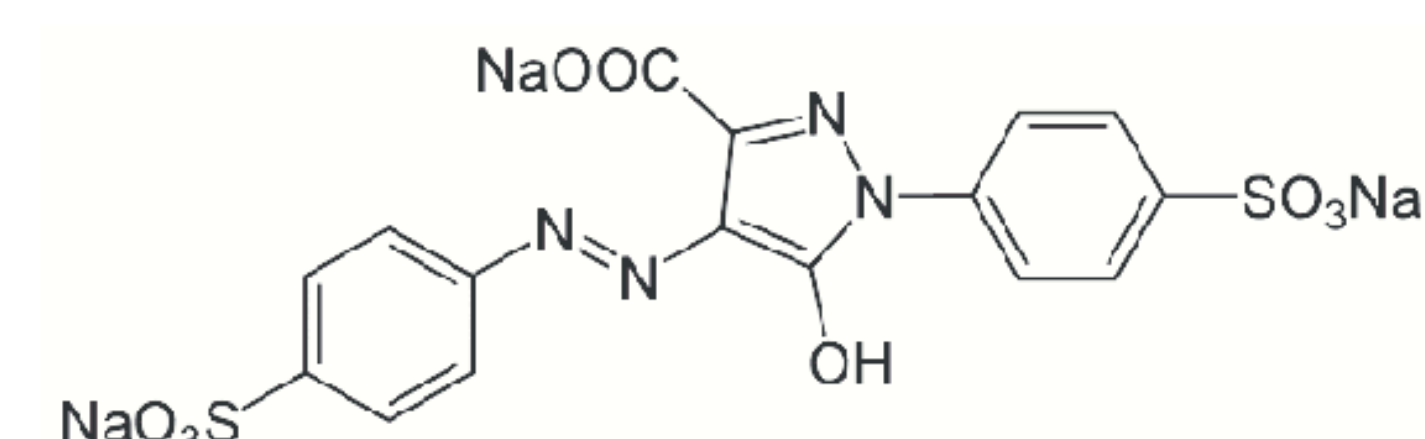
2. A student conducted an investigation into the dyes present in the **green** coloured sugar coating of a certain brand of chocolate lollies. To do this a small amount of the dye was obtained by dissolving it from the candy coating using a few drops of water. A **pencil line** was drawn across the bottom end of a chromatography paper strip and a spot of the green dye solution was placed onto it. The prepared paper strip was then developed by placing it into a beaker of **0.1% salt solution** while ensuring the solution was below the pencil line. A lid was placed onto the beaker and the chromatogram was allowed to develop. The following questions relate to this procedure. (See Fig 12.)

- Use the above example to demonstrate your understanding of **stationary phase**, **mobile phase** and **chromatogram** as applied to paper chromatography.
- A **pencil line** is drawn where the green dye is added to the chromatography paper. What is the **purpose** of this line and why shouldn't an **ink** pen be used to draw the line?
- What **problem** if any would be caused if the student had overfilled the beaker with 0.1% salt solution so that the spot of green dye was below the liquid level?
- After eight minutes two distinct colours began to appear on the chromatography strip, a **blue colour** and a **yellow colour**. These had travelled **5 cm** and **3 cm** respectively. Briefly **explain** why the dyes have travelled different distances along the chromatography paper.

**FIGURE 12** The paper chromatography arrangement for Question 2.



**FIGURE 13** The molecular structure of the food dye **tartrazine** or **yellow #5** (E102).



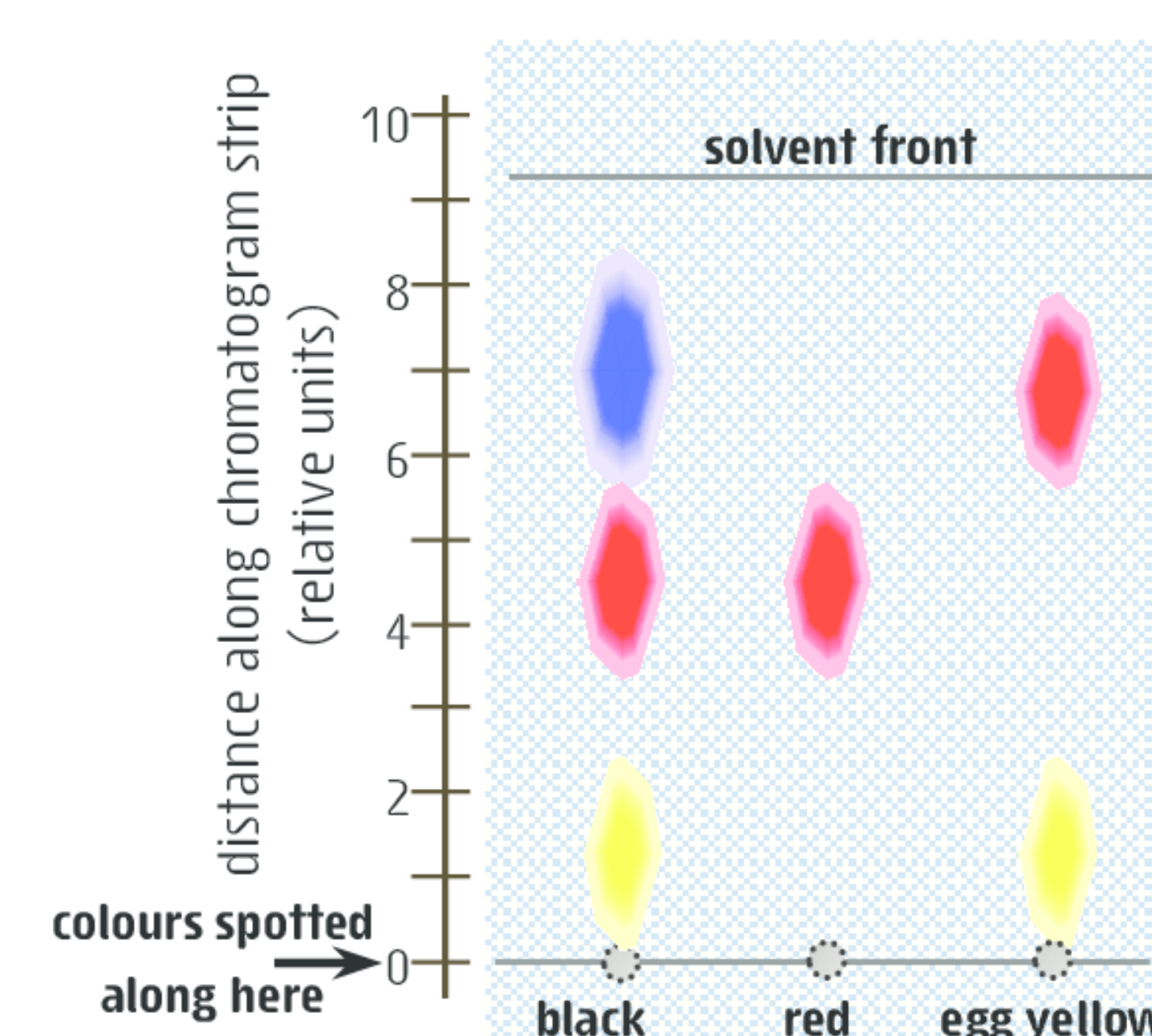
3. The student suspects the **yellow dye** in the green coloured candy (Question 2) may be a dye called yellow #5 (**tartrazine**). (See Fig 13.) This dye causes allergic reactions in some people and so its presence is usually named as an ingredient in products that contain it.

- Briefly **describe** how the student can use **TLC** to determine whether the yellow dye in the green coloured candy is indeed tartrazine?
- Sketch** the expected appearance of the chromatogram(s) from part (a) if the yellow dye in the candy was indeed tartrazine. Assume the blue dye has a greater  $R_f$  and the dyes have separated.

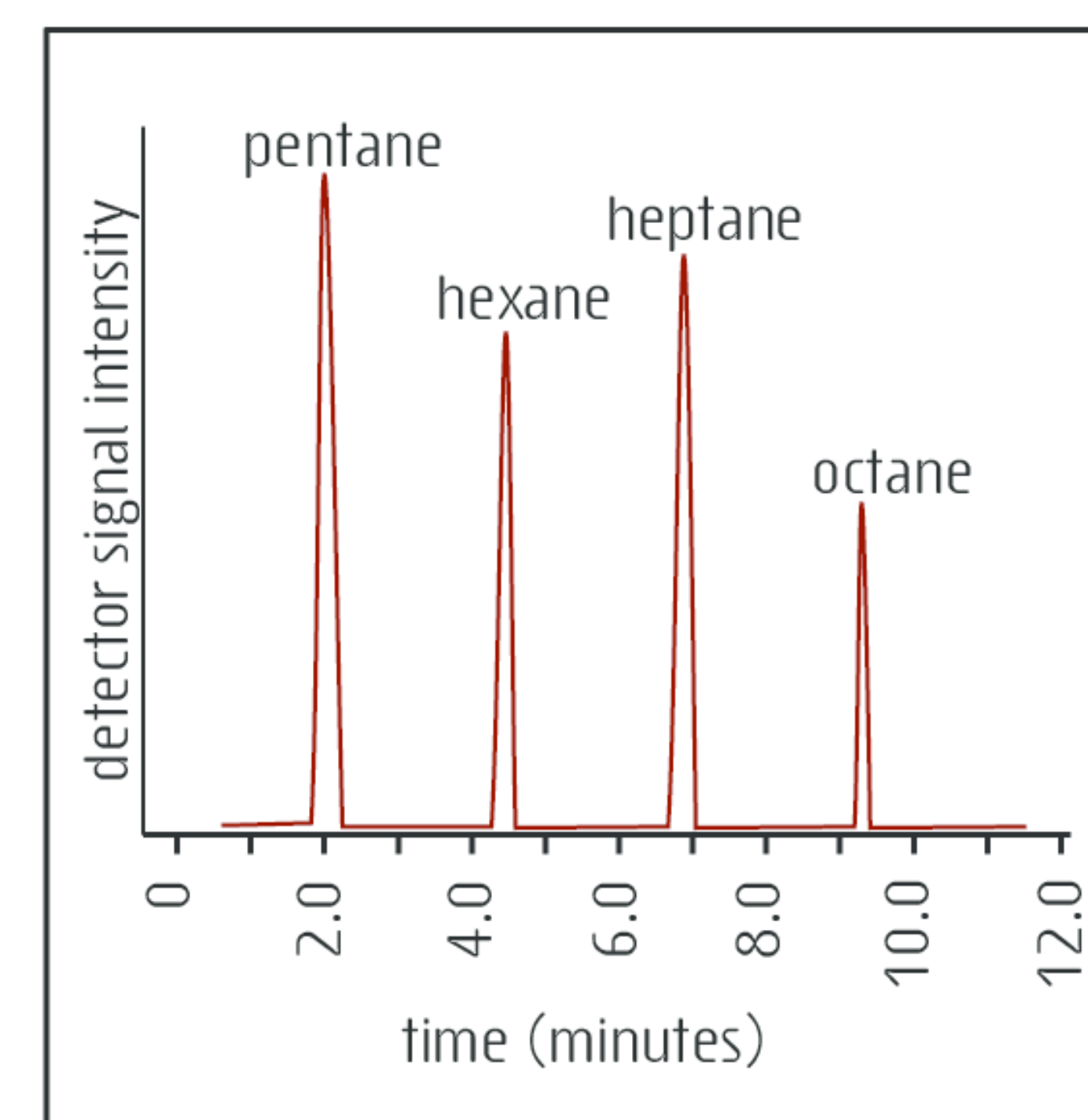
4. A student conducted an investigation into the composition of several different **food colourings**. This involved preparing a thin-layer chromatogram of a sample of **black**, **red** and **egg yellow** food colourings all of the same brand. (See Fig 14.)

- Refer to her results (Fig 14) then describe and **compare** the **dye** composition of the three food colourings.
- Determine the **retardation factor**,  $R_f$  of each of the different dyes.
- Is the **red dye** from the egg yellow food colouring and the black food colouring the same compound? Support your answer with reference to  $R_f$  data obtained from the TLC chromatogram.
- The student suspected the red food dye present in one or more of the food colourings may have been **E123**, also known as **amaranth**. To test this she prepared a chromatogram of the food colouring E123, using the same solvent and TLC plate. She found the dye moved 3.3 cm while the solvent had moved 6.9 cm. Were her suspicions correct? **Explain**.
- The silica gel used on the TLC plate in Fig 14 is very polar in nature while the solvent used is only moderately polar. With this in mind rank the polarity of the components of the black food colouring. Give a brief **justification** for your choice

**FIGURE 14** TLC chromatograms for three food colourings, **black**, **red** and **egg yellow**.



**FIGURE 15** A **GC** chromatogram for a mixture of four hydrocarbons,  $C_5H_{12}$ ,  $C_6H_{14}$ ,  $C_7H_{16}$  and  $C_8H_{18}$ .

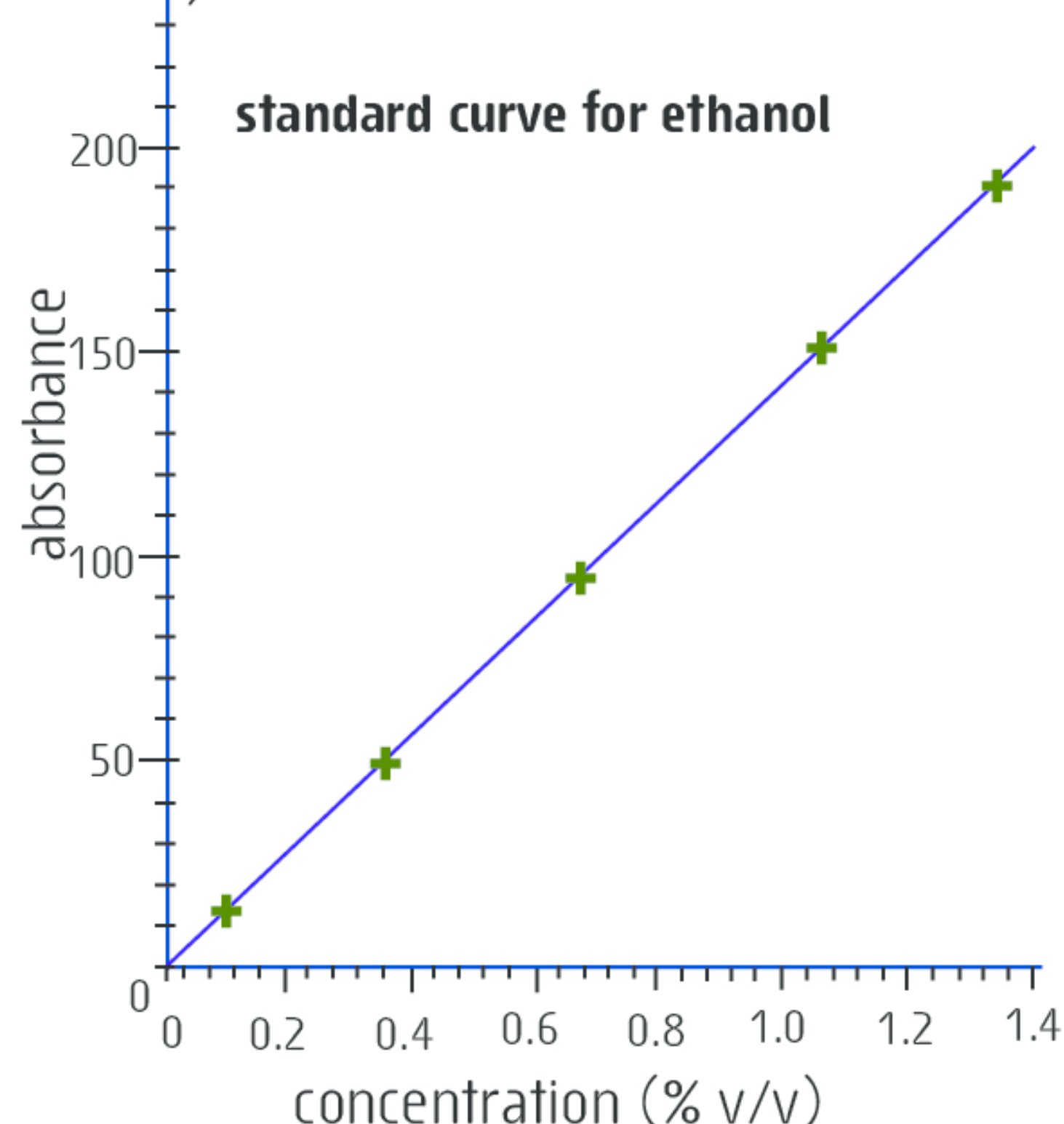


5. The **GC** chromatogram in Fig 15 is for a mixture of four hydrocarbons,  $C_5H_{12}$ ,  $C_6H_{14}$ ,  $C_7H_{16}$  and  $C_8H_{18}$ . The following questions refer to this chromatogram.

- Use pentane and heptane to illustrate your understanding of **retention time**.
- What **factors** affect the retention time of an analyte in GC and hence **explain** why these hydrocarbons have different retention times.
- What is the significance of the **height** and **area** of these peaks?



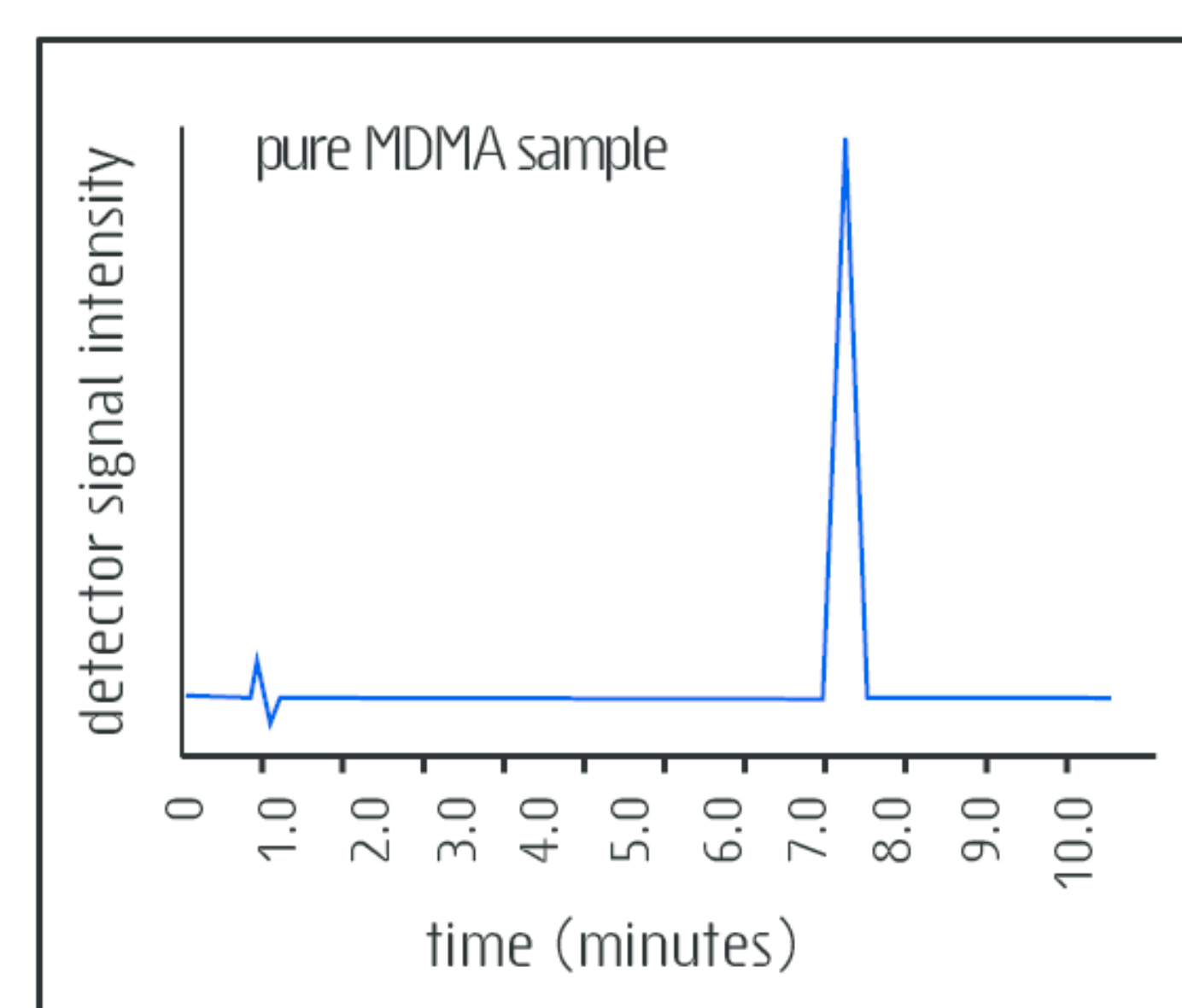
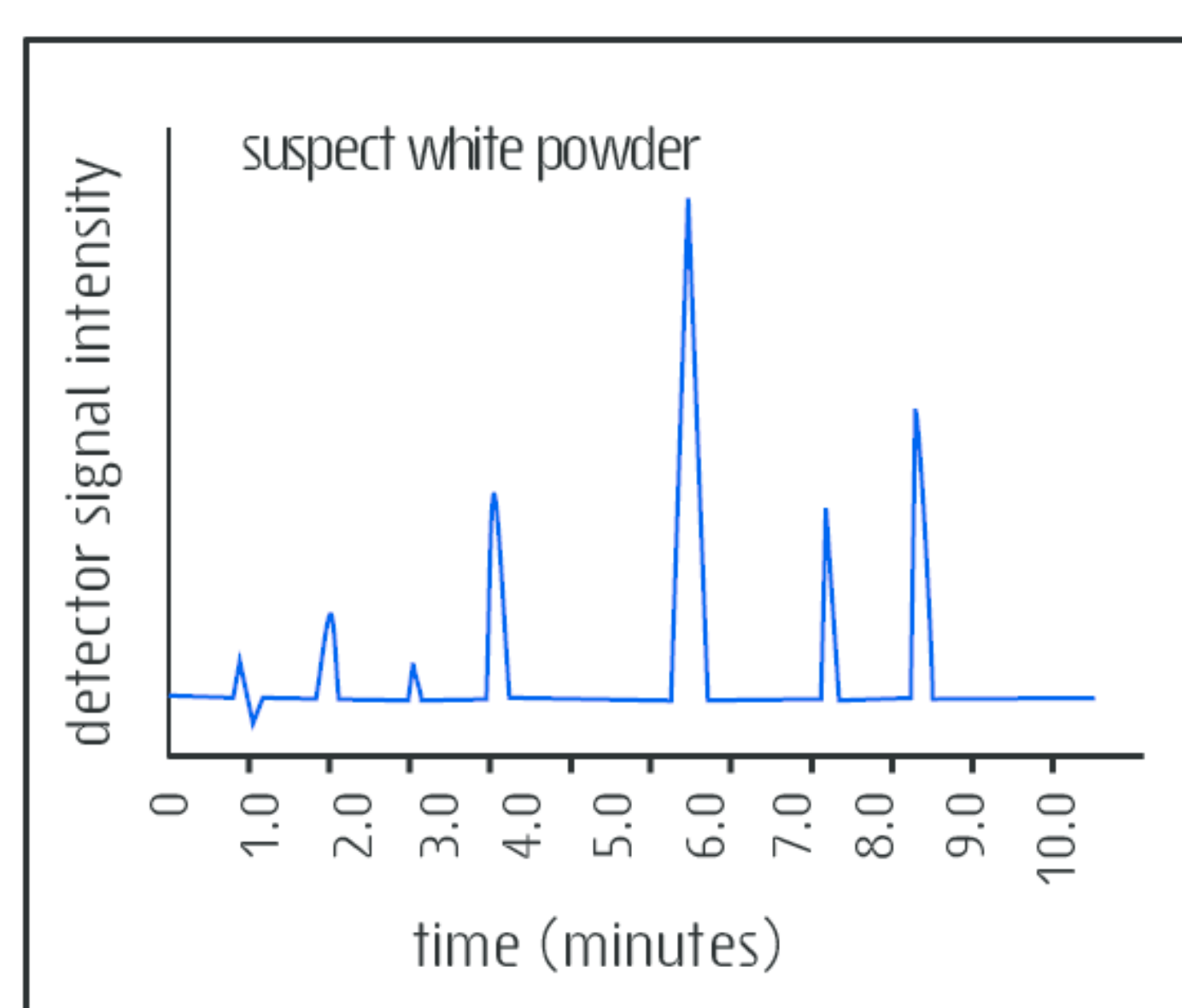
**FIGURE 16** Standard curve for ethanol. The alcohol concentration is shown as a percent by volume, % v/v.



6. **Drug testing** of thoroughbred race horses is a routine procedure used to protect the safety and welfare of horses and to ensure the fairness of the sport. To do this a urine sample can be analysed using GC. The resulting chromatogram will have many peaks produced over several minutes. **How** is it possible to tell if any of the peaks in such a chromatogram represent prohibited equine stimulants such as amphetamine or methylphenidate (Ritalin)?

7. The sale of **liquor** in Western Australia is controlled by the 'Liquor Control Act 1988' and as such can only be sold from suitably licensed premises. The term liquor generally applies to beverages containing **1.15%** or more alcohol (**ethanol**) by volume. For this reason beverages with very low alcohol concentration may be sold from general unlicensed retail premises. A brewery producing a low alcohol beer is hoping to market its product through unlicensed retail outlets. To check the suitability of their beer for this type of sale they need to verify its alcohol content. This is done using GC analysis. To do this a **standard curve** for ethanol is produced (Fig 16) using several carefully prepared ethanol solutions. Three different beer samples from slightly different brewing techniques are also prepared and tested. The absorbances of the tested beer samples were **Beer X**: 136, **Beer Y**: 45 and **Beer Z**: 198. Use these absorbance values and the standard curve for ethanol to determine the alcohol content of these beers and decide if any is suitable for sale from unlicensed premises.

8. A **forensic sample** of a white powder obtained from a suspected drug laboratory is tested for the presence of the prohibited drug **MDMA** (3,4-methylenedioxy-N-methylamphetamine). The HPLC chromatograms for the white powder and a pure sample of MDMA are shown here. The following questions refer to these.



- On the basis of the HPLC **chromatograms** does the suspected white powder contain the drug MDMA? **Explain**.
  - Briefly **explain** how the various analytes in the white powder mixture are able to be separated by the process of HPLC.
  - A calibration curve can be used to determine the concentration of a drug like MDMA in a sample such as the white powder. Briefly **describe** what this involves.
9. **GC** is suitable for analysing hydrocarbons as shown in Fig 15 but is probably not suitable for the forensic analysis of **high** molar mass substances like **enzymes** or **blood proteins**. Suggest **why** and what chromatographic technique could be used instead.
10. Consider the following situations and suggest which of the chromatographic techniques would apply. Briefly **state** a reason for your choice.
- A technique suitable for analysing **minute** samples (microlitre amounts) of **volatile** fuel residues extracted from the burnt remains at a suspected arson scene.
  - A technique suitable for separating the components of a plant leaf extract. **Several millilitres** of the extract are available.
  - A pharmacological analysis of a mixture of **very high molar mass proteins** and **polypeptides** present in a solution of biological fluids.
  - Analysis of **air** samples for pollutants like sulphur dioxide, nitrogen oxides and various hydrocarbon compounds.
  - Analysis of the **sugar** content of a fruit juice.