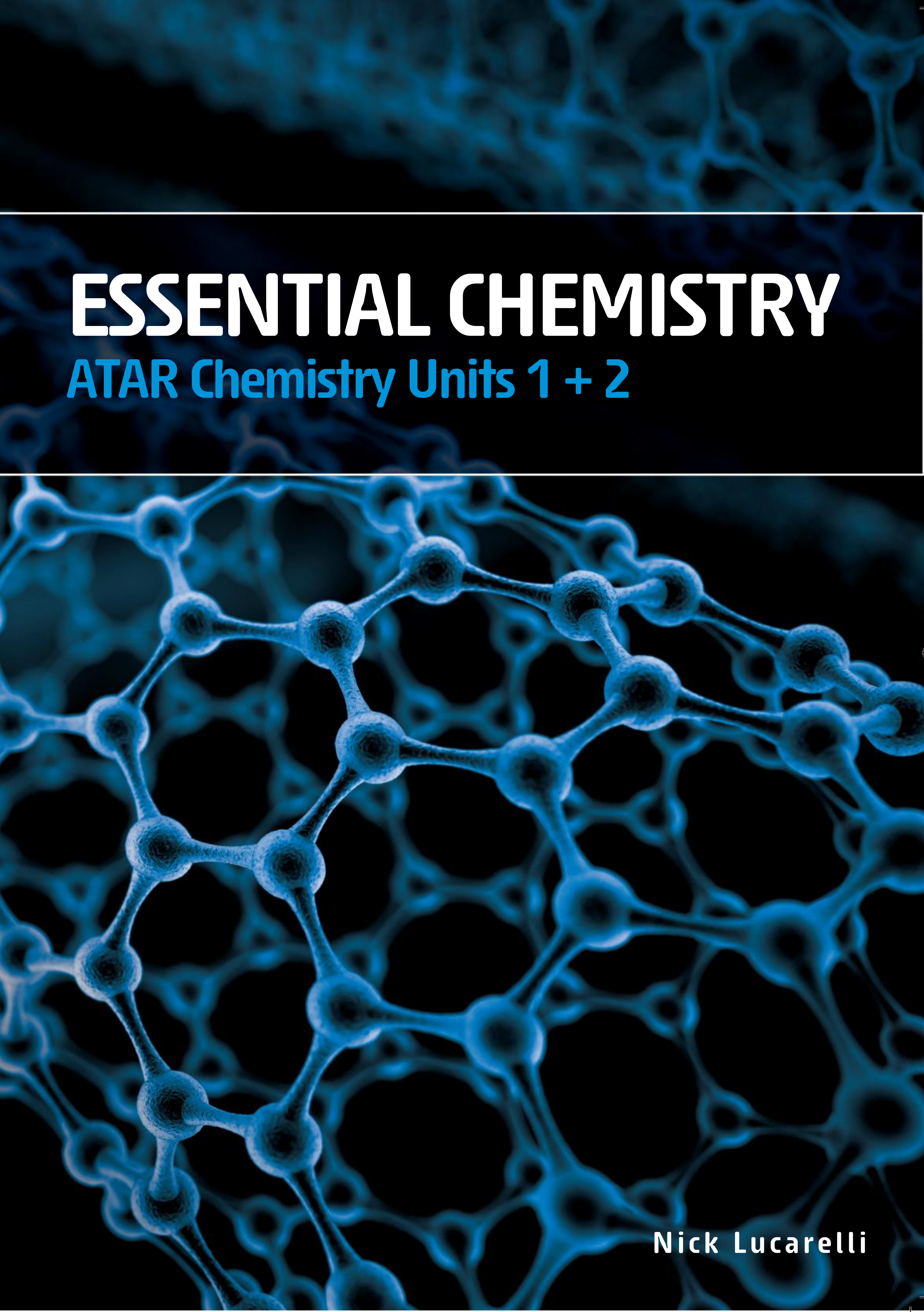
ESSENTIAL CHEMISTRY

ATAR Chemistry Units 1 + 2



Nick Lucarelli

ESSENTIAL CHEMISTRY

ATAR CHEMISTRY UNITS 1 + 2

Nick Lucarelli

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About this book

Essential Chemistry covers the West Australian ATAR Chemistry Course Units 1 and 2 as outlined by the School Curriculum and Standards Authority of Western Australia. It provides a complete coverage of the Science Understanding and Science as a Human Endeavour strands and includes studies in the Science Inquiry Skills strand.

Extension (E)

Great care has been taken to ensure the depth and breadth of chemistry content within this text accurately reflects the course outlined by the School Curriculum and Standards Authority. There are however, some inclusions identified with a purple letter **(E)**. These may not be directly outlined in the Chemistry Course Units 1 and 2. They either cover content the author considers desirable for developing a good understanding of the Chemistry Course Units 1 or 2 or they overlap content specified in Chemistry Course Units 3 or 4. Their inclusion is for the convenience of teachers and students and is not intended to reflect content specific to the Chemistry Course Units 1 or 2.

Features

- Nineteen chapters conveniently sequenced to form a logical learning and teaching programme.
- Coverage and integration of the three course strands: '**Science Inquiry Skills**', '**Science as a Human Endeavour**' and '**Science Understanding**'.
- **Clear** and **easy to read** text that is **stimulating** and **concise**.
- Extensive use of **examples**, **illustrations**, **diagrams**, **tables** and **margin notes**.
- **Contextual situations** integrated into both the body of the text and study questions. These highlight the role of chemistry and chemists in society.
- **33 sets** of questions and problems thoughtfully sequenced to allow mastery of single principles and concepts before leading into more challenging and complex tasks.
- **Solutions manual** with complete answers to all **written** and **calculation** questions. Answers include supplementary explanations and notes that allow students to have greater control over their learning and progress.
- Fully **indexed** for convenient use.

Acknowledgements

In particular the author would like to acknowledge the meticulous efforts of Norm Kingwell in reviewing this publication. His input has been invaluable. Andrew Foreman's assistance with his knowledge of and access to chromatographic instrumental analysis equipment was extremely helpful. Thanks to Joanne Lucarelli for generously sharing her research skills and time in accessing some of the information and graphics used. The engaging cover design owes its presence to Cameron James' creative efforts and outstanding desktop skills. To my wife Carolyn, thank you very much for your huge contribution in proofing for grammar and ensuring the syntax in this book is as dependable as the chemistry.

Nick Lucarelli
August 2014

Images

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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_2 (21%), N_2 (78%) and **Ar** (1%) with variable amounts of **water vapour** and traces of other gases such as CO_2.

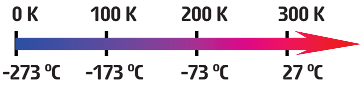
At sea level, normal air pressure due to these atmospheric gases is:

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.



eBook⁺ Quiz 1.2

Attempt Set 1 # 1 and 2.

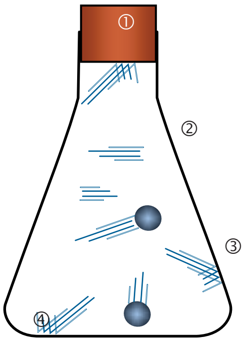


FIGURE 4 The particles of a gas move freely within the entire volume of their container. At 27 °C for example, the molecules in a sample of $H_2(g)$ move at an average speed of about 5650 km hr^{-1}. Gas **pressure** is a result of random elastic collisions between such gas particles and their **container 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.

eBook⁺ Quiz 1.1 @ lucaspublications.com.au.

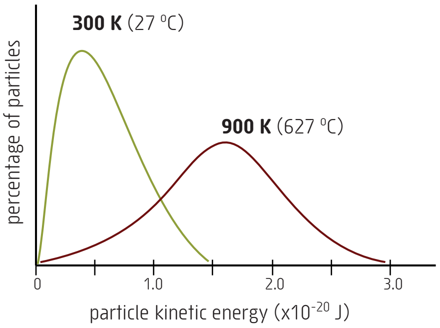
1.2 The kinetic theory of gases

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_k) given by, $E_{k(\text{particle})} = \frac{1}{2}mv^2$, 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_k (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

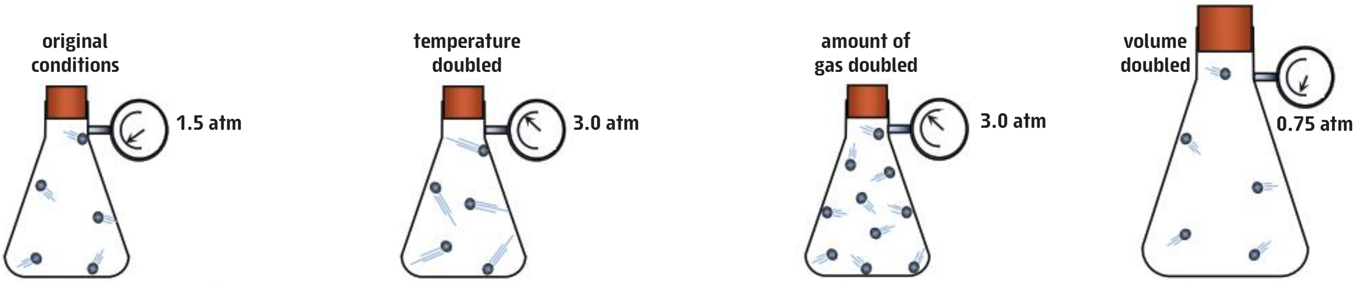
Gases, irrespective of their particular chemical make up, all have a number of common physical properties. They always take the **shape** of their container, have a very **low density**, **exert pressure**, can be **compressed** and readily **diffuse** through other gases. The kinetic theory, as outlined 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.



Flask A: The gas is originally at 200 K in a 1.0 L flask and exerts a pressure of **1.5 atm**.

Flask B: Doubling the **temperature** to 400 K doubles the pressure to 3 atm. (The amount and volume of gas are kept constant.)

Flask C: Doubling the **amount** of gas (number of particles) doubles the pressure to 3 atm. (The temperature and volume of gas are kept constant.)

Flask D: Doubling the **volume** to 2.0 L halves the pressure to 0.75 atm. (The temperature and amount of gas are kept constant.)

TABLE 2 Understanding gas pressure

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

eBook+ Quiz 1.3 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 $H_2(g)$, $N_2(g)$ or HCl(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 °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.

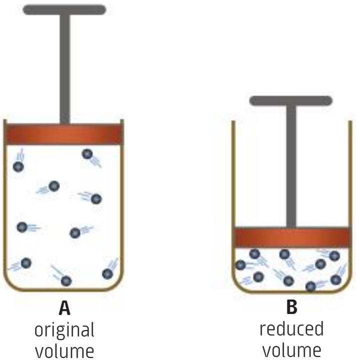


FIGURE 6 Significantly reducing the volume occupied by a **real gas** (by increasing the pressure applied) can cause a situation where the volume of the particles of the gas become a significant factor in determining the volume occupied by the gas. When this happens, as in situation **B**, the gas volume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

eBook+ Quiz 1.4.

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.

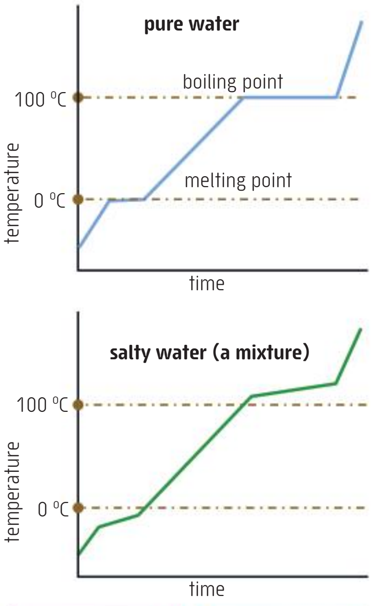
FIGURE 7 Particle movement in the **solid** phase is restricted to vibrating about fixed positions within the solid. The particles are packed very tightly and so there is little opportunity for the solid to be compressed.

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.



eBook Quiz 1.6. 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.)

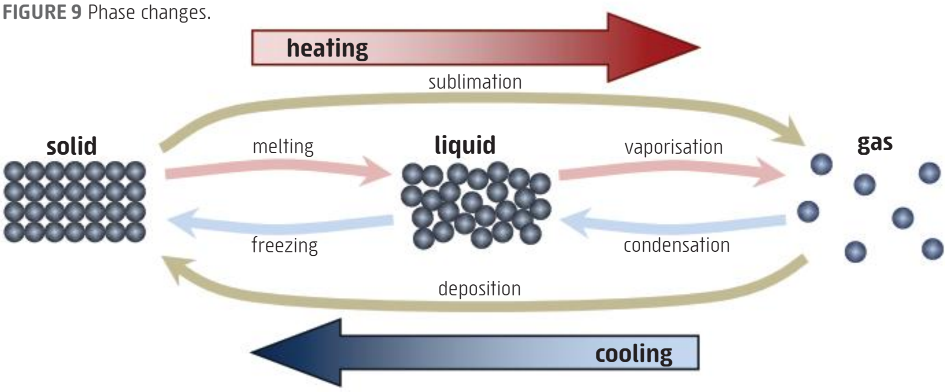
In **liquids,** the strong attractive forces between particles also cause them to pack closely. Here however, the particles are able to jostle past one another within the liquid volume. This arrangement of particles explains why liquids can flow to fill the bottom of a container but have a fixed volume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

eBook Quiz 1.5. 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

1. 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 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.

distributed
temperature
random motion
motion
negligible
volume
physical
attraction
kinetic energy
average kinetic energy
particles
chemical
elastically

2. According to the kinetic theory the particles of any gas have the same **average kinetic energy** when at the same temperature.
   a. What is meant by average kinetic energy in this context?
   b. How does **temperature** affect particle **average kinetic energy** and particle **speed**?

3. If a laboratory gas tap is accidently 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.
   a. What is the **name** of the process by which the leaking gas spreads throughout the room?
   b. Use the **kinetic theory** to describe at a particle level how this mixing process occurs.
   c. 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.

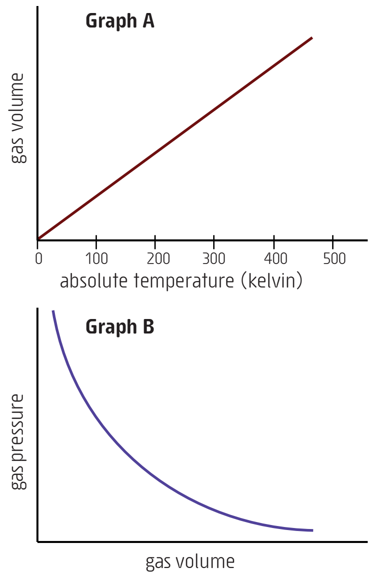
4. Use the **kinetic theory** to explain why gases exert pressure.

5. 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.
   a. The car tyre becomes quite **hot** during a long journey.
   b. A faulty tyre valve allows some air to **leak** out. (Assume tyre volume doesn't change.)

6. Refer to the graphs in Fig 11 and answer the following questions.
   a. What does **Graph A** show about the volume of an ideal gas and its absolute temperature?
   b. Use the kinetic theory to account for the volume of an ideal gas at zero kelvin.
   c. 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.

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.)



7. The kinetic theory is a model used to explain the properties of an ideal gas.
   a. Describe two assumptions in the kinetic theory apply to an ideal gas but are only approximations for a real gas.
   b. State **one** physical property that applies to a real gas but not to an ideal gas.

8. 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.
   a. Why is the gas phase of wax referred to as a **vapour**?
   b. Which of the processes occurring on a burning candle; melting, vaporising or combustion, are easily **reversible**?
   c. 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.
   d. 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.

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.

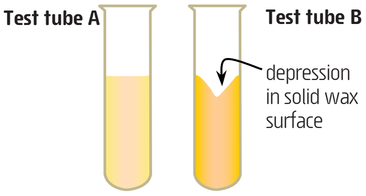


FIGURE 13 Cream, milk, sugar and vanilla are the main ingredients in **ice cream**. One way to convert this mixture into ice cream is to mix in liquid nitrogen.

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, $N_2(l)$ 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 °C), most of its cooling effect is produced when it boils. **Explain** how this happens.

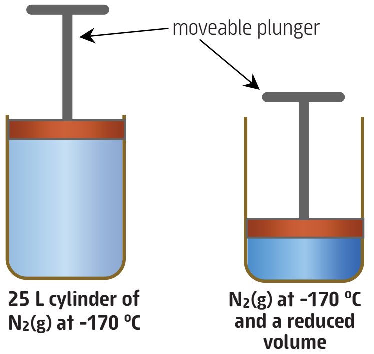


FIGURE 14 Pushing the plunger in reduces the volume of the 25 L cylinder of nitrogen gas. The temperature is kept at -170 °C.

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 °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 °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?

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

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'.

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.

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.)

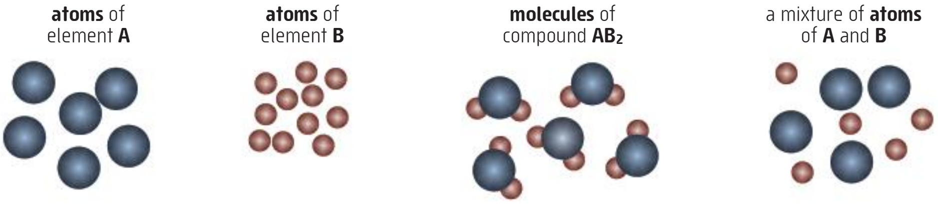


FIGURE 17 Dalton's atomic theory tells us that each type of element is composed of its own unique atoms. (See p13.) When atoms of different elements chemically combine in a definite atomic ratio they form a **compound**. In a **mixture** the components are not chemically combined and may be present in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

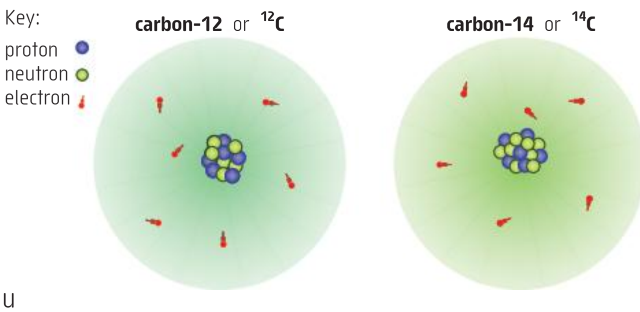
eBook Quiz 1.7. Attempt Set 2 # 1, 2, 3, 4 and 5.

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.

TABLE 3 Subatomic particles

particle	relative mass (u)	relative charge	location
proton	1.0	+1	nucleus
neutron	1.0	0	nucleus
electron	≈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.

${}^{A}_{Z}X$ eg ${}^{56}_{26}Fe$

${}^{A}X$ eg ${}^{56}Fe$

or **iron-56**

eBook+ Quiz 1.8.

Attempt Set 2 # 6, 7 and 8.

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 ${}^{15}N$, ie nitrogen-15? (See border note at left.)

$Z = N_p = 7$

$A = N_p + N_n$

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

and $N_e = N_p = 7$

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.

∴ the isotope nitrogen-15 contains **7 protons**, **8 neutrons** and **7 electrons**.

1.9 Ions

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**.

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.

Ion charge $= N_p - N_e$ where: N_p is the number of protons in the ion.

thus $N_e = N_p -$ **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	$= N_p$ - ion charge = 8 - (-2) = 10 electrons
Al^{3+}	The atomic number of Al is 13 (see periodic table) $\therefore Al^{3+}$ has 13 protons	and	N_e	$= N_p$ - ion charge = 10 electrons

eBook+ Quiz 1.9.

Attempt Set 2 # 9.

1.10 Relative atomic mass (Ar)

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 u (ie 1.67262×10^{-24} g)

m_n=1.008665 u (ie 1.67493×10^{-24} g)

m_e=0.000549 u (ie 0.00091×10^{-24} g)

The unified atomic mass unit is now sometimes referred to as a **dalton (Da)**.

1 Da = 1u = $1.660538782 \times 10^{-24}$ g

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 (Ar)** 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: % is the percentage of isotope a in the element
A a
% b
A b
A 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.

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

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

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 $A_{r(b)}$.

eBook+ Quiz 1.10.

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, $Cl_2(g)$ sample shows its isotopic composition. The +1 ionised atomic fragments, $^{35}Cl^+$ and $^{37}Cl^+$, form as Cl_2 molecules enter the mass spectrometer through a high energy electron beam. A majority of the Cl_2 molecules will be ionised to Cl_2^+ without being fragmented into separate atoms. These also appear in the mass spectrum and correspond to various combinations of ^{35}Cl and ^{37}Cl.

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

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

^{37}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.

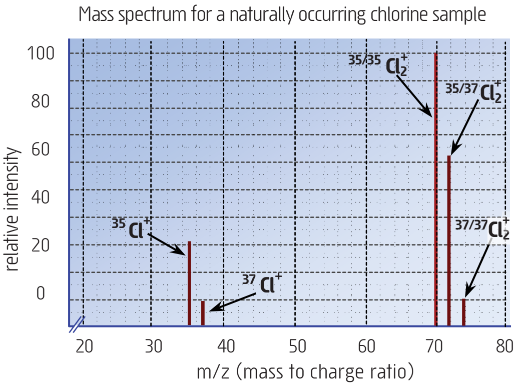
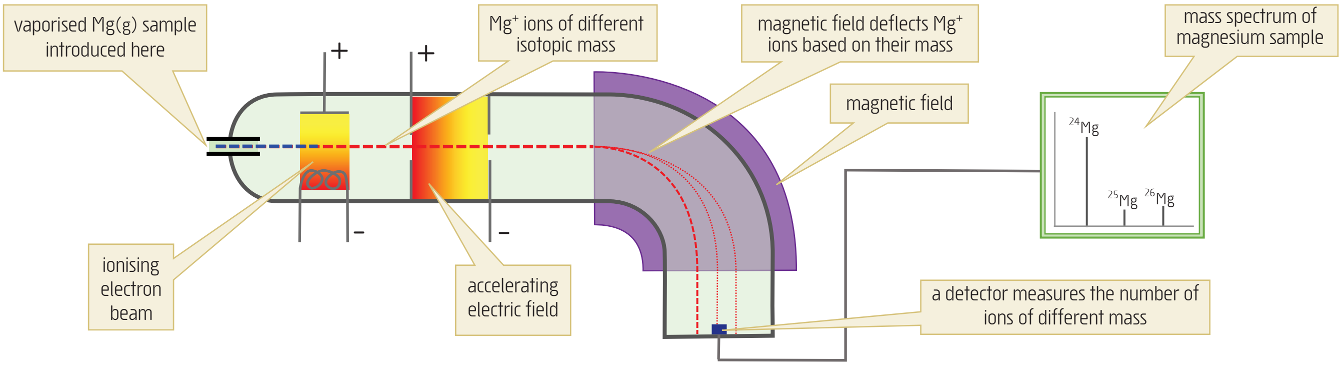


FIGURE 21 Schematic view of a **mass spectrometer** being used to analyse a sample of naturally occurring **magnesium**. Naturally occurring magnesium consists of **magnesium-24, magnesium-25** and **magnesium-26**. The actual mass and abundance of each isotope can be accurately measured by the mass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

eBook+ Quiz 1.11.

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

1. 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) __________.

Subscripts written alongside a formula show its phase.

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

2. Identify the following materials as **elements**, **compounds** or **mixtures**.
   a. hydrogen gas [$H_2(g)$]
   b. carbon dioxide gas [$CO_2(g)$]
   c. salt solution [$NaCl(aq)$]
   d. bronze [$Cu(s) + Sn(s)$]
   e. iron [$Fe(s)$]
   f. water [$H_2O(l)$]

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.

3. Classify the following materials as **pure** or **mixtures**, **homogeneous** or **heterogeneous** and state which are **solutions**.
   a. copper [$Cu(s)$]
   b. sugar dissolved in water [$C_{12}H_{22}O_{11}(aq)$]
   c. vinegar, a combination of two miscible liquids [$CH_3COOH(l) + H_2O(l)$]
   d. orange juice [$C_{12}H_{22}O_{11}(aq) + H_2O(l)$ + pieces of orange pulp]
   e. a glass of distilled water [$H_2O(l)$]
   f. a glass of mineral water [$H_2O(l)$ containing various dissolved minerals]
   g. a gas jar full of clean air [$N_2(g) + O_2(g) + Ar(g)$]
   h. Alka-Seltzer tablet [powdered $C_6H_8O_7(s)$ combined with powdered $NaHCO_3(s)$]

4. 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.
   a. **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.
   b. Which if any of the three substances is **homogeneous**? **Explain** your answer.

5. **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.
   a. Would you classify bronze as an element, compound or mixture? **Justify** your answer.
   b. **Justify** the statement, 'Alloys like bronze are solid solutions.'
   c. Use your knowledge of the kinetic theory of matter to **explain** why the mixture of metals melts when heated and then solidifies when cooled.
   d. 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. $^{127}_{53}I$ c. ^{23}Na

7. How many **protons**, **neutrons** and **electrons** are in one atom of the following isotopes?

   a. $^{7}_{3}Li$ b. ^{35}Cl c. ^{12}C d. ^{52}Cr

8. Most elements have more than one isotope, hydrogen for example has three isotopes, ^{1}**H**, ^{2}**H** and ^{3}**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	Mg^{2+}	S^{2-}	Cl^{-}	I^{-}	N^{3-}	Fe^{2+}	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**.

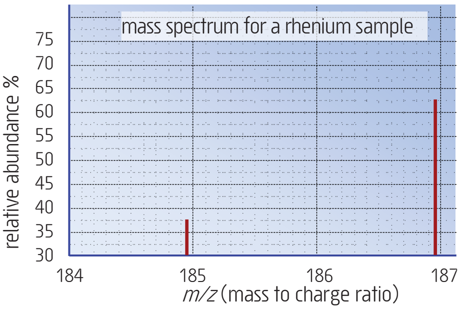


FIGURE 22 The metallic element **rhenium.**

Image courtesy of Heinrich Pniok, heinrich@pniok.de.

16. The mass spectrum of a sample of an unknown metal element reveals a single peak with a mass of 4.4804 x 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 x 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.

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'.

eBook+ Quiz 2.1. **Attempt Set 3 # 1.**

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.

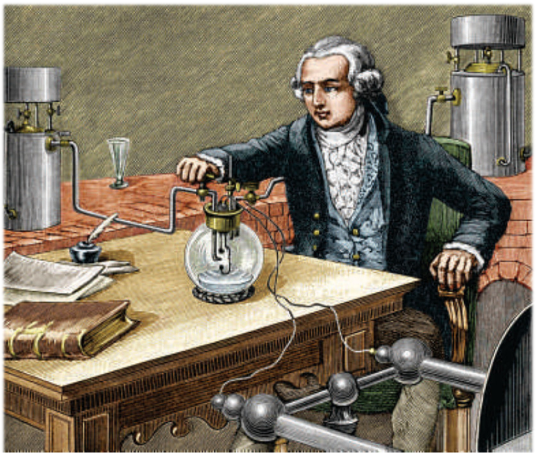


FIGURE 2 The French chemist **Antoine Laurent Lavoisier** (1743-1794) making water in 1783. The two cylinders (grey, left and right) hold oxygen and hydrogen. A static electricity generator (right) supplies a spark to the glass vessel (centre). The product of the reaction is water, proving water to be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

eBook+ Quiz 2.2.

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 **5**Ca:**2**O. This ratio is different to the **atomic ratio** (**1**Ca:**1**O) 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_2. 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_2. 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

	Wt		Wt
Hydrogen	1	Strontian	46
Azote	5	Barytes	68
Carbon	54	Iron	50
Oxygen	7	Zinc	56
Phosphorus	9	Copper	56
Sulphur	13	Lead	90
Magnesia	20	Silver	190
Lime	24	Gold	190
Soda	28	Platina	190
Potash	42	Mercury	167

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 $\mathbf{H_2O}$ and ammonia **NH**, instead of $\mathbf{NH_3}$. 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.)

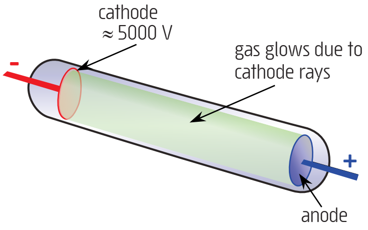
Experiments conducted by Michael Faraday in about 1833 showed that passing an electric current through an aqueous solution would cause chemical changes to take place. The amount of chemical change (ie mass of products formed) was directly proportional to the current flowing and the amount of time for 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.

eBook+ Quiz 2.3.

Attempt Set 3 # 5.

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.

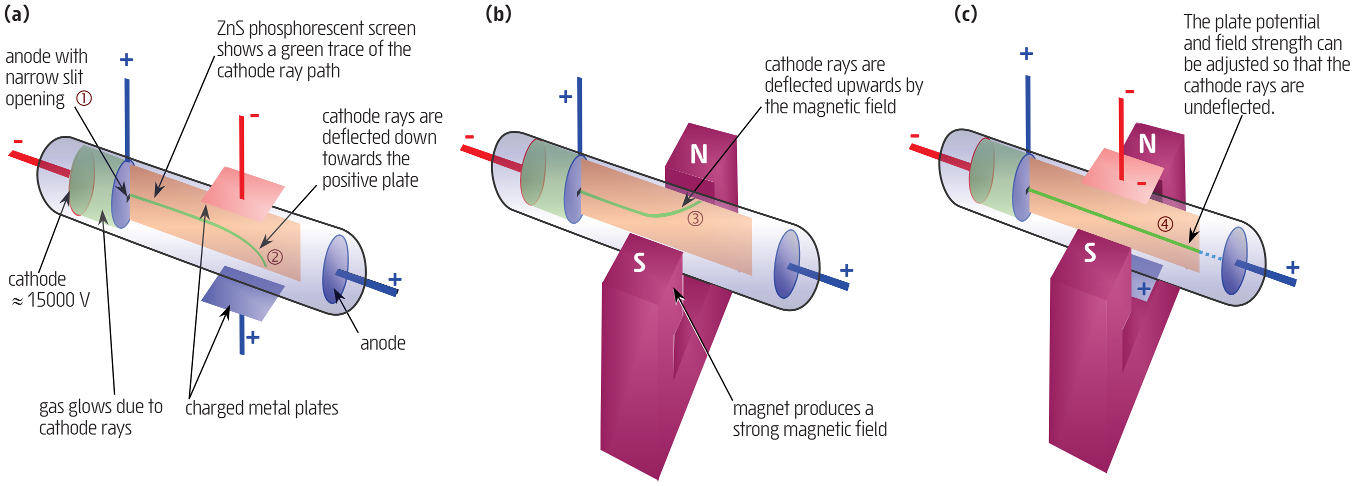


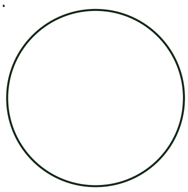
FIGURE 5 In the **CRT**, a cathode ray beam is formed using a narrow slit in a positive plate, ①. The beam can be seen as it creates a green trace on the phosphorescent ZnS coated screen. Notice how the cathode ray beam is deflected by the charged metal plates, ②. A magnetic field is also observed to 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 1.76×10^{-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 1.602×10^{-19} coulomb. Importantly, with Thomson's charge to mass ratio (**q_e/m_e**) now known to be 1.76×10^{-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 **9.11×10^{-31} kg** or approximately 1/1800 of the mass of a hydrogen atom.

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



eBook+ Quiz 2.4.

Attempt Set 3 # 6.

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 1/1000th that of the smallest known atom. This lead 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).

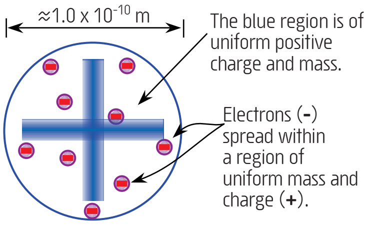


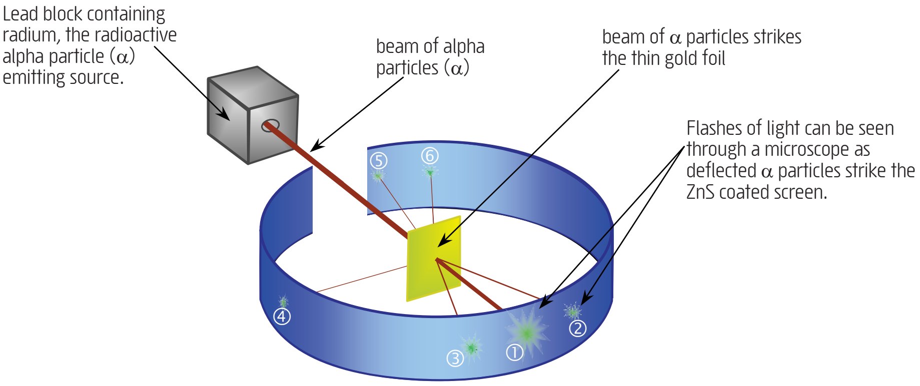
FIGURE 7 J.J.Thomson's 1904 **'plum-pudding'** model of the atom. Small negatively charged electrons are imbedded within a sphere of uniformly positive charged mass.

eBook+ Quiz 2.5.

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**, α (+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 α particles towards a thin sheet of gold foil. The scattered α 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 α particles are deflected backwards, ④, ⑤ and ⑥.



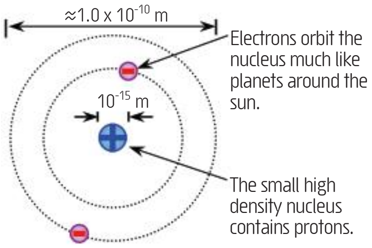
Rutherford was particularly interested in how the alpha particles would be deflected as they passed through the thin gold foil. If Thomson's 'plum-pudding' model of the atom was correct then all of the alpha particles would pass through the gold foil with little or no deflection. This he concluded as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

FIGURE 9 Portrait of New Zealand born physicist **Sir Ernest Rutherford** (1871-1937), painted by Janssens in 1917.

Rutherford, graduated from the University of New Zealand, Wellington receiving his B.Sc. degree in 1894. That year he was awarded a scholarship enabling him to attend Trinity College, Cambridge, as a research student at the Cavendish Laboratory.

There he worked under the guidance of J.J.Thomson, the scientist who had earlier discovered the electron and proposed the 'plum-pudding' model of the atom. Rutherford's later discoveries would disprove Thomson's atomic model.

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 (≈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 (≈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)**.

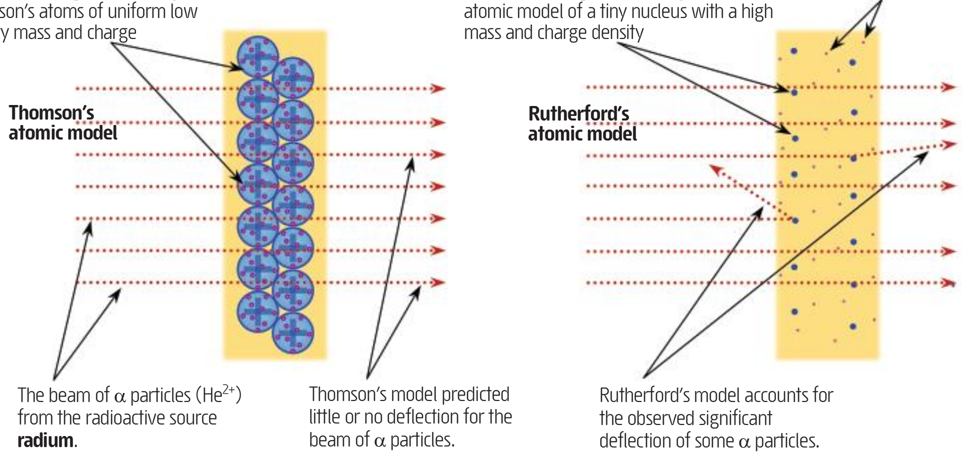


FIGURE 11 (a) cross section of **gold foil** using Thomson's atoms of uniform low density mass and charge

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

eBook+ Quiz 2.6.

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.

eBook+ Quiz 2.7.

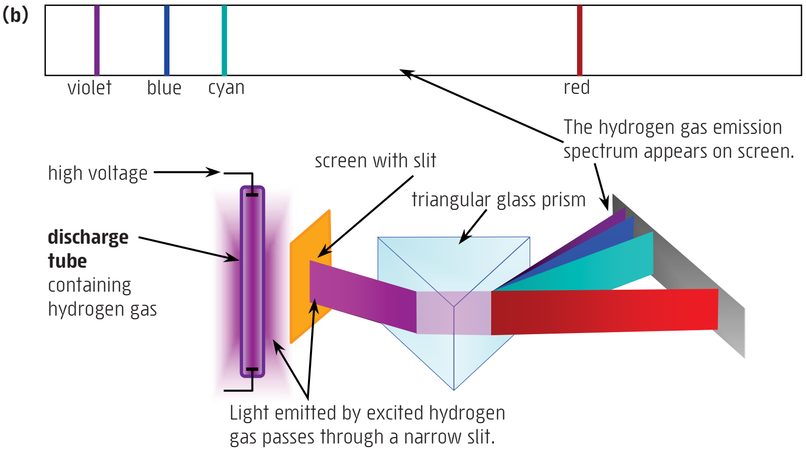
Attempt Set 3 # 8.

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_{upper}) to a lower energy one (E_{lower}). (See Fig 14.) The energy of the emitted photon (E_{photon}) would equal the difference in energy of the two orbits. The frequency (and wavelength) of the emitted photon depends upon its energy ($E_{photon} = hf$ where $h = 6.626 \times 10^{-34}$ and f = frequency).

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.

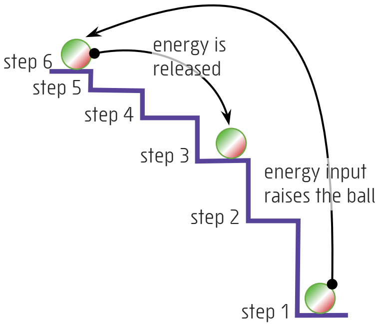
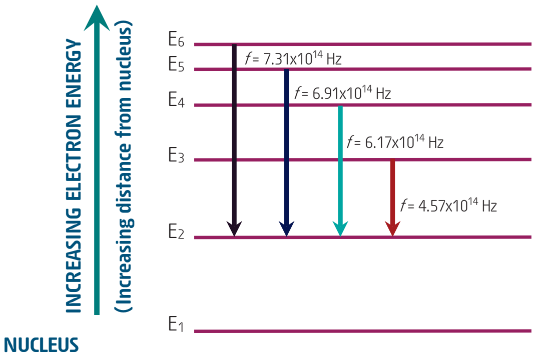


FIGURE 14 The simplified sketch at right shows some of the electron **energy levels** (E_1 to E_6) of the **hydrogen atom** as visualised by Bohr. The **electron transitions** shown here correspond to the formation of the visible part of the hydrogen emission spectrum shown in Fig 12(b).

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 $\mathbf{E_2}$ and releases energy in the form of a **visible light photon** where, $E_{photon} = E_3 - E_2$ and so on. The wavelength and associated colour of the emitted light depends upon its energy, ie E_{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.



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.

eBook$^+$ Quiz 2.8.

Attempt Set 3 # 9.

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.

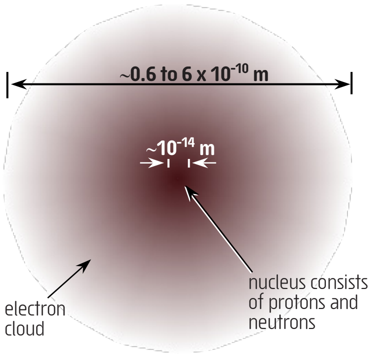


FIGURE 15 The **current** atomic model has a central nucleus of protons and neutrons. The electrons, however, do not orbit the nucleus as in Bohr's model but instead move within regions of characteristic electron distribution and energy called orbitals. The lowest energy orbital for the hydrogen atom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

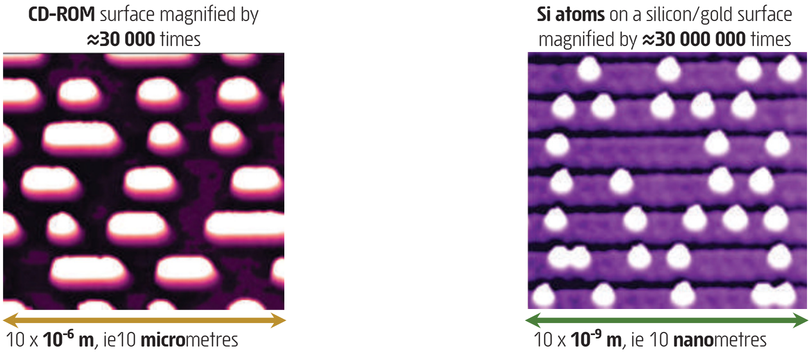
Although the nucleus contains all of the positive charge and over 99.95% of the atom's mass it only represents a tiny fraction of its total volume. This gives the nucleus a very high charge and mass density. The low mass and negatively charged electrons occupy the electron cloud region which comprises over 99.999999999% of the atom's total volume but almost none of its mass.

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 He^+, Li^{2+}, 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**.

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.


CD-ROM surface magnified by ≈**30 000** times

10 x **10^{-6} m**, ie10 **micro**metres

Si atoms on a silicon/gold surface magnified by ≈**30 000 000** times

10 x **10^{-9} m**, ie 10 **nano**metres

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.)

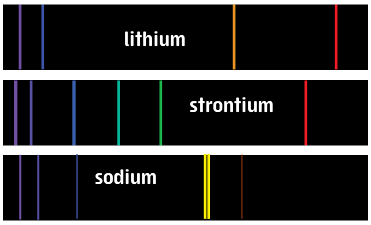
This research was conducted at the Universities of Basel, Switzerland and Madison, Wisconsin, USA.

eBook$^+$ Quiz 2.9.

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.

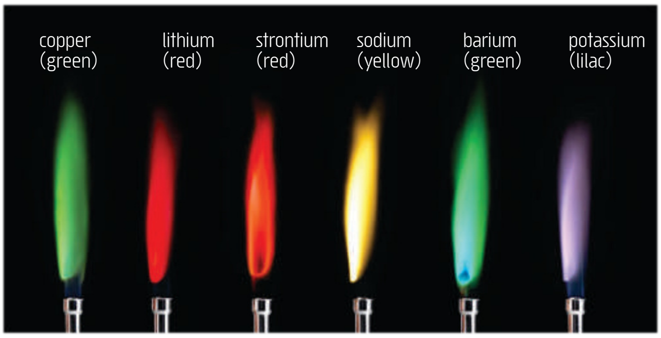
FIGURE 17 The **emission spectrum** for an element can be viewed with a **spectroscope**. Some of the major lines in the visible emission spectrum of lithium, strontium and sodium are shown here.



- **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.

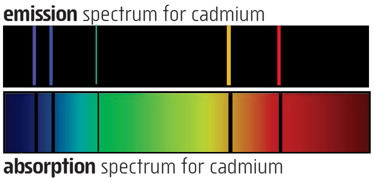
FIGURE 18 (b) Flame tests
A clean platinum wire loop is used to introduce a salt solution or paste into a hot, non-luminous Bunsen flame. The heat of the flame vaporises the salt and excites electrons in the vaporised metal ions. When these excited electrons return to their ground state they emit light 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 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.

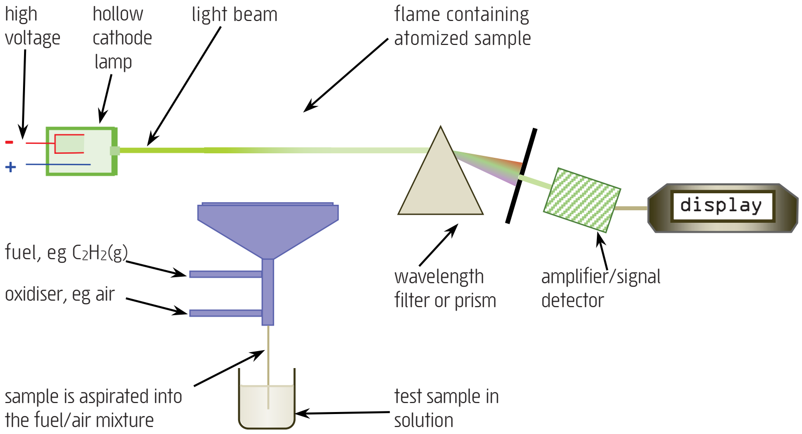


FIGURE 20 **Atomic absorption spectrometer** schematic. In this example of the AAS, a **hollow cathode lamp** is used as the light source. The metal of the cathode is chosen to match the target metal being analysed from the test solution. In this way the light it produces is of the precise wavelengths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

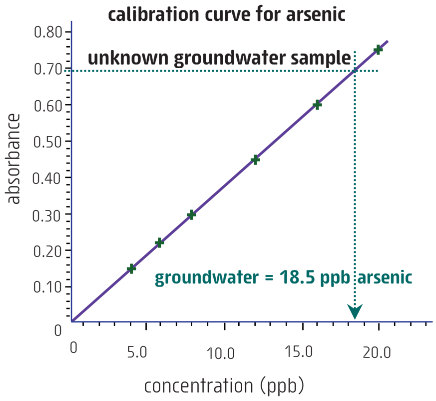


FIGURE 21 Groundwater supplies are sometimes found to be contaminated with naturally occurring arsenic. Water like this may be unsuitable for drinking. In Australia the NHMRC guideline for arsenic in drinking water recommends a threshold of 0.01 mg L^{-1}, ie 10 ppb. AAS can be used to monitor the concentration 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	**groundwater**
absorbance	0.750	0.600	0.450	0.300	0.225	0.150	**0.695**

eBook+ Quiz 2.10. **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, 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 $CuCO_3(s)$ 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.

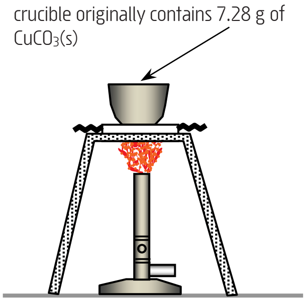


FIGURE 22 As the crucible with $CuCO_3(s)$ is strongly heated its contents decompose leaving behind only CuO(s). The other product, $CO_2(g)$ escapes from the crucible.

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?

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 $Na^+(aq)$ mg L^{-1}	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

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, H_2O(l) that is used for example in a steam iron, table salt, NaCl(s) for cooking or gold, Au(s) and diamonds, C(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 °C and boiled at 100 °C you could be confident (though not certain) the substance was pure water, H_2O(l). By comparison, sea water, a mixture of water and various soluble salts will boil at some temperature above 100 °C, and freeze at some temperature below 0 °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 g mL^{-1} whereas the density of sea water may be as high as 1.24 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, Fe(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.

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.

eBook+ Quiz 3.1.

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

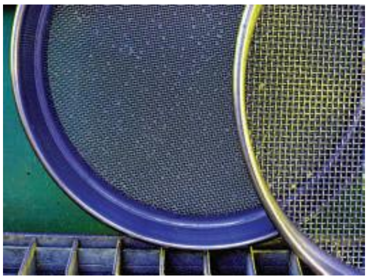
3.2 Mixture separation using physical properties

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.)

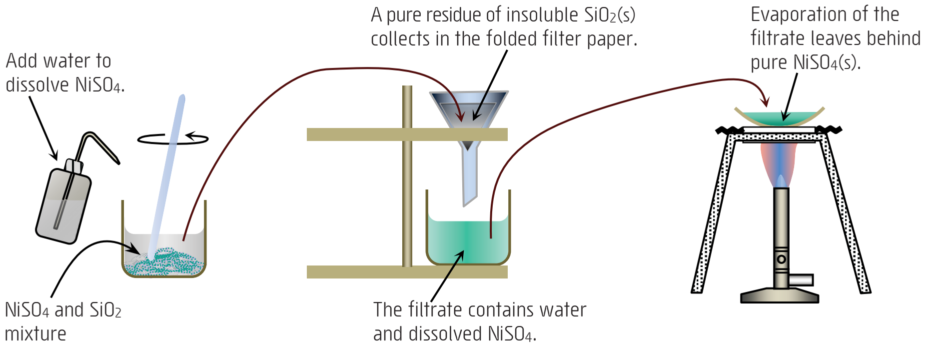


FIGURE 3 Filtration and evaporation
A mixture of $NiSO_4$ (soluble) and powdered quartz granules, $SiO_2(s)$ (insoluble) can be separated using **filtration** and **evaporation**.

Adding distilled water to this mixture dissolves only the soluble component, ie $NiSO_4(s)$. The insoluble, undissolved solid, SiO_2 can be separated by passing the mixture through a folded **filter paper** placed inside a **filter funnel**. Insoluble SiO_2 collects in the filter paper while the solution of $NiSO_4$, 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 $NiSO_4(s)$ crystals.

In the mixture from Fig 3, nickel sulfate, $NiSO_4(s)$ can be separated from the powdered quartz granules, $SiO_2(s)$ as $NiSO_4(s)$ is soluble in water while $SiO_2(s)$ is not. Adding water to this mixture dissolves only $NiSO_4(s)$ leaving $SiO_2(s)$ as an undissolved residue. The resulting $NiSO_4(aq)$ solution is then **filtered** to separate it from the undissolved $SiO_2(s)$. Pure $NiSO_4(s)$ 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 $NiSO_4(s)$, 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 **μm** 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 1×10^{-10} m to filter fine particles, microorganisms and even molecules or ions from solution.

Note: 1 micrometre = **1 μm** = 1×10^{-6} metres
also
1 nanometre = **1 nm** = 1×10^{-9} metres

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 g mL^{-1}) from within quartz rock (density 2.6 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.

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 g mL^{-1}), iron ore (5.2 g mL^{-1}), tantalum (5.2 g mL^{-1}), heavy mineral sands and chromite.

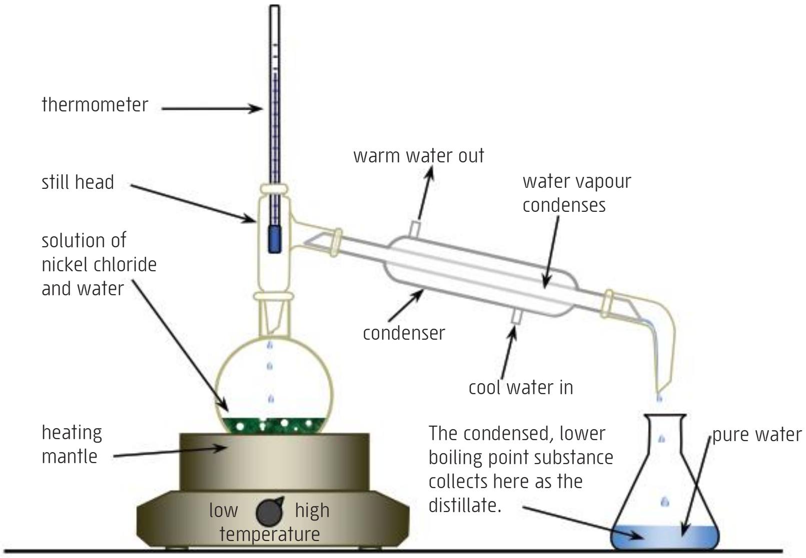
The ore to be concentrated (partially separated) is crushed then mixed with water to form a slurry that flows down the spirals (green). Higher density minerals in the mixture accumulate to the inside of the spirals and are siphoned off from here. The lower density minerals travel faster and accumulate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

- **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_2O) 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.

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, $NiCl_2$ 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.



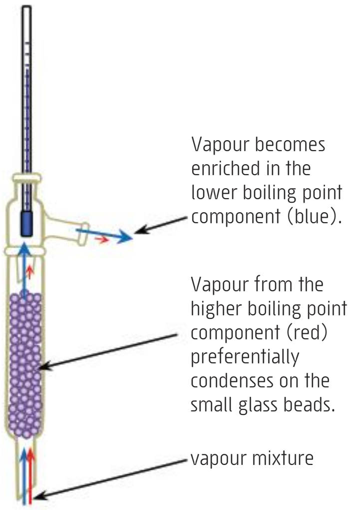


FIGURE 6 Including a **fractionating column** (shown above) below the distillation still head (Fig 5) greatly improves the efficiency of separation of volatile components. This is especially important if the components have similar boiling points.

- **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.

eBook+ Quiz 3.2.

Complete Set 4.

Set 4 Mixtures, pure substances and separation techniques

1. Classify the following materials as pure substances or mixtures.

   a. a solid cube of zinc, Zn
   b. sweat on an athlete's skin
   c. the mineral calcite, $CaCO_3$
   d. the air in a balloon
   e. a glass of milk
   f. a glass of water

2. 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**?

3. **Elemental gold** is yellow in colour with a density of 19.3 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.

   a. **Classify** the quoted properties of elemental gold as physical or chemical.
   b. What does the **well defined melting point** of 1063 °C indicate about elemental gold?
   c. **Suggest** a reason why rose gold has a melting point range rather than a specific melting point as does elemental gold.
   d. 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, CH_3COOH 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**, $CuCl_2(s)$, **sodium chloride**, NaCl(s) and **graphite**, C(s). Their respective solubilities in water are, 61 g $CuCl_2$ per 100 g of water, 36 g 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, C(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 $CuCl_2(s)$ and NaCl(s) from the remaining filtrate mixture.

6. It is possible to use filtration to separate pure **sodium chloride**, NaCl(s) from a mixture of **copper chloride**, $CuCl_2(s)$ and **sodium chloride**, NaCl(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 NaCl per 100 g of ethanol and 67 g $CuCl_2$ per 100 g of ethanol.

   The procedure involves placing the $CuCl_2(s)$/NaCl(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**, ($Fe.TiO_3$), **rutile**, (TiO_2), and **zircon** ($ZrSiO_4$). (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 mL^{-1} to 5.0 g mL^{-1}. A major impurity occurring along with heavy minerals is **quartz sand**, $SiO_2(s)$ which has a much lower density, 2.7 g 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

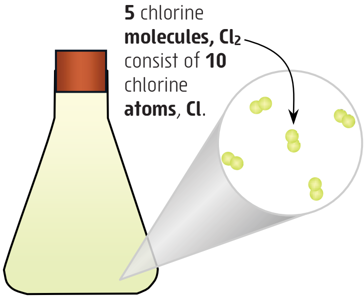


FIGURE 1 A 250 mL flask of the gaseous element chlorine at normal laboratory conditions contains around 6.2 x 10^{21} chlorine **molecules** of formula Cl_2. Each molecule is a single cluster of **two** strongly bonded chlorine **atoms**.

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	H	fluorine	F	F
carbon	C	C	chlorine	Cl	Cl
silicon	Si	Si	bromine	Br	Br
nitrogen	N	N	iodine	I	I
phosphorus *	P	P	helium	He	He
oxygen	O	O	argon	Ar	Ar
sulfur *	S	S	neon	Ne	Ne

* It is generally accepted to write the **formula P** for $\mathbf{P_4}$ and **S** for $\mathbf{S_8}$.

eBook Quiz 4.1.

Attempt Set 5 # 1.

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 (SiC), silicon dioxide (SiO_2), carbon (diamond and graphite) and silicon (Si). Other exceptions are compounds containing **ammonium**, eg NH_4Cl and NH_4NO_3. These form **ionic compounds**. (See Chapter 8.)

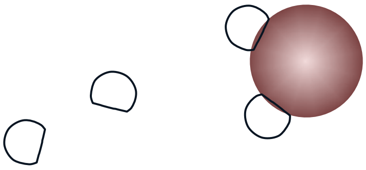


FIGURE 2 This sketch shows two water molecules. Each molecule consists of two hydrogen atoms (small blue spheres) and one oxygen atom (large brown sphere). The chemical formula H_2O shows this.

EXAMPLE 1 What information is conveyed by the following formulas?

$\mathbf{H_2O}$ (water)	Since H and O are non-metal elements then H_2O is a molecular compound. It has two H atoms and one O atom in each water molecule. (See Fig 2.)
$\mathbf{NH_3}$ (ammonia)	NH_3 is a molecular compound (contains non-metal elements only) with one N atom and three H atoms in each ammonia molecule.
$\mathbf{C_2H_6}$ (ethane)	C_2H_6 is a molecular compound (contains non-metal elements only) with two C atoms and six H atoms in each of its molecules.
SiC (silicon carbide)	Although 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 **covalent network** 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.

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

$H_2O(l)$	water
$H_2O_2(l)$	hydrogen peroxide
$NH_3(g)$	ammonia
$NO(g)$	nitric oxide
$H_2CO_3(aq)$	carbonic acid
$CH_3COOH(aq)$	acetic acid
$HCl(aq)$	hydrochloric acid
$H_2SO_4(aq)$	sulfuric acid
$H_3PO_4(aq)$	phosphoric acid
$HNO_3(aq)$	nitric acid
$C_2H_2(g)$	acetylene

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.

NO_2	Each molecule has one N atom (no prefix) and two O atoms (prefix di) in every molecule of NO_2. Add the suffix ide. Thus the systematic name is **nitrogen dioxide**.
N_2O_4	Each molecule has two N atoms (prefix di) and four O atoms (tetr) in every molecule of N_2O_4. Add the suffix ide. Thus the systematic name is **dinitrogen tetroxide**.
SO_3	Each molecule has one S atom (no prefix) and three O atoms (prefix tri) in every molecule of SO_3. Add the suffix ide. Thus the systematic name is **sulfur trioxide**.

eBook+ Quiz 4.2.
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^+, Br^-, Mg^{2+} or N^{3-} or they may be **polyatomic** like OH^-, NH_4^+ or SO_4^{2-}. (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.)

Metal or non-metal? Two special cases. Although the **ammonium ion, NH_4^+** consists of non-metal elements only, it behaves like a **metal ion** by forming ionic compounds with non-metal elements. Thus compounds like **NH_4NO_3** and **NH_4Cl** 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_2S, H_2SO_4, HCl, H_3PO_4 and HNO_3. Interestingly the formula of these compounds can be found as if the compound were ionic.

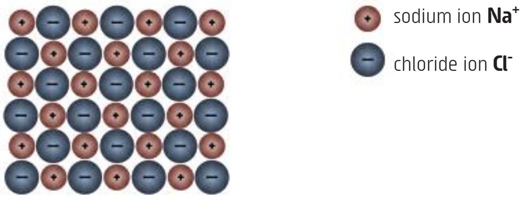


FIGURE 3 Ionic substances consist of a continuous **three-dimensional array** of ions. The **ratio of ions** depends upon the ion charges. This simplified two-dimensional view shows the NaCl(s) structure. Its lattice contains one sodium ion for every one chloride ion.

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.

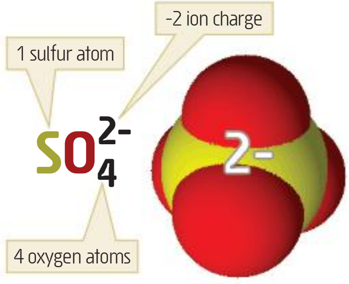


FIGURE 4 A **polyatomic ion** is a **charged cluster** of two or more atoms. The sulfate polyatomic ion, pictured above, consists of a cluster of 5 atoms that includes 1 sulfur atom and 4 oxygen atoms. The ion has a total of 50 electrons, 8 from each of the O atoms (32) plus 16 from the S atom and 2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

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

	sodium sulfide	**ammonium chloride**	**iron(III) hydroxide**	**aluminium sulfate**
Step ①	This is ionic as Na is a metal and S is a non-metal.	This is ionic as NH_4^+ 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.
Step ②	**Na^+ S^{2-}**	**NH_4^+ Cl^-**	**Fe^{3+} OH^-**	**Al^{3+} SO_4^{2-}**
Step ③	Two Na^+ ions and one S^{2-} ion have a charge of 2+ and 2- which together give a charge of zero.	One NH_4^+ ion and one Cl^- ion have a charge of 1+ and 1- which together give a charge of zero.	One Fe^{3+} ion and three OH^- ions have a charge of 3+ and 3- which together give a charge of zero.	Two Al^{3+} ions and three SO_4^{2-} ions have a charge of 6+ and 6- which gives a net charge of zero.
Step ④	**Na_2S**	**NH_4Cl**	**$Fe(OH)_3$**	**$Al_2(SO_4)_3$**
	Remove all ion charges. The formula shows a ratio of two Na^+ ions for every one S^{2-} ion.	( ) are not used as the polyatomic ion NH_4^+ has no added subscript. This formula shows a ratio of one NH_4^+ ion for every one Cl^- ion.	( ) are used as the polyatomic ion OH^- has a subscript of 3. The formula shows a ratio of one Fe^{3+} ion for every three OH^- ions.	( ) are used as the polyatomic ion SO_4^{2-} has a subscript of 3. The formula shows a ratio of two Al^{3+} ions for every three SO_4^{2-} ions.

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

$ZnCl_2$ (zinc chloride)	**$ZnCl_2$** is an ionic compound (Zn is a metal and Cl a non-metal) containing the ions Zn^{2+} and Cl^- in a ratio of one Zn^{2+} ion for every two Cl^- ions.
$Fe_2(SO_4)_3$ (iron(III) sulfate)	**$Fe_2(SO_4)_3$** is an ionic compound (Fe is a metal, S and O are non-metals) containing the ions Fe^{3+} and SO_4^{2-} in a ratio of two Fe^{3+} ions for every three SO_4^{2-} ions.
$(NH_4)_2S$ (ammonium sulfide)	**$(NH_4)_2S$** is an ionic compound (NH_4^+ behaves as a metal ion and S is a non-metal) containing the ions NH_4^+ and S^{2-} in a ratio of two NH_4^+ ions for every one S^{2-} ion.

eBook$^+$ Quiz 4.3.

Attempt Set 5 # 4, 5 and 6.

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

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.

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 H_2O for every formula unit of $CuSO_4$.	$CuSO_4.5H_2O$	copper sulfate-5-water or copper sulfate pentahydrate
Oxalic acid containing two molecules of H_2O for every molecule of $H_2C_2O_4$.	$H_2C_2O_4.2H_2O$	oxalic acid-2-water or oxalic acid dihydrate

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.

eBook$^+$ Quiz 4.4. **Attempt Set 5 # 7.**

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	N_2O_4	÷ by 2	NO_2
3-octenedioic acid	$C_8H_{12}O_4$	÷ by 4	C_2H_3O
potassium oxalate	$K_2C_2O_4$	÷ by 2	KCO_2
glucose	$C_6H_{12}O_6$	÷ by 6	CH_2O
ammonia	NH_3	÷ by 1	NH_3
ethanoic acid	CH_3COOH	÷ by 2	CH_2O

Ammonia (NH_3), **ethanoic** acid (CH_3COOH) and **glucose** ($C_6H_{12}O_6$) 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.

eBook$^+$ Quiz 4.5. **Attempt Set 5 # 8 and 9.**

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**:

$$\textbf{\% element in compound} = \frac{\boldsymbol{\Sigma A_r} \textbf{ for the element in the formula x 100}}{\boldsymbol{A_r}\textbf{(compound)}}$$

Note: **ΣA_r** is the Ar for the element multiplied by the number of times it appears in the formula, eg:

$\Sigma A_r(H)$ in H_2O = **2** x $A_r(H)$ = 2 x 1.008 =2.016

$\Sigma A_r(H)$ in CH_4 = **4** x $A_r(H)$ = 4 x 1.008 =4.032

$\Sigma A_r(H)$ in $Al(OH)_3$ = **3** x $A_r(H)$ = 3 x 1.008 =3.024

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

$$\textbf{\% element in compound} = \frac{\textbf{mass of element in sample x 100}}{\textbf{total mass of sample}}$$

EXAMPLE 7 Determine the **percentage composition** of Na_2CO_3.

$$\textbf{\%Na} = \frac{\Sigma A_r(Na) \text{ x } 100}{A_r(Na_2CO_3)} = \frac{2 \text{ x } 22.99 \text{ x } 100}{105.99} = \textbf{43.38\%}$$

$$\textbf{\%C} = \frac{\Sigma A_r(C) \text{ x } 100}{M(Na_2CO_3)} = \frac{12.01 \text{ x } 100}{105.99} = \textbf{11.33\%}$$

$$\textbf{\%O} = \frac{\Sigma A_r(O) \text{ x } 100}{A_r(Na_2CO_3)} = \frac{3 \text{ x } 16.00 \text{ x } 100}{105.99} = \textbf{45.29\%}$$

Thus Na_2CO_3 contains 43.38% Na, 11.33% C and 45.29% O by mass.

Attempt Set 5 # 10 and 11.

EXAMPLE 8 Determine the **percentage composition** of **water** in crystalline nickel sulfate-6-water [$NiSO_4.6H_2O$]. (See Fig 6.) **(E)**

$$\%H2O = \frac{\Sigma A_r(H_2O) \times 100}{A_r(NiSO_4.6H_2O)} = \frac{6 \times 18.016 \times 100}{262.846} = \mathbf{41.12\%}$$

Thus $NiSO_4.6H_2O$ 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)**

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

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.

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

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

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

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

eBook+ Quiz 4.6. **Complete Set 5.**

FIGURE 6 **Blue-green** crystals of hydrated **nickel(II) sulfate**, $NiSO_4.6H_2O$.

Set 5 Chemical formulas

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

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

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

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

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

   a. carbon dioxide (CO_2)
   b. ammonia (NH_3)
   c. hydrogen sulfide (H_2S)
   d. propane ($CH_3CH_2CH_3$)
   e. hydrogen sulfate (H_2SO_4)
   f. ethanoic acid (CH_3COOH)

4. The **polyatomic ions** hydroxide and ammonium have the respective formulas, **OH^-** and **NH_4^+**. **Describe** the composition of each of these ions and use this to **explain** why they have a net charge.

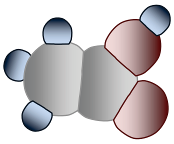


FIGURE 7 **Ethanoic acid** (acetic acid) is the active ingredient in vinegar. Its molecules consist of a cluster of 8 atoms. The space filling model shows how these atoms are arranged in a single molecule of ethanoic acid CH_3COOH.

● carbon atom

● oxygen atom

○ hydrogen atom

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. $LiCl$
   b. $KMnO_4$
   c. MgO
   d. $(NH_4)_2SO_4$
   e. Al_2S_3
   f. $Zn(HSO_4)_2$
   g. FeO
   h. $Cr_2(SO_3)_3$
   i. Fe_2O_3
   j. $Au(CN)_3$

6. Write the **ionic formula** for each of the following compounds.

   a. zinc chloride
   b. copper(I) bromide
   c. calcium sulfate
   d. sodium nitrite
   e. ammonium sulfate
   f. aluminium sulfate
   g. sodium sulfide
   h. iron(III) oxide
   i. silver chromate
   j. iron(II) nitrate
   k. sodium dichromate
   l. zinc phosphate
   m. calcium oxide
   n. silver sulfate
   o. barium hydroxide
   p. potassium hydroxide
   q. copper(II) hydrogensulfate
   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)**

   a. Blue copper(II) sulfate crystals contain five molecules of water for every formula unit of copper(II) sulfate.
   b. Iron(III) chloride is a yellow solid with six molecules of water for every formula unit of iron(III) chloride.
   c. Green hydrated iron(II) chloride crystals contain two molecules of water for every formula unit of iron(II) chloride.
   d. White crystalline zinc nitrate has two molecules of water for every formula unit of zinc nitrate.
   e. 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)**

   a. The household bleach and antiseptic hydrogen peroxide (H_2O_2).
   b. Ozone (O_3) the substance found in the upper atmosphere and responsible for absorbing harmful ultra violet light.
   c. Lactic acid ($CH_3CH(OH)COOH$ or simply $C_3H_6O_3$) an acid involved in many biochemical processes.
   d. Arginine ($C_6H_{14}N_4O_2$) an amino acid essential to living things.

The formula for the ionic salts of organic acids like ethanoic acid (CH_3COOH) can be written with the positive metal ion at the end or the start of the formula, eg:

silver ethanoate:
$AgCH_3COO$ or CH_3COOAg
sodium ethanoate:
$NaCH_3COO$ or CH_3COONa

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_2
   b. K_2S
   c. $NaHSO_4$
   d. SiO_2
   e. NH_4Cl
   f. $H_2C_2O_4$
   g. CH_4
   h. HCl
   i. $ZnSO_3$
   j. H_2SO_3
   k. CO_2
   l. BaC_2O_4
   m. $CaSO_4$
   n. NO_2
   o. $AgCH_3COO$ (See border note at left.)
   p. $Fe(HSO_3)_2$
   q. CH_3COOH
   r. SiC

10. Calculate the **percentage composition of each element** in the following compounds.

   a. methane (CH_4)
   b. barium nitrate [$Ba(NO_3)_2$]
   c. ammonium sulfate
   d. copper(II) chloride-2-water

11. Three compounds often used as sources of **nitrogen** in garden fertilisers are ammonium sulfate [$(NH_4)_2SO_4$], ammonium nitrate [NH_4NO_3] and urea [$(NH_2)_2CO$]. 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.]

12. Determine the **percentage composition of water** in each of the hydrated compounds. **(E)**
    a. cobalt ethanoate-6-water [$Co(CH_3COO)_2.6H_2O$]
    b. 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 °C. By contrast, copper sulfate itself is quite stable and does not decompose unless heated to above 650 °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 °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.
    a. **Account** for the weight loss of 1.67 g.
    b. Determine the **percentage of water** in the sample of hydrated copper sulfate. **(E)**
    c. 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.

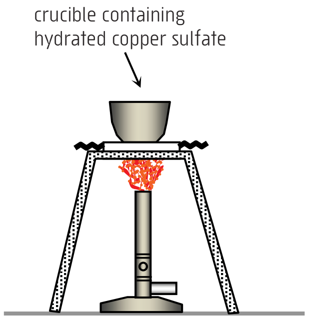


FIGURE 8 If the crucible of hydrated copper sulfate is strongly heated it will lose mass as the water of crystallisation is driven off.

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 °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 °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

    a. Determine the mass of **silver oxide** used in the experiment.
    b. **Account** for the loss of mass when silver oxide is heated?
    c. From the experimental data determine the mass of **silver** and **oxygen** in the sample.
    d. What is the **experimental** percentage composition of **silver** in the silver oxide sample? **(E)**
    e. Determine the **theoretical** percentage composition of **silver** in silver oxide, ie from the known chemical formula Ag_2O?
    f. 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

    a. Explain why the increase in mass of the crucible during this reaction does not contradict the **law of conservation of mass**.
    b. Use the student's experimental data to determine the **percentage of magnesium** in magnesium oxide? **(E)**
    c. The chemical formula of magnesium oxide is known to be MgO. Using this formula, determine the **theoretical** percentage of magnesium in magnesium oxide.
    d. 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

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.)

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.

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.

eBook+ Quiz 5.1.

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.

eBook+ Quiz 5.2.

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.'

a. For each of these determine the **dependent** and **independent** variable.

b. According to Hypothesis 4, what should be produced when iron nails are added to a sulfuric acid solution?

c. 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?

d. 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.

FIGURE 2 **Dry ice** is the common name for solid carbon dioxide. It is a peculiar substance as it **sublimes** (at -78 ºC) 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 ºC) 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 $CO_2(g)$ is not toxic, if large volumes are formed then room air may be replaced with $CO_2(g)$ leading to asphyxiation due to lack of oxygen.

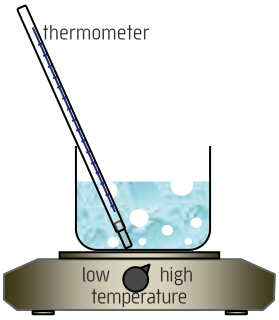
2 The students who wrote the hypotheses in Question 1 decided to proceed with an investigation for Hypothesis 3, ie 'When zinc dissolves in hydrochloric acid the **volume** of **hydrogen** gas produced increases **in direct proportion** to the **mass of zinc** used.' Answer the following regarding their planned investigation.

a. 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.

b. What **data** should the students record in order to test their hypothesis?

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



Note: Solute concentration can be found using:

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

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 (NaCl) as its solute.

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........ **mol** s^{-1}

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

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

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.

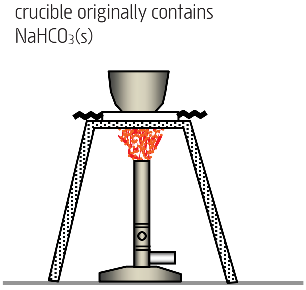


FIGURE 4 As the crucible with $NaHCO_3(s)$ is strongly heated its contents decompose leaving behind only $Na_2CO_3(s)$. The other products, $CO_2(g)$ and $H_2O(g)$ escape from the crucible.

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 $NaHCO_3(s)$ and measured the mass of $Na_2CO_3(s)$ 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 $NaHCO_3(s)$ before heating
- the mass of the crucible with the reaction product $Na_2CO_3(s)$ 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.

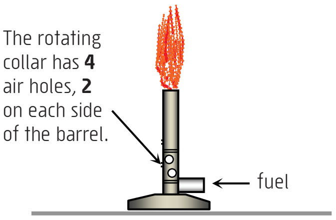


FIGURE 5 Heat produced from a Bunsen burner comes from the combustion of the fuel natural gas (essentially methane, CH_4). On this Bunsen a rotating collar surrounding the four air holes can be adjusted to vary the amount of air mixing with the fuel.

Diameter of each Bunsen air hole opening (mm)	Total opening area of four Bunsen air holes (mm^2)	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

a. What are the **independent** and **dependent variables** in this investigation?

b. What are four other variables that the student should be careful to keep constant during the investigation?

c. **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.

d. 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.

a. Clearly identify the **dependent variable** and the two possible **independent variables** referred to by Mitch.

b. Write two **hypotheses** that relate to Mitch's question.

c. 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.

d. Briefly outline how you would **process or present your data** in order to determine the validity of your hypothesis.

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**.

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	**8.99 g**
2	8.67, 8.65, 8.65, 8.67	**8.66 g**
3	8.75, 7.98, 9.55, 8.81	**8.77 g**

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**.

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.

eBook+ Quiz 5.3.

Attempt Set 7 # 1.

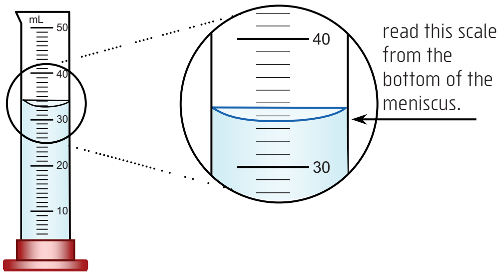
5.4 Making and recording measurements

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.

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.

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 1/10th 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**, ± amount. This indicates the actual measured amount could be higher or lower than the recorded value by the ± amount. (See Table 1.) For instruments with a scale the random error is usually ± half the smallest scale division, for a digital display instrument it is ± 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 ±	Measurement examples	
			Using significant figures only	Including ± random error
10 mL	0.1 mL	± 0.05 mL	3.45 mL 7.80 mL	3.45 mL ± 0.05 mL (ie 3.40-3.50 mL) 7.80 mL ± 0.05 mL (ie 7.75-7.85 mL)
50 mL	1 mL	± 0.5 mL	15.5 mL 42.5 mL	15.5 mL ± 0.5 mL (ie 15.0-16.0 mL) 42.5 mL ± 0.5 mL (ie 42.0-43.0 mL)
250 mL	2 mL	± 1 mL	153 mL 227 mL	153 mL ± 1 mL (ie 152-154 mL) 227 mL ± 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 ± **random error** in each of the balances used.

Measurement	Comment
20.670 g	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 ± 0.0005 g, ie half the value of the last displayed digit.
20.7 g	The recorded mass has three significant figures. This balance is capable of measuring to one tenth of a gram with a random error of ± 0.05 g.
21 g	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 ± 0.5 g.

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, ±
graduations) shown on this 50 mL cylinder.

eBook+ Quiz 5.4.

Attempt Set 7 # 2 and 3.

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 x 10^4 (four SF), 3.50 x 10^4 (three SF) or 3.5 x 10^4 (two SF).

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

1**00**819.5**0**4..........②

0.
0. ③

181954**.0** ....④
181954**.000**..........④

181954**0** ....⑤
181954**000**...........⑤

181954**.0** ....④
181954**000.0**.........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.

EXAMPLE 4 How many significant figures are present in each of the following volume measurements?

7.08×10^3 mL	**three** significant figures	see rule ① and ②
7.800×10^3 mL	**four** significant figures	see rule ① and ④
7.0800×10^3 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

Attempt Set 7 # 4, 5 and 6.

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.

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.

EXAMPLE 5 Evaluate the following and give the answer to the correct number of significant figures.

a. $1.498\ g \div 6.2 \times 10^{-1}\ L$ $= 2.416129\ g\ L^{-1}$ $= \mathbf{2.4\ g\ L^{-}}$	This calculation involves division so the answer only has as many SF as the number with the least SF. As 6.2×10^{-1} L has the least SF (two) so the answer is rounded to two significant figures even though 1.498 g has four SF.
b. $\frac{1.04\ g \times 7.000}{12.01\ g\ mol^{-1}}$ $= 0.6061615$ $= \mathbf{0.606\ mol}$ (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.

Attempt Set 7 # 7.

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. $1.49 \times 10^2\ g + 6.2\ g$ $= 149\ g + 6.2\ g$ $= 155.2$ $= \mathbf{155\ g}$ (0 DP)	This calculation involves addition so the answer only has as many DP as the number with the least DP. As the measurement 1.49×10^2 g has the least decimal places (nil) when written to the same powers of ten as 6.2, ie 1.49×10^2 g becomes 149 g so the answer has nil decimal places.
b. $7.5530 \times 10^3\ L - 6.790\ L$ $= 7553.0\ L - 6.790\ L$ $= 7546.21\ L$ $= \mathbf{7546.2\ L}$ (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.

eBook⁺ Quiz 5.5.

Complete Set 7.

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^{-1}**.
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.

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

Density is calculated as follows:

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

Trial	Volume of water (mL)	Mass of empty beaker (g)	Mass of beaker + water (g)	Mass of water (g)	Density of water (g mL^{-1})
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^{-1} 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.

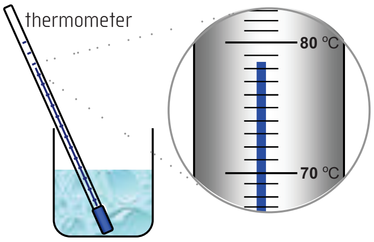


FIGURE 10 Monitoring the temperature of some hot water as it cools. An enlarged section of the thermometer's temperature scale is shown.

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?

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 **$H_2C_2O_4.2H_2O$**, which means they should contain **14.3%** by mass H_2O. To measure this value the student weighed a sample of the crystals, ($H_2C_2O_4.2H_2O$) into a preweighed crucible. The crucible and crystals were heated for three minutes to expel the water of crystallisation thus forming anhydrous oxalic acid (**$H_2C_2O_4$**). 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 + $H_2C_2O_4.2H_2O$.........................24.10 g
   mass of crucible + $H_2C_2O_4$ (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
   b. 10.1 Pa
   c. 4.04×10^4 mg
   d. 400 kPa
   e. 6250 L
   f. 1000 g
   g. 6.6×10^3 kPa
   h. 1000.0 Pa
   i. 0.09000 kg
   j. 0.4 °C
   k. 0.0032 g
   l. 1.00110×10^6 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

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

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

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	6.02×10^{23}
mass of a proton	1.67×10^{-24} g
thickness of a page	2.1×10^{-5} m

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
   b. 4.990 L to mL
   c. 3.72×10^6 mL to L
   d. 989.27 MPa to Pa
   e. 78631 Pa to kPa
   f. 14.99 mg to g
   g. 2.266 MPa to kPa
   h. 7.62 atm to kPa
   i. 7.25 tonne to kg
   j. 3.4 tonne to g
   k. 356.9 °C to K
   l. 775 K to °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**.

   a. 265.3 x 0.16

   b. $\dfrac{3.8265}{0.07250}$

   c. $\dfrac{1.350 \times 10^3 \times 350}{0.59962}$

   d. $\dfrac{9.379 \times 10^2 \times 3.50}{0.59962 \times 17.008}$

8. **Some experimental measurements are processed as shown here. Evaluate** these and round your answer to the correct number of significant figures.

   a. 3.042 + 192.1
   b. 0.08193 + 0.0032
   c. $1.731 \times 10^2 + 3.296 \times 10^3$
   d. 192.1 - 3.042
   e. $8.192 \times 10^5 - 7.791 \times 10^4$

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.)

   a. $\dfrac{4.64 \times 10^3 + 14.592}{0.3766 \times 6.312}$ b. $\dfrac{7.332 \times 10^4 - 21}{9.728 \times 3.4741}$

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:

    a. 1×10^2 mm^2 b. 1.0×10^2 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.

    a. What value can Michelle **reasonably quote** for the combined volume of distilled water and sulfuric acid? Assume the two volumes are additive.
    b. What can Michelle do to obtain a **more precise** final result?

CHAPTER 6 | CHEMICAL EQUATIONS

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, → 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, ⇄
reaction meaning both forward and reverse reactions are occurring.

eBook+ Quiz 6.1 @ lucaspublications.com.au.

Attempt Set 8 # 1.

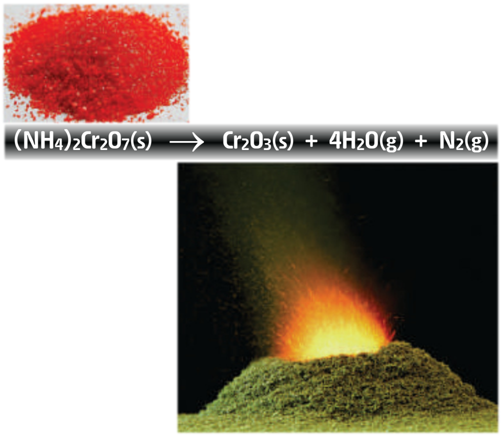


FIGURE 1 The decomposition of **ammonium dichromate**, $(NH_4)_2Cr_2O_7$ (orange-red crystals, top left) is a spectacular exothermic chemical reaction producing plumes of dark green chromium(III) oxide (bottom right), large amounts of water vapour, nitrogen gas and considerable heat.

6.2 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.

$\mathbf{2}H_2O$ = $\mathbf{4}H$ + $\mathbf{2}O$ atoms

$\mathbf{4}N_2O_4$ = $\mathbf{8}N$ + $\mathbf{16}O$ atoms

$\mathbf{3}HNO_3$ = $\mathbf{3}H$ + $\mathbf{3}N$ + $\mathbf{9}O$ atoms
or = $\mathbf{3}H^+$ + $\mathbf{3}NO_3^-$ ions

$\mathbf{2}Ca(NO_3)_2$ = $\mathbf{2}Ca$ + $\mathbf{4}N$ + $\mathbf{12}O$ atoms
or = $\mathbf{2}Ca^{2+}$ + $\mathbf{4}NO_3^-$ ions

$\mathbf{3}Fe_2(SO_4)_3$ = $\mathbf{6}Fe$ + $\mathbf{9}S$ + $\mathbf{36}O$ atoms
or = $\mathbf{6}Fe^{3+}$ + $\mathbf{9}SO_4^{2-}$ ions

To write a balanced chemical equation:

① formula of products (separated by a + sign) to the right of the arrow.

② 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 (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.

Step① $Al_2(CO_3)_3 + HNO_3 \rightarrow Al(NO_3)_3 + CO_2 + H_2O$

The reactants are aluminium carbonate, $Al_2(CO_3)_3$ and nitric acid, HNO_3. These substances are written first followed by an arrow pointing to the products aluminium nitrate [$Al(NO_3)_3$], carbon dioxide [CO_2] and water [H_2O]. Ensure all **formulas** are correct.

Step② $Al_2(CO_3)_3 + \mathbf{6}HNO_3 \rightarrow \mathbf{2}Al(NO_3)_3 + \mathbf{3}CO_2 + \mathbf{3}H_2O$

Al is balanced first [$\mathbf{2}Al(NO_3)_3$] as it appears in only two formulas. **N** is balanced next as it is now fixed at **6N** on the product side [$\mathbf{2}Al(\mathbf{N}O_3)_\mathbf{3}$] and also appears in two formulas only, ∴ write $\mathbf{6}H\mathbf{N}O_3$. H is now fixed at **6H** on the reactant side [$\mathbf{6H}NO_3$] 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.

Step③ $Al_2(CO_3)_3(s) + 6HNO_3\mathbf{(aq)} \rightarrow 2Al(NO_3)_3\mathbf{(aq)} + 3CO_2\mathbf{(g)} + 3H_2O\mathbf{(l)}$

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

eBook+ Quiz 6.2.

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 , (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.

Step ① $_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$

Step ② $_3(s) + 6H^+(aq) + \underline{\mathbf{3}}SO_4^{2-}(aq) \rightarrow 2Al^{3+}(aq) + \underline{\mathbf{3}}SO_4^{2-}(aq) + 6H_2O(l)$

As $H_2SO_4(aq)$ is a strong acid and is dissolved in water, ie **(aq)**, then $3H_2SO_4$ is written as $\mathbf{6H^+}$ $\mathbf{3SO_4}$ product $Al_2(SO_4)_3$ is ionic and dissolved in water so it is written as $\mathbf{2Al^{3+}}$ $\mathbf{3SO_4}$ solids, liquids or gases, therefore their formulas are left as they are.

Step ③ $_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 6H_2O(l)$

The equation contained spectator ions (SO_4^{2-}) so $\mathbf{3SO_4}$ 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**.

$$Na_2SO_3(s) + 2CH_3COOH(aq) \rightarrow 2NaCH_3COO(aq) + SO_2(g) + H_2O(l)$$

$$Na_2SO_3(s) + 2CH_3COOH(aq) \rightarrow 2Na^+(aq) + 2CH_3COO^-(aq) + SO_2(g) + H_2O(l)$$

$Na_2SO_3(s)$, $H_2O(l)$ and $SO_2(g)$ are in solid, liquid and gas phase respectively so their formulas are left as they are. Although $CH_3COOH(aq)$ is dissolved it is neither ionic nor a strong acid and so its formula is left as is. The product $2NaCH_3COO(aq)$ is dissolved and ionic so its formula is rewritten as $\mathbf{2Na^+}$ $\mathbf{2CH_3COO^-}$. This equation does not contain spectator ions and so is left as it is.

eBook+ Quiz 6.3. 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**.

$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$ .... ①

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ .... ②

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 $H_2(g)$ in both equations. To do this multiply the coefficients of equation ① ②

$\mathbf{3}H_2O(g) + \mathbf{3}C(s) \rightarrow \mathbf{3}CO(g) + \mathbf{3H_2}(g)$ .... ①

$N_2(g) + \mathbf{3H_2}(g) \rightarrow 2NH_3(g)$ .... ②

Add both to give a single equation.

$$3H_2O(g) + 3C(s) + N_2(g) + \mathbf{3H_2}(g) \rightarrow 3CO(g) + \mathbf{3H_2}(g) + 2NH_3(g)$$

Simplify the result, ie remove $3H_2(g)$ from both sides of the equation.

$$3H_2O(g) + 3C(s) + N_2(g) \rightarrow 3CO(g) + 2NH_3(g)$$

Ionic substances include any compounds that contain a combination of metal elements (or NH_4^+) and non-metal elements.

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

$NaOH(aq)$............$Na^+(aq)$ and $OH^-(aq)$

$CaBr_2(aq)$............$Ca^{2+}(aq)$ and $2Br^-(aq)$

$Al(NO_3)_3(aq)$.......$Al^{3+}(aq)$ and $3NO_3^-(aq)$

$NH_4Cl(aq)$............$NH_4^+(aq)$ and $Cl^-(aq)$

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

$H_2SO_4(aq)$ ....$2H^+(aq)$ and $SO_4^{2-}(aq)$

$HNO_3(aq)$ ....$H^+(aq)$ and $NO_3^-(aq)$

$HCl(aq)$ ....$H^+(aq)$ and $Cl^-(aq)$

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 (P_4) in air (O_2) to form phosphorus(V) oxide (P_4O_{10}). Adding water to P_4O_{10} produces phosphoric acid. The two sequential reactions and the overall reaction for this process are shown here.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$

$P_4(s) + 5O_2(g) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$

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.

eBook+ Quiz 6.4. 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 [$H_2(g)$] on the surface of the zinc strip.

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

   $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

   a. **Name** the reactants and products of this reaction.

   b. In this reaction what substances are consumed and what substances are formed?

   c. 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**.

   d. 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 $ZnCl_2$ and 2.55 g of H_2. Clearly the student has made a significant error. **Explain**.

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

   a. $HCl(aq) + Fe(OH)_3(s) \rightarrow FeCl_3(aq) + H_2O(l)$

   b. $HNO_3(aq) + BaO(s) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$

   c. $NO_2(g) + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$ ($\rightleftharpoons$

   d. $N_2(g) + H_2(g) \rightleftharpoons NH_3(g)$

   e. $NaOH(aq) + Al(s) + H_2O(l) \rightarrow NaAl(OH)_4(aq) + H_2(g)$

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

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

   a. solid copper(II) carbonate + nitric acid solution gives copper(II) nitrate solution + carbon dioxide gas + water liquid

   b. sulfuric acid solution + copper(II) hydroxide suspension gives copper sulfate solution + water liquid

   c. solid aluminium oxide + nitric acid solution gives aluminium nitrate solution + water liquid

   d. granulated zinc + hydrochloric acid solution gives zinc chloride solution + hydrogen gas

   e. sulfur dioxide gas + potassium hydroxide solution gives potassium sulfite solution + water (**This is a reversible reaction**.)

   f. 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. $CO_2(g)$ is injected into soft drink under pressure. When this is done most of the $CO_2(g)$ dissolves in the drink forming $CO_2(aq)$. A portion of the dissolved $CO_2(aq)$ then reacts with water producing the unstable compound carbonic acid, $H_2CO_3(aq)$. All of these reactions are reversible.

$CO_2(g) \rightleftharpoons CO_2(aq)$

then

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Releasing the cap on a soft drink bottle causes the unstable $H_2CO_3(aq)$ to decompose thus reforming $CO_2(aq)$ then $CO_2(g)$. The $CO_2(g)$ 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	$Na_2CO_3(s)$	carbonic acid	$H_2CO_3(aq)$
sodium sulfate	$Na_2SO_4(s)$	carbon dioxide	$CO_2(g)$
rust	$Fe_2O_3.3H_2O(s)$	ethanoic acid	$CH_3COOH(aq)$
sodium hydrogencarbonate	$NaHCO_3(s)$	sodium ethanoate	$NaCH_3COO(aq)$
sodium hydrogensulfate	$NaHSO_4(aq)$	iron	$Fe(s)$
citric acid	$H_3C_6H_5O_7(s)$	oxygen gas	$O_2(g)$
sodium citrate	$Na_3C_6H_5O_7(aq)$	water	$H_2O(l)$

   a. **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**.

   b. 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.)**

   c. 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.)

a. $Fe^{3+}(aq) + CO_3^{2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$

b. $Ca^{2+}(aq) + PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

c. $Al(s) + H^+(aq) \rightarrow Al^{3+}(aq) + H_2(g)$

d. $SO_3^{2-}(aq) + H^+(aq) \rightleftharpoons SO_2(aq) + H_2O(l)$

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^+ .... has a charge of +1

$\mathbf{2}Zn^{2+}$ ..... has a charge of +4

SO_4^{2-} .... has a charge of -2

$\mathbf{3}PO_4^{3-}$ ..... has a charge of -9

6. **Rewrite** the following balanced chemical equations in **net ionic** form. (See border note.)

a. $Al_2(CO_3)_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3CO_2(g) + 3H_2O(l)$

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

c. $MgO(s) + 2CH_3COOH(aq) \rightarrow Mg(CH_3COO)_2(aq) + H_2O(l)$

d. $Co(s) + 2HCl(aq) \rightarrow CoCl_2(aq) + H_2(g)$

e. $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$

f. $3NH_3(g) + H_3PO_4(aq) \rightarrow (NH_4)_3PO_4(aq)$

g. $3Pb(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Pb_3(PO_4)_2(s) + 6NaNO_3(aq)$

h. $2AgNO_3(aq) + H_2SO_4(aq) \rightarrow Ag_2SO_4(s) + 2HNO_3(aq)$

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 $NaOH$, $CaCl_2$, NH_4NO_3, $Fe_2(SO_4)_3$ or a **strong acid**, eg H_2SO_4, HCl or HNO_3.

7. **Convert** the following word equations to balanced **net ionic equations**.

a. solid calcium carbonate + nitric acid solution → calcium nitrate solution + carbon dioxide gas + water liquid

b. hydrochloric acid solution + aluminium hydroxide suspension → aluminium chloride solution + water liquid

c. solid magnesium oxide + nitric acid solution → magnesium nitrate solution + water liquid

d. calcium granules + sulfuric acid solution → calcium sulfate solid + hydrogen gas

e. carbon dioxide gas + sodium hydroxide solution → sodium carbonate solution + water

f. barium chloride solution + sodium sulfate solution → 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)**

a. 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.

$C(s) + CO_2(g) \rightarrow 2CO(g)$ (In this reaction C and CO_2 react to form CO.)

$CO(g) + FeO(s) \rightarrow Fe(l) + CO_2(g)$ (Here, CO reduces FeO to Fe.)

b. **Ozone** (O_3) 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.

$O_2(g) \rightarrow 2O(g)$ (This reaction absorbs UV energy.)

$O_2(g) + O(g) \rightarrow O_3(g)$ (O_3 goes on to absorb UV in other reactions.)

Allotropes are alternative forms of an element that differ in the way the atoms are bonded. Graphite and diamond are two allotropes of carbon (C). Ozone (O_3) and oxygen (O_2) are also allotropes.

c. 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.

$CFCl_3(g) \rightarrow CFCl_2(g) + Cl(g)$ (CFC decomposes in the upper atmosphere.)

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ (Cl atoms destroy ozone, O_3.)

$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$ (ClO depletes O needed for O_3 formation as well as producing more Cl that goes on to destroy more O_3.)

CHAPTER 7 | ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

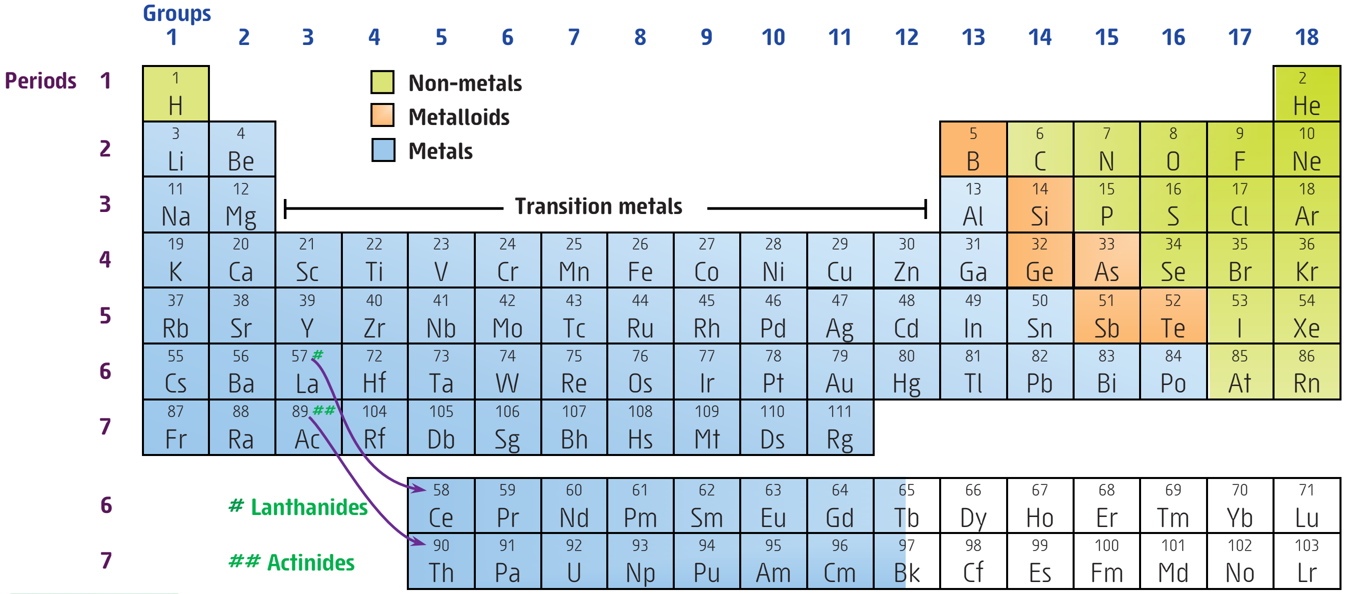
7.1 The periodic table and chemical periodicity

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.

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.

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



Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 # La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 ## Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							
6	# Lanthanides				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	## Actinides				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

eBook⁺ Quiz 7.1.

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, $CaCl_2$, and $AlBr_3$.
- **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_2S, and K_3PO_4.
- **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 $MgCl_2$, CaS and $Sr_3(PO_4)_2$.

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.

eBook⁺ Quiz 7.2.

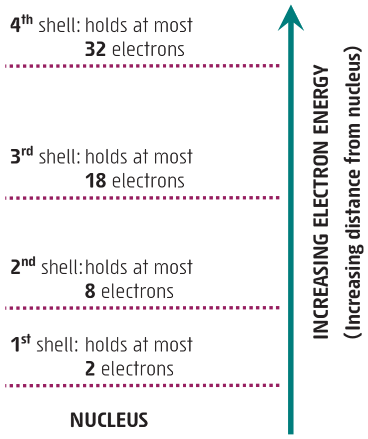
Attempt Set 9 # 1, 2, 3, 4 and 5.

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) = 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.)

eBook^{+} Quiz 7.3.

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.



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 1st shell, then 8 electrons fill the 2nd shell, then a further 8 electrons fill the 3rd shell and finally 2 electrons fill the 4th shell.

It may be interesting to note however, for atoms with more than 20 electrons the 3rd shell recommences filling to its ultimate capacity of 18 electrons and only then does the 4th shell fill to 8 electrons and the 5th 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					
	1st shell	2nd shell	3rd shell	4th shell	5th shell	6th 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

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.

eBook^{+} Quiz 7.4.

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**.

calcium
2, 8, 8, **2**
2 valence electrons

aluminium
2, 8, **3**
3 valence electrons

oxygen
2, **6**
6 valence electrons

chlorine
2, 8, **7**
7 valence electrons

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.

eBook+ Quiz 7.5.

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	3	3	2	2	helium
O	8	8	10	2, 8	neon
F	9	9	10	2, 8	neon
Al	13	13	10	2, 8	neon
S	16	16	18	2, 8, 8	argon
Cl	17	17	18	2, 8, 8	argon
Ca	20	20	18	2, 8, 8	argon
Br	35	35	36	2, 8, 18, 8	krypton

calcium 2+ ion
2, 8, **8**

aluminium 3+ ion
2, **8**

oxygen 2- ion
2, **8**

chlorine 1- ion
2, 8, **8**

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.

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**.

eBook+ Quiz 7.6.

Complete Set 9.

Set 9 Electronic structure and the periodic table

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

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.

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

3. 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.

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

4. 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.
   a. N and P
   b. Ar and He
   c. C and O
   d. oxygen and selenium
   e. potassium and bromine
   f. magnesium and sulfur

5. From each of the following pairs of elements choose the one the most likely to be a good conductor of electricity and heat. **(E)**
   a. Be and Ca
   b. B and Tl
   c. Sc and Ge
   d. selenium and titanium

6. Give the **electron configuration** and **Lewis structure** for the following atoms.
   a. Na b. S c. Ca d. P e. Cl f. Ga

7. Give the **electron configuration** and **Lewis structure** for the following ions.
   a. Na^+ b. S^{2-} c. Mg^{2+} d. Ca^{2+} e. Cl^- f. O^{2-}

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

FIGURE 5 The most abundant **isotopes** of carbon occurring on Earth are ^{12}**C** (98.9%) and ^{13}**C** (1.1%). The isotope ^{14}**C** is extremely rare, and constitutes <0.01% of naturally occurring carbon in atmospheric CO_2.

^{14}C is formed in the upper atmosphere by the interaction of cosmic rays on ^{14}**N** atoms. However, ^{14}C is radioactive and slowly decays back to ^{14}N. It takes about 5730 years for half of a ^{14}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 CO_2, or from the food they eat. When the tissue dies the amount of ^{12}C remains constant, but ^{14}C decays. Measuring the ratio of ^{14}C to ^{12}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	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 number	Electron
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	Ion	Ion e	Nearest	Noble gas e
K	2, 8, 8,1	K^+	2, 8, 8	Ar	2, 8, 8
Mg		Mg^{2+}			
S		S^{2-}			
F		F^-			
N		N^{3-}			
Sr		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.

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_2), zinc sulfate ($ZnSO_4$), sodium chloride (NaCl)	carbon dioxide (CO_2), water (H_2O), oxygen (O_2), sugar ($C_{12}H_{22}O_{11}$)	silicon (Si), silicon dioxide (ie quartz, SiO_2), 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_3 or H_2SO_4) 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.

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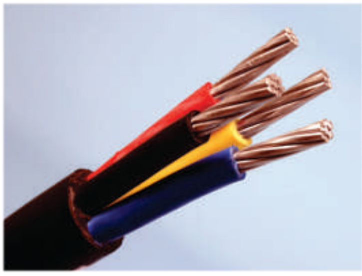


FIGURE 2 This **electric power cable** consists of four copper wires coated with a plastic material. The copper conducts the electric current while the plastic coating is an insulator that is non-conducting.

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.)

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 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.

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.

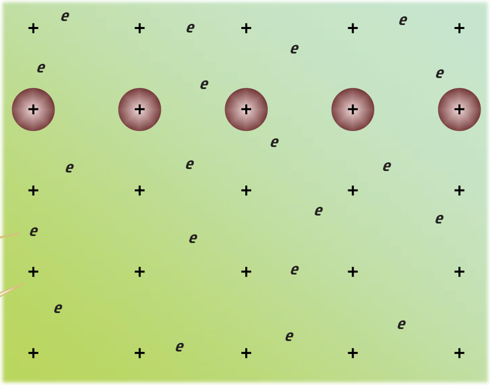
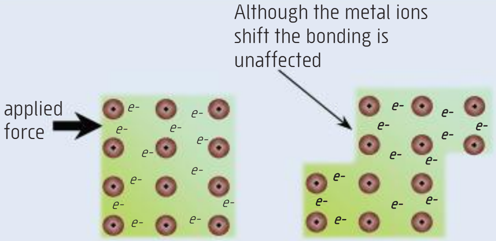


TABLE 2 Understanding metallic properties

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.

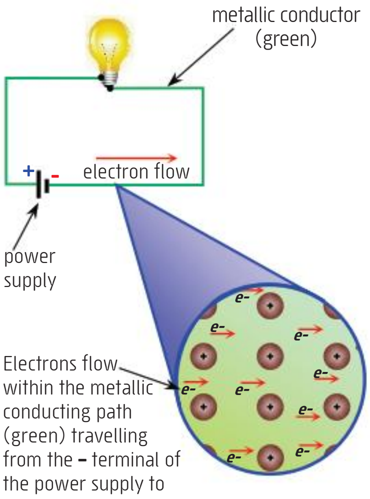
Malleable and ductile: Bonding between metal ions and the sea of electrons is non-directional. This means individual metal atoms can move in relation to each other without breaking the bonds between them and the sea of electrons. This allows a metal to change shape, ie be dented, bent or stretched without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

eBook^{+} Quiz 8.2. Complete Set 10.

FIGURE 5 Electrical **conductivity** in metals.



Electrons flow within the metallic conducting path (green) travelling from the **–** terminal of the power supply to the **+** terminal, see red arrows.

Set 10 Metallic substances

1. 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.

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

2. 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.)

3. Use your knowledge of metallic bonding to account for the following typical physical properties of metals.
   a. Metals are known to be good conductors of electricity.
   b. Metallic elements are both malleable and ductile.
   c. Metals are good conductors of heat.

4. 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?

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 $J\ s^{-1}\ m^{-1}\ K^{-1}$	Electrical conductivity $\Omega^{-1}\ m^{-1}$
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

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

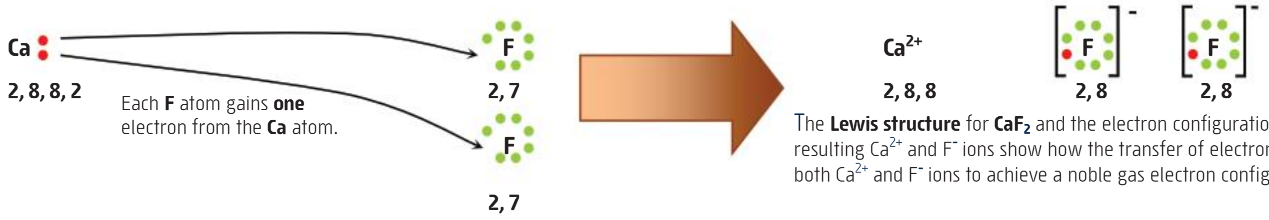
Similarly the higher the **electrical conductivity value** the better the metal is able to conduct electricity.

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 NH_4^+ ions) with **non-metallic** elements, eg NaCl, CaO, $MgSO_4$, $Al(NO_3)_3$, NH_4Cl 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.

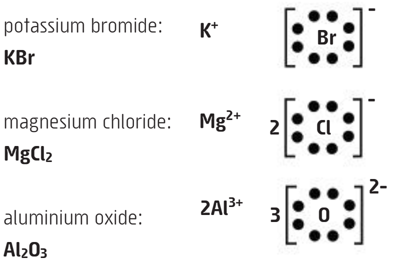
FIGURE 6 **Electron configurations** and **Lewis structures** are used here to show the transfer of electrons in the formation of the **ionic compound** CaF_2



Each **F** atom gains **one** electron from the **Ca** atom.

The **Lewis structure** for **CaF_2** and the electron configuration for the resulting Ca^{2+} and F^- ions show how the transfer of electrons allows both Ca^{2+} and F^- ions to achieve a noble gas electron configuration.

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.

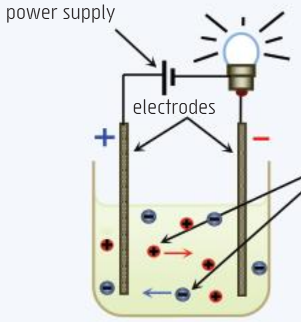
FIGURE 8 This two dimensional diagram is a representation of the sodium chloride (NaCl) ionic lattice. It shows the typical structure of an ionic lattice. Note the **unlike** charged ions are **closer** together than like charged ions. This ensures attractive forces within the lattice are greater than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

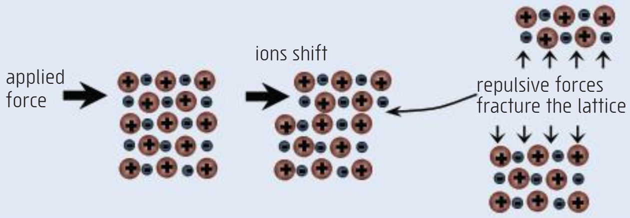
Good conductors of electricity when molten: In the **molten phase**, ions are mobile and free to move and carry charge throughout the ionic liquid. Both positive and negative ions carry charge. Positive ions move towards the negative electrode while negative ions move towards the positive electrode.

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.



In the **molten** and **aqueous** phase both positive and negative ions are mobile and can conduct an electric current.

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.

eBook Quiz 8.3. Complete Set 11.

Set 11 Ionic compounds

1. 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.

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

2. **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.

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

a. NaF b. K_2S c. CaO d. $AlCl_3$ e. Al_2S_3 f. $MgBr_2$

4. 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.'

5. 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.

6. Ping and Sindhu wanted to explore the **electrical conductivity** of an ionic compound in its different phases. They chose to test $AgNO_3(s)$, $AgNO_3(l)$ and $AgNO_3(aq)$.

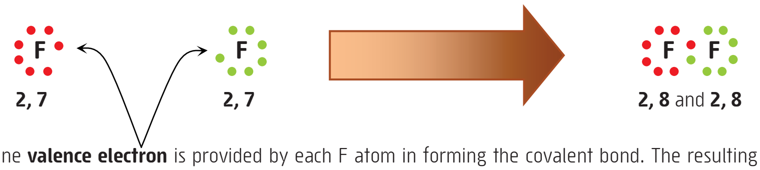
   a. **Compare** the structure and composition of $AgNO_3(s)$, $AgNO_3(l)$ and $AgNO_3(aq)$.
   b. **Sketch** an apparatus that Ping and Sindhu could use to perform their tests.
   c. What **safety precautions** should Ping and Sindhu consider?
   d. What conductivity results would you **predict** for each of their experiments?
   e. **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 F_2 molecule



One **valence electron** is provided by each F atom in forming the covalent bond. The resulting **Lewis structure** of the **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, ie **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.)

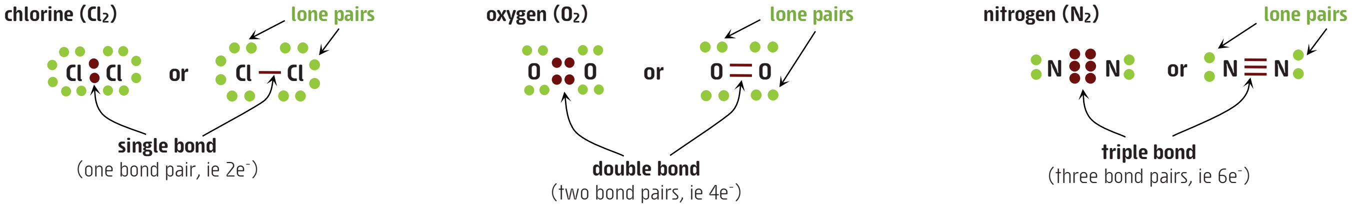


FIGURE 10 Pairs of atoms form covalent bond(s) by sharing 2, 4 or 6 electrons. Lewis structures can be used to shows this. Shared pairs of valence electrons are placed between bonded atoms and are known as **bond pairs**. Unshared (non bonding) pairs of valence electrons are known as **lone pairs**.

eBook⁺ Quiz 8.4.

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 (Cl_2), oxygen (O_2), nitrogen (N_2) (Fig 10) and most compounds formed from a combination of non-metal elements only, eg CH_4, H_2O, HBr, NH_3, HNO_3 and H_2SO_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 x 10^{21} H_2O 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**.

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, 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**.

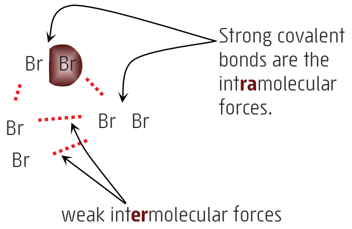


TABLE 4 Understanding the properties of covalent molecular substances

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 HCl, H_2SO_4 and 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.)

eBook Quiz 8.5. Attempt Set 12 # 2, 3 and 4.

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.

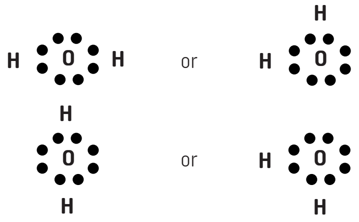
To draw a **Lewis structure** for a molecular substance:

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.

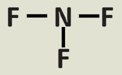
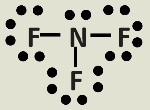
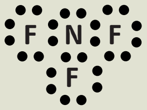
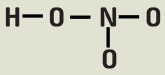
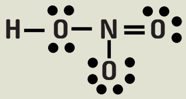
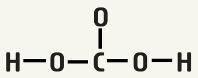
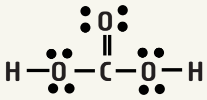
② Calculate the number of valence electrons still to be allocated. This is the total number available to the molecule, less those already allocated to single bonds in step ①.

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.

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 NF_3, HCN, HNO_3, and H_2CO_3.

 $F-\underset{\underset{F}{\vert}}{N}-F$ NF_3 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.  or 	$H-C-N$ HCN 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.  or  Using a triple bond, instead of two more lone pairs ensures both C and N achieve an octet with the available valence electrons.	 $H-O-\underset{\underset{O}{\vert}}{N}-O$ HNO_3 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.  Using a double bond, instead of another lone pair ensures all N and O atoms achieve an octet with the available valence electrons.	 $H-O-\overset{\overset{O}{\vert}}{C}-O-H$ H_2CO_3 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.  A double bond is used as this enables all C and O atoms to achieve an octet with the available valence electrons.

eBook Quiz 8.6. Complete Set 12.

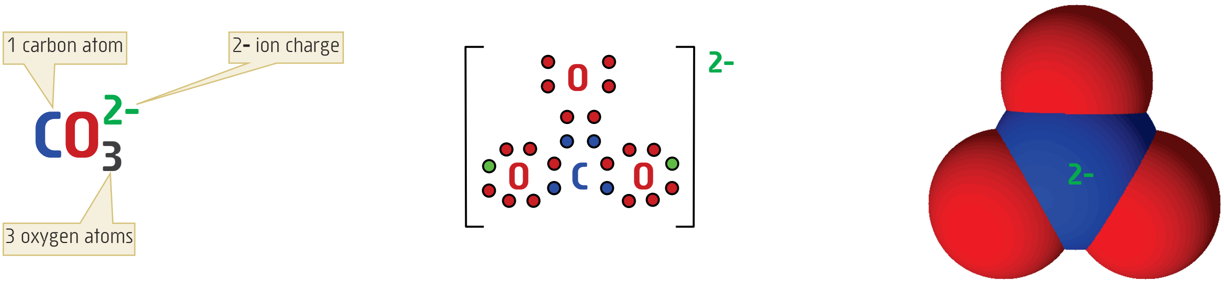
Note: Sections identified in this text with an **(E)** may be considered an extension to the Chemistry Course Units 1 and 2. These cover content considered desirable for developing a good understanding of the Chemistry Course Units 1 or 2 or they lead into content covered later in Chemistry Course Units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

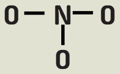
FIGURE 12 **Polyatomic ions** like carbonate, **CO_3^{2-}**, nitrate, **NO_3^-** and so on consist of a cluster of **covalently bonded** atoms that has a net positive or negative charge. For this reason a polyatomic ion is not a molecule or compound in its own right but instead can only exist along with 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, **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.

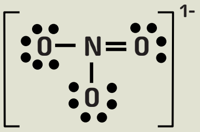


For a **positive ion**, reduce the number of valence electrons by an amount equal to its charge. Thus an ammonium ion, **NH_4^+** has **8** valence electrons in total, **5** from the **N** atom, **1** from each **H** atom and **one less** because of its **1+** charge. Remember, the square brackets around the ion are a reminder that their valence electrons are exclusively associated with the ion. These valence electrons are not shared with other ions.

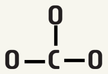
EXAMPLE 2 Draw Lewis structures for the nitrate ion (NO_3^-) and the carbonate ion (CO_3^{2-}). **(E)**



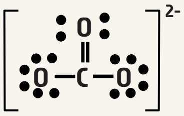
NO_3^- has 24 valence electrons in total, 6 from each O, 5 from N and 1 extra for the 1- charge. The skeleton structure uses 6 valence electrons so 18 more electrons need to be allocated. Multiple bonds are needed for each atom to achieve an octet.



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



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.

eBook+ Quiz 8.7 @ lucaspublications.com.au.

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

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)

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_2, 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.

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**.

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 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 $^{\circ}$C. This extremely high temperature is needed to break all of the strong covalent bonds between neighbouring carbon atoms in the diamond structure.

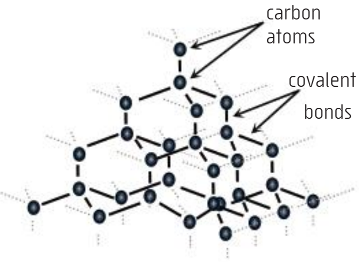


Figure 15 The unusual covalent network structure of **graphite** (at right) has strong covalent bonding within two dimensional layers of carbon atoms. Only weak van der Waals forces occur between these layers with some valence electrons free to move throughout the structure. As a result graphite is soft,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

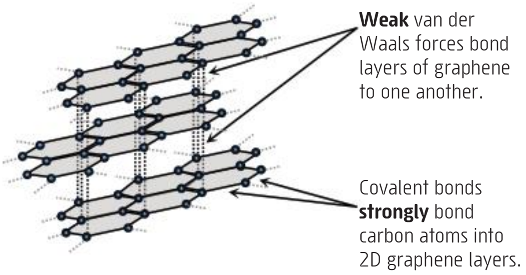


TABLE 5 Understanding the properties of covalent network substances

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.

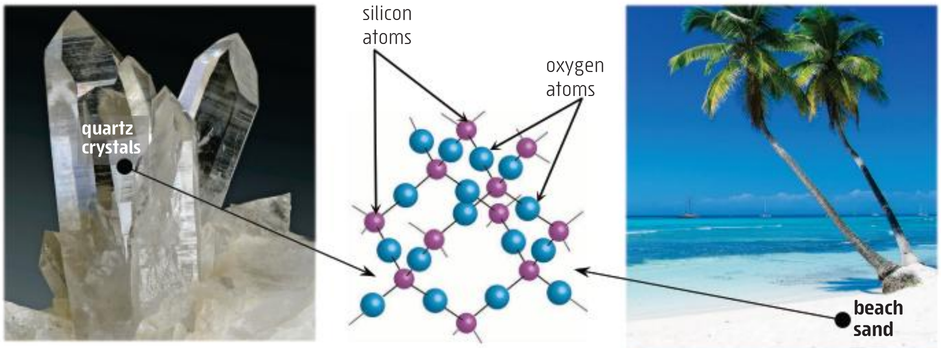


FIGURE 16 **Quartz** is one of the more common compounds found in the Earth's crust. It is a crystalline form of **silica** (SiO_2) where each silicon atom is covalently bonded to **four** neighbouring oxygen atoms while each oxygen atom is covalently bonded to **two** neighbouring silicon atoms. This 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.

eBook$^+$ Quiz 8.8.

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.

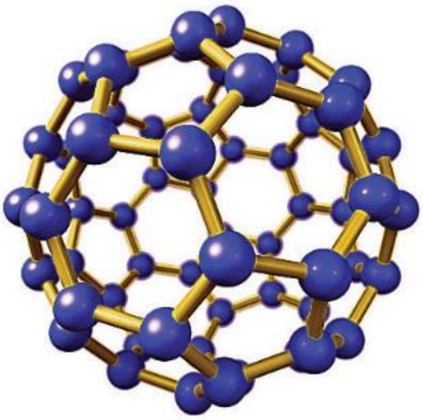


FIGURE 17 The 1985 discovery of C_{60} was the result of a **collaborative effort** between Harold W. Kroto from the University of Sussex, Richard E. Smalley and Robert F. Curl of Rice University in Houston along with several of their undergraduate students.

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 know 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** (1x10^{-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**).

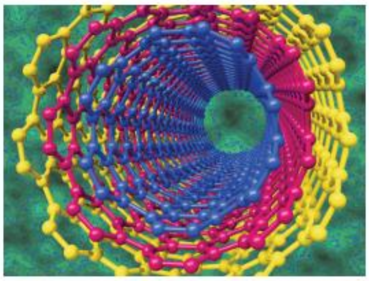
Every atom in a single carbon nanotube (CNT) is bonded to its neighbouring atoms by strong covalent bonds. This gives an individual CNT great strength and flexibility. Although individual CNTs are very tiny, when compared to a steel sample of the same dimensions, they are much stronger and lighter with 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 x 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.



eBook Quiz 8.9.

Complete Set 13.

Set 13 Covalent network substances and carbon allotropes

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

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

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.

2. **Carbon dioxide** (**CO_2**) is a gaseous substance present in low concentrations in the Earth's atmosphere (≈0.04% by volume). The substance **silicon dioxide** (**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 (CO_2) with that of silicon dioxide (SiO_2). Thus **account** for the different phase of carbon dioxide and silicon dioxide.

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.)

3. **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.

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

4. 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.
   a. What physical properties would you expect for hexagonal BN?
   b. Draw a section of a single layer of the hexagonal BN. Clearly indicate the boron and nitrogen atoms as well as the covalent bonds.
   c. 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?
   d. 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.

5. The group of substances called **fullerenes** are recently discovered **allotropes** of carbon. The following questions relate to these allotropes.
   a. 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 C_{60} to **elaborate** on these points.
   b. Briefly describe the **structure** of a C_{60} molecule.
   c. Materials like C_{60} are sometimes referred to as **nanoparticles**. What does the prefix '**nano**' mean and how is this related to the particles of C_{60}?
   d. Would you expect a solid sample of 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.
   a. 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.
   b. 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?
   c. 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 x 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 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 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 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.

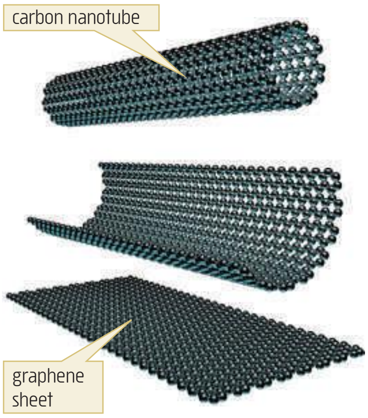
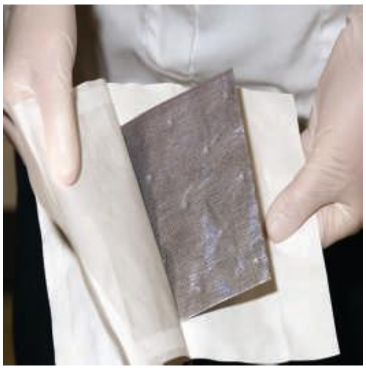
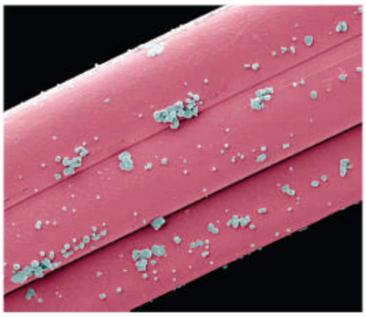


FIGURE 24 The '**Acticoat 7**' wound dressing shown here is impregnated with **nanosize** particles of **silver**. The silver particles have an **antimicrobial** effect, helping to prevent some bacterial and fungal infections. This dressing is designed to be used on wounds like leg ulcers, pressure sores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



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.

eBook+ Quiz 8.10.

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.

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.

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.

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 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, ≈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.

eBook+ Quiz 8.11.

8.12 Imaging and manipulating nanoparticles

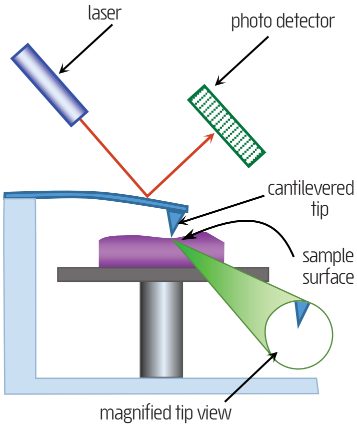
Optical microscopes rely on magnifying an image produced by **visible light** that is transmitted through or reflected from an object. However, because of diffraction effects this only works if the object being viewed is larger than the wavelength of light being used to view it. As the wavelength of 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.

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.



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.

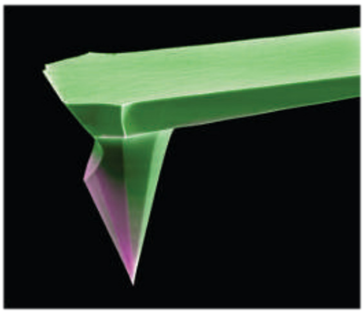


FIGURE 28 A coloured scanning electron micrograph, **SEM** image of a cantilever and tip (magnified by 1000 times), as used in the atomic force microscope, AFM.

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.

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.

eBook+ Quiz 8.12.

8.13 Manufacturing nanoparticles

A variety of **chemical** and **physical** means can be used to create nanoparticles. Nanosized particles of metal oxides like TiO_2 and 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 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 (≈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.

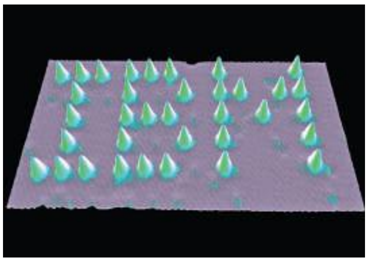


FIGURE 29 IBM Fellow Don Eigler became the first person in history to move and control an individual atom. On November 11 1989, Eigler and his team used a custom-built **scanning tunnelling microscope** (STM) to spell out the letters IBM with 35 xenon atoms. This unprecedented ability to manipulate individual 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.

eBook+ Quiz 8.13.

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, 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.

eBook+ Quiz 8.14 @ lucaspublications.com.au. **Complete Set 14.**

Set 14 Review: Bonding, structure and nanotechnology

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

   a. NaI
   b. Mg
   c. SO_2
   d. Al_2O_3
   e. SiO_2
   f. CO_2
   g. C
   h. CH_4
   i. H_2SO_4
   j. CaC_2
   k. CH_3OH
   l. TiO_2
   m. Sc
   n. Si
   o. SiC
   p. CS_2
   q. HCl
   r. Sr

2. Distinguish between the terms '**covalent bond**' and '**covalent molecular**'.

3. 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 ($CaCl_2$)
   b. chlorine gas (Cl_2)
   c. hydrogen cyanide (HCN)
   d. lithium oxide (Li_2O)
   e. phosphorous trifluoride (PF_3)
   f. magnesium nitride Mg_3N_2
   g. formaldehyde (H_2CO)
   h. hydrogen phosphate (H_3PO_4)

4. **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 yes/no/semi	Hard and yes/no	Malleable and yes/no
Zn(s)						
$Zn(NO_3)_2$(s)						
$Zn(NO_3)_2$(l)		☒			☒	☒
$Zn(NO_3)_2$(aq)		☒			☒	☒
$C_{12}H_{22}O_{11}$(s)						
$C_{12}H_{22}O_{11}$(l)					☒	☒
SiO_2(s)						
C(graphite)(s)						
C(diamond)(s)						
C_{60}(s)						☒

5. 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^-
   b. carbonate CO_3^{2-}
   c. cyanide CN^-
   d. nitrate NO_3^-
   e. nitrite NO_2^-
   f. chlorate ClO_3^-

Remember! When drawing the Lewis structure for a polyatomic ion like NH_4^+ or SO_4^{2-}, **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 (Al_2O_3)	**diamond** (C)	**copper** (Cu)
graphite (C)	**tungsten** (W)	**marble** (essentially $CaCO_3$)
candle wax (assume to be $C_{25}H_{52}$)	**woods metal** (a low MP alloy)	**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 °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 C_x. This is unlike a molecule of buckminsterfullerene which has a defined formula, 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 Na_2O (≈13%), CaO (≈11%), K_2O (≈4%) and SiO_2 (≈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 $FeO.Fe_2O_3$.
    a. The passage referred to a **crystalline** $FeO.Fe_2O_3$ layer. What does the term crystalline tell us about the structure of the $FeO.Fe_2O_3$ layer?
    b. The major component of the rocks onto which chitons attach themselves is silica (SiO_2). How does the presence of SiO_2 affect rock hardness? **Explain**.
    c. **Explain** why the presence of a crystalline $FeO.Fe_2O_3$ layer on chiton teeth can be an advantage to the chiton?

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.

11. **Nanotechnology** involves the study of nanoparticles including their structure, properties, manufacture and potential use.
    a. **Define** a nanoparticle and give two examples that do not involve carbon.
    b. 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**.
    a. **What** is a nanocomposite? Use an example to illustrate your answer.
    b. **Why** are nanocomposites potentially superior to fiberglass 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.

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.

eBook+ Quiz 9.1.

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.

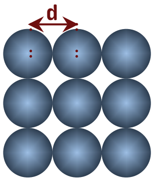
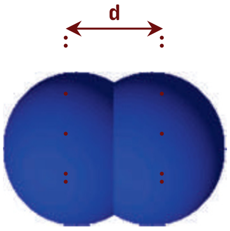


FIGURE 1 The **atomic radius** of a **metal** atom is defined as being half the distance between the centres of two adjacent atoms in the metallic lattice, ie ½**d**.



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 ½**d**.

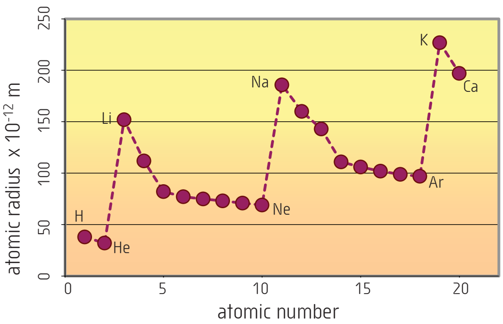


FIGURE 2 Graphing the **atomic radius** of the elements against their **atomic number** reveals two clear trends.

- 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.

eBook+ Quiz 9.2.

Attempt Set 15 # 1 and 2.

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.

$Na(g) + \mathbf{E_1} \rightarrow Na^+(g) + e^-$ **E_1** represents the **first ionisation energy** for sodium

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.

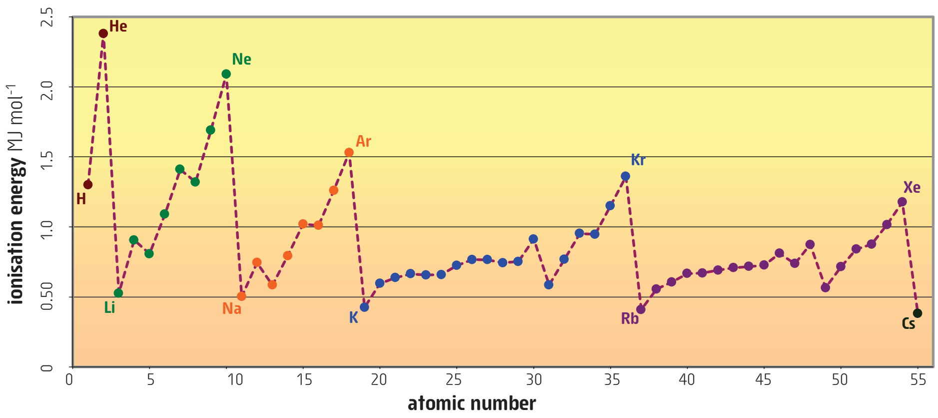


FIGURE 3 A graph of the **first ionisation energy** of the elements plotted against their **atomic number**. A different colour is used to highlight the elements of each period, ie **brown** 1st period, **green** 2nd period and so on. The graph reveals two clear trends:

- Ionisation energy increases from left to right in any period of the periodic table, eg the elements **Li through to Ne**.
- Ionisation energy decreases down any group of the periodic table, eg **Li**, **Na**, **K**, **Rb** and **Cs**.

The trends in first ionisation energy of the elements as seen in Figure 3 can be explained in terms of three factors:

① **The atom's nuclear charge**: An atom's nuclear charge depends upon its number of protons (atomic number). A greater nuclear charge (**+**) means electrons (**-**) are attracted more strongly to the nucleus and so ionisation energy increases with increasing nuclear charge.

② **The distance between the nucleus and the outermost electron (atomic radius)**: As atomic radius increases so the strength of attraction between the nucleus (**+**) and the outer electron (**-**) decreases. Thus ionisation energy decreases with increasing atomic radius.

③ **Shielding by inner electrons**: Each electron in the atom's electron cloud repels each other electron. Thus the more electrons there are between the outer electron (the one to be removed) and the nucleus (to which it is attracted) the more easily the electron is removed and the lower the ionisation energy. (See border note.)

Using these ideas, the trend to increasing ionisation energy that occurs for elements further to the right in any period is due to the atom's **increasing nuclear charge** (①
atomic radius (②

the atom's increasing nuclear charge. Instead the reducing ionisation energy is a result of the outer electrons being located in progressively **higher shells**. Thus electrons are further from the nucleus (increasing atomic radius) and ionisation energy will decrease (②
effect (③

Shielding is mainly due to core electrons, ie those in the filled inner shells. These cause the **effective nuclear charge** (Z_{eff}) felt by valence shell electrons to be significantly less than the actual nuclear charge (Z). This then reduces the overall attraction between the outer electrons and the nucleus.

Shielding due to neighboring electrons in the valence shell is much less significant. For this reason a major increase in the shielding effect occurs at the start of each new period.

eBook+ Quiz 9.3.

Attempt Set 15 # 3 and 4.

9.4 Periodic trends: Electronegativity

The property of **electronegativity** is defined as the ability of an atom in a molecule to attract electrons to itself. Of all the elements **caesium** (Cs) has the **lowest** electronegativity, **0.7** while **fluorine** (F) has the **highest** electronegativity, **4.0**. Generally non-metal elements have the highest values of electronegativity. This is to be expected as these elements typically gain electrons to form negative ions. Conversely, metals have low electronegativity.

Within the periodic table there is a general trend of increasing electronegativity from left to right in any period. Down any group the electronegativities show a gradual decrease. (See Fig 4.)

eBook+ Quiz 9.4. Attempt Set 15 # 5.

FIGURE 4 **Electronegativities** of the main group elements.

2.1 H						
1.0 Li	1.5 Be	2.0 B	2.5 C	3.0 N	3.5 O	4.0 F
0.9 Na	1.2 Mg	1.5 Al	1.8 Si	2.1 P	2.5 S	3.0 Cl
0.8 K	1.0 Ca	1.6 Ga	1.8 Ge	2.0 As	2.4 Se	2.8 Br
0.8 Rb	1.0 Sr	1.7 In	1.8 Sn	1.9 Sb	2.1 Te	2.5 I
0.7 Cs	0.90 Ba	1.8 Tl	1.8 Pb	1.9 Bi	2.0 Po	2.2 At
0.7 Fr	0.9 Ra					

9.5 Periodic trends: Valence electrons and bonding capacity

Valence electrons are those electrons in the outermost shell (highest numbered shell) of an atom. (See p50.) All elements in any given group of the periodic table have the same number of valence electrons. Group 1 elements for example all have one valence electron while group 2 elements all have two valence electrons. (See Table 1.)

For the main group elements there exists a strong relationship between the element's group number and its **ionic bonding capacity**. Metallic elements from group 1, 2 and 13 for example typically form 1+, 2+ and 3+ ions respectively when forming ionic compounds. Thus the fluorides for these elements are ionic with the general formulas MF, MF_2 and MF_3 where M is the group 1, 2 or 3 element respectively (eg, NaF, MgF_2 and AlF_3). Non-metal elements from groups 15, 16 and 17 typically form 3-, 2- and 1- ions respectively when forming ionic compounds, eg Na_3P, Na_2S and NaCl.

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.)

C, group 14, forms
4 covalent bonds

N, group 15, forms
3 covalent bonds

O, group 16, forms
2 covalent bonds

F, group 17, forms
1 covalent bond

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.

eBook+ Quiz 9.5. Attempt Set 15 # 6.

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).

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).

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).

Oxygen reacts with most metal elements to produce a metal oxide containing the $\mathbf{O^{2-}}$ ion. With the alkali metals the reactions are more complex. While **Li** does produce an oxide, Li_2O, the other alkali metals; Na, K, Rb, Cs and Fr, produce either a peroxide (containing the peroxide ion, $\mathbf{O_2^{2-}}$, eg Na_2O_2) or a superoxide (containing the superoxide ion $\mathbf{O_2^-}$ eg KO_2). Sodium can also form an oxide, ie Na_2O if the oxygen supply is limited.

$$2Na(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2(g)$$

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

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 [$H_2O(g)$] the remaining metals calcium, strontium and barium (lowest ionisation energies) are all readily oxidised by cold water [$H_2O(l)$].

$Be(s) + H_2O(g) \rightarrow$ No reaction

$Mg(s) + 2H_2O(g) \rightarrow Mg(OH)_2(s) + H_2(g)$

$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$

$Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(s) + H_2(g)$

↓ increasing metal reactivity

↓ decreasing metal ionisation energy

eBook+ Quiz 9.6.

Attempt Set 15 # 7.

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

9.7 Understanding non-metal properties (E)

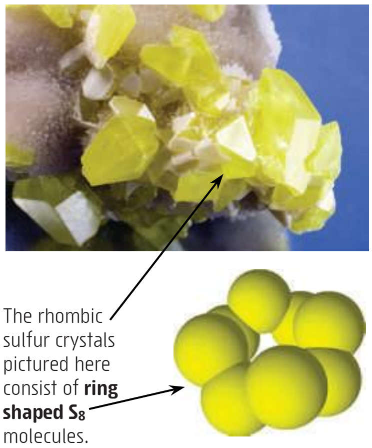
Left to right across each period of the periodic table the elements show **increasing ionisation energy**. As a result elements further to the right in a period become progressively less able to form positive ions and hence less able to form metallic structures. At some point in each period the tendency 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**.

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

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 F_2, Cl_2, Br_2 and 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 $N_2(g)$, $P_4(s)$, $O_2(g)$, $S_8(s)$, $Se_8(s)$, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$ and $I_2(s)$. (See Fig 6.)

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 **O_2** however, it also exists as **ozone**, **O_3**. The yellow, solid form of sulfur commonly used in the laboratory is **rhombic** sulfur which consists of puckered **S_8** rings of sulfur atoms.



The rhombic sulfur crystals pictured here consist of **ring shaped S_8** molecules.

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 F_2, Cl_2, Br_2 and I_2.

$Cl_2(g) + 2Na(s) \rightarrow 2NaCl(s)$

$Cl_2(g) + Ca(s) \rightarrow CaCl_2(s)$

$3Cl_2(g) + 2Al(s) \rightarrow 2AlCl_3(s)$

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 F_2 is most reactive while I_2 and At_2 are the least reactive). This pattern is in line with the decreasing electronegativity (tendency to gain electrons) going down the group.

Heating rhombic sulfur above its melting point (113 °C) causes it to change to a viscous red liquid. In this allotrope of sulfur the S_8 rings have broken open and joined to one another to form long **chains** of sulfur atoms with no specific molecular formula.

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.

$O_2(g) + 4Li(s) \rightarrow 2Li_2O(s)$

$O_2(g) + 2Ca(s) \rightarrow 2CaO(s)$

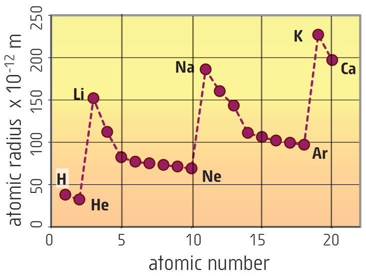
$3O_2(g) + 4Al(s) \rightarrow 2Al_2O_3(s)$

eBook+ Quiz 9.7.

Complete Set 15.

Set 15 Periodic trends

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



1. 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.
   a. Use a **labelled sketch** to show what is meant by atomic radius of a metal element.
   b. **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".
   c. **Account** for the trend in atomic radius across a **period** of the periodic table.
   d. **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.
   e. **Account** for the trend in atomic radius within a **group** of the periodic table.

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

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

3. **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 (**E₁**) is represented here:

   $$Na(g) \; + \; \mathbf{E_1} \; \rightarrow \; \_\_\_\_\_\_\_\_\_\_ \text{ (e).}$$

   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.

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

	Magnesium	Calcium	Strontium
First ionisation energy	0.738 MJ mol^{-1}	0.596 MJ mol^{-1}	0.556 MJ mol^{-1}

   a. **Where** do these three elements occur in the **periodic table**?
   b. **Account** for the **trend** in first ionisation energy of these elements. In your answer you should refer to refer to atomic radius, nuclear charge and electron to nucleus attraction.
   c. 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. **Ionisation energy**: Mg, Ar, P lowest _______________ highest	
b. **Ionisation energy**: Cl, F, Br lowest _______________ highest	
c. **Atomic radius**: Ga, Ca, Br lowest _______________ highest	
d. **Atomic radius**: I, F, Cl lowest _______________ highest	
e. **Electronegativity**: N, O, C lowest _______________ highest	
f. **Electronegativity**: O, Br, Mg lowest _______________ highest	
g. **Number of valence electrons**: 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		
16 (non-metal)	**17**		
13 (not boron)	**16** (non-metal)		
14 (not Sn or Pb)	**14** (not Sn or Pb)		
1 (not H)	**15** (non-metal)		
13 (not boron)	**17**		
2	**16**(non-metal)		
17	**17**		

7. The elements in any group of the periodic table are said to increase in **metallic character** down the group. **(E)**

   a. **State** the physical properties that are typical of metallic elements.

   b. **Name** two groups where this trend is most evident. Briefly **justify** your choice.

   c. 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:

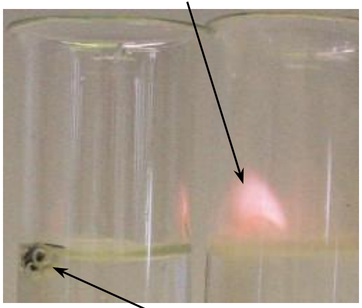
   a. **covalent bonding capacity** with hydrogen

   b. **ionic bonding charge** (valence).

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.

   a. Write **ionic equations** for the reaction of **potassium** and **calcium** with **water**.
   b. 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.
   c. 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.
      i. Use your knowledge of ionisation energy to **account** for the differing **reactivity** of group **2** metals with water compared to group **1** metals.
      ii. 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.
      iii. Use your knowledge of ionisation energy to **account** for the variation in **reactivity** of the different group **2** metals with water.

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.

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
A	Medium	4	2.6
B	Low	1	1.2
C	High	7	3.5
D	High	6	1.1

   a. an element most likely to form ions with a **1+** charge
   b. the element most likely to form a **single covalent bond** with other non-metal elements
   c. an element whose properties favour a **metallic** structure
   d. the element most likely to form a **covalent network** structure
   e. the element belonging to **group 18** of the periodic table
   f. an element whose properties are **inconsistent** with known elements.

11. Consider the fluorides of the third period elements.

NaF MgF_2 AlF_3 SiF_4 PF_3 SF_2 ClF

   a. Classify the bonding in these fluorides as **ionic bonding** or **covalent bonding**? Justify your answer with reference to electronegativity and ionisation energy.
   b. Account for the different **covalent bonding capacity** of Si, P, S and Cl.
   c. Account for the different **ionic bonding capacity** of Na, Ca, and Al.

CHAPTER 10 | INTRODUCING MOLES

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 6.02×10^{23}, known as **Avogadro's number**. One mole of a substance contains 6.02×10^{23} particles (ie atoms, ions, molecules or formula units) of that substance. (See Fig 1.)

FIGURE 1 The Latin translation of **mole** is '**massive heap**'. **Avogadro's number** is so large that this many grains of sand (of diameter ≈ 0.5 mm) could cover the surface of Australia to a depth of ≈7 m and have a mass of around 200 million million tonnes!

In quantitative chemistry the particular value of **6.022×10^{23}**, ie one **mole**, has a special significance.

A **single atom** of the isotope **^{12}C** (carbon-12) has a very small mass, 1.99265×10^{-23} g. **Avogadro's number** however, is such that this number of ^{12}C atoms (ie 6.022×10^{23} atoms of ^{12}C) has a mass of exactly 12 g. This mass is equal to the **relative atomic mass** of ^{12}C, ie exactly **12**, expressed in grams.

In every case, **one mole** of atoms (ie **6.022×10^{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.

eBook$^+$ Quiz 10.1 @ lucaspublications.com.au.

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 1.9926×10^{-23} g while a sulfur-32 atom has a mass of 5.3091×10^{-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

M(Na) = 22.99 g mol^{-1}
M(S) = 32.07 g mol^{-1}
M(Cl) = 35.45 g mol^{-1}
M(Sn) = 118.7 g mol^{-1}
M(Fe) = 55.85 g mol^{-1}

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 6.02×10^{23} atoms of the element. Quote your answer in g mol^{-1}.

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 6.02×10^{23} atoms of sodium. Similarly weighing 32.07 g of sulphur is equivalent to counting out one mole or 6.02×10^{23} atoms of sulfur.

eBook$^+$ Quiz 10.2.

Attempt Set 16 # 1.

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.

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 O_2. Similarly a single particle (molecule) of water, H_2O consists of two hydrogen atoms and one oxygen atom.

A single **formula unit**, (a hypothetical particle) of the ionic substance $Al_2(SO_4)_3$ consists of two Al^{3+} ions and three SO_4^{2-} ions.

EXAMPLE 2 Calculate the molar mass of oxygen gas (O_2).

M(O_2) = 2 x M(O)
= 2 x 16.00
= **32.00 g mol^{-1}**

Each particle (molecule) of O_2 consists of two O atoms. Adding the molar mass of these components gives the molar mass of O_2.

EXAMPLE 3 Determine the molar mass of ethanoic acid (CH_3COOH).

M(CH_3COOH) = 2 x M(C) + 4 x M(H) + 2 x M(O)
= 2 x 12.01 + 4 x 1.008 + 2 x 16.00
= **60.05 g mol^{-1}**

Each particle (molecule) of CH_3COOH has two C atoms, two O atoms and four H atoms. Adding the molar mass of these components gives the molar mass of CH_3COOH.

EXAMPLE 4 What is the molar mass of calcium nitrate [$Ca(NO_3)_2$]?

M[$Ca(NO_3)_2$] = M(Ca) + 2 x M(N) + 6 x M(O)
= 40.08 + 2 x 14.01 + 6 x 16.00
= **164.10 g mol^{-1}**

Each formula unit ('particle') of $Ca(NO_3)_2$ contains one Ca atom, two N atoms and six O atoms. The combined molar masses of these components gives the molar mass of $Ca(NO_3)_2$.

eBook$^+$ Quiz 10.3.

Attempt Set 16 # 2.

10.4 Relating mass and moles

The mass and moles of a substance are related as shown below.

m = n x M also expressed as $n = \frac{m}{M}$ where: **n** = the moles of the substance in mol
m = the mass of the substance in g
M = the molar mass of the substance in g mol^{-1}

EXAMPLE 5 The compound ammonium sulfate [$(NH_4)_2SO_4$], is an active ingredient in some garden fertilisers. Calculate the number of moles of $(NH_4)_2SO_4$ contained in a 38.5 g sample of $(NH_4)_2SO_4$.

n[$(NH_4)_2SO_4$] $= \frac{m}{M} = \frac{38.5}{132.15} =$ **0.291 mol**	Simply substitute the mass of the substance, 38.5 g and molar mass, 132.15 g mol^{-1} to obtain the number of moles present.

eBook+ Quiz 10.4.
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 Fe^{3+} ions and SO_4^{2-} ions are contained in 1.8 moles of $Fe_2(SO_4)_3$?

n(Fe^{3+} ions) = 2 x n[$Fe_2(SO_4)_3$] = 2 x 1.8 = **3.6 mol**	The subscript 2 alongside Fe^{3+} in the formula for iron(III) sulfate means there are two Fe^{3+} ions in each formula unit of $Fe_2(SO_4)_3$. Thus the moles of Fe^{3+} are twice the moles of $Fe_2(SO_4)_3$ formula units.
n(SO_4^{2-} ions) = 3 x n[$Fe_2(SO_4)_3$] = 3 x 1.8 = **5.4 mol**	The subscript 3 alongside SO_4^{2-} in the formula for iron(III) sulfate means there are three SO_4^{2-} ions in each formula unit of $Fe_2(SO_4)_3$. Thus the moles of SO_4^{2-} are three times the moles of $Fe_2(SO_4)_3$.

EXAMPLE 7 How many moles of N atoms and H atoms are contained in 3.2 moles of ammonia (NH_3)?

n(N atoms) = 1 x n(NH_3) = 1 x 3.2 = **3.2 mol**	The subscript 1 (implied) alongside N in the formula for ammonia (NH_3) means there is one N atom in each molecule of NH_3. Thus the moles of N atoms are equal to the moles of NH_3 molecules.
n(H atoms) = 3 x n(NH_3) = 3 x 3.2 = **9.6 mol**	The subscript 3 alongside H in the formula for ammonia (NH_3) means there are three H atoms in each molecule of NH_3. Thus the moles of H are three times the moles of NH_3 molecules.

eBook+ Quiz 10.5.
Attempt Set 16 # 5.

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 L = 1000 mL also 1 L = 1000 cm^3 = 1 dm^3 and 1000 L = 1 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.)

normal atmospheric pressure = 1.000 atm = 101.325 kPa = 1.01325 x 10^5 Pa

The SI unit of temperature is the **kelvin (K)** though it is often recorded in **celsius** (°C). (See Fig 3.) By definition, **absolute zero**, **0 K** (or -273.15 °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.

Temperature (kelvin) = Temperature (celsius) + 273.15

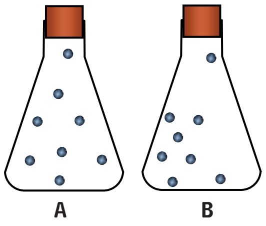


FIGURE 2 The volume of gas on its own is not a reliable measure of the moles of gas present. Flasks **A** and **B** have the same volume but flask B contains twice as much gas as flask A. This can happen because the gas in flask B is at twice the pressure as that in flask A. Similarly the temperature of a gas can affect the moles of gas present in a given volume. (See p2-3.)

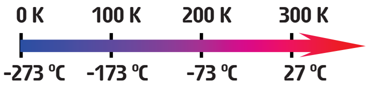


FIGURE 3 **Kelvin** and **Celsius** temperature scales compared.

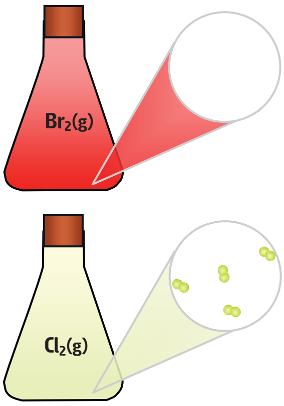


FIGURE 4 These two **22.71 L** flasks contain the gases **bromine** and **chlorine** both at 100.0 kPa and 273 K (0 °C). Each flask contains exactly **1.00 mole of gas**. This occurs despite the obvious difference in the molecular size and molar mass of the two gases. Thus one mole of any gas irrespective 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.

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.

$$n(\text{gas}) = \frac{V_{stp}}{22.71}$$

where: **n(gas)** = the moles of gas (mol)
V_{stp} = 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?

$$n(H_2) = \frac{V_{(stp)}}{22.71} = \frac{4.39}{22.71} = 0.193 \text{ mol}$$

Since the gas volume is measured at STP then one mole of it will have a volume of 22.71 L.

eBook Quiz 10.6. Complete Set 16.

Set 16 Relating moles, mass and gas volume

1. Use a periodic table to find the **molar mass** of the following elements.
   - a. lithium (Li)
   - b. zinc (Zn)
   - c. oxygen atoms (O)
   - d. nitrogen atoms (N)
   - e. lead
   - f iron

2. Calculate the **molar mass** of the following substances.
   - a. oxygen gas (O_2)
   - b. hydrogen gas (H_2)
   - c. calcium chloride ($CaCl_2$)
   - d. copper(II) sulfate ($CuSO_4$)
   - e. ammonium sulfate [$(NH_4)_2SO_4$]
   - f. chlorine gas
   - g. iron(III) oxide
   - h. copper(II) hydrogensulfate
   - i. aluminium sulfate
   - j. barium hydroxide
   - k. **sodium carbonate-10-water ($Na_2CO_3.10H_2O$)**
   - l. copper(II) ethanoate-1-water

3. Determine the **mass** in grams of each of the following.
   - a. 3.15 mol of magnesium bromide ($MgBr_2$)
   - b. 1.74×10^{-3} mol of iron(III) oxide (Fe_2O_3)
   - c. 0.395 mol of copper(II) hydrogensulfate [$Cu(HSO_4)_2$]
   - d. 1.25×10^{3} mol of sodium carbonate-10-water ($Na_2CO_3.10H_2O$)
   - e. 7.38×10^{-2} mol of sulfuric acid
   - f. 4.72×10^{2} mol of **oxalic acid-2-water** (oxalic acid dihydrate, see border note)

4. The mass of each substance is given in grams. Convert this to an equivalent amount in **moles**.
   - a. 250 gram of water (H_2O), about the amount in a glass of water
   - b. 1.29×10^{-3} gram of ammonium sulfate-2-water [$(NH_4)_2SO_4.2H_2O$]
   - c. 4.29 grams of **ethanoic acid** (see border note)

5. Many substances consist of particles that are themselves a combination of smaller particles. In this way 3.0 mol of oxygen gas (O_2) 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.
   - a. How many moles of nitrogen (N) atoms and hydrogen (H) atoms are present in 4.50 mol of ammonia (NH_3)?
   - b. Determine the number of moles of hydrogen atoms (H), sulfur atoms (S) and oxygen atoms (O) in 0.25 mol of sulfuric acid (H_2SO_4).
   - c. Find the moles of iron ions (Fe^{3+}) and oxide ions (O^{2-}) present in 1.7 mole of iron(III) oxide (Fe_2O_3).
   - d. How many moles of calcium ions (Ca^{2+}) and phosphate ions (PO_4^{3-}) are present in 0.28 moles of calcium phosphate [$Ca_3(PO_4)_2$]?

Sodium carbonate decahydrate ($Na_2CO_3.10H_2O$) 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_2) and calcium carbonate ($CaCO_3$).

Oxalic acid ($H_2C_2O_4$) 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^{2+}, Mg^{2+} and Fe^{2+} 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_3COOH) 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.

6. Determine the **molar amount** of each of the following gases. All volumes are measured at **STP**. (See border note.)

   a. 472.0 L of carbon dioxide gas (CO_2)

   b. 3.50×10^3 L of hydrogen gas (H_2)

   c. 1.700×10^2 mL of chlorine gas (Cl_2)

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.

7. Determine the **volume** that would be occupied by the following gases at STP conditions.

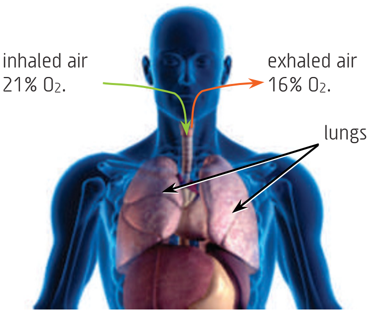
   a. 2.50 moles of carbon dioxide gas (CO_2)

   b. 0.550 moles of oxygen gas (O_2)

   c. 8.32 gram of hydrogen gas (H_2). Take care, the quantity given is in grams.

   d. 6.50×10^{-2} grams of ammonia gas (NH_3)

FIGURE 5 On average an adult will inhale about 0.50 L of air per breath. The inhaled air contains 21% by volume $O_2(g)$ while the exhaled air still contains around 16% by volume $O_2(g)$.



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.

   a. Calculate the **mass** of oxygen (O_2) that has been inhaled in this breath if the volume was measured at STP.

   b. 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.

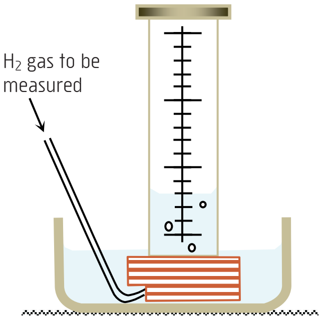
9. The complete combustion of a tank of petrol produced 219 kg of carbon dioxide gas.

   a. What **volume** of carbon dioxide is produced when measured at STP?

   b. 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.)

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 (O_2) and carbon dioxide (CO_2). Gases like ammonia (NH_3), hydrogen chloride (HCl) and chlorine (Cl_2) should not be collected this way as they are quite soluble in water.

11. **Dry ice** (Fig 2 p35) is the common name used for solid carbon dioxide. Dry ice sublimes (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 sublimed? Use a calculation to support your answer.

12. A 9.00×10^2 kg sample of **bauxite**, the ore from which aluminium is obtained, contains 4.70×10^3 moles of hydrated alumina ($Al_2O_3.3H_2O$) along with other impurities. What is the maximum **mass** of Al that can be extracted from this ore sample?

CHAPTER 11 | STOICHIOMETRY WITH MOLES, MASS AND GAS VOLUMES

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 (C_2H_6)?

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

Substances involved in the reaction	$C_2H_6(g)$	$O_2(g)$	$CO_2(g)$	$H_2O(g)$
Relative number of **molecules**	**2** molecules	**7** molecules	**4** molecules	**6** molecules
Relative number of **moles**	**2** moles	**7** moles	**4** moles	**6** moles

eBook Quiz 11.1 @ lucaspublications.com.au.

Stoichiometry is a specialised science term. It is 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 H_2O produced can vary but it must always be **three times** (**6**/**2**) the molar amount of C_2H_6 used. The molar amount of CO_2 produced however, is always **twice** (**4**/**2**) the molar amount of C_2H_6 used.

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).

$$aA + bB \rightarrow cC + dD$$

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: $\dfrac{\textbf{moles of A in the reaction}}{\textbf{moles of B in the reaction}} = \dfrac{\text{coefficient of A in the reaction}}{\text{coefficient of B in the reaction}}$ ie $\dfrac{n(A)}{n(B)} = \dfrac{a}{b}$

thus for A, $n(A) = \dfrac{a}{b} \times n(B)$ or $n(A) = \dfrac{a}{c} \times n(C)$ or $n(A) = \dfrac{a}{d} \times n(D)$

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.

EXAMPLE 2 Determine the molar amount of oxygen (O_2) used and carbon dioxide (CO_2) produced when 0.795 mole of ethane (C_2H_6) is burnt in air.

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

$n(O_2) = \frac{7}{2} \times n(C_2H_6) = \frac{7}{2} \times 0.795 = \mathbf{2.78\ mol}$	The coefficient of O_2 is **seven**, while that of C_2H_6 is **two**, thus the molar amount of O_2 in the reaction is **3.5 times** (7/2) the molar amount of C_2H_6.
$n(CO_2) = \frac{4}{2} \times n(C_2H_6) = \frac{4}{2} \times 0.795 = \mathbf{1.59\ mol}$	The coefficient of CO_2 is **four**, while that of C_2H_6 is **two**, thus the molar amount of CO_2 is **twice** (4/2) the molar amount of C_2H_6.

eBook Quiz 11.2.

Attempt Set 17 # 1, 2 and 3.

11.3 Calculations involving mass and moles

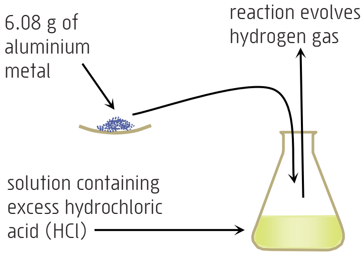
If the mass of any one substance involved in a reaction is known, then by converting this to an equivalent amount in moles (**n = m/M**), the molar amounts of all the other substances involved in the reaction can be found. The relationship **m = nM** can be used to find the mass of a substance once the molar amount of it is found.

EXAMPLE 3 Determine the moles of hydrochloric acid (HCl) used and hydrogen (H_2) produced when 6.08 g of aluminium (Al) reacts with excess hydrochloric acid. (See Fig 1.)

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

$n(Al) = \frac{m}{M} = \frac{6.08}{26.98} = \mathbf{0.225\ mol}$	Find the moles of Al from the given mass.
$n(HCl) = \frac{6}{2} \times n(Al) = \frac{6}{2} \times 0.225 = \mathbf{0.676\ mol}$	The coefficient of HCl is **six**, while that of Al is **two**, thus the molar amount of HCl in the reaction is **three times** (6/2) that of Al.
$n(H_2) = \frac{3}{2} \times n(Al) = \frac{3}{2} \times 0.225 = \mathbf{0.338\ mol}$	The coefficient of H_2 is **three**, while that of Al is **two**, thus the molar amount of H_2 is **one and a half times** (3/2) the molar amount of 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 ($AlCl_3$) is formed if 1.22×10^{-2} g of hydrochloric acid (HCl) reacts with excess aluminium (Al)?

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

n(HCl) = $\frac{m}{M} = \frac{1.22 \times 10^{-2}}{36.458}$ = **3.35×10^{-4} mol**	Find the moles of HCl from the given mass.
n($AlCl_3$) = $\frac{2}{6}$ n(HCl) = $\frac{2}{6} \times 3.35 \times 10^{-4}$ = **1.12×10^{-4} mol**	The coefficient of $AlCl_3$ is **two**, while that of HCl is **six**, thus the molar amount of $AlCl_3$ is **one third** (2/6) that of HCl.
m($AlCl_3$) = n x M = $1.12 \times 10^{-4} \times 133.33$ = **1.49×10^{-2} g**	Convert the moles of $AlCl_3$ to an equivalent mass.

eBook⁺ Quiz 11.3.

Complete Set 17.

Set 17 Stoichiometry with mass and moles

1. The explosive **trinitrotoluene** (TNT or $C_7H_5O_6N_3$, see Fig 2) reacts with oxygen according to the equation shown below. Refer to this equation to complete the partially written mole equations.

$$4C_7H_5O_6N_3(s) + 21O_2(g) \rightarrow 28CO_2(g) + 6N_2(g) + 10H_2O(g)$$

a. $n(CO_2) = \frac{28}{?} \times n(C_7H_5O_6N_3)$ c. $n(H_2O) = \frac{?}{?} \times n(O_2)$

b. $n(O_2) = \frac{?}{4} \times n(C_7H_5O_6N_3)$ d. $n(CO_2) = \frac{?}{?} \times n(N_2)$

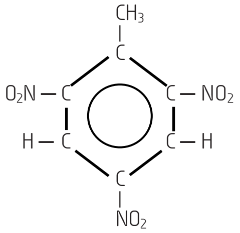


FIGURE 2 A single molecule of **TNT** (**trinitrotoluene**) consists of three nitro groups (NO_2) and one methyl group (CH_3) attached to a flat hexagonal ring of six carbon atoms. TNT was first prepared in 1863 by the German chemist Joseph Wilbrand. Today TNT is a widely used explosive. It has the advantage 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.

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.

$$2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

3. A small **spirit burner** of the type used in camping, contains 200 mL of ethanol (C_2H_5OH), which is equivalent to 3.41 moles of it. Find the **moles of oxygen** used during its complete combustion.

$$2C_2H_5OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

4. Propane is commonly used for **gas barbeques**. A particular cylinder contains 4.5 kg of propane. If the gas is pure propane (C_3H_8), determine the **molar amounts** of **carbon dioxide** and **water** produced from its complete combustion.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

5. **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 (Na_2SiO_3).

$$Na_2SiO_3(s) + 8HF(aq) \rightarrow H_2SiF_6(aq) + 2NaF(aq) + 3H_2O(l)$$

   a. How many **moles of sodium silicate** can be dissolved by 3.72 g of HF?
   b. How many **moles of sodium fluoride** are formed when 16.77 g of Na_2SiO_3 dissolves by the action of excess HF?
   c. Determine the number of **moles of H_2SiF_6** formed when 82.59 g of HF reacts with excess sodium silicate.

Hydrogen fluoride's (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.

6. Hydrogen gas is produced in the laboratory by reacting zinc with hydrochloric acid.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

   a. What **mass of zinc** is needed to produce 9.25×10^{-2} g of hydrogen gas?
   b. What **mass of zinc chloride** in **mg** is formed when 7.00×10^{-3} g of zinc is used?

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:

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$

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:

$$\%\text{purity} = \frac{m(\text{compound in mixture}) \times 100}{m(\text{mixture})}$$

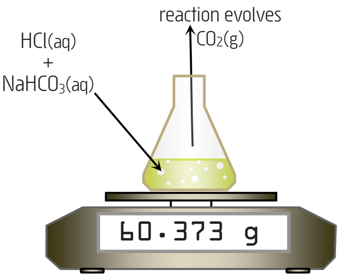


FIGURE 3 **Carbon dioxide** has a very low solubility in warm acid solutions like the reaction mixture involved in this experiment. So as the gas CO_2 is formed it escapes from the reaction mixture. The loss of mass in the reaction mixture can be assumed to be equal to the mass of CO_2 produced.

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.

   $S(s) + O_2(g) \rightarrow SO_2(g)$

   a. How many **moles of sulfur** are contained in these fuels?
   b. 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 (CaO) inside a 'wet scrubber'. (See Fig 4 p155.) The following reaction occurs.

      $CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$

      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 $SO_2(g)$.
   c. 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 **$Na_2CO_3.10H_2O$** 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.

   $Na_2CO_3.10H_2O(s) + 2HCl(aq) \rightarrow CO_2(g) + 11H_2O(l) + 2NaCl(aq)$

   a. From the mass of carbon dioxide formed, find the **mass of $Na_2CO_3.10H_2O$** present in the 3.312 g sample of washing soda.
   b. Determine the **% purity** of $Na_2CO_3.10H_2O$ 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 ($NaHCO_3$) sample to a conical flask containing a concentrated hydrochloric acid solution. The recorded data is shown here. (See Fig 3.)

   $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

   mass of impure $NaHCO_3$ ....4.362 g
   mass of flask + HCl(aq) solution ....57.982 g
   mass of flask + HCl(aq) solution + impure $NaHCO_3$ after reaction ....60.373 g

   a. Determine the **mass** of **$CO_2(g)$** that was formed. You may assume the weight loss of the flask and its contents is entirely due to evolution of $CO_2(g)$. (See Fig 3.)
   b. Use your answer from (a) to find the **mass** of **sodium hydrogen carbonate** ($NaHCO_3$) actually present in the impure measured sample.
   c. What is the **% purity** of $NaHCO_3$ in the sodium hydrogen carbonate sample? **(E)**
   d. 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.
   e. 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 MnO_2) of **hydrogen peroxide**.

    $2H_2O_2(aq) \xrightarrow{MnO_2} O_2(g) + 2H_2O(l)$

    a. What **mass of hydrogen peroxide** is needed to produce 3.47 g of oxygen gas?
    b. 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.

$S(s) + O_2(g) \rightarrow SO_2(g)$

$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$

$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

a. 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)**

b. 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.)

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.

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)**

$C(s) + O_2(g) \rightarrow CO_2(g)$

$C(s) + CO_2(g) \rightarrow 2CO(g)$

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$

a. Write an **overall equation** showing the formation of Fe from Fe_2O_3. (See 6.4 p45.)

b. Assuming no other reactions are involved, determine the **minimum mass of carbon** needed for every tonne of iron ore if the ore contains 97% Fe_2O_3 by mass.

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:

$\mathbf{V_{stp} = n(gas) \times 22.71}$

where: **n(gas)** = the moles of gas (mol)
$\mathbf{V_{stp}}$ = the STP volume of gas in litres (L)

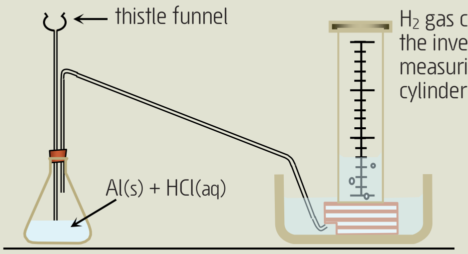
Using this relationship it is possible to find the volume of a gas involved in a chemical reaction from the mass of another reagent.

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.

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?

$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$



$\mathbf{n(HCl)} = \frac{m}{M} = \frac{1.22}{36.46} = \mathbf{3.35 \times 10^{-2}\ mol}$	Find the moles of HCl from the given mass.
$\mathbf{n(H_2)} = \frac{3}{6} \times n(HCl) = \frac{3}{6} \times 3.35 \times 10^{-2} = \mathbf{1.67 \times 10^{-2}\ mol}$	The molar amount of H_2 involved in the reaction is half (3/6) the molar amount of HCl.
$\mathbf{V(H_2\ stp)} = n \times 22.71 = 1.67 \times 10^{-2} \times 22.71 = \mathbf{0.380\ L}$	Since at STP the volume of one mole of gas is 22.71 L.

eBook⁺ Quiz 11.4.

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.

$$n(\text{gas}) = \frac{V_{stp}}{22.71}$$

where: V_{stp} = the STP volume of gas in litres L
n = 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?

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

$n(H_2) = \frac{V_{(stp)}}{22.71} = \frac{3.98}{22.71} = \mathbf{0.175\ mol}$	Since at STP one mole of gas occupies 22.71 L.
$n(Al) = \frac{2}{3} \times n(H_2) = \frac{2}{3} \times 0.175 = \mathbf{0.117\ mol}$	The coefficient of H_2 is three, while that of Al is two, thus the molar amount of Al is two thirds (2/3) that of H_2.
$m(Al) = n \times M = 0.117 \times 26.98 = \mathbf{3.15\ g}$	Convert the moles of Al to an equivalent mass.

eBook+ Quiz 11.5.

Complete Set 18.

Set 18 Stoichiometry with mass and gas volumes

1 In some vehicles the safety **air bag** is inflated by the rapid decomposition of the compound **sodium azide** (NaN_3). The impact of collision triggers the reaction shown.

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

A particular airbag contains 12 g of sodium azide. What **volume** (STP) would the air bag inflate to on collision?

2 **Cellular respiration**, (see border note) releases energy from sugars like glucose. The overall equation for the respiration of glucose is shown here.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

a. Determine the **STP volume of oxygen** used to metabolise 8.5 g of glucose, the amount in a typical barley sugar lolly.

b. Approximately what **number of breaths** would be needed to supply this much oxygen to your body cells? (**See border note**.)

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.

3 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.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

a. 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_2O.) All volumes are measured at STP.

b. The 150 g of H_2O 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.

4 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 1.55×10^2 L of carbon dioxide gas measured at STP is absorbed into a sodium hydroxide solution as shown?

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

5 The rising of pastries, cakes and bread products is largely due to the addition of **baking soda** ($NaHCO_3$) 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.

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

6 Nitrogen, phosphorus and potassium are the three major elements needed for healthy plant growth. (See Fig 5.) **Urea** [$(NH_2)_2CO$] 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.

$2NH_3(g) + CO_2(g) \rightarrow (NH_2)_2CO(s) + H_2O(g)$

What **mass of urea** can be formed by the complete reaction of 5.00×10^3 L (STP) of ammonia and excess carbon dioxide?

7 A typical **butane gas lighter** can release 6.50 L of butane gas (C_4H_{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.

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

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 [$NH_4^+(aq)$] or nitrate ions [$NO_3^-(aq)$] 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.

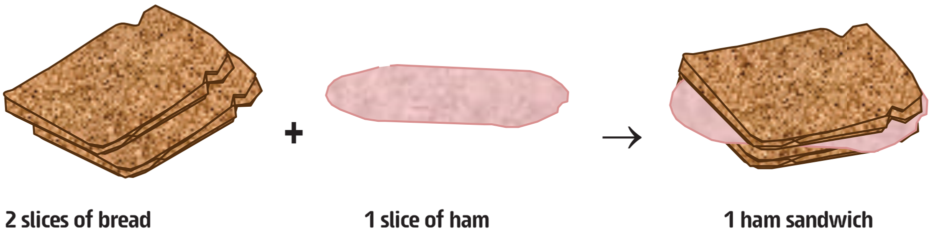


FIGURE 6 **A party problem?** You are having friends over for a party and need to make as many ham sandwiches as possible. You have 24 slices of bread and 16 slices of ham. Each sandwich needs two slices of bread and one slice of ham.

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**.

eBook+ Quiz 11.6.

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.)

EXAMPLE 7 Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

actual ratio = $\frac{n(HCl)}{n(Al)} = \frac{24.5}{9.87} = \mathbf{2.48}$	Find the actual mole ratio of the two reagents using the amounts given. Either reagent can be the numerator.
stoichiometric ratio = $\frac{n(HCl)}{n(Al)} = \frac{6}{2} = \mathbf{3}$	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.

numerator

$\frac{24.5}{9.87}$

denominator

EXAMPLE 8 Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Let Al	Either reagent, Al or HCl is assumed to be the limiting reagent.
n(HCl) = $\frac{6 \times n(Al)}{2} = \frac{6 \times 9.87}{2} = \mathbf{29.6\ mol}$	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.

eBook⁺ Quiz 11.7.

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.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

n(HCl) = $\frac{m}{M} = \frac{10.50}{36.46} = \mathbf{0.2880\ mol}$	Find the moles of HCl from the given mass.
n(Zn) = $\frac{m}{M} = \frac{10.5}{65.38} = \mathbf{0.1606\ mol}$	Find the moles of Zn from the given mass.
Let Zn	Either reagent, Zn or HCl is assumed to be the limiting reagent.
n(HCl) = $\frac{2}{1} \times n(Zn) = \frac{2}{1} \times 0.1606 = \mathbf{0.3212\ mol}$	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($ZnCl_2$) = $\frac{1}{2} \times n(HCl) = \frac{1}{2} \times 0.2880 = \mathbf{0.1440\ mol}$	Use the limiting reagent to find the amount of $ZnCl_2$ formed.
m($ZnCl_2$) = n x M = 0.1440 x 136.28 = **19.62 g**	Convert n($ZnCl_2$) to an equivalent mass.
n(Zn used) = $\frac{1}{2} \times n(HCl) = \frac{1}{2} \times 0.2880 = \mathbf{0.1440\ mol}$	Use the limiting reagent to find the amount of Zn used.
m(Zn used) = n x M = 0.1440 x 65.38 = **9.415 g**	Convert the moles of Zn used to an equivalent mass.
m(Zn remaining) = m(Zn original) - m(Zn used) = 10.50 - 9.415 = **1.09 g** (2DP, ie 3 SF)	Originally 10.50 g of Zn was added and only 9.415 g is consumed by the HCl.

eBook⁺ Quiz 11.8.

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)**

   $MnO_2(s) \ + \ 4HCl(aq) \ \rightarrow \ MnCl_2(aq) \ + \ Cl_2(g) \ + \ 2H_2O(l)$

   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**.

   a. 0.600 mol HCl and 0.251 mol of MnO_2
   b. 7.08×10^{-2} mol HCl and 1.92×10^{-2} mol of MnO_2
   c. 0.655 mol HCl and 0.142 mol of MnO_2

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 [$NaClO(s)$] and calcium hypochlorite [$Ca(ClO)_2(s)$]. These react with water to produce the familiar chlorine (Cl_2) odour found around swimming pools.

2. Sodium carbonate readily reacts with a hydrochloric acid solution.

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

   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)**

   a. 5.00 g of Na_2CO_3 and 4.00 g of HCl
   b. 1.926 g of Na_2CO_3 and 1.205 g of HCl

3. Sodium hydroxide and sulfuric acid react by the neutralisation reaction shown here:

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

   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 1.740×10^{-1}g of barium nitrate with another solution containing 9.260×10^{-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)**

   $Na_2SO_4(aq) \ + \ Ba(NO_3)_2(aq) \ \rightarrow \ 2NaNO_3(aq) \ + BaSO_4(s)$

5. Solutions of copper nitrate and potassium carbonate readily react to produce insoluble copper carbonate and a solution of potassium nitrate.

   $K_2CO_3(aq) \ + \ Cu(NO_3)_2(aq) \ \rightarrow \ 2KNO_3(aq) \ + \ CuCO_3(s)$

   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 K_2CO_3 and 14.00 g of $Cu(NO_3)_2$
   b. 3.380×10^{-2} g of K_2CO_3 and 5.980×10^{-2} g of $Cu(NO_3)_2$

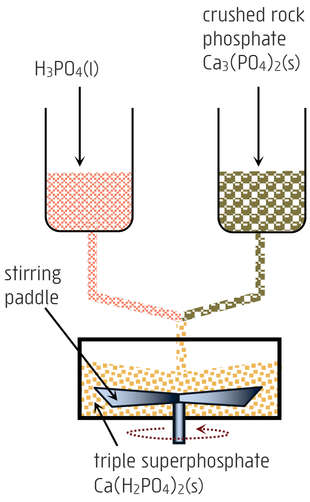
6. Triple superphosphate is a water soluble fertiliser produced by mixing phosphoric acid with insoluble rock phosphate. (See Fig 7.) It is important to add the reagents in the correct stoichiometric ratio so that there is no wastage of rock phosphate and no excess of phosphoric acid in the resulting 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)**

   $Ca_3(PO_4)_2(s) \ + \ 4H_3PO_4(l) \ \rightarrow \ 3Ca(H_2PO_4)_2(s)$

   rock phosphate — triple superphosphate

   a. 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.
   b. What **mass of triple superphosphate** is formed when the two reagents are present in the stoichiometric equivalent amounts as calculated in (a)?

FIGURE 7 Producing water soluble **triple superphosphate** from $H_3PO_4(l)$ and water insoluble rock phosphate $Ca_3(PO_4)_2(s)$.



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.

eBook+ Quiz 12.1.

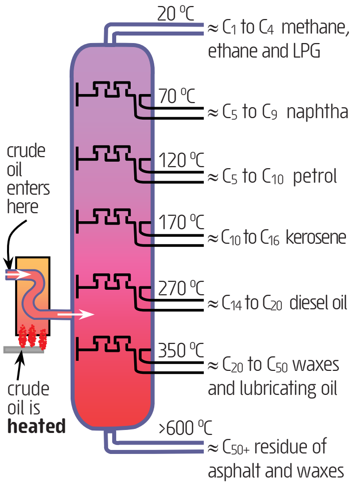


FIGURE 1 Crude oil is separated into various fractions using a fractionating tower like this one. Each **fraction** is a **mixture** of hydrocarbons with its own **boiling point range**. The temperatures and C numbers indicated here for the different fractions are an approximate guide only.

Attempt Set 20 # 1.

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.

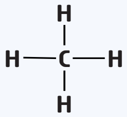
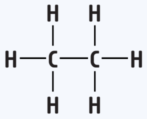
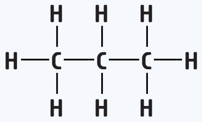
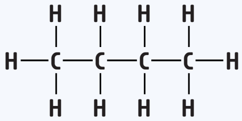
12.3 Alkanes: Structure and nomenclature

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}).

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

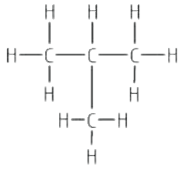
TABLE 1 Structure and nomenclature of selected alkanes

Name	Structural formula	Condensed formula	Molecular shape
methane CH_4		CH_4	
ethane C_2H_6		CH_3CH_3	
propane C_3H_8		$CH_3CH_2CH_3$	
butane C_4H_{10}		$CH_3CH_2CH_2CH_3$	

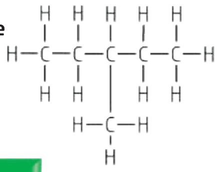
The alkanes shown in Table 1 are all **straight chain** alkanes. Their terminal carbon atoms (ie end ones) are bonded to three hydrogen atoms (CH_3) while the inner carbon atoms bond to two hydrogen atoms (CH_2). Sometimes alkanes form **branched** structures (see Fig 2) where an inner carbon atom is 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 2 Structures like these **branched alkanes** contribute to the great variety and number of possible alkane compounds.

methylpropane



3-methylpentane



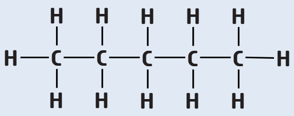
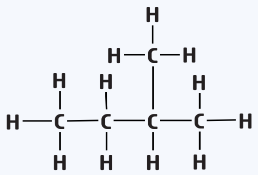
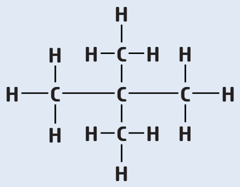
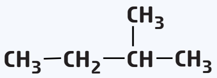
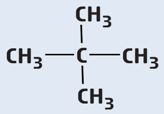
eBook+ Quiz 12.3

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.

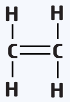
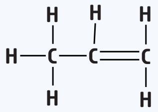
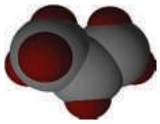
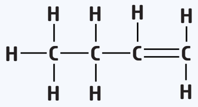
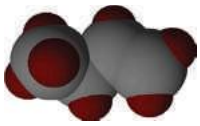
TABLE 2 Structural and condensed formulas for three structural isomers of C_5H_{12}

pentane	methylbutane	dimethylpropane
		
$CH_3-CH_2-CH_2-CH_2-CH_3$	 $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$	 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$
$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CHCH_3CH_3$	$CH_3C(CH_3)_2CH_3$

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 $\mathbf{C_nH_{2n}}$. Alkene names have the suffix **-ene**.

TABLE 3 Structure and nomenclature of some alkenes

Name	Structural formula	Condensed structural formula	Molecular shape
ethene C_2H_4		CH_2CH_2 or $CH_2=CH_2$	
propene C_3H_6		CH_3CHCH_2 or $CH_3CH=CH_2$	
but-1-ene (1-butene) C_4H_8		$CH_3CH_2CHCH_2$ or $CH_3CH_2CH=CH_2$	

eBook$^+$ Quiz 12.5.

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.)

***trans*-but-2-ene** (*trans* means across)

***cis*-but-2-ene** (*cis* means the same side)

FIGURE 5 These two molecules have the **same sequence** of bonding yet the molecules have a **different geometry**. These substances are the *cis* *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.

eBook$^+$ Quiz 12.6.

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.

eBook$^+$ Quiz 12.4.

Attempt Set 20 # 5.

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 **un**saturated or **polyun**saturated (more than one double bond). Olive oil, shown above, contains **monoun**saturated 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**.

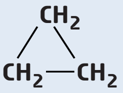
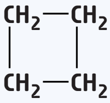
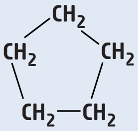
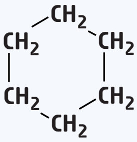
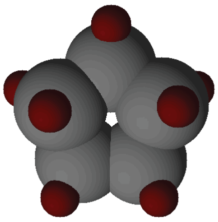
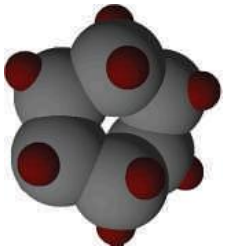
Nutritionists recognise that fats are an important part of our diet. The risk of developing heart disease does not so much depend upon the amount of fat in our diet as on the type of fat consumed. Unsaturated fats are thought to be much better for our cardiovascular system than saturated fats. In particular, 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})
			
			

eBook+ Quiz 12.7.

Attempt Set 20 # 9.

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.

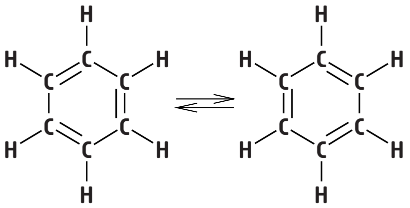
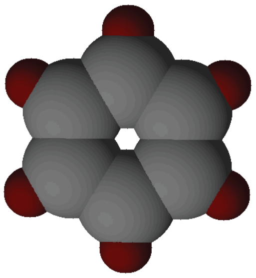
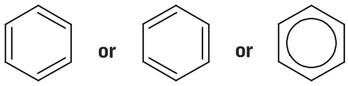


FIGURE 6 The **benzene** molecule (C_6H_6) consists of six C atoms arranged into a flat hexagonal ring structure with each C atom bonded to a single H atom.



A benzene molecule can be represented by any one of the following **shorthand notations**.

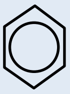
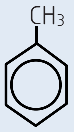
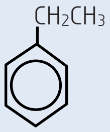
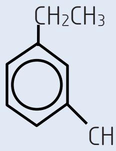


Research has shown benzene and some of its aromatic derivatives to be **carcinogenic** (cancer-causing). Excessive exposure may affect bone marrow and blood production and can lead to leukaemia. Even short-term exposure to high levels of benzene can cause drowsiness, dizziness, unconsciousness and death.

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.

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

			
benzene	**methylbenzene (toluene)**	**ethylbenzene**	**1-ethyl-3-methylbenzene**

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**.

eBook+ Quiz 12.8.

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.)

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 ($-C=C-$) is present then the parent chain must be chosen to include it; even if this does not give the longest chain.

② **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.

③ 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.

④ 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.

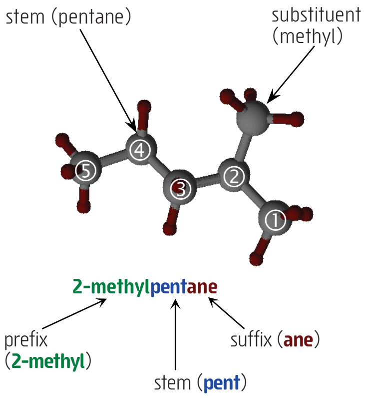
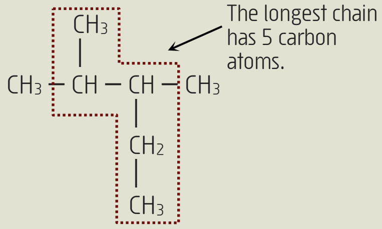
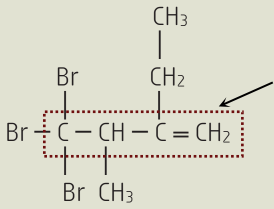
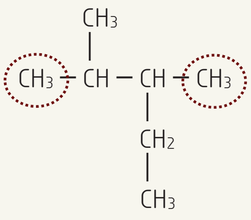
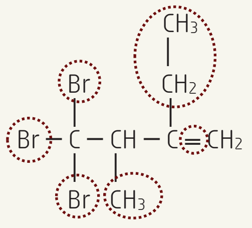
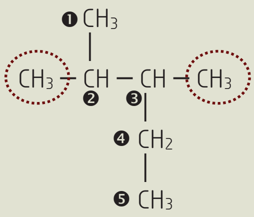
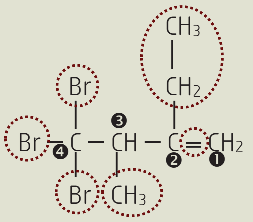


FIGURE 7 IUPAC names are based on a compound's **parent** or **stem** structure. **Prefixes** and **suffixes** along with **numbers** are used to show the identity and location of substituent groups.

TABLE 6 Alkyl groups (side chains)

Name	Condensed formula
methyl	CH_3-
ethyl	CH_3CH_2-
propyl	$CH_3CH_2CH_2-$
butyl	$CH_3CH_2CH_2CH_2-$

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.	 The longest chain has 5 carbon atoms. The stem name is pentane	 The longest chain that includes all of the substituents has 4 carbon atoms. The longer chain of 5 carbon atoms is not used as the double bond is not part of this chain, see ①. The stem name is butene
Identify any **substituents** attached to the main chain. (These have been circled.)	 Two methyl groups are present.	 One double bond, an ethyl group, three bromo groups and a methyl group are present.
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)		 The double bond has numbering priority.
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**

eBook+ Quiz 12.9. 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

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}

The **wax** found naturally occurring on apple skins is a straight chain **paraffin** of molecular formula $C_{27}H_{56}$.

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)**

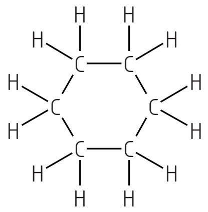
6. What is the structural difference between an **alkane** and an **alkene**? Explain how this affects the general formula of an alkene. Use propane and propene to support your answer.

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)**

FIGURE 8 A molecule of **cyclohexane** (C_6H_{12}).



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.

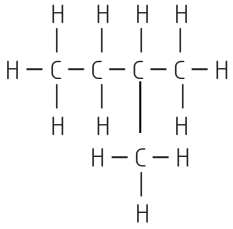
11. Draw **full structural formula** for the following hydrocarbons and other **halogenated** compounds. (See border note.) **Show all bonds**.

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. *cis*-1,2-dibromoethene **(E)**
d. 1,1,3-tribromopent-1-ene	i. *trans*-but-2-ene **(E)**
e. 1,2-dichlorohexane	j. 1-fluoro-3-methylbenzene **(E)**

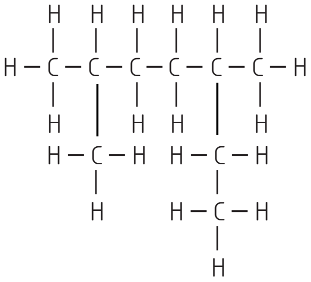
Halogenated hydrocarbons are a most useful class of organic compound. (See border note p101.) They are formed when one or more of the hydrogen atoms of a hydrocarbon are replaced with a halogen atom (ie **F**, **Cl**, **Br** or **I**).

12. Give the **IUPAC name** for the substances with the molecular structures shown below.

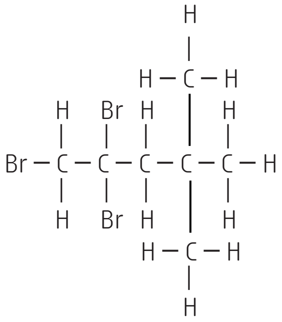
a.



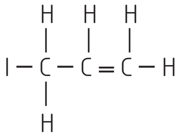
b.



c.



d.

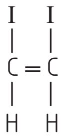


e. $CH_3CH_2(CH_3)CHCHCHCH_3$
(**Hint**: Draw the structural formula first.)

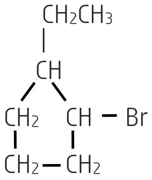
f. $CH_3(CH_3)_2CCH_2CHCH_2$

g. $Cl_2CHCH_2CHCH_3CHBrCH_3$
(**Hint**: Draw the structural formula first.)

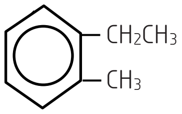
h. **(E)**



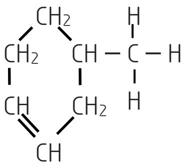
i. **(E)**



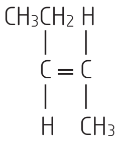
j.



k. **(E)**



l. **(E)**



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**

a. Draw the structural formula of these compounds. How are these compounds related? Justify your answer.
b. Describe one factor that affects the octane rating of a hydrocarbon fuel. (See Fig 9.) Use the data provided to support your answer.

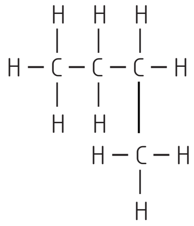
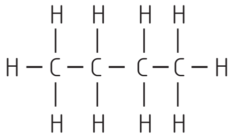
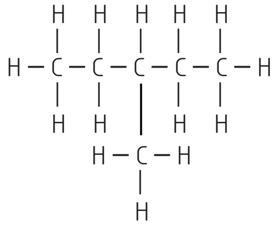
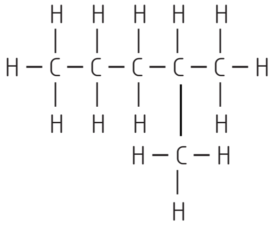
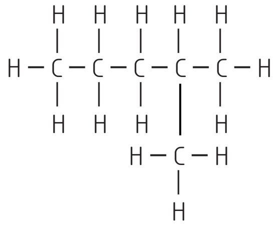
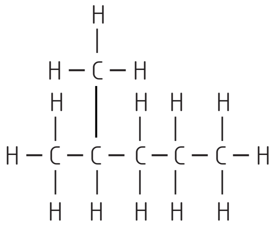
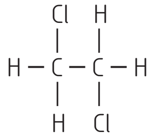
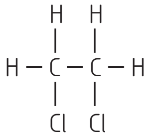
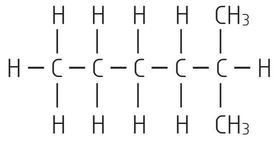
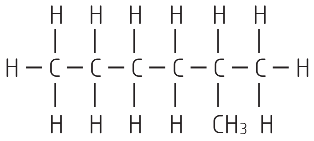
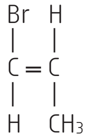
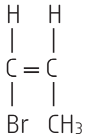
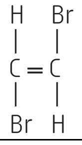
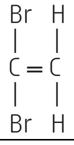
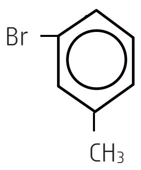
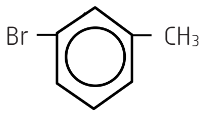
FIGURE 9 **Petrol** is a complex mixture of many different hydrocarbon compounds. One measure of the combustion characteristics of petrol is its **octane rating**. This measures a fuel's tendency to resist exploding when pressure is applied to its vapour and is known as its **anti-knock quality**. Depending 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** (**C_7H_{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.

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.)

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.

Molecular formula	Structure 1		Structure 2
a. **C_4H_{10}**		and	
b. **C_6H_{14}**		and	
c. **C_6H_{14}**		and	
d. **$C_2H_4Cl_2$**		and	
e. **C_7H_{16}**		and	
f. **$C_3H_5Br_2$** **(E)**		and	
g. **$C_2H_2Br_2$** **(E)**		and	
h. **C_7H_7Br** **(E)**		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

b. 2-methylbut-3-ene

c. 1-methylpropane

d. 2,2-diethylbutane

e. 1-bromo-5-methylbenzene

f. 1,2-dichloroethene **(E)**

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. $CH_2{=}CHCH_2CH_3$

b. $CH_2{=}CCl_2$

c. $CHCl{=}CHCl$

d. $CH_2{=}CHCl$

e. $CH_3CH{=}CHCH_2CH_3$

f. CH_2BrCH_2Br

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** ($CH_2OHCHOHCH_2OH$). 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.

$\mathbf{CH_3(CH_2)_{16}}COOH$	$\mathbf{CH_3(CH_2)_4(CH)_2CH_2(CH)_2(CH_2)_7}COOH$	$\mathbf{CH_3(CH_2)_7(CH)_2(CH_2)_7}COOH$
stearic acid	linoleic acid	oleic acid

18. **Name** an organic compound that matches each description.

a. This compound has a molecular formula of C_3H_6 and is unsaturated.

b. A branched, saturated hydrocarbon with four carbon atoms per molecule.

c. A high octane fuel of molecular formula C_6H_{14} that has two methyl groups per molecule.

d. An aromatic hydrocarbon produced from the catalytic reforming of certain petroleum fractions. It contains seven carbon atoms per molecule and eight hydrogen atoms.

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.

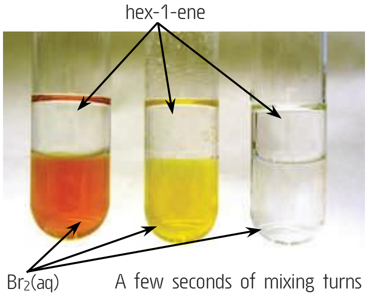
Reagents used in addition reactions include H_2 (with a Pt catalyst), Cl_2, Br_2, HCl, HBr and HI. In the laboratory it is most convenient to use $Br_2(g)$ and $Cl_2(g)$ in aqueous solution form, ie $Br_2(aq)$ and $Cl_2(aq)$. These are known as bromine water and chlorine water respectively. (See Fig 10.)

TABLE 7 Addition reactions of alkenes

Example	Observation
$CH_2{=}CHCH_2CH_2CH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_2CH_2CH_3$ **hex-1-ene** → **1,2-dibromohexane** $CH_3CH{=}CHCH_2CH_2CH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_2CH_2CH_3$ **hex-2-ene** → **2,3-dibromohexane**	In each case two immiscible layers form. With mixing, the bromine water changes colour from **orange** to **colourless**. (See Fig 10.)
$CH_2{=}CH_2 + HCl \rightarrow CH_2ClCH_3$ **ethene** → **chloroethane** $CH_3CH{=}CH_2 + HCl \rightarrow CH_3CHClCH_3$* **propene** → **2-chloropropane**	In both cases two colourless gases react to form a colourless liquid.

* 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.

FIGURE 10 **Bromine water** is essentially a solution of Br_2 in water. It has an orange colour due to the presence of bromine. **Hex-1-ene** is a colourless liquid hydrocarbon (BP=63.5 °C) that does not dissolve in water. When bromine water is added to hex-1-ene they naturally form two separate layers as seen below. If the layers are mixed, the orange colour of bromine quickly disappears. This is due to a rapid **addition reaction** involving bromine and hex-1-ene.



A few seconds of mixing turns the $Br_2(aq)$ layer colourless.

eBook$^+$ Quiz 12.10.

Attempt Set 21 # 1.

12.11 Substitution reactions of hydrocarbons

Substitution reactions occur when an **alkane** or **benzene** is combined with $\mathbf{Cl_2}$ or $\mathbf{Br_2}$. 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_2 or Br_2 **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
$CH_3CH_3 + Br_2(aq) \xrightarrow{UV} CH_3CH_2Br + HBr$ **ethane** → **bromoethane**	Bromine water [ie $Br_2(aq)$] slowly changes colour from **orange** to **colourless**.
$C_6H_6 + Cl_2(aq) \xrightarrow{UV} C_6H_5Cl + HCl$ **benzene** → **chlorobenzene**	Chlorine water slowly changes colour from **pale yellow** to **colourless**.

*Note: If **excess** Br_2 or Cl_2 is present in the reaction mixture then substitution of hydrogen atoms will continue until complete. This would result in the formation of **hexabromoethane** (C_2Br_6) and **hexachlorobenzene** (C_6Cl_6).

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.

eBook$^+$ Quiz 12.11.

Attempt Set 21 # 2.

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.

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g) + 5754\ kJ$$

butane **considerable 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.)

$$2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO(g) + 10H_2O(g) + 3490\ kJ$$

butane **less heat energy**

Incomplete combustion is an inefficient way to burn hydrocarbon fuels as it produces significantly less energy than complete combustion.

FIGURE 11 Methane (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.

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^2 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.

eBook$^+$ Quiz 12.12 @ lucaspublications.com.au.

Complete Set 21.

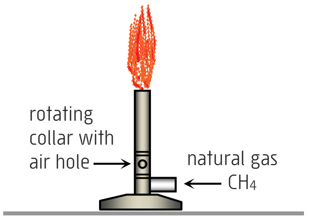


FIGURE 12 The heat produced from a Bunsen burner comes from the combustion of natural gas (essentially methane, CH_4). A rotating collar surrounding the air hole can be adjusted to vary the amount of air mixing with methane. Less air results in **incomplete combustion** forming CO, C (soot) and less 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** (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.

Set 21 Reactions of hydrocarbons

1. Write a balanced equation for each of the **addition** reactions described here.

   a. $CH_2=CH_2(g) + Cl_2(g) \rightarrow$ ____________?

   b. $CH_2=CH_2(g) + HCl(g) \rightarrow$ ____________?

   c. $CH_2=CHCH_3(g)$ is combined with $H_2(g)$.

   d. Propene gas is bubbled through bromine water.

   e. Chlorine water is mixed with cyclopentene.

   f. Propene gas is bubbled into an HBr(aq) solution.

Hint!
Having trouble visualising the reaction products? Try drawing full structural formula for the organic reactant and its product.

2. Write a balanced equation for each of the following **substitution** reactions. Assume the reaction conditions permit **single substitution only**, unless otherwise indicated.

   a. $CH_3CH_3(g) + Cl_2(g) \rightarrow$ ____________ + ____________

   b. A mixture of $CH_4(g)$ and **excess** $Br_2(g)$ is exposed to ultraviolet radiation. (Assume complete substitution occurs.)

   c. A few drops of bromine water is mixed with **excess** liquid hexane.

   d. A few drops of bromine solution and **excess** benzene are mixed and exposed to ultraviolet radiation.

   e. Ethane gas and **excess** chlorine gas are combined and react until **no further** reaction occurs.

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 ($CH_2=CHCl$), 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** ($Cl_2C=CCl_2$) is excellent for dissolving grease and oil. It can be used for **dry-cleaning** clothes that would otherwise be damaged by soap or water.

3. Write **balanced equations** for the combustion of the following fuels. Assume an excess air supply (complete combustion) unless otherwise stated. (See border note.)

   a. Burning methane in a Bunsen flame (Fig 12), $CH_4(g) + O_2(g) \rightarrow$ ________ + ________

   b. Incomplete combustion of propane, a major component of LPG.

      $C_3H_8(l) + O_2(g) \rightarrow$ ________ + ________

   c. $C_{24}H_{50}(s)$, a wax, is burnt with a limited air (O_2) supply.

   d. Burning octane, a major component of petrol. Assume complete combustion.

   e. Acetylene (C_2H_2) in an oxyacetylene torch and excess oxygen is ignited.

   f. Complete combustion of benzene, an important petrol additive.

A wide variety of **hydrocarbon fuels** are available for different specific applications.

methane (C_1) (major component of NG)
home heating and cooking

acetylene (C_2) (ethyne)
high temperature flames

LPG ($C_{3\text{-}4}$) (mainly propane and butane)
motor cars and portable cookers

petrol ($C_{5\text{-}10}$) motor cars

jet fuel ($C_{8\text{-}16}$) aircraft

diesel ($C_{10\text{-}15}$) heavy vehicles

wax ($C_{20\text{-}40}$) candles

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?

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 Al_2O_3/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.

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 C_6 to 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.

Fluorine (**F_2**) reacts explosively with all hydrocarbons causing both addition and substitution.

Iodine (**I_2**) shows no tendency to undergo addition or substitution reactions with hydrocarbons.

7. Addition and substitution reactions can be used to make halogenated compounds. This is done by reacting a suitable hydrocarbon with an appropriate halogen (F_2, Cl_2 or Br_2) or an appropriate hydrogen halide (HCl, HBr or 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, $CHCl_3$
   b. 1,2-dibromobutane
   c. 2-chlorobutane
   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 C_3H_6 **(E)**

CHAPTER 13 | ENERGY FLOW AND CHEMICAL CHANGE

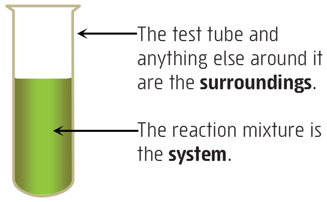


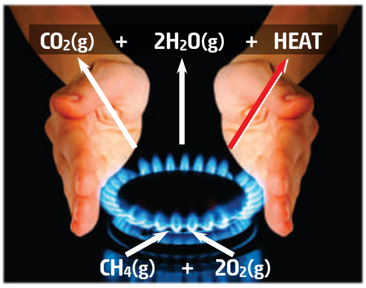
FIGURE 1 When analysing energy changes in a chemical reaction it is convenient to define the **reaction mixture** as the **system** and its container and everything else around it as the **surroundings**.

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**.

eBook Quiz 13.1.

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**.



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

weak bonds, ie **high** chemical potential energy ⟶ **strong** bonds, ie **low** chemical potential 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**, **ΔH** is defined as:

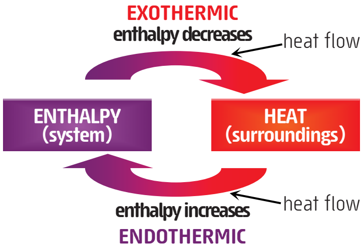
$$\Delta H = H_{(products)} - H_{(reactants)}$$

where: **H** = **enthalpy**
ΔH = **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 (ΔH)**. In these situations ΔH is also referred to as the **heat of reaction**.

eBook Quiz 13.2.

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.

13.3 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 **ΔH**, 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 **ΔH is negative**.

Reactions that **gain heat from the surroundings** are called **endothermic** reactions. These reactions have a **positive** value for **ΔH**, 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 **ΔH is positive**. (See border note.)

eBook Quiz 13.3.

13.4 Representing energy changes in chemical reactions

The enthalpy change, **ΔH** 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.)

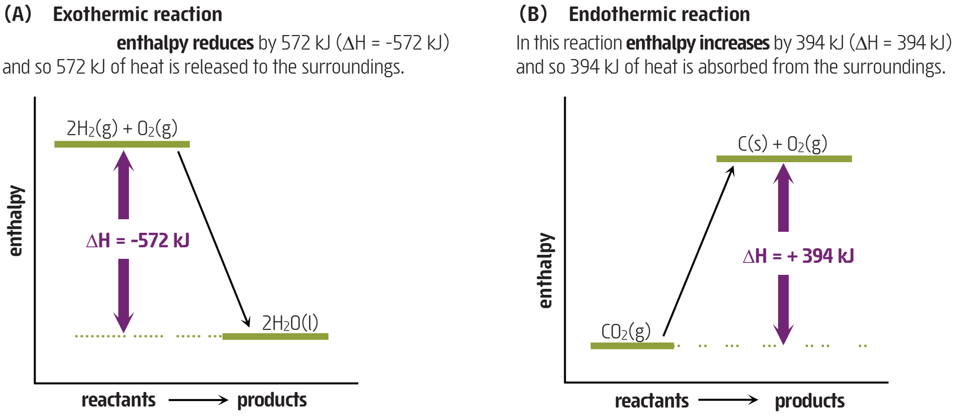


FIGURE 3 The energy profile diagram **(A)** shows the reduction in enthalpy for an **exothermic** reaction. In the **endothermic** reaction **(B)** there is an increase in enthalpy as products have more enthalpy than reactants.

For convenience **ΔH** can be written along with the balanced equation, as shown for ① and ②

absorbed or released in the reaction can be written into the equation, as shown for ③ and ④

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** (**ΔH**), as in equation ① ② flow, as in equation ③ ④

Exothermic equation showing **enthalpy change**, **ΔH**

$2H_2$(g) + O_2(g) → $2H_2O$(l) **ΔH = -572 kJ** ...... ①

Endothermic equation showing **enthalpy change**, **ΔH**

(g) → C(s) + O_2(g) **ΔH = +394 kJ** .....②

equation showing **heat released**

$2H_2$(g) + O_2(g) → $2H_2O$(l) + **572 kJ** .... ③

Endothermic equation showing **heat absorbed**

(g) + **394 kJ** → C(s) + O_2(g)...........④

eBook⁺ Quiz 13.4.

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, I_2(s) to form iodine vapour, I_2(g) (Fig 4 and reaction ① **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

I_2(s) + **62 kJ** → $_2$(g)............①

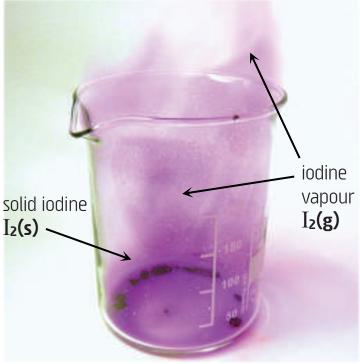
I_2(g) → $_2$(s) + **62 kJ**............②

①

②

eBook⁺ Quiz 13.5.

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.



I_2**(s)** + **62 kJ** → I_2**(g)** ....①

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 ④

breaking or forming the weak bonds (IMFs) during its sublimation, ① and ②

$_2$(g) + **214 kJ** → (g) ....③

2I(g) → $_2$(g) + **214 kJ** ....④

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.

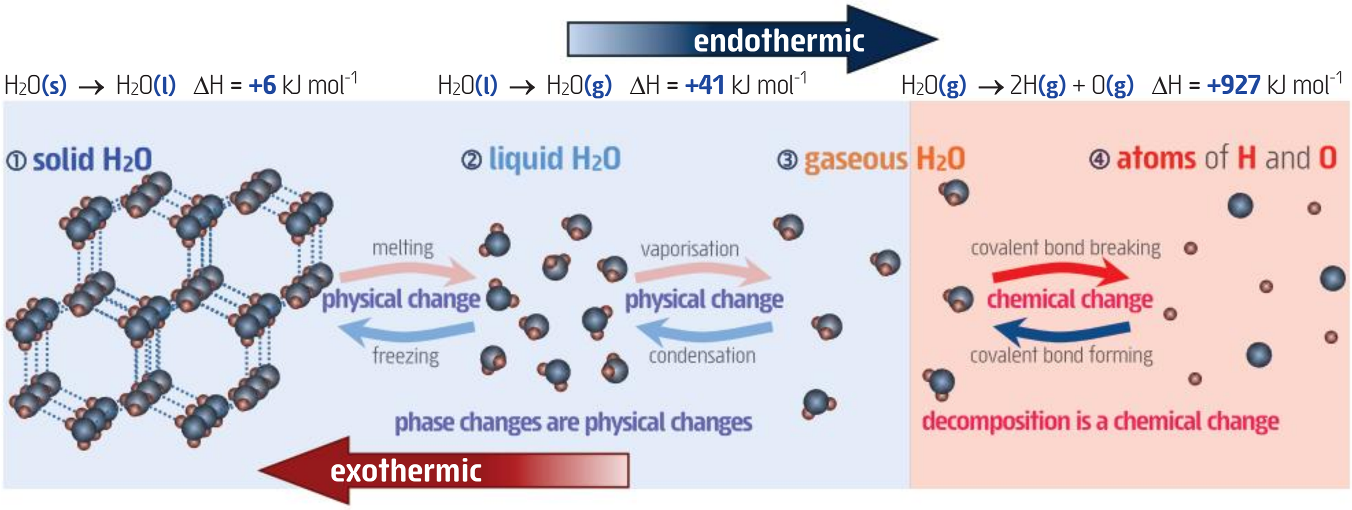


FIGURE 5 Ice, $H_2O(s)$ consists of water molecules bound into a regular array, ① by **weak intermolecular forces** (shown here as dotted lines). Heating ice above its melting point, 0 °C causes the weak attractive forces to be partially overcome. As a result the water molecules move freely in the liquid phase, ②. Further heating above 100 °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 °C then a significant number of the H_2O 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.

eBook$^+$ Quiz 13.6. **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**, $C_6H_{12}O_6(s)$.

respiration: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2870\ kJ$

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 $CO_2(g)$ absorbed in this endothermic reaction is returned to the environment when cells carry out respiration.

photosynthesis: $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H = 2870\ kJ$

eBook$^+$ Quiz 13.7.

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**.

13.8 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 fuels** 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.

combustion of ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2\mathbf{CO_2}(g) + 3H_2O(l) + \mathbf{1367\ kJ}$

combustion of methane: $CH_4(g) + 2O_2(g) \rightarrow \mathbf{CO_2}(g) + 2H_2O(l) + \mathbf{890\ kJ}$

combustion of octane: $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16\mathbf{CO_2}(g) + 18H_2O(l) + \mathbf{10940\ kJ}$

These fuels produce varying amounts of **energy** and **carbon emissions** (CO_2).

eBook$^+$ Quiz 13.8.

Attempt Set 22 # 9.

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^{-1}**, **MJ kg^{-1}** or **MJ L^{-1}**. For pure compounds this can be calculated from the standard heat of combustion for the fuel, **ΔH_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.)

Fuel value$_{\text{(compound)}} = \dfrac{\Delta H_c}{M}$ where: **ΔH_c** = standard heat of combustion of 1 mol of the fuel
M = the molar mass of fuel (ie the mass that is burnt, 1 mole)

Example 1 What is the fuel value
$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H = -2870$ kJ mol^{-1} of $C_6H_{12}O_6(s)$

Fuel value $\dfrac{\Delta H_c}{M} = \dfrac{2870}{180.156}$ = 15.9 kJ g

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 $CO_2(g)$, 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 CO_2 concentration (see Fig 8) is contributing to rising average global temperatures which in turn are resulting in climate change.

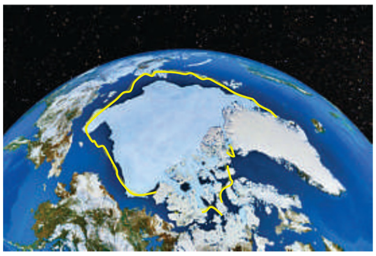


FIGURE 7 **Carbon emissions** in the form of **$CO_2(g)$** are believed to contribute to global warming. One clearly visible effect of this is the well documented annual reduction in the area of summer Arctic sea ice. The image here shows the extent of Arctic sea ice on Sept. 12, 2013, the day before 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.

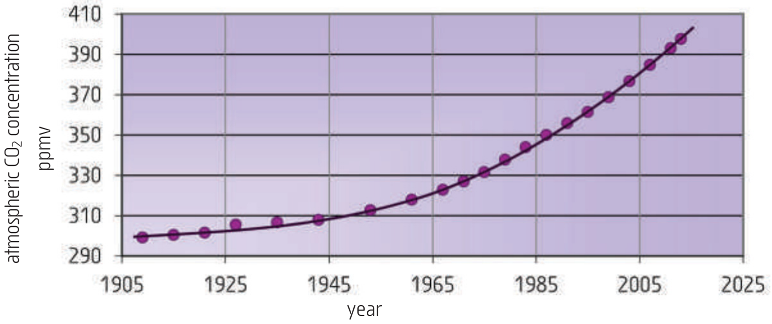


FIGURE 8 The graph at left shows the atmospheric concentration of CO_2 in parts per million by volume (**ppmv**). Data from 1910 till 1953 is from the **Siple Station ice core** in Antarctica. Data from 1953 onwards is from **Mauna Loa** in Hawaii.

A clear trend is evident showing an increased rate of growth in the atmospheric CO_2 concentration. The current rate of increase is around **2 ppmv per year**, equivalent to 2 x 10^{10} tons of 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(CO_2) MJ^{-1}**. (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(CO_2) MJ^{-1}. (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(CO_2) MJ^{-1}.

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/)

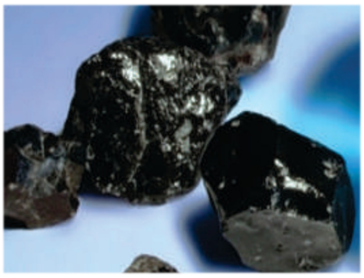


FIGURE 9 The fossil fuel coal consists mainly of carbon chemically combined to varying amounts of hydrogen, oxygen, sulfur and nitrogen. Its carbon content can vary considerably. Anthracite coal for example (shown above) may contain up to 98% carbon by mass while lignite contains as little as 50% carbon.

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_2 is a known greenhouse gas that is believed to contribute to global warming and climate change.

eBook Quiz 13.9.

Attempt Set 22 # 10, 11 and12.

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^{-1} (Australian black coal) **90-95 g(CO_2) MJ^{-1}):** 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_2O). 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^{-1}/0.039 MJ L^{-1}, 51 g(CO_2) MJ^{-1}): 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_2, O_2, CO_2 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^{-1} 51 g(CO_2) MJ^{-1}): 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^{-1}/26 MJ L^{-1} 59 g(CO_2) MJ^{-1}): 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^{-1}/34 MJ L^{-1} 66 g(CO_2) MJ^{-1}): 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_8H_{18} is often used as an 'average' representation of the compounds in petrol.

Diesel (46 MJ kg^{-1}/39 MJ L^{-1} 70 g(CO_2) MJ^{-1}): 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^{-3} 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_2) MJ^{-1}) 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^{-1} when compared to petrol, 34 MJ L^{-1}, 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, $C_2H_5OH(l)$ for example can be produced by the fermentation of plant sugars such as in the conversion of **glucose** to **ethanol** by **yeast**.

ethanol by fermentation: $C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$

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_2.

glucose from photosynthesis: $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$

Ultimately, all of the atmospheric CO_2 absorbed during plant photosynthesis is recycled to the atmosphere during fermentation (above) or by its combustion as a fuel (below).

combustion of ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

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_2 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_2 emissions due to fossil fuel use in biomass farming, fertiliser manufacture, fuel synthesis and transportation. While the extent of this extra CO_2 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_2 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 $CO_2(g)$ 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.

eBook+ Quiz 13.10.

FIGURE 11 Biogas is essentially a mixture of methane, CH_4 and carbon dioxide CO_2 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_4 and CO_2).

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.

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 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. GDF SUEZ Australian Energy.

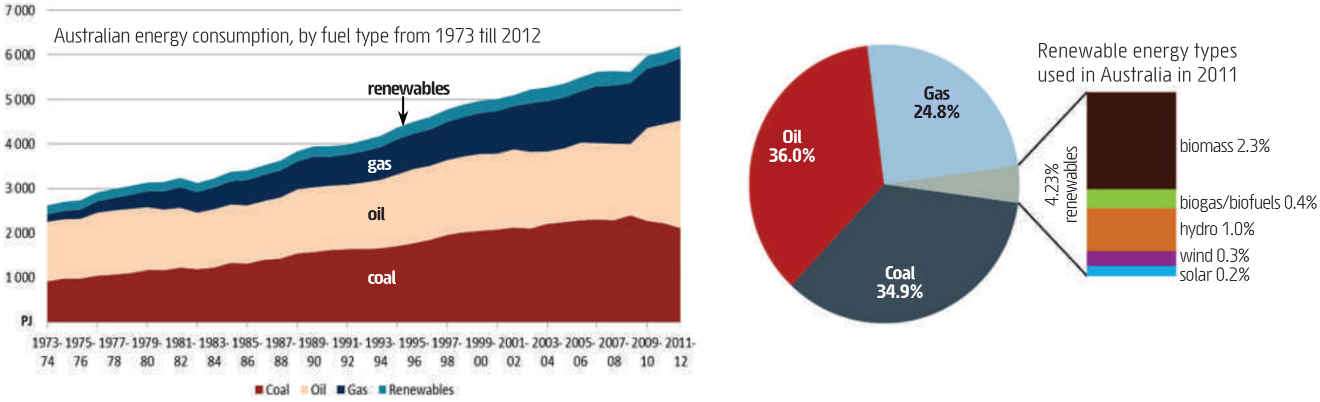
eBook+ Quiz 13.11.

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 x 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.)



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, $CO_2(g)$. Although $CO_2(g)$ 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/)

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.

eBook+ Quiz 13.12.

Complete Set 22.

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. M		
c. The to		
d. T a		
e. Can be changed into other forms of energy		
f. A		
g. R		
h. Includes chemical potential energy that is stored		

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 ΔH. In an exothermic reaction ΔH has a negative value and the temperature of the reaction mixture will increase. What is the significance of the negative value of ΔH 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.)

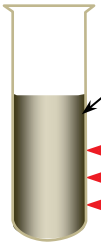
FIGURE 15 Instant sports cold packs like these use an **endothermic** reaction to produce freezing temperatures. Sports hot packs use an **exothermic** reaction to produce a heating effect.

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.
   a. Is this reaction endothermic or exothermic? **Explain**.
   b. Write an **equation** for the combustion of acetylene in excess oxygen gas.
   c. Include **heat** in your equation given that each mole of acetylene releases 1.255 megajoules of heat energy when burnt this way.
   d. Now write your equation to include the enthalpy change, **ΔH**.
   e. Draw an **enthalpy change diagram** for this reaction. Label the axes, reactants, products, enthalpy of reactants, enthalpy of products and ΔH (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.
   a. Is this reaction endothermic or exothermic? **Explain**.
   b. Write an **equation** for this reaction.
   c. 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.)
   d. Include the enthalpy change, **ΔH** in your equation.
   e. Draw an **enthalpy change diagram** for this reaction. Label the axes, reactants, products, enthalpy of reactants, enthalpy of products and ΔH.

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.)



The system temperature falls as heat is converted to chemical potential energy. As a result of its temperature drop **heat then flows from the surroundings into the reacting system**.

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, $H_2O(l) \rightarrow H_2O(g)$
   b. Sublimation of gaseous carbon dioxide to its solid phase, $CO_2(g) \rightarrow CO_2(s)$
   c. Decomposition of molecular sulfur to atomic sulfur, $S_8(g) \rightarrow 8S(g)$

7. Choose from the following pairs of substances, the one having the **highest enthalpy**.
   a. equal masses of $H_2O(l)$ and $H_2O(g)$, both at 100 °C
   b. equal masses of $CO_2(s)$ and $CO_2(g)$, both at the same temperature
   c. equal masses of $H_2O(s)$ and $H_2O(l)$, both at 0 °C
   d. equal masses of $H_2O(l)$ at 10 °C and $H_2O(l)$ at 80 °C

8. These two equations both represent the combustion of methane. Explain why the **enthalpy change**, ΔH is greater for reaction ① kJ.

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + \Delta H = -890$ kJ .... ①

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \Delta H = -802$ kJ .... ②

9. Consider the chemical changes described here and **complete the following table**.

   Natural gas is essentially methane (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.

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + 890$ kJ

   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.

   $C_2H_5OH(l) + 43$ kJ $\rightarrow C_2H_5OH(g)$

   Ice is an excellent cooling agent and is often used to cool drinks. The equation shows the melting of ice.

   $H_2O(s) \rightarrow H_2O(l) \quad \Delta H = 6.0$ kJ

   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 [$C_6H_{12}O_6$]. The overall chemical equation for respiration is shown here.

   $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2870$ kJ

   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	Glass cleaner, ethanol	Ice melting in a glass drink	Respiration, where	Photosynthesis, where
Is the reaction endothermic or					
Is enthalpy increased or					
Is there an increase or decrease					
Is there an increase or decrease					
Is the total energy of the					
Overall, which have the					

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^{-1}**.

   $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_c = -394$ kJ

   b. Use the information given in the combustion equation for carbon in part (a) to determine the amount of CO_2 produced in grams for every MJ of heat released from the burning of pure carbon, ie carbon emissions in **g(CO_2) MJ^{-1}**.

   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.

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.

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_4) 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_2 when burning coal to produce heat? Answer in **g(CO_2) MJ^{-1}**. (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^{-1}**? (See border note and Table 1.) Why is this difference an issue when replacing petrol with LPG as a transport fuel?

Energy density of a fuel may be defined as the energy available per unit volume of the fuel (eg **kJ L^{-1}** or **MJ L^{-1}**). 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.

13. **Bioethanol** (C_2H_5OH) 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.)

   $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1367$ kJ

   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^{-1}**.

   d. Ethanol has a density of 789 g L^{-1}. Use this information and your answer to part (c) to determine its **fuel density** in **MJ L^{-1}**. Does its fuel density impact on the use of ethanol as a petrol replacement?

The standard enthalpy of combustion **ΔH_c** of a fuel gives ΔH for the complete combustion of 1 mole of the fuel at 25 ^oC 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.

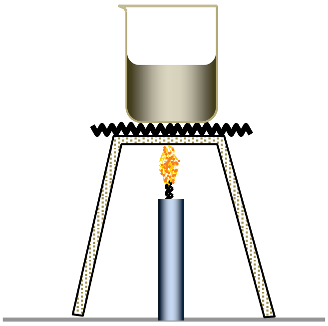
The Australian government has legislated to restrict the use of higher ethanol blends due to vehicle manufacturer warranties on locally available cars.

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 $CO_2(g)$ into the atmosphere. The following questions refer to the use of biofuels and their $CO_2(g)$ emissions.

   a. The combustion of both ethanol and petrol releases about 1.5 mole of $CO_2(g)$ 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 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, ΔH_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, $C_{46}H_{92}O_2$. (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, $C_{46}H_{92}O_2$.
   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 **ΔH_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 **ΔH_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 **ΔH_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.

eBook+ Quiz 14.1.

Attempt Set 23 # 1 and 2.

14.2 Measuring reaction rate

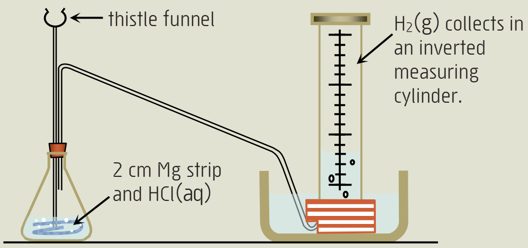
Just how fast or slow a reaction proceeds can be described in terms of the rate of **formation of products** or the rate of **consumption of reactants**. Thus the rate of a chemical reaction can be calculated using:

$$\textbf{rate of reaction} = \frac{\textbf{amount substance used or produced}}{\textbf{time taken}}$$

Various units can be used to express rate; eg moles per second (mol s^{-1}), grams per second (g s^{-1}) or millilitres per second (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 mol L^{-1} 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 H_2(g) produced as the reaction progressed to completion.

volume of H_2(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

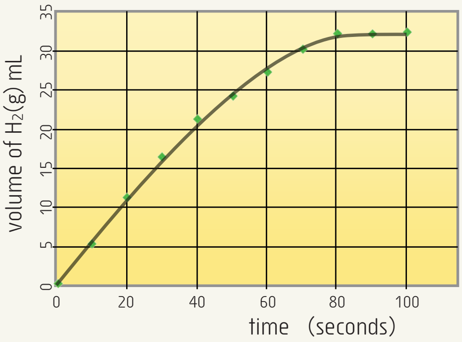


(a) Construct a graph of volume of hydrogen gas produced against time.

(b) Examine the gradient of this graph and comment on the rate of formation of hydrogen gas as the reaction proceeded to completion.

(c) 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.

(a)

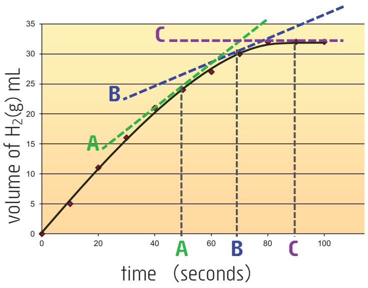


(b) The rate of this reaction is shown by the gradient of the graph for the formation of hydrogen gas with time. As the gradient is fairly constant for the first 50-60 seconds then this means the reaction rate is also constant for the first 50-60 seconds. From 60 seconds onwards to the end of the reaction 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.

(c) 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 $H_2(g)$ 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.

FIGURE 2 Formation of $H_2(g)$ from Example 1.



This graph shows the total volume of $H_2(g)$ 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.

eBook⁺ Quiz 14.2.

Attempt Set 23 # 3, 4 and 5.

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 $H_2(g)$ (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 s to t = 30 s.
(b) The last 30 seconds of the reaction, ie from t = 50 s to t = 80 s.

(a) $\text{rate} = \dfrac{\text{amount produced}}{\text{time taken}} = \dfrac{16}{30} = 0.53 \text{ mL s}^{-1}$

The data table shows 16 ml of $H_2(g)$ is collected from the start to 30 seconds.

(b) volume of $H_2(g)$ collected = 32 – 24 = 8 mL

$\text{rate} = \dfrac{\text{amount produced}}{\text{time taken}} = \dfrac{8}{30} = 0.27 \text{ mL s}^{-1}$

Since 24 mL of $H_2(g)$ 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
  The reacting particles must collide with a suitable **orientation**. (See Fig 3.)

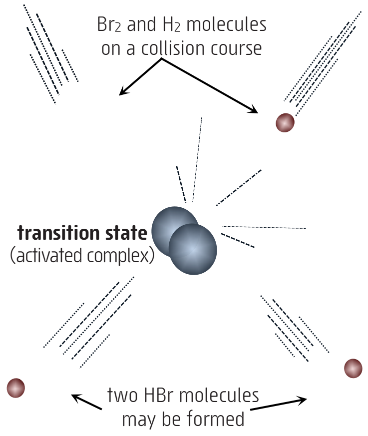
If the reacting particles collide with sufficient energy and a suitable orientation then they can form a transition state. Here the original bonds are breaking while new bonds are forming. The transition state exists for a very short time only and when it decomposes it may lead to the formation of new products or may reform to the original reactants.

eBook⁺ Quiz 14.3.

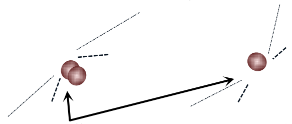
FIGURE 3 According to the **collision theory**, chemical reactions like the one shown here,

$Br_2(g) + H_2(g) \rightarrow 2HBr(g)$

involve a collision between particles. In this example, a $\mathbf{H_2}$ molecule and a $\mathbf{Br_2}$ 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.



Poor collision orientation means the molecules are not suitably aligned to allow new bonds to form.

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** $\mathbf{E_a}$. (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.

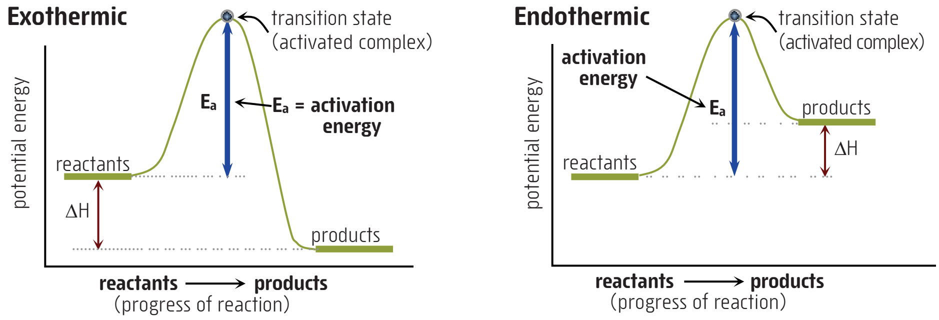


FIGURE 4 A **potential energy profile** shows the change in potential energy for reacting particles as they approach and form an activated complex. If the colliding particles have too little kinetic energy they will rebound before the activated complex forms and so there would be no reaction. The minimum collision energy needed to form an activated complex is the **activation energy**. This is labelled $\mathbf{E_a}$.

eBook⁺ Quiz 14.4.

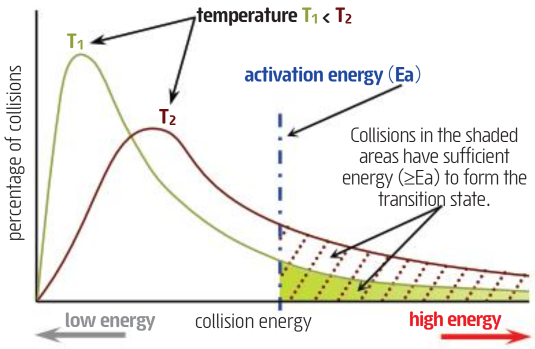
Attempt Set 23 # 6 and 7.

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.)

eBook⁺ Quiz 14.5.

Attempt Set 23 # 8.



Collisions in the shaded areas have sufficient energy (≥Ea) to form the transition state.

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 ≥ E_a** at the lower temperature T_1.

14.6 Understanding the factors that affect reaction rate

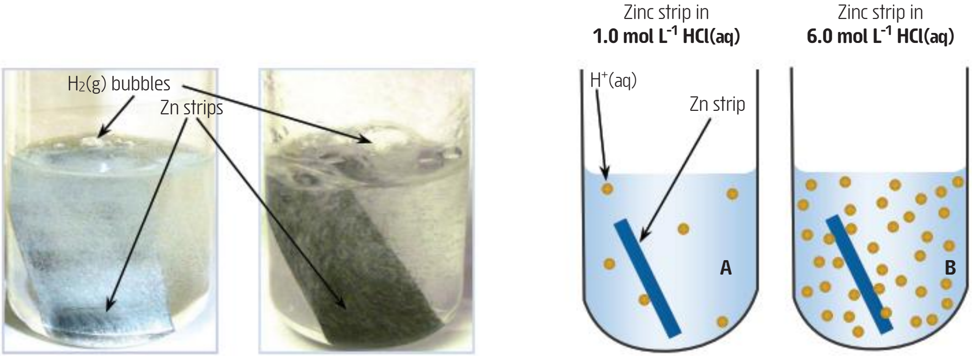
The collision theory gives us a basis for **understanding** and **explaining** the effects of concentration, temperature, pressure, state of sub-division and catalysts on reaction rate.

- **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).

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

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.



Zinc strip in **1.0 mol L^{-1} HCl(aq)**

Zinc strip in **6.0 mol L^{-1} HCl(aq)**

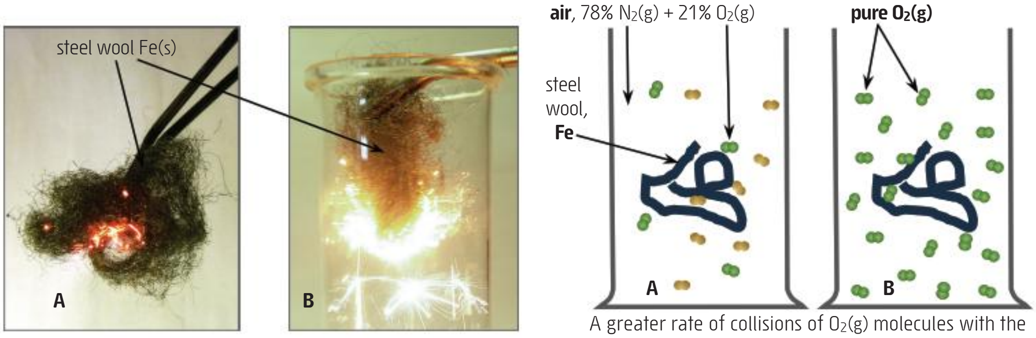
A greater rate of collisions of $H^+(aq)$ ions with the Zn surface (6x greater) will occur in the **6.0 mol L^{-1} HCl(aq)**.

- **Gas pressure:** Raising the pressure, by reducing volume or adding more gas to the same container, creates a greater concentration of reacting gas molecules. This causes an increase in the rate of collisions between these molecules, hence an increase in rate of reaction. Typically doubling the pressure of a gaseous reagent will usually (but not always) double the reaction rate. As with concentration in aqueous solutions the collision theory can explain the rate change in terms of **collision rate** of the reacting particles. (See Fig 7.)

FIGURE 7 Iron, in the form of steel wool, burns slowly in air as it reacts with $O_2(g)$ to produce $Fe_3O_4(s)$.

$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$

The $O_2(g)$ pressure in air is around 21 kPa. A gas jar of pure oxygen, however, contains $O_2(g)$ at a pressure of around 100 kPa. Here the same reaction is much more vigorous. The increased rate is due to the higher $O_2(g)$ pressure which gives rise to a greater rate of collisions between O_2 molecules and Fe atoms on the steel wool surface. This is visualised at the particle level by **diagram A**, low $O_2(g)$ pressure (air) and **diagram B**, high $O_2(g)$ pressure (pure oxygen).



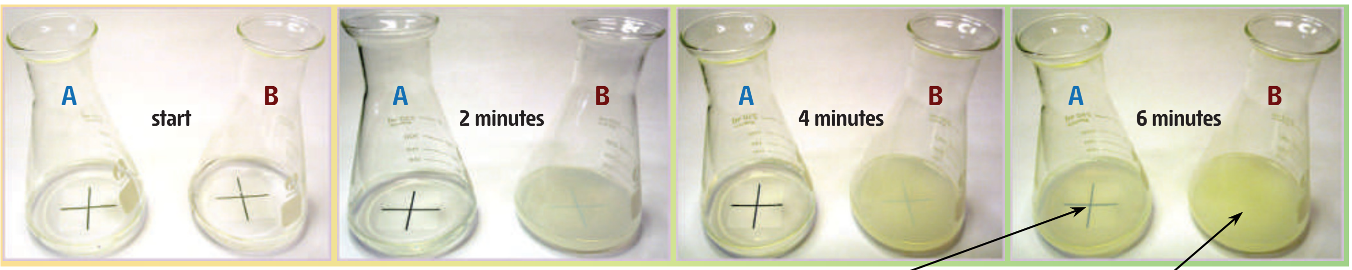
Steel wool burns slowly in **air**, ie **$O_2(g)$ at ≈ 21 kPa**.

Steel wool burns rapidly in **pure** $O_2(g)$, ie **$O_2(g)$** at **≈100 kPa**.

A greater rate of collisions of $O_2(g)$ molecules with the Fe surface (≈5x greater) will occur in pure oxygen (**B**) than air (**A**).

- **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** ($Na_2S_2O_3$) and **hydrochloric acid**: $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow \mathbf{S(s)} + SO_2(aq) + H_2O(l)$ 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, $\mathbf{S_2O_3^{2-}(aq)}$ and hydrogen ions, $\mathbf{H^+(aq)}$ have a collision energy equal to or greater than the activation energy.



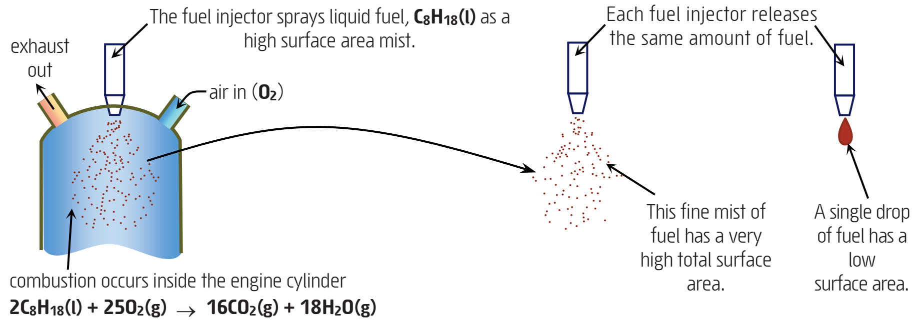
flask **A** is at **15 °C** flask **B** is at **65 °C**

After 6 minutes the black cross in flask **A** is still visible while that in flask **B** is no longer visible.

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.)

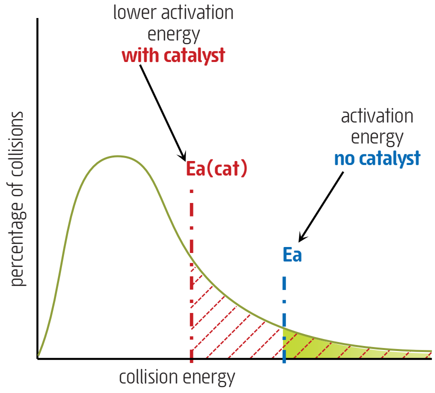
FIGURE 9 Car engine fuel injectors spray liquid fuel into the combustion chambers (cylinders) forming a fine mist of fuel (high surface area). This increases the rate of collision between oxygen molecules (gas phase) and the fuel molecules (liquid phase), thus increasing the rate of fuel combustion.



- **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, $MnO_2(s)$ 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 ≥ Ea (activation energy) when a catalyst is present.



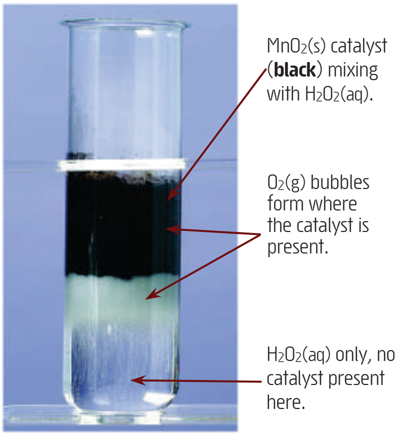
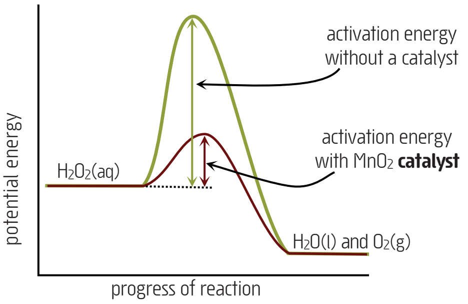


FIGURE 11 The **uncatalysed** and **catalysed** potential energy profile for the decomposition of H_2O_2(aq) (at left).

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

A high activation energy makes this reaction slow under normal laboratory conditions. Adding a catalyst like MnO_2(s) provides the reaction with a pathway of lower activation energy. Thus with the catalyst present a greater percentage of collisions between H_2O_2 molecules have sufficient energy to form the activated complex. Such collisions may go on to produce H_2O(aq) and O_2(g). As a result the rate of decomposition of H_2O(aq) is much greater with a catalyst present.



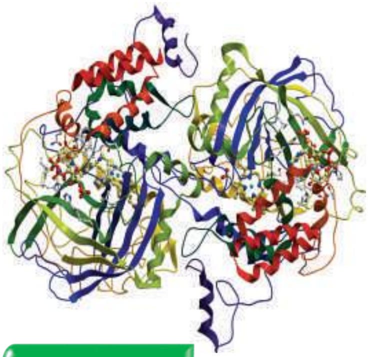
eBook+ Quiz 14.6. **Attempt Set 23 # 9, 10 and 11.**

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 12 Hydrogen peroxide, **H_2O_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.

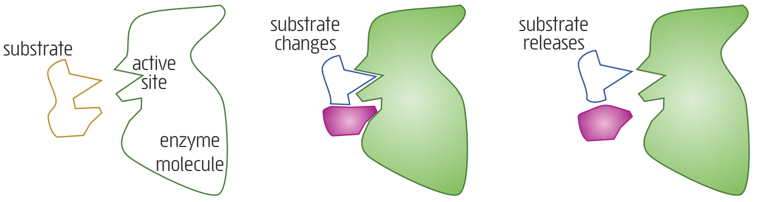
In the human body and the tissue of almost all living organisms an **enzyme** called **catalase** is responsible for the rapid catalytic decomposition of H_2O_2. Catalase is one of the **fastest acting catalysts known**. A single molecule can decompose several million H_2O_2 molecules per second. The schematic model below shows the complex structure of the catalase molecule.



eBook+ Quiz 14.7.

Attempt Set 23 # 12.

FIGURE 13 Schematic representation of the **lock and key model** of enzyme action.



The substrate approaches an enzyme's active site.

Weak intermolecular forces keep the substrate in place while bonds break and new ones form.

The changed substrate releases from the active site as the products are no longer bonded.

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 $CO(NH_2)_2$ (urea), $(NH_4)_2SO_4$, and $NH_4H_2PO_4$, are only possible due to the catalytic synthesis of ammonia, 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.

$N_2(g) + 3H_2(g) \rightleftharpoons \quad (g) \qquad \Delta H = -92$ kJ

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, N_2(g) with hydrogen, H_2(g) to produce ammonia, NH_3(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, NO_x in the exhaust are converted into harmless N_2 and 80% of the unburnt hydrocarbons, HCs and poisonous carbon monoxide CO are converted into H_2O and 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 NO_x and some CO to N_2 and 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 H_2O and 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.

eBook+ Quiz 14.8.

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 $H_2(g)$ and $O_2(g)$ into $H_2O(l)$ 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, CO(g). This gas is typically present in the hydrogen fuel obtained from the **catalytic reforming** of hydrocarbons. **Catalytic poisoning** occurs as CO(g) molecules attach very strongly to the catalyst surface. This prevents the catalyst from interacting with $H_2(g)$ and $O_2(g)$ and catalysing their conversion into $H_2O(l)$. 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 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 (NOx) and various unburnt hydrocarbons (HCs). CO is a **toxic gas** while NOx 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.

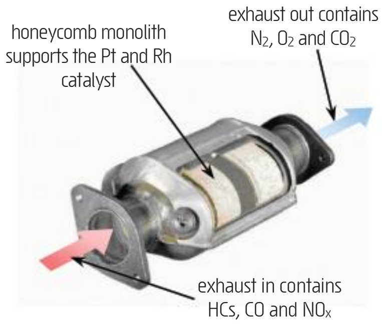
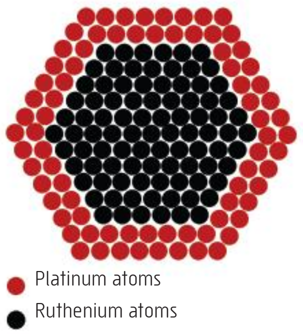


FIGURE 16 Researchers at Brookhaven National Laboratory have developed a new type of nanocatalyst that shows great potential in advancing the versatility of the **hydrogen oxygen fuel cell**. The catalytic nanoparticles they created consist of a ruthenium core coated with a double layer shell of platinum 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.

eBook+ Quiz 14.9.

Complete Set 23.

Set 23 Reaction rate

1. 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 mol L^{-1} hydrogen peroxide (H_2O_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 (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. A piece of zinc added to a **1.0 mol L^{-1}** hydrochloric acid solution produced 2 mL of hydrogen gas per minute. When using **5 mol L^{-1}** hydrochloric acid with a similar piece of zinc, 40 mL of hydrogen gas is produced per minute.

   b. 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.

   c. 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.

   d. A single piece of aluminium added to a 1.0 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.

   e. 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.

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.

2. State **three alterations** that could increase the rate of the reaction shown here.

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

3. 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.

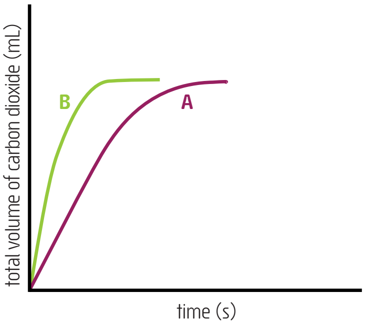
   $NaHCO_3(s) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$

   Graph **A** shows the result when using **20.0 mL** of **0.50 mol L^{-1}** $HNO_3(aq)$ at **25 °C**. Graph **B** is for the same reaction performed at a different **temperature**.

   a. 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.

   b. This reaction is repeated once more using **100.0 mL** of **0.10 mol L^{-1}** $HNO_3(aq)$ 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.

FIGURE 18 This graph shows the total volume of carbon dioxide produced over time when nitric acid reacts with sodium



4. 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.

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

   The investigation involved using a 1.0 cm^3 cube of calcite (pure $CaCO_3$) placed into a 250 mL conical flask containing 150.0 mL of 0.50 mol L^{-1} 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^{-1})	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_2) s^{-1}]					

The following questions relate to this investigation.

a. **Briefly account** for the mass loss that occurs during the course of the reaction.

b. Calculate the average reaction rate in grams of carbon dioxide produced per second, **g(CO_2) s^{-1}**. Do this for each acid concentration and thus complete the table.

c. 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_2(g) produced? Would this be a **systematic** or **random** error and how would it affect the calculated rate of reaction for each experiment? **Explain**.

d. Construct a **graph** of rate of reaction against concentration of HCl(aq). You may assume the rate of evolution of CO_2(g) is zero when the concentration of HCl(aq) is zero.

e. Do the processed results as seen in your graph support the student's hypothesis?

f. The procedure the student used involved allowing the reaction mixture to lose 0.20 g in mass, equivalent to an STP volume of CO_2 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.

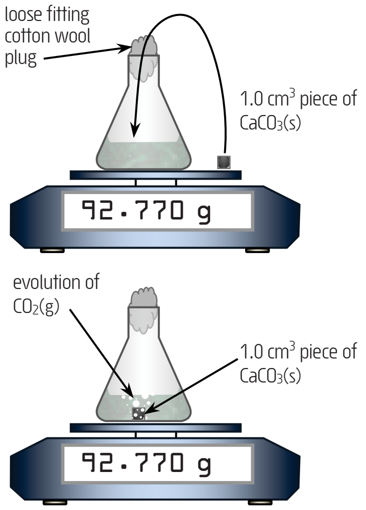


FIGURE 19 Carbon dioxide gas has a very low solubility in acid solutions. Thus as CO_2(g) forms it leaves the solution and escapes from the flask. Hence the mass loss of the reaction mixture and flask can be assumed to be equal to the mass of CO_2(g) produced.

Using a cotton wool plug in the mouth of the flask helps reduce loss of liquid by spattering while still allowing CO_2(g) to escape.

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.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

6. The following passage describes the events taking place at the particle level when hydrogen gas, H_2(g) and oxygen gas, O_2(g) are mixed in a sealed container and react to form water, H_2O(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) ___________.

breaking
collide
repel
reactants
orientation
water
kinetic energy
activation energy
randomly
activated complex
forming
electron clouds
molecules
decompose

7. Synthetic petroleum products like petrol can be manufactured from natural gas (CH_4) 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.

syngas reaction: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \quad \Delta H = 206\ kJ$

a. **Suggest** a reason for converting natural gas to synthetic petrol.

b. 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.

c. Briefly explain what the **high** activation energy of the syngas reaction indicates about the nature of the **bonds** in the reactants of this reaction.

d. Why is the activation energy of this reaction significant from an **industrial synthesis** point of view?

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.

$$Ni(s) + 2HCl(aq) \rightarrow NiCl_2(aq) + H_2(g)$$

The original reaction conditions used were as follows:

a. 45 mL of 1.0 mol L^{-1} 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 °		
b. Use 90 mL of acid		
c. Use 2.0 mol L^{-} HCl(aq)		
d. Add 45 mL of distilled water		
e. Use smaller pieces of nickel (same total mass)		
f. Heat the reaction to 95 °		

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_2 was added to a 50.0 ml sample of 5% hydrogen peroxide bleaching solution. Upon adding MnO_2(s) the bleaching solution fizzed rapidly and became quite hot. When the reaction appeared to have stopped the remaining **MnO_2** 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_2(s). Label **reactants**, **products**, **ΔH** and **activation energy** with and without MnO_2(s).
   d. What is **catalase** (Fig 12 p120) and how is its action related that of MnO_2(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.

$$nC_6H_{12}O_6 \xrightarrow{\text{enzyme}} (C_6H_{12}O_6)n$$

a. What is the role of the **enzyme** shown in this equation?

b. In the equation above, the enzyme is written above the arrow. Why isn't it included as a reactant or product?

c. How is the action of an enzyme different to that of inorganic catalysts?

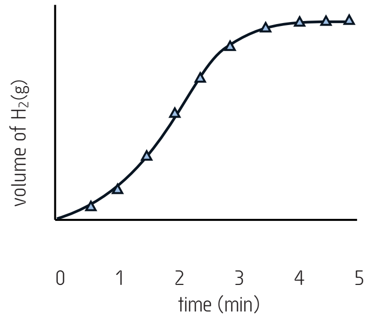


FIGURE 20 Shows how the rate of formation of hydrogen gas changes during the course of the reaction.

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 mol L^{-1} HCl(aq) initially at 21°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.

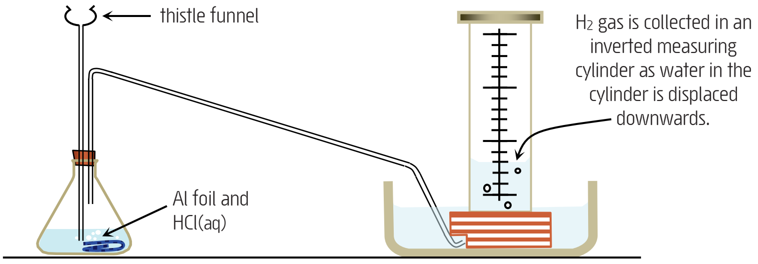
$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g) \qquad \Delta H = -1060 \text{ kJ}$$

a. Suggest a reason for using a **thistle funnel** as part of the apparatus. (See Fig 21.)

b 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?

c. 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 21 Initially the flask contains aluminium foil only. The reaction commences when HCl(aq) is added via the **thistle funnel**. H_2 gas from the reaction of HCl(aq) with 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 (NO_x), unburnt hydrocarbons (HCs) and carbon monoxide (CO) from the car's exhaust stream. It does this by converting these substances to nitrogen (N_2), oxygen (O_2), water (H_2O) and carbon dioxide (CO_2).

a. 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 (NOx) in the exhaust pass through the honeycomb section their molecules become temporarily bonded to the metals. During this time the atoms in NOx molecules rearrange to form N_2 and O_2 molecules which become released back into the exhaust stream. These two reactions can be visualised as shown.

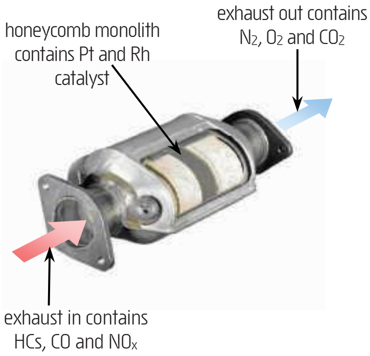
$$NO_2(g) + Pt(s) \rightarrow PtNO_2(s) \qquad \textbf{then} \qquad 2PtNO_2(s) \rightarrow N_2(g) + 2O_2(g) + 2Pt(s)$$

Write an **overall equation** for these two reactions (see 6.4 p45) and **justify** the statement that platinum is acting as a catalyst.

b. 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.

c. 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**

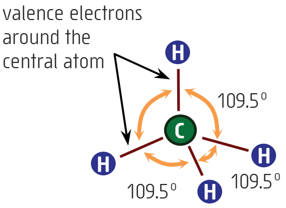


CHAPTER 15 | INTERMOLECULAR FORCES

15.1 Molecular shape

Shapes of simple molecules include linear, triangular planar, tetrahedral, pyramidal and bent.

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 (CH_4), the highest angular separation for the four groups of valence electrons of the carbon atom is 109.5°. 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°. This angle is known as the **bond angle** for methane.

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

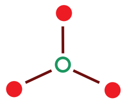
● other attached atoms

— covalent bond(s) (2, 4 or 6 electrons)

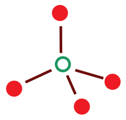
: lone pairs (2 valence electrons)

- **1 or 2** groups of electrons gives
  a **linear shape** with a 180° bond angle..

- **3** groups of electrons and none of these are lone pairs gives
  a **triangular planar** shape with 120° bond angles.......................................

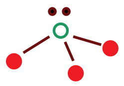


- **4** groups of electrons and none of these are lone pairs gives
  a **tetrahedral** shape with 109.5° bond angles...

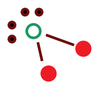


Pyramidal and **bent** (V shape) molecular shapes are versions of the tetrahedral arrangement where one or two atoms respectively are missing and a lone pair of electrons is in its place.

- **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° ....

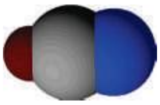
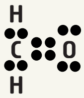
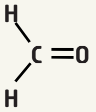
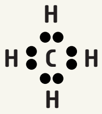
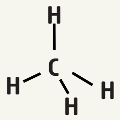
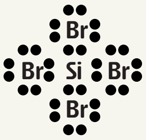
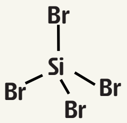
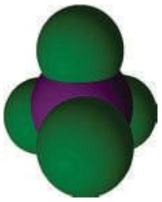
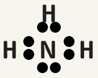
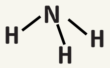
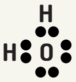
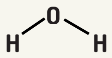


- **4** groups of electrons and **two** of these are **lone pairs** gives
  a **bent** or **V** shape with bond angles several degrees less than 109.5° ....



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 Example1.

EXAMPLE 1 Using VSEPR theory to find molecular shape and bond angles

Substance	Lewis structure	Central atom + number and type of valence electron groups	Shape	Molecular appearance	Bond angle
carbon dioxide **CO_2**		**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** $H-C\equiv N$		180°
methanal **H_2CO**		**C** has 3 groups of valence shell electrons and none of these are lone pairs.	**triangular planar** 		120°
methane **CH_4**		**C** has 4 groups of valence shell electrons and none of these are lone pairs.	**tetrahedral** 		109.5°
silicon bromide **$SiBr_4$**		**Si** has 4 groups of valence shell electrons and none of these are lone pairs.	**tetrahedral** 		109.5°
ammonia **NH_3**		**N** has 4 groups of valence shell electrons and one of these is a lone pair.	**pyramidal** 		ideal: 109.5° actual: 107°
water **H_2O**		**O** has 4 groups of valence shell electrons and two of these are lone pairs.	**bent** 		ideal: 109.5° actual: 104.5°

eBook+ Quiz 15.1.

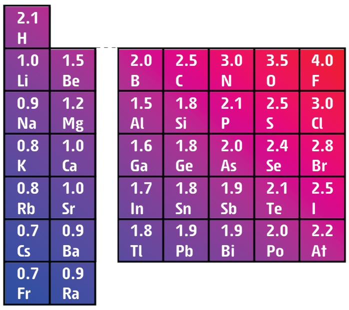
Attempt Set 24 # 1, 2 and 3.

15.2 Electronegativity and covalent bond dipoles

Electronegativity measures the tendency of an atom to attract electrons. It is defined as the ability of an atom in a molecule to attract electrons to itself and is measured on a scale of 0 to 4. Atoms of higher electronegativity have a greater tendency to attract electrons. Within the periodic table, electronegativity of the elements increases left to right in a period and decreases down a group. (See Fig 2 for values.)

If two atoms of different electronegativity form a covalent bond then an uneven sharing of the bonding electrons will occur. This happens as the shared electrons of the covalent bond spend more time closer to the more highly electronegative element. As a result of this uneven sharing of electrons, the more electronegative atom develops a **small** (much less than 1) negative charge represented as δ , see border note) and the less electronegative atom develops a **small** positive charge represented as δ this are said to have a **bond dipole**. (See Fig 3.) The greater the difference in electronegativity of two covalently bonded atoms, the greater the size of the bond dipole.

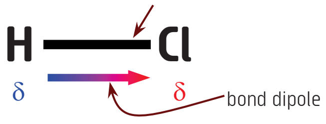
FIGURE 2 **Electronegativities** for the main group elements.



2.1 H						
1.0 Li	1.5 Be	2.0 B	2.5 C	3.0 N	3.5 O	4.0 F
0.9 Na	1.2 Mg	1.5 Al	1.8 Si	2.1 P	2.5 S	3.0 Cl
0.8 K	1.0 Ca	1.6 Ga	1.8 Ge	2.0 As	2.4 Se	2.8 Br
0.8 Rb	1.0 Sr	1.7 In	1.8 Sn	1.9 Sb	2.1 Te	2.5 I
0.7 Cs	0.9 Ba	1.8 Tl	1.9 Pb	1.9 Bi	2.0 Po	2.2 At
0.7 Fr	0.9 Ra					

FIGURE 3 The significant difference in the electronegativity of **Cl** and **H** (**3.0** and **2.1** respectively) results in an uneven sharing of bonding electrons from the covalent bond. The arrow alongside the bond represents the resulting **bond dipole**. It points toward the **slightly negative end**, δ^- of the covalent bond, ie the **Cl** end. This shows the direction in which the shared electrons will be more strongly attracted.

On average the shared pair of electrons are closer to the **Cl** atom.



Note: The symbol δ **delta**, is used to represent a small factional amount, ie **much less than one**. Thus δ represents a fractional charge of **much less than 1+**. Similarly δ « **1-**.

eBook+ Quiz 15.2.

Set 24 # 4.

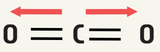
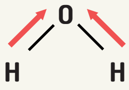
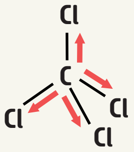
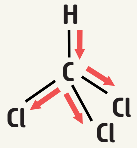
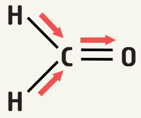
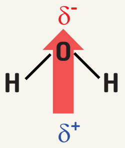
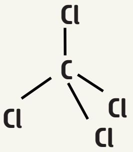
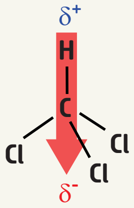
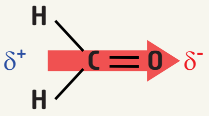
15.3 Polar and non-polar molecules

Polar molecules are those with **slight positive** (δ^+) and **slight negative** (δ^-) 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.)

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** (δ^-) while the other end has a permanent **slight positive charge** (δ^+).

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_2	H_2O	CCl_4	$CHCl_3$	H_2CO
Shape and bond dipoles (arrows)					
Bond dipole symmetry	symmetrical	not symmetrical	symmetrical	not symmetrical	not symmetrical
Net dipole (large arrow)	 zero net dipole		 zero net dipole		
Molecular polarity	non-polar	polar	non-polar	polar	polar

eBook+ Quiz 15.3. Complete Set 24.

Set 24 Molecular shape and polarity

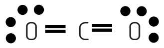
1. The following passage explores how the **VSEPR** theory can be used to find the shape of a molecule. Use the list of terms to complete the passage.

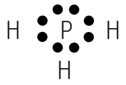
VSEPR
lone pairs
molecule
six
linear
three
central
bent
valence shell
triangular planar
groups
tetrahedral

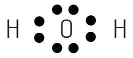
When two or more atoms covalently bond to one another they can form a tightly bound cluster known as a (a) ___________. The shape of a simple molecule describes the arrangement of atoms around the (b) ___________ atom of the molecule. From the valence shell electron pair repulsion theory or (c) ___________, 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.

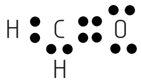
Molecules form a (h) ___________ shape when the central atom has two groups of valence shell electrons. Three groups of valence shell electrons on the central atom result in a (i) ___________ shape. If the central atom has four groups of valence shell electrons but only (j) ___________ atoms attached 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) ___________.

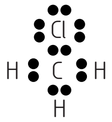
2. Refer to the Lewis structure for the following compounds and determine their **molecular shape**. (See Fig 5.)

a.


b.


c.


d.


e.


3. Both CO_2 and H_2O (see Question 2) consist of molecules with two atoms bonded to a central atom yet their shapes are different. CO_2 is linear while H_2O 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 fluorine (HF) is said to have a bond dipole whereas the covalent bond between fluorine atoms in fluorine gas (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 (**CH_3Cl**), dichloromethane (**CH_2Cl_2**) and trichloromethane (**$CHCl_3$**) all have a net dipole moment, ie they are polar molecules yet the compounds methane (**CH_4**) and tetrachloromethane (**CCl_4**) both have a zero dipole moment, ie are non-polar. These molecules contain the same polar C — Cl or C — 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.

a. F_2
b. H_2O
c. HCl
d. CH_4
e. NH_3
f. CBr_4
g. PCl_3
h. CS_2
i. SO_2
j. H_2CO
k. H_2Se

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)**

a. CO_3^{2-}
b. NH_4^+
c. SO_4^{2-}
d. NO_3^-
e. SO_3^{2-}

8. **Rank** the following groups of compounds in order of increasing molecular polarity. Give a brief statement that **justifies** your ranking.

a. HBr HI HF
b. H_2O H_2Te H_2S H_2Se
c. CH_4 CF_4 CH_3F
d. CH_2I_2 CH_2F_2 CH_2Cl_2

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 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 °C and 100 °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 °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!

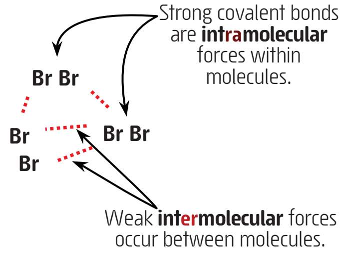
15.4 Intramolecular forces and Intermolecular forces

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.

eBook+ Quiz 15.4. **Attempt Set 25 # 1, 2.**

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.**

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.)

FIGURE 7 **Dipole-dipole** attraction occurs between the oppositely charged ends of **polar molecules**.

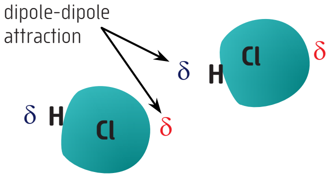


TABLE 1 Polarity and its effect on melting point and boiling point

Substance	Molecular size (ie molar mass, g mol^{-1})	Molecular polarity (debye)	Melting point (°C)	Boiling point (°C)
propane ($CH_3CH_2CH_3$)	44	0 (ie non-polar)	-188	-42
methoxymethane (CH_3OCH_3)	46	1.3	-139	-25
ethanal (CH_3CHO)	44	2.7	-123	21
acetonitrile (CH_3CN)	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.)

eBook+ Quiz 15.5. **Attempt Set 25 # 3.**

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.

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_2, O_2 and CO_2. 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.)

* 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**.

increasing molecular electrons (ie increasing molecular mass or size) →

compound	methane, CH_4	ethane, C_2H_6	propane, C_3H_8	butane, C_4H_{10}	pentane, C_5H_{12}
boiling point	-161.5 °C	-88.6 °C	-42.1 °C	-0.50 °C	36.1 °C

increasing boiling points indicate increasing dispersion forces →

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.)

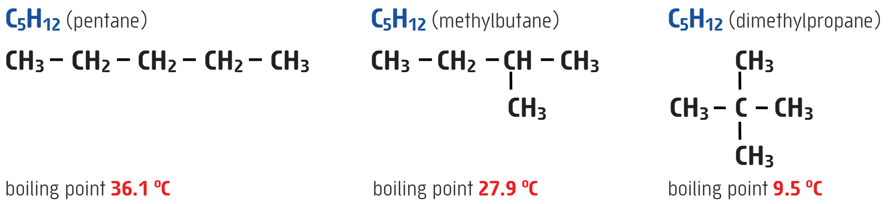
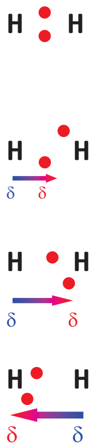


FIGURE 8 The three compounds at left, **pentane**, **methylbutane** and **dimethylpropane** all have the same molecular formula, C_5H_{12}, ie same size and number of electrons per molecule. Their differing strength of dispersion forces, as shown by their different boiling points, is due to their different 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.

FIGURE 9 Temporary dipole in a H_2 molecule



The H_2 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_2 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.

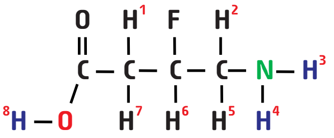
eBook$^+$ Quiz 15.6. **Attempt Set 25 # 4.**

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.)

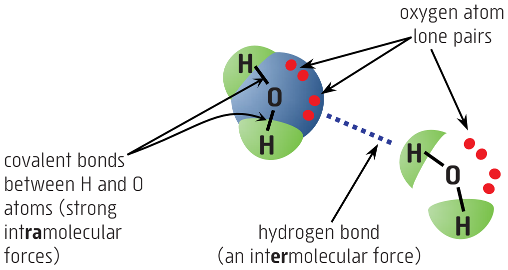
Hydrogen bonding is sometimes described as a form of **extreme dipole-dipole attraction** where the strong positive dipole of an H atom, ie one bonded to a **highly electronegative** F, O or N atom, is attracted to a strongly negative dipole of another F, O or N atom. The lone pair of electrons of the 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.)

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.



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.



eBook$^+$ Quiz 15.7.

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.)

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)
F_2	38 g mol^{-1}	-220	-188
Cl_2	71 g mol^{-1}	-101	-35
Br_2	160 g mol^{-1}	-7	59
I_2	254 g mol^{-1}	114	184

Such data supports the idea that dispersion forces increase with increasing molar mass, ie increasing molecular size/number of molecular electrons.

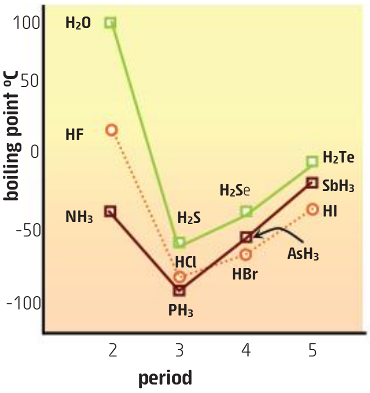
Substances that can also interact by dipole-dipole forces will have slightly higher melting and boiling points compared to other substances of similar molecular size that cannot interact this way. (See Table 3.)

TABLE 3 Polarity and its effect on boiling point

Compound	Molecular formula	Molecular mass	Molecular polarity*	Boiling point
propane	C_3H_8	44 g mol^{-1}	nil (0.0 D)	-42 °C
methoxymethane	CH_3OCH_3	46 g mol^{-1}	low (1.3 D)	-25 °C
ethanal	CH_3CHO	44 g mol^{-1}	moderate (2.7 D)	21 °C

* Molecular polarity is in debye units, D. Polarity increases with D.

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_2O and NH_3. 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.



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_2O), hydrogen fluoride (HF) and ammonia (NH_3) 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.

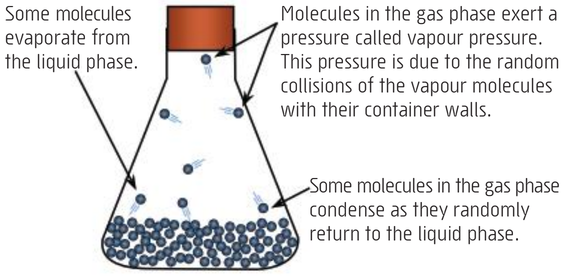
- **Solubility:** A **solute** and **solvent** can only form a solution if the attractive forces acting between the solute molecules and solvent molecules are **comparable in strength** to the attractive forces acting within the pure solvent or pure solute. Generally, this happens for substances whose 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_5-C_{11} hydrocarbons) is very soluble in non-polar kerosene (a mixture of C_{10}-C_{15} 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 ($C_{12}H_{14}O_3(OH)_8$), ethanol (C_2H_5OH) and ammonia (NH_3), which all interact strongly by hydrogen bonding, are extremely soluble in water which also interacts most strongly by hydrogen bonding.

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.

- **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.

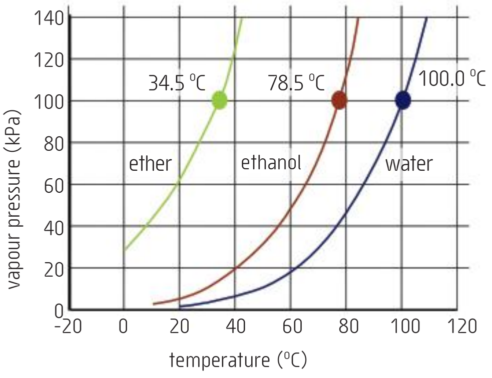
FIGURE 13 If a liquid is kept in a sealed container then at some point the rate of evaporation of the liquid and the rate of condensation of the vapour become equal. At this point the pressure of the vapour reaches a steady value called the **equilibrium vapour pressure**. The greater the tendency for a liquid to evaporate, the higher its equilibrium vapour pressure will be.



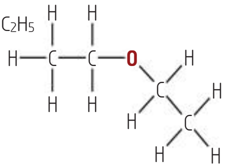
All substances show a greater tendency to evaporate with increasing temperature and so their vapour pressure also increases with temperature. (See Fig 14.) This is to be expected, as higher temperatures mean higher average molecular kinetic energies that better enable molecules to escape their intermolecular 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.

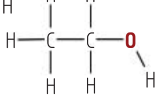
Although **ether** is polar and has the strongest dispersion forces, it has the weakest overall intermolecular forces. **Ethanol** has stronger intermolecular forces as it has up to two hydrogen bonds per molecule. Despite **water** having the weakest dispersion forces it is very polar and capable of 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.



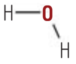
ether
$C_2H_5OC_2H_5$



ethanol
C_2H_5OH



water
H_2O



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.

eBook⁺ Quiz 15.8.

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_4) or hydrogen sulfide (H_2S) 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^{-1}** 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^{-1}**. (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.)

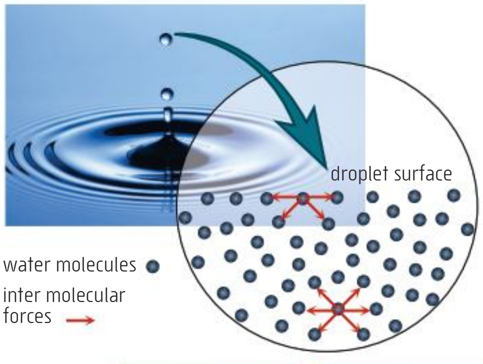
remember, $\textbf{density} = \dfrac{\textbf{mass}}{\textbf{volume}}$

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**.



eBook+ Quiz 15.9. Complete Set 25.

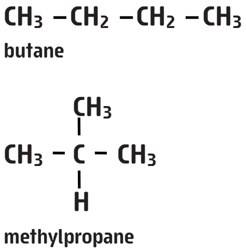
Set 25 Intermolecular forces

1. 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**.
   a. the bonding between the oxygen **atoms** (O) in an oxygen **molecule** (O_2)
   b. the bonding between neighbouring water **molecules** (H_2O) in liquid water (H_2O)
   c. the bonding found in solid **sodium chloride** (NaCl)
   d. the bonding between carbon **atoms** (C) in diamond (C)
   e. the bonding that is overcome when **liquid** pentane (C_5H_{12}) **boils**
   f. the bonding that is overcome when solid **sugar** ($C_{12}H_{22}O_{11}$) is heated to the point that a black residue of **carbon** (C) **remains**
   g. the bonding that is overcome when molten iron is **vaporised**
   h. the bonding that is overcome when the wax $C_{22}H_{46}$ **melts** and then **vaporises**

2. 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**.

3. **Explain** the formation of **dipole-dipole forces** in molecular compounds using hydrogen sulfide as an example (H_2S). You must include a sketch as part of your answer.

FIGURE 18 The two **isomeric structures** of butane (**C_4H_{10}**).



$CH_3-CH_2-CH_2-CH_3$

butane

$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

methylpropane

4. All molecular substances can interact by **dispersion** forces.
   a. **Describe** the origin of these forces.
   b. 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.
      i. chlorine (Cl_2) BP = -35 °C and nitrogen (N_2) BP = -196 °C
      ii. ethane (C_2H_6) BP = -88.6 °C and methane (CH_4) BP = -161.5°C
      iii. butane (C_4H_{10}) BP = -0.5 °C and its isomer methylpropane [$CH_3CH(CH_3)_2$] BP = -11.7 °C. (See Fig 18.)

5. **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.

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

Continued over page.

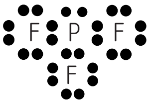
5. *(continued)* The nature of intermolecular forces and molecular polarity also has a significant effect on the solubility or miscibility of different substances. It is generally found that substances of similar polarity are (p) ___________ in one another while substances of unlike polarity are (q) ___________ in one another. Hydrogen bonding has a strong effect on solubility. If two substances can interact by hydrogen bonding they may be (r) ___________ 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.
   a. Name the types of intermolecular forces common to **both** H_2O and H_2S.
   b. It can be said that the **dipole-dipole** forces in water are stronger than those in hydrogen sulfide. Explain why this should be so.
   c. In which of the two molecular substances are dispersion forces the **strongest**?
   d. 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 H_2O.
   e. Use a **diagram** to show the formation of **hydrogen bonds** in water.

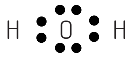
7. Refer to the Lewis structures shown below and **determine** the types of **intermolecular forces** present in each of the substances.

   a. carbon dioxide

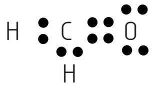
   b. phosphorous trifluoride



   c. water



   d. methanal

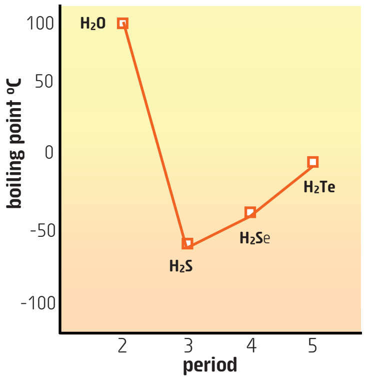


8. **Determine** the type of **intermolecular force(s)** present in each of the listed substances. You may need to draw their **Lewis structure** to determine the shape and polarity of these substances.
   a. Cl_2
   b. H_2S
   c. HF
   d. CH_4
   e. NH_3
   f. CH_2F_2
   g. CF_4
   h. CS_2
   i. CH_3OH
   j. HCN
   k CH_3COOH
   l. H_2O_2

9. Choose the substance from each pair that you would expect to have the **higher boiling point**. **Justify** your answer.
   a. fluorine (F_2) and chlorine (Cl_2)
   b. methoxymethane (CH_3OCH_3) and ethanol (CH_3CH_2OH)
   c. methane (CH_4) and butane (C_4H_{10})

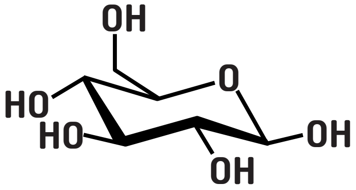
10. Water is a **liquid** at room temperature, which was a determining factor for the evolution of life on Earth. It has a freezing point of 0 °C and a boiling point of 100 °C (at normal atmospheric pressure). Similar compounds of other group 16 elements, like hydrogen sulfide (**H_2S**), hydrogen telluride (**H_2Te**) and hydrogen selenide (**H_2Se**) are all gases at normal laboratory conditions. (See Fig 19.) Discuss the **role** of **intermolecular forces** in affecting the **boiling point** of these compounds.

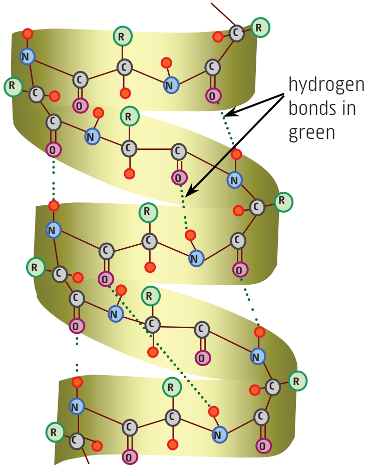
FIGURE 19 The boiling points of the hydrides formed by the elements from group 16.



11. A student has a choice of two liquids: **water** (H_2O) or **decane** ($C_{10}H_{22}$, 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.
   a. **glycerol**, $CH_2OHCHOHCH_2OH$
   b. **petrol**, essentially C_8H_{18}
   c. **diesel** fuel, a mixture of hydrocarbons containing components like $CH_3(CH_2)_{15}CH_3$
   d. the monosaccharide **glucose**, $C_6H_{12}O_6$ (See Fig 20.)

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.

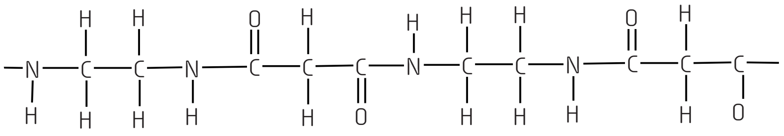




hydrogen bonds in green

FIGURE 21 A section of a **protein** molecule showing how hydrogen bonds form the α **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 α **helical** form, this structure resembles a **right handed coiled spring**. (See Fig 21.) The following structure shows part of a protein molecule.



$-NH-CH_2-CH_2-NH-CO-CH_2-CO-NH-CH_2-CH_2-NH-CO-CH_2-CO-$

a. 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.
b. What is **unique** about the hydrogen atoms identified above that allows them to be involved in hydrogen bonding?
c. Determine from Figure 21 which lone pairs are **actually** involved in forming the hydrogen bonds responsible for the α 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.

a. **methanol** (CH_3OH), boiling point 65 °C and **methane** (CH_4), boiling point -162 °C

b. **methanol** (CH_3OH), boiling point 65 °C and **octane** (C_8H_{18}), boiling point 126 °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.

a. 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.
b. **Explain** why solid ice has a **less dense** structure than liquid water.

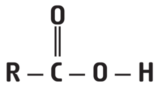
15. The **solubility** of **alcohols** in water varies with the molar mass of the alcohol as shown here.

Alcohol	Molecular formula	Molar mass	Solubility in water g alcohol per 100 g of water
methanol	CH_3OH	32	infinitely soluble
ethanol	C_2H_5OH	46	infinitely soluble
propan-1-ol	C_3H_7OH	60	infinitely soluble
butan-1-ol	C_4H_9OH	74	8.1
pentan-1-ol	$C_5H_{11}OH$	88	2.6
hexan-1-ol	$C_6H_{13}OH$	102	0.59
heptan-1-ol	$C_7H_{15}OH$	116	0.093

a. Suggest a **reason** why alcohols like methanol would be expected to be very soluble in solvents like water.
b. How does the solubility of the listed alcohols vary with increasing **molar mass**?
c. **Suggest** an **explanation** for the trend you outlined in part (b) above.

16. Short chain carboxylic acids (see border note) like methanoic acid, HCOOH and ethanoic acid, CH_3COOH are infinitely soluble, ie **miscible** in water. Higher chain carboxylic acids like palmitic acid, $CH_3(CH_2)_{14}COOH$ 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:

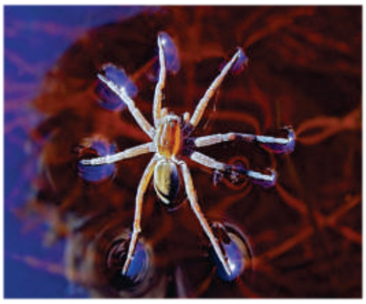


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

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_3** and in palmitic acid **R = $CH_3(CH_2)_{14}$**.

17. The spider shown in Fig 22 is able to walk on water without getting wet.
    a. What is the **name** of the property that allows the insect to do this?
    b. **Explain** in terms of intermolecular forces why liquids have a surface tension.
    c. Overall, the intermolecular forces in benzene, C_6H_6 are much less than in water. How would the surface tension of benzene **compare** to that of water? **Explain**.
    d. Detergents improve the ability of water to wet a surface. How must this affect its surface tension?

FIGURE 22



CHAPTER 16 | SOLUTIONS

16.1 Solutions and the dissolving process

A solution is a mixture where the particles of a **solute** are homogenously 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.

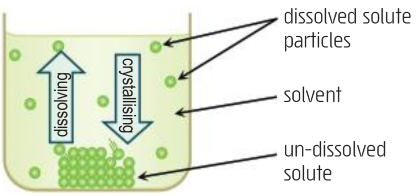


FIGURE 1 The formation of an aqueous solution involves two opposing processes, dissolving and crystallising. As the solute dissolves the solution concentration increases. Crystallisation however, returns some of the dissolved solute to the solid form, thus reducing the solute concentration. When the 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.)

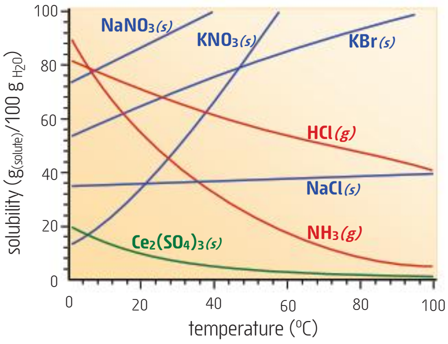
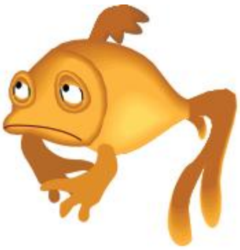


FIGURE 2 Graph of solubility in water with temperature for various substances. Most solids (blue) become more soluble with increasing temperature. $Ce_2(SO_4)_3$ (green) is an exception to the rule.

Gases by comparison (shown in red) all become less soluble as temperature rises.



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** mg L^{-1} at 0 °C and **6.5** mg L^{-1} at 40 °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.)

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.)

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.

eBook$^+$ Quiz 16.1.

Attempt Set 26 # 1 and 2.

16.2 Solutes and ion formation (E)

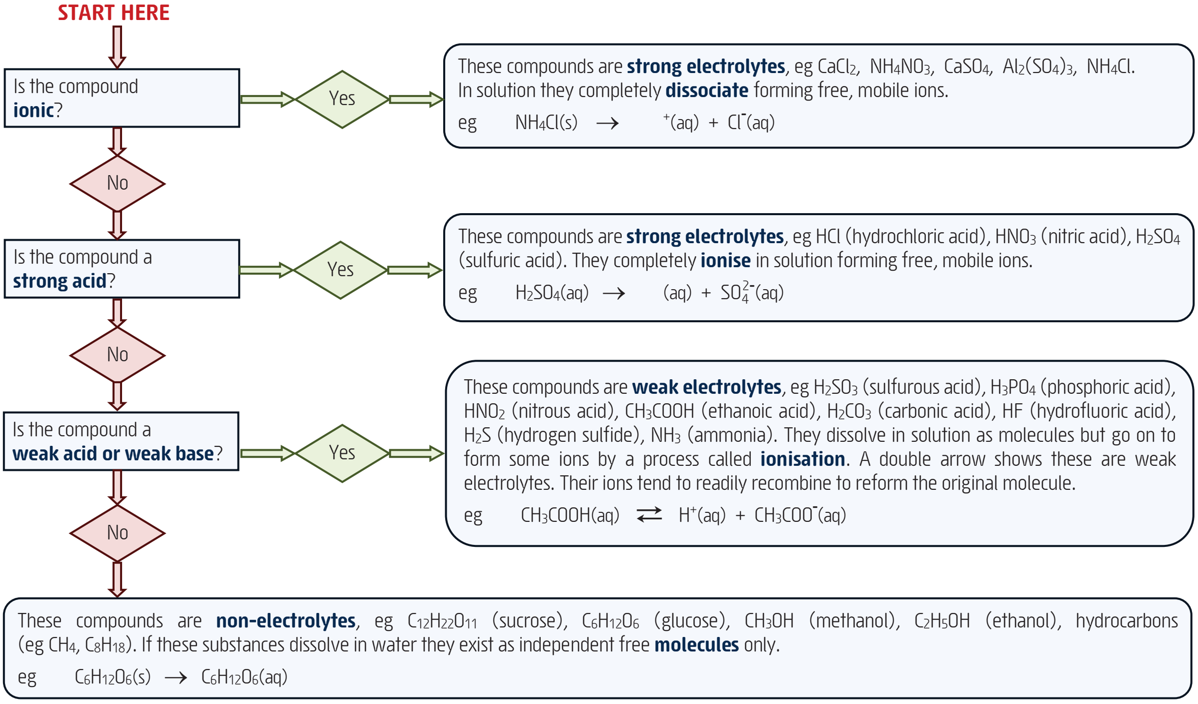
Some solutes dissolve in water producing molecules while others form ions. Aqueous solutes that produce ions when dissolved in water are classified as electrolytes as follows:

- **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.)

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.

FIGURE 3 Use the flow chart below to determine the type of electrolyte.



These compounds are **strong electrolytes**, eg $CaCl_2$, NH_4NO_3, $CaSO_4$, $Al_2(SO_4)_3$, NH_4Cl. In solution they completely **dissociate** forming free, mobile ions.

eg $NH_4Cl(s) \rightarrow {}^{+}(aq) + Cl^{-}(aq)$

These compounds are **strong electrolytes**, eg HCl (hydrochloric acid), HNO_3 (nitric acid), H_2SO_4 (sulfuric acid). They completely **ionise** in solution forming free, mobile ions.

eg $H_2SO_4(aq) \rightarrow (aq) + SO_4^{2-}(aq)$

These compounds are **weak electrolytes**, eg H_2SO_3 (sulfurous acid), H_3PO_4 (phosphoric acid), HNO_2 (nitrous acid), CH_3COOH (ethanoic acid), H_2CO_3 (carbonic acid), HF (hydrofluoric acid), H_2S (hydrogen sulfide), NH_3 (ammonia). They dissolve in solution as molecules but go on to form some ions by a process called **ionisation**. A double arrow shows these are weak electrolytes. Their ions tend to readily recombine to reform the original molecule.

eg $CH_3COOH(aq) \rightleftarrows H^{+}(aq) + CH_3COO^{-}(aq)$

These compounds are **non-electrolytes**, eg $C_{12}H_{22}O_{11}$ (sucrose), $C_6H_{12}O_6$ (glucose), CH_3OH (methanol), C_2H_5OH (ethanol), hydrocarbons (eg CH_4, C_8H_{18}). If these substances dissolve in water they exist as independent free **molecules** only.

eg $C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq)$

eBook⁺ Quiz 16.2.

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_2SO_4 or HNO_3) 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** (→

is the case for a strong electrolyte. Certain **molecular** substances such as CH_3COOH, NH_3 or H_2CO_3 (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** (⇄

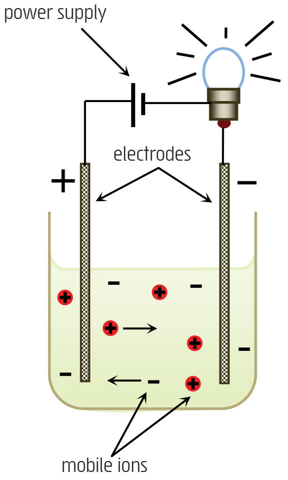


FIGURE 4 Pure water is a non-conductor of electricity. When an electrolyte dissolves in water the resulting mobile ions allow the solution to conduct a current.

Conductivity involves positive ions moving towards the negative electrode and negative ions moving towards the positive electrode.

EXAMPLE 1 Write equations showing how the following electrolytes dissolve in water to form ions.

Al aluminium sulfate	$Al_2(SO_4)_3(s) \rightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$ dissociation	$Al_2(SO_4)_3$ is ionic ∴ a strong electrolyte. A single arrow shows its dissociation goes to completion. The dissolved $Al_2(SO_4)_3(s)$ is present entirely as independent mobile $Al^{3+}(aq)$ and $SO_4^{2-}(aq)$ ions.
HNO nitric acid	$HNO_3(aq) \rightarrow H^{+}(aq) + NO_3^{-}(aq)$ ionisation	HNO_3 is a strong acid ∴ a strong electrolyte. Its ionisation goes to completion so the solution consists of independent mobile $H^{+}(aq)$ and $NO_3^{-}(aq)$ ions. It contains very few, if any HNO_3 molecules.
CH ethanoic acid	$CH_3COOH(aq) \rightleftarrows H^{+}(aq) + CH_3COO^{-}(aq)$ partial ionisation	CH_3COOH is a weak acid ∴ a weak electrolyte. Its ionisation is partial, so the solution contains mainly CH_3COOH molecules with some $H^{+}(aq)$ and $CH_3COO^{-}(aq)$ 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.

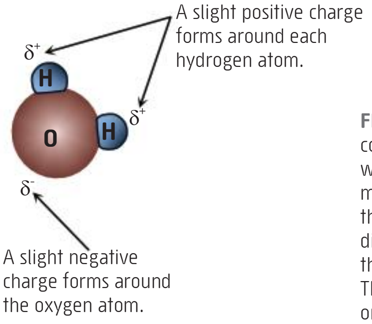
eBook⁺ Quiz 16.3.

Attempt Set 26 # 3, 4 and 5.

16.4 Ionic solubility and solvation

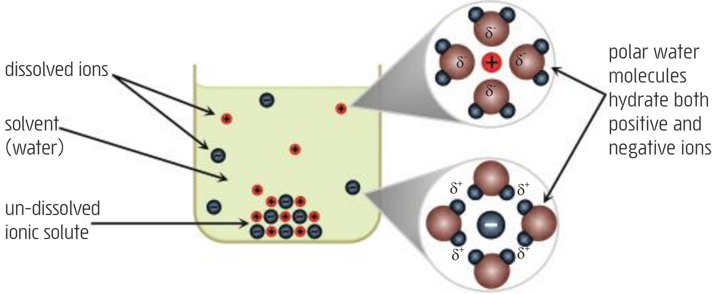
The solubility of ionic compounds depends largely on the **solvation** properties of polar solvents. Solvation involves the attraction of polar solvent molecules to both the positive and negative ions of an ionic solid. The highly polar nature of water molecules (Fig 5) allows water to be an excellent solvent for many ionic solutes.

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** (**«1**) positive charge (δ^+) while a slight (**«1**) negative charge (δ^-) develops around the oxygen atom. Molecules like this are said to have a **dipole**, ie a slightly positive (δ^+) and a slightly negative (δ^-) end, overall the molecule remains neutral.



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 (δ^+) hydrogen atoms in a water molecule being attracted to a negative ion while the slightly negative (δ^-) 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**.



eBook+ Quiz 16.4

Complete Set 26.

Set 26 Electrolytes in solution

1. Give the **term(s)** that describes each of the following:
   a. The two components that make up a solution.
   b. The uniform way in which the components of a solution are mixed.
   c. A solution of $CaCl_2(aq)$ that can dissolve more $CaCl_2(s)$.
   d. A saturated solution of $NaNO_3$ that is carefully cooled from 80 °C to 45 °C.
   e. The degree to which a solute can dissolve in water.

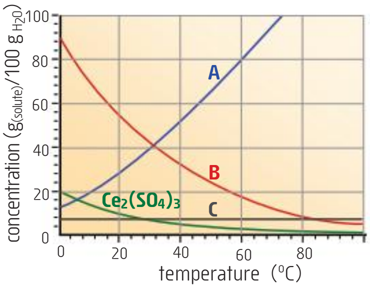


FIGURE 7 Graph of solubility in water with temperature for various substances, A, B, C and cerium sulfate.

2. 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.
   a. Which graph has a shape typical of the solubility curve for a gas? **Explain**.
   b. What is **unusual** about the solubility curve for $Ce_2(SO_4)_3$?
   c. 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**.

FIGURE 8 Solution **concentration** refers to the quantity of solute dissolved in a given quantity of solution. **Molarity** (**M** or **mol L^{-1}**) is one way of expressing the concentration of a solute in solution. (See p145.)

This 0.1 mol L^{-1} (0.1 mole per litre) copper sulfate solution contains 0.1 mole of copper sulfate dissolved in every one litre of solution.

3. 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)
   b. ethanoic acid liquid (CH_3COOH)
   c. copper(II) ethanoate solid [$Cu(CH_3COO)_2$]
   d. ethanol liquid (C_2H_5OH)
   e. iron(III) chloride solid ($FeCl_3$)
   f. sucrose solid ($C_{12}H_{22}O_{11}$)
   g. ammonium sulfate solid [$(NH_4)_2SO_4$)]
   h. hydrogen chloride gas (HCl)
   i. hydrogen sulfide gas (H_2S)
   j. chloroform liquid ($CHCl_3$)
   k. potassium dichromate solid
   l. nitric acid liquid

4. 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)**
   a. 1.0 mol L^{-1} KCl(aq) or 0.1 mol L^{-1} KCl(aq)
   b. 1.0 mol L^{-1} $FeCl_2$(aq) or 1.0 mol L^{-1} $FeCl_3$(aq)
   c. 1.0 mol L^{-1} CH_3COOH(aq) or 1.0 mol L^{-1} HCl(aq)

5. Use your understanding of electrolytes and their properties to **account** for the following: **(E)**
   a. A solution made by dissolving hydrogen chloride gas in water contains very few HCl molecules, even though HCl(g) is composed entirely of molecules.
   b. 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.
   c. Despite AgCl being a strong electrolyte, its solution can never contain a high concentration of $Ag^+(aq)$ and $Cl^-(aq)$ ions.
   d. A solution of $Cu(NO_3)_2$ contains no particles of formula $Cu(NO_3)_2(aq)$.

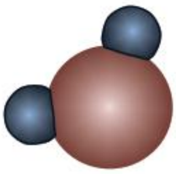
6. The following passage describes the formation of an ionic solution of sodium chloride by mixing NaCl(s) and $H_2O(l)$. Complete the passage by selecting the correct terms from the ones listed. Note, some of these terms are distractors and will not be used.

   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.

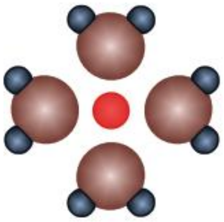
   Polar molecules are ones that have an uneven distribution of (d) ________________. This causes part of the molecule to have a slight positive charge while elsewhere the molecule has a (e) ________________. The strong polarity of water molecules allows both sodium ions and chloride ions to become (f) ________________ 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) ________ + _______.

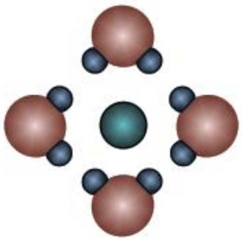
electrostatically
$Na^+(aq)$ + $Cl^-(aq)$
ionisation
aqueous
ion-dipole
electrons
hydrated
dipolar
slight negative charge (δ^-)
dissolves
polar
dissociation

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^+)
      - slightly negative region (δ^-).



   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^-, K^+, δ^+ and δ^-.





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:

$Cl^-(aq)$……… 0.55 mol L^{-1}
$Na^+(aq)$……. 0.47 mol L^{-1}
$SO_4^{2-}(aq)$…… 0.028 mol L^{-1}
$Mg^{2+}(aq)$….. 0.054 mol L^{-1}
$Ca^{2+}(aq)$…… 0.010 mol L^{-1}
$K^+(aq)$……… 0.010 mol L^{-1}

Sea water also contains some other very important dissolved substances like **oxygen** and **carbon dioxide**. In water CO_2 dissolves to produce $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$ 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 $CaCO_3(s)$ from dissolved $Ca^{2+}(aq)$ and $HCO_3^-(aq)$.

8. Common table salt (NaCl) is very soluble in water (36 g per 100 g of water) yet only slightly soluble in methanol, $CH_3OH(l)$ (1.4 g per 100 g of methanol) and insoluble in hexane, $C_6H_{14}(l)$.
   a. **Account** for the high solubility of salt in water. You should include a sketch and refer to ion-dipole forces in your answer.
   b. 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**.

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.

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.

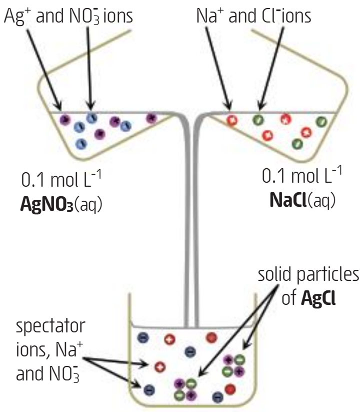


FIGURE 9 Mixing 0.1 mol L^{-1} NaCl(aq) and 0.1 mol L^{-1} AgNO$_3$(aq) produces a solution that is super saturated with Ag$^+$(aq) and Cl$^-$(aq) ions. This happens as AgCl has a very low solubility. As a result, insoluble AgCl(s) immediately precipitates and causes the mixture to go cloudy white. Precipitation continues until the mixture is no longer super saturated with Ag$^+$(aq) and Cl$^-$(aq).

eBook+ Quiz 16.5

Attempt Set 27 # 2, 3, 4 and 5.

EXAMPLE 2 Solutions of Pb(NO$_3$)$_2$(aq) and NaI(aq) are combined and mixed. Will a precipitate form? If so, give its formula. All solution concentrations are 1 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: **Pb^{2+}**(aq) and **NO$_3^-$**(aq) [from Pb(NO$_3$)$_2$(aq)] **Na$^+$**(aq) and **I$^-$**(aq) [from NaI(aq)]
Write the formula for possible precipitates by combining pairs of oppositely charged ions.	Possible precipitates are: **PbI$_2$** and **NaNO$_3$**
Refer to the solubility rules (Table p249) and determine the solubility of these substances.	PbI$_2$ is **insoluble** NaNO$_3$ is **soluble**
Any insoluble or slightly soluble compound can be expected to form a precipitate.	∴ a precipitate of **PbI$_2$**(s) (bright yellow) will form.

Attempt Set 27 # 1.

EXAMPLE 3 Write a net ionic equation for the precipitation of Al$_2$(CO$_3$)$_3$ from a mixture of AlCl$_3$(aq) and Na$_2$CO$_3$(aq).

Write the precipitate formula on the product side of the equation.	?			→	**Al$_2$(CO$_3$)$_3$**(s)
On the reactant side write the ions that form the precipitate.	**Al^{3+}**(aq)	+	**CO$_3^{2-}$**(aq)	→	Al$_2$(CO$_3$)$_3$(s)
Balance the equation.	**2**Al^{3+}(aq)	+	**3**CO$_3^{2-}$(aq)	→	Al$_2$(CO$_3$)$_3$(s)

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, Pb^{2+}(aq) for example then the addition of some sodium iodide solution, 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, Pb(NO$_3$)$_2$(s) can be distinguished from the white solid calcium nitrate, Ca(NO$_3$)$_2$(s). To do this each solid is first dissolved in distilled water in two separate test tubes. A few drops of sodium iodide solution, NaI(aq) are then added to each solution. The Pb(NO$_3$)$_2$(aq) will be distinguished as it produces a bright yellow precipitate while the Ca(NO$_3$)$_2$(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 NaNO$_3$(aq) and KNO$_3$(aq). Although these solutions contain different cations, ie Na$^+$(aq) and K$^+$(aq), these cations have the same pattern of solubility.

FIGURE 10 Mixing a few drops of 0.1 mol L^{-1} NaI(aq) and 0.1 mol L^{-1} Pb(NO$_3$)$_2$(aq) produces a bright yellow precipitate of PbI$_2$(s). This reaction can be used to verify the presence of Pb^{2+}(aq) in solution.

EXAMPLE 4 Describe how you could use a chemical test based on precipitation to distinguish between the two aqueous solutions **barium chloride** [BaCl$_2$(aq)] and **barium iodide** [BaI$_2$(aq)]. Indicate the observations you would expect and the inferences you could make.

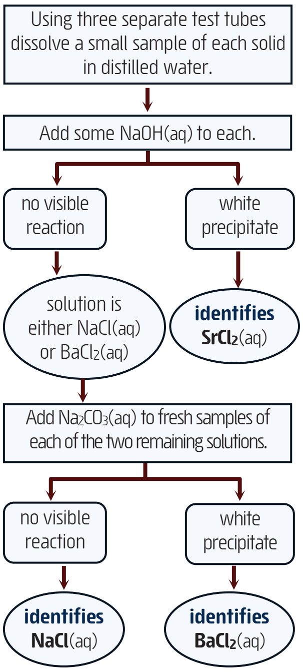
List the ions present in each solution.	Ions present: **BaCl$_2$**(aq) contains **Ba^{2+}**(aq) and **Cl$^-$**(aq) **BaI$_2$**(aq) contains **Ba^{2+}**(aq) and **I$^-$**(aq)
Using solubility rules identify any different pattern of solubility for the ions present.	The same cation, **Ba^{2+}**(aq) is present 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 **Ag$^+$**(aq). Chloride, **Cl$^-$**(aq) produces a white precipitate, **AgCl**(s) while **I$^-$**(aq) produces a pale yellow precipitate, **AgI**(s).
Based on this, choose a suitable test reagent.	The test reagent needs to be an aqueous solution of **Ag$^+$**(aq). As all nitrates are soluble use a solution of **AgNO$_3$**(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 AgNO$_3$(aq) to each. The solution producing a **white precipitate** must be BaCl$_2$(aq). The **creamy yellow precipitate** identifies BaI$_2$(aq).

Attempt Set 27 # 6, 7, and 8.

EXAMPLE 5 Describe a procedure using precipitation that distinguishes the three white solids, **barium chloride** [$BaCl_2(s)$], **strontium chloride** [$SrCl_2(s)$] 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: $BaCl_2(aq)$ contains $\mathbf{Ba^{2+}}(aq)$ and $\mathbf{Cl^-}(aq)$ $SrCl_2(aq)$ contains $\mathbf{Sr^{2+}}(aq)$ and $\mathbf{Cl^-}(aq)$ $NaCl(aq)$ contains $\mathbf{Na^+}(aq)$ and $\mathbf{Cl^-}(aq)$
Identify any solubility differences for the ions present.	The same anion, $Cl^-(aq)$ is present in each of the unknown solutions so this can't be used to distinguish them. Of the cations, $Sr^{2+}(aq)$ produces a white precipitate with $\mathbf{OH^-}(aq)$ while the other two cations, $Na^+(aq)$ and $Ba^{2+}(aq)$ would give no reaction.
Based on this, choose a suitable test reagent.	The test reagent needs to be an aqueous solution of $\mathbf{OH^-}(aq)$. As all sodium compounds are soluble use a solution of **NaOH**(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 **white precipitate** is the $SrCl_2(aq)$ solution. The other two solutions produce no reaction.
Repeat Step 3 for the remaining two unknowns.	The same anion, $Cl^-(aq)$ is present in each of the two remaining unknown solutions so this can't be used to distinguish them. Of the cations, $Ba^{2+}(aq)$ produces a white precipitate with $CO_3^{2-}(aq)$, $PO_4^{3-}(aq)$ or $SO_4^{2-}(aq)$ while $Na^+(aq)$ gives no reaction.
Based on this, choose a suitable test reagent.	Use an aqueous solution of $CO_3^{2-}(aq)$, $PO_4^{3-}(aq)$ or $SO_4^{2-}(aq)$ as the test reagent. All sodium salts are soluble so use a solution of $Na_2CO_3(aq)$, $Na_3PO_4(aq)$ or $Na_2SO_4(aq)$ as the test reagent.
Conduct the test and identify the remaining two unknowns.	Add a few drops of the test reagent, eg $Na_2CO_3(aq)$ to fresh samples of the two remaining unknown solutions. The one that produces a **white precipitate** is the $BaCl_2(aq)$ solution. The solution showing no reaction is $NaCl(aq)$.

FIGURE 11 This flow diagram shows how the three solids **BaCl₂**, **SrCl₂** and **NaCl** can be identified and distinguished from each other by a series of precipitation reactions.



eBook⁺ Quiz 16.6.

Complete Set 27.

Set 27 Precipitation reactions

1. Alicia and Lara carried out several experiments in which they mixed two different 0.1 mol L^{-1} 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**.
   a. $Zn(NO_3)_2(aq)$ and $Na_2CO_3(aq)$
   b. $FeCl_2(aq)$ and $KOH(aq)$
   c. $(NH_4)_2SO_4(aq)$ and $MgCl_2(aq)$
   d. sodium chloride solution and lead II nitrate solution
   e. calcium nitrate solution and sodium sulfate solution
   f. barium chloride solution and potassium sulfate solution

2. Write a **net ionic equation** for the precipitation of each the following compounds.

   a. AgBr b. $Zn(OH)_2$ c. $Fe_2(CO_3)_3$ d. Boiler scale (Fig12) a mixture of $MgCO_3$ and $CaCO_3$

3. 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. A Na_2CO_3 solution is mixed with a $CaCl_2$ solution.
   b. KBr(aq) and NaOH(aq) are mixed.
   c. A NaCl solution is mixed with a $AgNO_3$ solution.
   d. $CaCl_2(aq)$ and $Ba(OH)_2(aq)$ are mixed.
   e. A few drops of NaOH solution is added to excess $CrCl_3$ solution.
   f. Some copper nitrate solution is added to a sodium hydroxide solution.
   g. A tin(II) chloride solution is combined with a sodium carbonate solution.
   h. Cobalt(II) chloride and sodium hydroxide solutions are mixed.
   i. Zinc chloride and lead nitrate solutions are combined.
   j. Some sodium sulfate solution is added to a calcium chloride solution.
   k. Sodium iodide solution and magnesium nitrate solution are combined.
   l. 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.

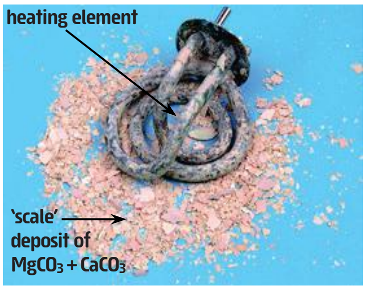


FIGURE 12 An undesirable precipitation reaction can sometimes occur in kettles and water boilers. This happens if boiled water contains dissolved impurities such as $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$. These soluble compounds are often present where water has passed through or over limestone. Water containing these dissolved minerals is termed **temporary hard water**. Heating these solutions decomposes the HCO_3^- ion.

$$2HCO_3^-(aq) \rightarrow H_2O(l) + CO_2(g) + CO_3^{2-}(aq)$$

The formation of carbonate ions, CO_3^{2-} then results in the precipitation of insoluble $MgCO_3$ or $CaCO_3$.

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

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.

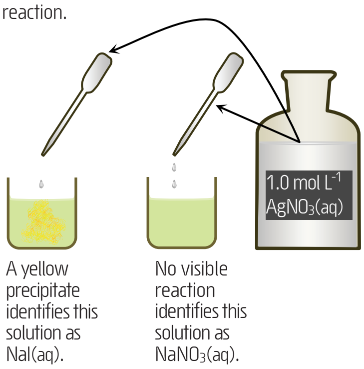
4. In a series of experiments the following observations were made. Unfortunately the student recording these results didn't record which combination of reagents produced each result. The reagents and observations are listed below. What is the most likely combination of reagents responsible for each 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.

$CoCl_2$ $CuSO_4$ $Pb(NO_3\;_2$ $Cr_2\quad_4\;_3$

$FeCl_3$ $Na_2\quad_3$ MgI_2 $FeSO_4$

a. A brown precipitate formed when a pale brown solution was mixed with a colourless solution.
b. A white precipitate was produced from two clear colourless solutions.
c. A colourless and a pale green solution were mixed and turned cloudy as a pale green precipitate formed.
d. A clear blue solution and a colourless solution were mixed and produced a green precipitate.
e. A bright yellow precipitate was formed from two clear colourless solutions.
f. A pink solution and a clear colourless solution were mixed and formed a red precipitate.

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 $NaNO_3$(aq) then NaI(aq) is identified as it produces a yellow precipitate [AgI(s)], while $NaNO_3$(aq) has no reaction.



5. Insoluble ionic compounds can be made in the laboratory by a precipitation process. For example, $ZnCO_3$(s) can be made by mixing $Zn(NO_3)_2$(aq) with Na_2CO_3(aq) then filtering, washing and drying the resulting precipitate. **Name** suitable solutions that when mixed together would precipitate the following compounds.

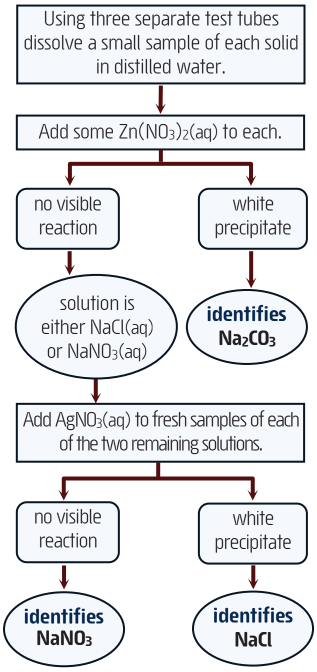
a. $CoCO_3$ b. $Ni(OH)_2$ c. $Cr(OH)_3$ d. $BaSO_4$

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 $NaNO_3$(aq) then NaI(aq) is identified as it produces a yellow precipitate (AgI(s) forms), while $NaNO_3$(aq) has no reaction. (See Fig 13.)

The two solutions **NaOH(aq)** and **Na_2CO_3(aq)** are both clear and colourless. These solutions contain the same cation, Na^+(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**.

$NaNO_3$(aq) **$Ca(NO_3)_2$(aq)** **$Fe(NO_3)_2$(aq)** **$Ba(NO_3)_2$(aq)**

FIGURE 14 This flow diagram shows how the three solids **NaCl**, **$NaNO_3$** and **Na_2CO_3** can be identified and distinguished from each other by a series of precipitation reactions.



7. **Explain** how a precipitation reaction can be used to distinguish the solutions of $Mg(NO_3)_2$(aq) and $Pb(NO_3)_2$(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_2CO_3(aq)** **$MgSO_4$(aq)** **$Pb(NO_3)_2$(aq)**

If so, **state** which **reagent** should be used and what **observation** would be noted.

a. $Pb(NO_3)_2$(aq) and $Ca(NO_3)_2$(aq)
b. $AgNO_3$(aq) and $Ca(NO_3)_2$(aq)
c. Na_2CO_3(aq) and K_2CO_3(aq)
d. $Fe(NO_3)_2$(aq) and $Fe(NO_3)_3$(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.

a. KOH(s), K_2SO_4(s) and KCl(s)
b. NaCl(s), NaI(s) and Na_2CO_3(s)
c. $MgCl_2$(s), $CaCl_2$(s) and $BaCl_2$(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:

$$\textbf{Concentration} \propto \frac{\textbf{quantity of solute}}{\textbf{quantity of solution}}$$

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 (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 (g L^{-1}) might be useful for everyday packaging information. (See Fig 15.)

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.

TABLE 1 Equations for calculating solution concentration

Concentration	Equation	Explanation
moles per litre (molarity) **mol L^{-1}**	$c = \frac{n}{V}$	**c** is the concentration of solute in moles per litre (mol L^{-1}) **n** is the amount of solute in moles (mol) **V** is the volume of solution (solvent + solute) in litres (L)
grams per litre g L^{-1}	$c_{gL^{-1}} = \frac{m}{V}$	$c_{gL^{-1}}$ is the concentration of solute in grams per litre (g L^{-1}) **m** is the mass of solute in grams (g) **V** is the volume of solution (solvent + solute) in litres (L)
parts per million (by mass) **ppm**	$c_{ppm} = \frac{m_s \times 10^6}{m_t}$	c_{ppm} is the concentration of solute in parts per million by mass (ppm) m_s is the mass of solute in grams (g) m_t is the mass of solution (solvent + solute) in grams (g)

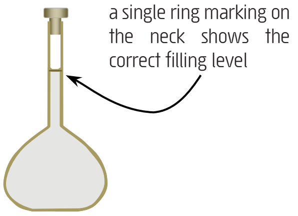
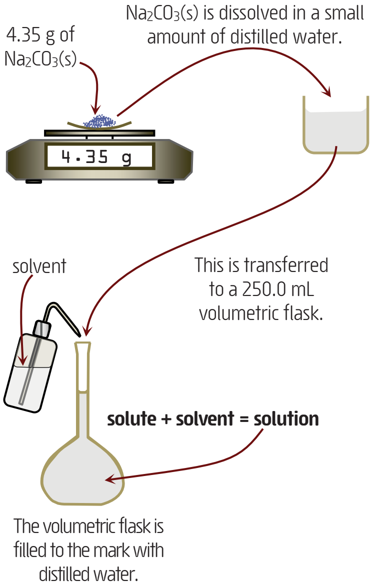


FIGURE 16 **A volumetric flask** is a piece of laboratory glassware used for preparing solutions of a precise concentration. The flask measures a specific volume such as 100.00 mL, 250.00 mL and so on. When filled to the correct volume, the bottom of the meniscus is aligned with a single ring graduation mark on the neck of the flask.

Here a **primary standard solution** of Na_2CO_3, ie a solution of an accurately known concentration is being prepared using a volumetric flask.



EXAMPLE 6 A solution of sodium carbonate was prepared by dissolving 4.35 g of Na_2CO_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. **mol L$^-$** **b.** **g L$^-$** **c.** **ppm.**

a. moles per litre

$$n(Na_2CO_3) = \frac{m}{M} = \frac{4.35}{105.99} = \mathbf{0.0410\ mol}$$

Find the moles of solute from its given mass.

$$c(Na_2CO_3) = \frac{n}{V} = \frac{0.0410}{0.2500} = \mathbf{0.164\ mol\ L^{-1}}$$

Find the solute concentration in mol L^{-1} by using the solution volume (0.2500 L) and the moles of solute (0.0410 mol).

b. grams per litre

$$c(Na_2CO_3) = \frac{m}{V} = \frac{4.35}{0.2500} = \mathbf{17.4\ g\ L^{-1}}$$

Using the volume of solution (0.2500 L) and mass of solute (4.35 g) find the solute concentration in g L^{-1}.

c. parts per million

$$c(Na_2CO_3) = \frac{m_s \times 10^6}{m_t} = \frac{4.35 \times 10^6}{252.4} = \mathbf{17200\ ppm}$$

Using the mass of solution (252.4 g) and the mass of solute (4.35 g) find the solute concentration in parts per million.

eBook+ Quiz 16.7. 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 (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (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 mol L$^-$ $_2(SO_4)_3$(aq)
b. 0.80 mol L$^-$ $_4)_2Fe(SO_4)_2$(aq)

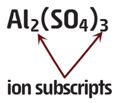
a. $\mathbf{c[Al^{3+}(aq)]} = 2 \times c[Al_2(SO_4)_3] = 2 \times 3.1 = \mathbf{6.2\ mol\ L^{-1}}$
$\mathbf{c[SO_4^{2-}(aq)]} = 3 \times c[Al_2(SO_4)_3] = 3 \times 3.1 = \mathbf{9.3\ mol\ L^{-1}}$

As Al^{3+} has a subscript of 2 and SO_4^{2-} has a subscript of 3.

b. $\mathbf{c[NH_4^+(aq)]} = 2 \times c[(NH_4)_2Fe(SO_4)_2] = 2 \times 0.80 = \mathbf{1.6\ mol\ L^{-1}}$
$\mathbf{c[Fe^{2+}(aq)]} = 1 \times c[(NH_4)_2Fe(SO_4)_2] = 1 \times 0.80 = \mathbf{0.80\ mol\ L^{-1}}$
$\mathbf{c[SO_4^{2-}(aq)]} = 2 \times c[(NH_4)_2Fe(SO_4)_2] = 2 \times 0.80 = \mathbf{1.6\ mol\ L^{-1}}$

Since NH_4^+ has a subscript of 2, Fe^{2+} has a subscript of 1 and SO_4^{2-} has a subscript of 2.

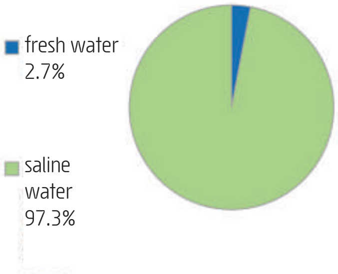
The two ions in aluminium sulfate, $Al_2(SO_4)_3$ are the aluminium ion, Al^{3+} and the sulfate ion, SO_4^{2-}. Their subscripts are **2** and **3** respectively.



eBook+ Quiz 16.8. Attempt Set 28 # 10 and 11.

16.9 Need a drink?

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.

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 mg L^{-1}'. Such dissolved substances are typically in the form of various non-toxic ions, eg Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, SiO_4^{2-}, F^-, Fe^{3+}, Mn^{2+}, NO_3^-, NO_2^-, 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.

eBook+ Quiz 16.9.

Attempt Set 28 # 12 and 13.

16.10 Potable water from seawater

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.

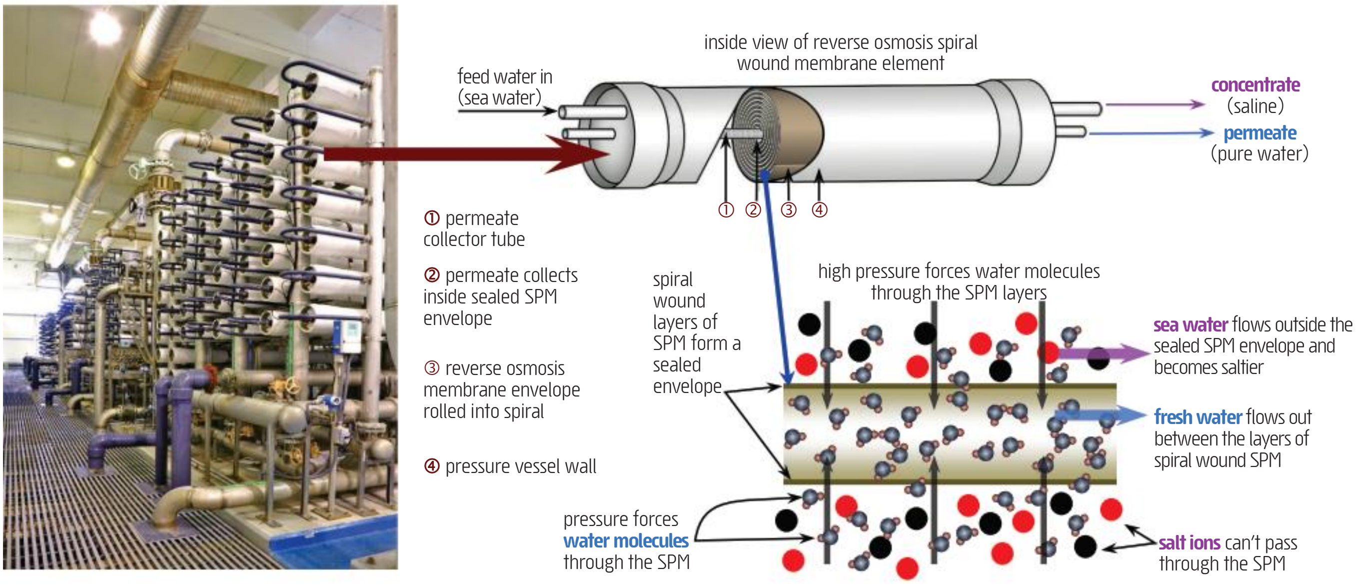
The most abundant water source on Earth is sea water. Its high salinity, typically greater than 35,000 mg L^{-1} TDS, make it unsuitable for drinking, washing or agriculture. Two approaches used to produce potable water from sea water are **distillation** and **reverse osmosis**. (See Fig 18.) The principle 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^{-1}.

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.

eBook$^+$ Quiz 16.10

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.

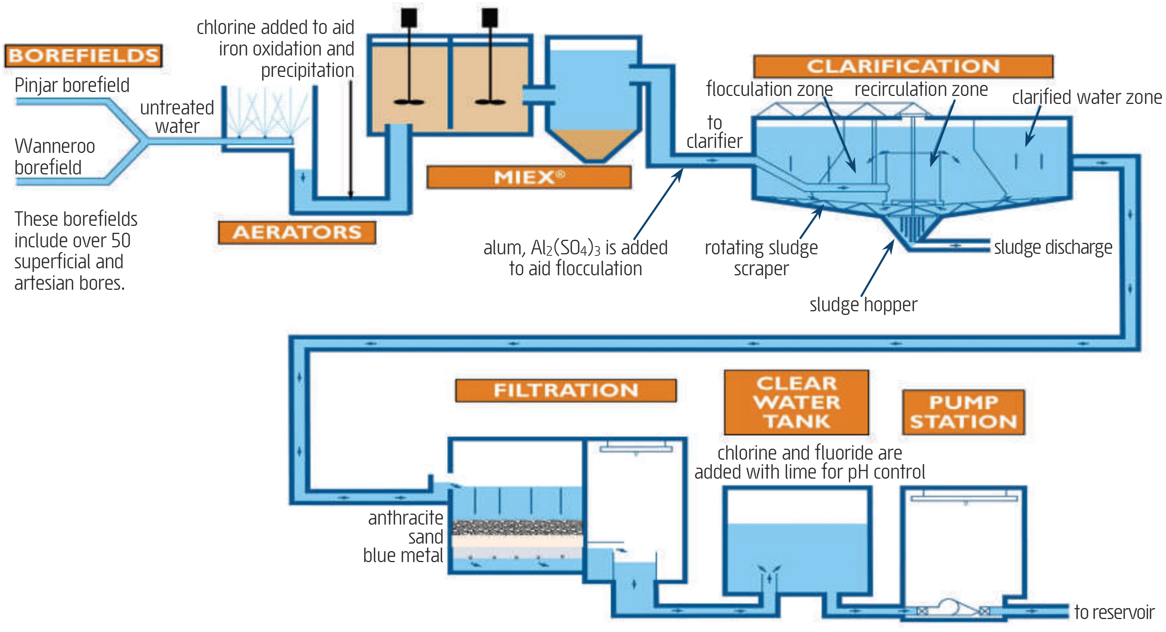
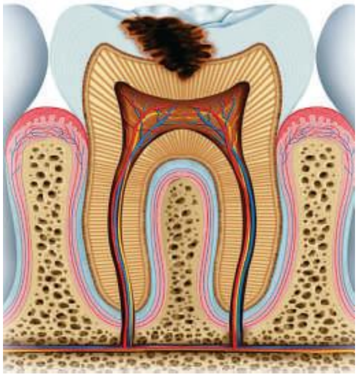


FIGURE 20 The **Wanneroo groundwater treatment plant** features an Australian developed **MIEX®1** Resin process (magnetised ion exchange) that prevents an intermittent 'swampy' odour occurring in treated groundwater supplied to Perth's northern suburbs. Unlike conventional ion exchange, the MIEX®1 resin 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^{-1} in surface waters through to greater than 1.5 mg L^{-1} in some groundwater sources. Health authorities have long recognised that fluoride levels of up to 1.5 mg L^{-1} reduce tooth cavity rates by strengthening tooth enamel. This occurs as fluoride changes the mineral in tooth enamel from **hydroxyapatite**, $Ca_5(PO_4)_3OH(s)$ into **fluorapatite**, $Ca_5(PO_4)_3F(s)$, 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^{-1}**. 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^{-1}) 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_2) and hydrogen sulfide (H_2S). These increase the acidity of water while H_2S 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 $Cl_2(aq)$ and $O_2(aq)$ 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, $Al_2(SO_4)_3$ 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^{-1} (0.85 mg L^{-1} is considered ideal). A maximum dose rate of 1 mg L^{-1} 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^{-1} and 1.0 mg L^{-1} by adding fluorosilicic acid, (H_2SiF_6). 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, CaO (for increasing pH) or by dissolving carbon dioxide gas, 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 $CaCO_3$ deposit, see Fig 12 p143), in kettles, hot water pipes and fittings. Hardness in water is due to the presence of **Mg^{2+}** and **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 Ca^{2+} ions as calcium carbonate onto seed crystals of calcite ($CaCO_3$).

eBook+ Quiz 16.11.

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 (NO_3^-), cyanides (CN^-) and iodides (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 pH<5.5. Of these bores, dissolved iron was recorded at concentrations up to 1300 mg L^{-1}, aluminium up to 290 mg L^{-1}, and arsenic up to 0.8 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 mg L^{-1}. Other tests on water from purpose drilled bores in the area have since recorded arsenic concentrations of up to 7.3 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.)

eBook+ Quiz 16.12. Complete Set 28.

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.

Set 28 Solution concentration and drinking water

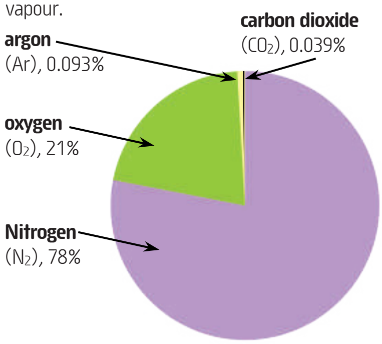
1. What is the **concentration** in mol L^{-1} of each solute in the following solutions?
   a. a 2.40 L solution of NaOH(aq) containing 1.41 mol of NaOH
   b. a 561 mL sample of vinegar solution containing 0.71 mol of CH_3COOH

2. What is the **molarity** (concentration in mol L^{-1}) of the solutes in the following solutions?
   a. 16.2 g of $CuSO_4$ dissolved in 1.94 L of solution
   b. 139 mg of NaCl dissolved in 0.494 L of solution
   c. 11.77 L of solution containing 129 g of iron(III) sulfate-9-water ($Fe_2(SO_4)_3.9H_2O$)

3. **Calculate** the concentration in **g L^{-1}** for the solute in each of following solutions.
   a. a 375 mL soda water solution containing 1.90 g of dissolved carbon dioxide (CO_2)
   b. a 375 mL soft drink containing 112 g of dissolved sucrose ($C_{12}H_{22}O_{11}$).

4. What **mass** of solute is contained in each of the following solutions?
   a. 15 L of 1.5 mol L^{-1} $Ca(NO_3)_2(aq)$
   b. 7.50 x 10^2 mL of 4.59 mol L^{-1} $Na_2CO_3(aq)$

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.



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 Na_2CO_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^{-1} sugar ($C_{12}H_{22}O_{11}$). 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.

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^3. This space would contain around 22000 L of air (1 m^3 = 1000L) consisting of around:

- 20 kg of $N_2(g)$
- 6.0 kg of $O_2(g)$
- 0.340 kg of Ar(g)
- 0.013 kg of $CO_2(g)$.

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 N_2, 4.97 g of O_2, 0.275 g of Ar and 0.0102 g of CO_2 gas.
   a. **Determine** the concentration of oxygen (O_2) and carbon dioxide (CO_2) in air in **g L^{-1}**.
   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 $Ca(ClO)_2$. 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 $Ca(ClO)_2$ concentration of 5.3 x 10^{-6} mol L^{-1}. What **mass** of $Ca(ClO)_2(s)$ 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 x 10^{-3} ppm. Given the world's oceans have a mass of 1.4 x 10^{21} kg determine the total **mass of gold** dissolved in the Earth's oceans.

FIGURE 24 These one ounce **gold ingots** (one troy ounce ≈ 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!

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^{-1} HCl
   b. 1.4 mol L^{-1} $Ca(NO_3)_2$
   c. 0.75 mol L^{-1} $Cr_2(SO_4)_3$

11. A saturated solution of aluminium sulfate contains 22.5 g of $Al_2(SO_4)_3$ dissolved in a litre of solution. Determine the **concentration** in mol L^{-1} 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.
    a. What is meant by **potable** water?
    b. **Suggest** why an increasing amount of water in WA is being sourced from the ocean.
    c. 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?
    d. 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.
    a. 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 Na^+ from H_2O molecules? **Explain** in terms of chemical bonding.
    b. 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, F^-(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.
    a. What **mass** of fluoride ion, **F^-(aq)** must be present in 45000 L of tap water ($\approx$ volume of a backyard swimming pool) to give it a fluoride, F^-(aq) concentration of 1.0 ppm? You may assume 1.0 L of tap water has a mass of 1.00 kg.
    b. Determine the **mass** of **sodium fluoride**, NaF that must be added to the 45 000 L of tap water in part (a).
    c. An NaF(aq) solution of concentration 2.0 ppm (4.8×10^{-5} mol L^{-1}) has a F^-(aq) ion concentration of around 0.90 ppm (4.8×10^{-5} mol L^{-1}). As you would expect, the molar concentrations of NaF(aq) and F^-(aq) in this solution are the same, ie both are 4.8×10^{-5} mol L^{-1}. However, the concentration in ppm of NaF(aq) and F^-(aq) are not the same, ie 2.0 ppm and 0.90 ppm respectively. **Account** for the difference.
    d. An alternative method of fluoridation involves adding a saturated solution of sodium fluoride (NaF) to drinking water. What is the **concentration** of **fluoride ions** (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 9.79×10^8 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.
    a. **Why** is chlorine added to drinking water as described?
    b. **What** total **mass** of chlorine, Cl_2 would need to be added daily to produce an initial 1.0 ppm Cl_2 concentration? Remember 1.0 L of water has a mass of 1.0 kg.
    c. In order to maintain a minimum 1 ppm chlorine level throughout the reticulated system more Cl_2 than calculated above needs to be added. **Suggest** why.

CHAPTER 17 | ACIDS AND BASES

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.

The distinctive properties of acids make them useful food additives. Vinegar, for example, contains the active ingredient **ethanoic acid** (CH_3COOH). 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 ($H_3C_6H_5O_7$), 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_3PO_4) for an enhanced tangy taste.

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 + $H_2(g)$

Example: Some hydrochloric acid solution is poured onto a strip of nickel metal.

$2HCl(aq) + Ni(s) \rightarrow NiCl_2(aq) + H_2(g)$

$2H^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + H_2(g)$

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, $MgCl_2$, $AlCl_3$

HNO_3..... $NaNO_3$, $AgNO_3$, $Fe(NO_3)_3$

H_2SO_4..... $KHSO_4$, $BaSO_4$, $Al_2(SO_4)_3$

The formula for the salts of organic acids, such as ethanoic acid (CH_3COOH) can be written with the positive metal ion at the end or the start of the formula.

eg sodium ethanoate:

NaCH_3COO or CH_3COO**Na**

- **Acidic** solutions react with **metal hydroxides** producing a salt and water.

ACID + METAL HYDROXIDE → SALT + H_2O

Example: A solution of nitric acid is poured onto some calcium hydroxide solid.

$2HNO_3(aq) + Ca(OH)_2(s) \rightarrow \quad)_2(aq) + 2H_2O(l)$

$2H^+(aq) + Ca(OH)_2(s) \rightarrow \quad (aq) + 2H_2O(l)$

- **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_2O

Example: A sulfuric acid solution is added to solid copper(II) oxide.

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

$2H^+(aq) + CuO(s) \rightarrow Cu^{2+}(aq) + H_2O(l)$

- **Acidic** solutions react with **carbonate compounds** producing a salt, water and carbon dioxide gas.

ACID + CARBONATE → SALT + H_2O **+** $CO_2(g)$

Example: Hydrochloric acid solution is added to solid nickel carbonate.

$2HCl(aq) + NiCO_3(s) \rightarrow NiCl_2(aq) + H_2O(l) + CO_2(g)$

$2H^+(aq) + NiCO_3(s) \rightarrow Ni^{2+}(aq) + H_2O(l) + CO_2(g)$

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_2CO_3) and a salt. Carbonic acid then rapidly **decomposes** forming **H_2O** and **CO_2**, ie $H_2CO_3 = H_2O + CO_2$. Thus carbonic acid does not appear in the final overall equation.

- **Acidic** solutions react with **hydrogencarbonate compounds** producing a salt, water and carbon dioxide gas.

ACID + HYDROGENCARBONATE → SALT + H_2O **+** $CO_2(g)$

Example: Hydrochloric acid solution is added to solid nickel hydrogencarbonate.

$2HCl(aq) + Ni(HCO_3)_2(s) \rightarrow NiCl_2(aq) + 2H_2O(l) + 2CO_2(g)$

$2H^+(aq) + Ni(HCO_3)_2(s) \rightarrow Ni^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$

- **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_2O **+** $SO_2(g)$

Example: Hydrochloric acid solution and sodium sulfite powder are mixed.

$2HCl(aq) + Na_2SO_3(s) \rightarrow 2NaCl(aq) + H_2O(l) + SO_2(g)$

$2H^+(aq) + Na_2SO_3(s) \rightarrow 2Na^+(aq) + H_2O(l) + SO_2(g)$

Sulfur dioxide is a poisonous colourless gas with a pungent choking odour.

- **Basic** solutions react with **ammonium salts** producing a salt, water and ammonia gas.

BASE + AMMONIUM SALT → SALT + H_2O + $NH_3(g)$

Example: A potassium hydroxide solution is mixed with an ammonium chloride solution.

$$KOH(aq) + NH_4Cl(aq) \rightarrow KCl(aq) + H_2O(l) + NH_3(g)$$

$$OH^-(aq) + NH_4^+(aq) \rightarrow H_2O(l) + NH_3(g)$$

Ammonia is a toxic colourless gas that has a characteristic irritating pungent odour.

- **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)**

BASE + NON-METAL OXIDE → SALT + H_2O

Example: Sulfur dioxide gas is bubbled through a potassium hydroxide solution.

$$2KOH(aq) + SO_2(g) \rightarrow K_2SO_3(aq) + H_2O(l)$$

$$2OH^-(aq) + SO_2(g) \rightarrow SO_3^{2-}(aq) + H_2O(l)$$

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.

initially $SO_2(g) + H_2O(l) \rightleftarrows SO_3(aq)$

then $H_2SO_3(aq) + 2OH^-(aq) \rightarrow 2H_2O(l) + SO_3^{2-}(aq)$

overall $SO_2(g) + 2OH^-(aq) \rightarrow H_2O(l) + SO_3^{2-}(aq)$

The margin notes at right show what acid(s) to expect from some common non-metal oxides.

Non-metal oxide	**Acid** formed in water
CO_2 ……………… carbon dioxide	**H_2CO_3** carbonic acid
SO_2 ……………… sulfur dioxide	**H_2SO_3** sulfurous acid
SO_3 ……………… sulfur trioxide	**H_2SO_4** sulfuric acid
NO_2 ……………… nitrogen dioxide	**HNO_3 and HNO_2** nitric and nitrous acid
P_4O_{10} ……………… phosphorous (v) oxide	**H_3PO_4** phosphoric acid

eBook⁺ Quiz 17.1.

Complete Set 29.

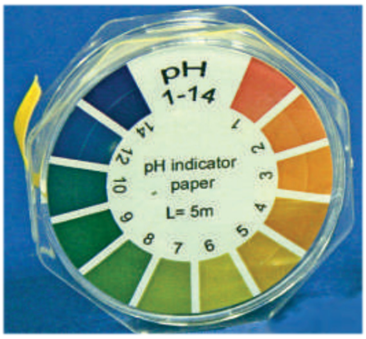
Set 29 Acid-base properties and reactions

1. 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**
A	This solution was tested with blue litmus. The litmus turned red.
B	This solution did not change the colour of blue or red litmus.
C	Rapid fizzing occurred when a strip of magnesium was added. The colourless gas formed was found to be hydrogen gas.
D	The solution was found to be a good electrical conductor and didn't change the colour of a piece of blue litmus.
E	The solution has a pH of 1 (see p156) and showed no reaction with a strip of copper metal.
F	This solution showed no reaction with powdered sodium carbonate. A piece of red litmus added to a fresh sample of the solution remained red.
G	When solid ammonium chloride was added to this solution it produced a strong pungent odour.
H	Universal indicator paper turns green in this solution. (See Fig 1.)

FIGURE 1 **Universal indicator** is a mixture of several indicators that produce a range of colours which gradually change with a solutions 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.



2. 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. $H_2SO_4(aq)$ and $MgCO_3(s)$
   b. $HCl(aq)$ and $Ca(s)$
   c. $HNO_3(aq)$ and $Na_2CO_3(s)$
   d. $H_2SO_4(aq)$ and $Zn(HCO_3)_2(s)$
   e. $CH_3COOH(aq)$ and $Mg(OH)_2(s)$
   f. $H_2SO_4(aq)$ and $Zn(s)$
   g. $HCl(aq)$ and $CaO(s)$
   h. $NH_4Cl(aq)$ and $NaOH(aq)$
   i. $SO_3(g)$ and $Ba(OH)_2(aq)$ **(E)**
   j. $CO_2(g)$ and $NaOH(aq)$ **(E)**

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. $HNO_3(aq)$ and $Al_2(CO_3)_3(s)$
   b. $HCl(aq)$ and $Fe(OH)_3(s)$
   c. $HNO_3(aq)$ and $BaO(s)$
   d. $NH_4Cl(aq)$ and $KOH(aq)$
   e. $HCl(aq)$ and $Fe(s)$
   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)**

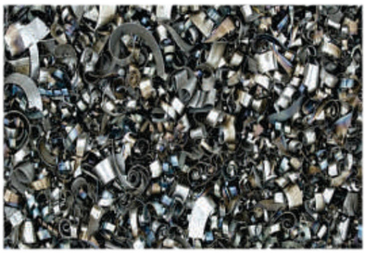


FIGURE 2 **Turnings** are small metal shavings. They have a high surface area that promotes a more rapid reaction rate.

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 $CuCO_3$ is added to a HNO_3 solution [ie $H^+(aq)$ and $NO_3^-(aq)$].
   b. Solid copper(II) oxide is added to a nitric acid solution.
   c. Powdered $Mg(OH)_2$ is added to a concentrated NaOH solution.
   d. Granulated Zn is added to a 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. SO_2 gas is bubbled through a KOH solution. **(E)**
   m. A Na_2SO_3 solution is added to a HCl solution. **(E)**

***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.

5. William and Natalie carried out several chemical tests on the following substances:

   $CuO(s)$ **$Ca(OH)_2(s)$** **$Cr_2(CO_3)_3(s)$** **$NH_4Cl(s)$** **$MgCO_3(s)$**

   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.

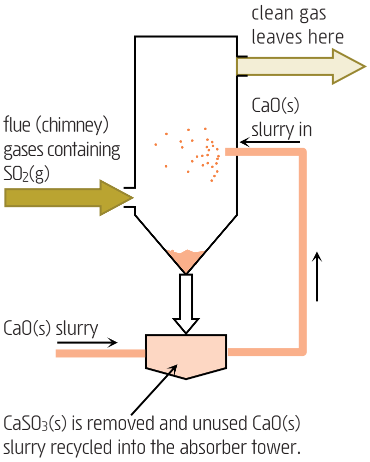
6. Craig and Nicole are presented with several groups of unlabelled substances. While they know what substances are in each group they aren't told which is which. Their objective is to identify each substance in the group. To do this Craig and Nicole must use a **chemical test** using any **acid** or **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.
   a. Zn(s) and Ag(s)
   b. Mg(s) and Fe(s)
   c. $CuCO_3(s)$ and $Cu(OH)_2(s)$
   d. 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 SO_2, SO_3 and 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 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, $CaCO_3$ or CaO producing a solid precipitate. This method removes 95%-98% of the SO_2 pollutants originally present in the flue gases of coal fired power stations. **(E)**

   a. Write an equation(s) to show how $SO_2(g)$ reacts with CaO in a 'wet scrubber'.
   b. How would acid rain containing sulfur trioxide affect metal structures like those made of iron? Explain with the aid of an equation(s).
   c. 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 NO_2, can cause the deterioration of limestone and marble structures. (Remember, $CaCO_3$ 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 $SO_2(g)$. The slurry is a mixture of water and fine particles of solid CaO. The small CaO particle size and fine spray ensure good contact between $SO_2(g)$ and CaO(s). This helps to promote a fast reaction rate where $CaSO_3(s)$ is the product.



17.2 Ionisation of water and pH

Water has a covalent molecular structure consisting of molecules of formula H_2O. Despite this molecular structure, some H_2O molecules (an extremely small number) change into **$H^+(aq)$** and **$OH^-(aq)$** ions. These ions are produced by a reversible reaction known as **ionisation**. (See Fig 5.)

$H_2O(l) \rightleftarrows \quad (aq) + OH^-(aq)$ **or** $2H_2O(l) \rightleftarrows \quad O^+(aq) + OH^-(aq)$

As can be seen, the ionisation process produces equal numbers of hydrogen ions and hydroxide ions. Consequently, in **pure water**, $H^+(aq)$ and $OH^-(aq)$ ions have the same concentration. For this reason pure water is said to be **neutral**.

Double arrows show this ionisation process is readily reversible. Rapid recombination of hydrogen ions with hydroxide ions keeps their concentration **very low**. In pure water both the $H^+(aq)$ and $OH^-(aq)$ ions have the same extremely low concentration of 1×10^{-7} mol L^{-1}. This hydrogen ion concentration corresponds to a pH of 7. (See Fig 6.)

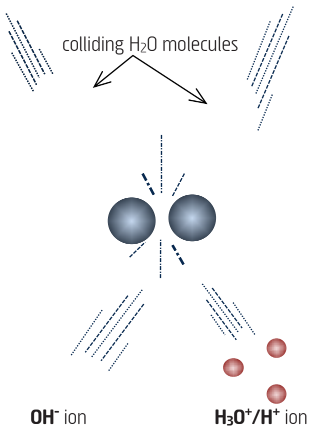


FIGURE 5 At 298K approximately one in 550 million water molecules (an extremely small percentage!!) are present as hydrogen ions (represented as H^+ or H_3O^+) and hydroxide ions (OH^-). The illustration (above) shows how these ions might form.

The aqueous **hydrogen ion**, also known as a **proton** or **hydronium ion** can be represented as **H^+**(aq) or **H_3O^+**(aq). The latter form shows that each hydrogen ion (H^+) is strongly attached to one water molecule, ie **$H^+ + H_2O = H_3O^+$**.

FIGURE 6 The pH of a solution is a measure of its hydrogen ion concentration and thus its acid-base characteristics. High hydrogen ion concentration, ie an acidic solution, corresponds to a low pH. Basic solutions have a high pH. Pure water is neutral and has a pH of 7.

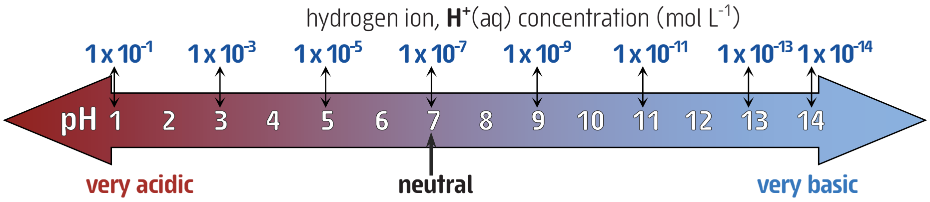


FIGURE 7 **Acid-base indicators** are pH sensitive dyes that change colour with solution acidity. Many are extracted from plants. **Litmus** is an indicator extracted from lichen. It has a **blue** colour in basic solutions and a **red** colour in acidic solutions. (See Fig 6.)

The **pH indicator paper** (at right) is impregnated with a mixture of indicators. Consequently, it has a range of colours that change with a solutions pH.

Dissolving an acid or base in water will change its pH. Adding an acid raises the concentration of $H^+(aq)$ to above 1×10^{-7} mol L^{-1} and hence lowers pH to below 7. Adding a base to water raises the $OH^-(aq)$ concentration and causes the $H^+(aq)$ concentration to fall to below 1×10^{-7} mol L^{-1}. This results in the pH rising to above 7.

eBook$^+$ Quiz 17.2. **Attempt Set 30 # 1.**

17.3 The Arrhenius theory of acids and bases

The role of hydrogen ions and hydroxide ions in acid-base behaviour was first recognised by the Swedish chemist, **Svante Arrhenius** (1859-1927). In 1884 he described a theory of acid-base behaviour centred on the ability of certain substances that contain H or OH to produce hydrogen ions, **$H^+(aq)$** or hydroxide ions, **$OH^-(aq)$** when dissolved in water. The **Arrhenius** theory states:

- An **acid** is a substance that will **ionise** (see 16.3) in solution producing **$H^+(aq)$** ions, eg:

  $HNO_3(aq) \rightarrow$ **H^+**$(aq) + NO_3^-(aq)$ .... ①

- A **base** is a substance that will **dissociate** (see 16.3) in solution releasing **$OH^-(aq)$** ions, eg:

  $NaOH(s) \rightarrow$ **OH^-**$(aq) + Na^+(aq)$ .... ②

Arrhenius's theory gives a good account of the acid-base behaviour of many acids and ionic hydroxides. However it is not able to explain or predict the acid-base behaviour of many other compounds, for example, why salts like sodium carbonate and potassium phosphate (which do not contain OH) are basic in nature and not neutral. The **Brønsted-Lowry** theory is a more comprehensive model of acid-base behaviour which first appeared in 1923. This theory gives a broader and more satisfactory account of acid-base behaviour. The theory was independently developed by the Danish chemist, Johannes Brønsted (1879-1947) and the English chemist, Thomas Lowry (1874-1936), hence the name Brønsted-Lowry theory.

eBook$^+$ Quiz 17.3. **Attempt Set 30 # 2.**

Ionisation and **dissociation**:
Acids, eg HCl and HNO_3 have a **covalent molecular** structure and so don't actually contain hydrogen ions. However, when dissolved in water they produce ions in a reaction called **ionisation**, see ① in the formation and release of hydrogen ions.

The **bases** referred to by Arrhenius are all **ionic** hydroxide compounds, eg NaOH, KOH, $Ba(OH)_2$ and so on. These compounds contain metal ions and **hydroxide ions**. When dissolved in water these ions are released into solution, as shown by reaction ② is called **dissociation**.

(E) The **Brønsted-Lowry** theory is a more comprehensive theory of acid-base behaviour that will be explored in Unit 3. It is able to account for the basic properties of many species like NH_3, CO_3^{2-} and S^{2-} that do not contain OH. It shows how these produce hydroxide ions, OH^- in solution by **reacting** with water in a process called **hydrolysis**, eg:

$CO_3^{2-}(aq) + \mathbf{H_2O}(l) \rightleftarrows \quad ^-(aq) + HCO_3^-(aq)$

$NH_3(aq) + \mathbf{H_2O}(l) \rightleftarrows \mathbf{OH^-}(aq) + NH_4^+(aq)$

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.)

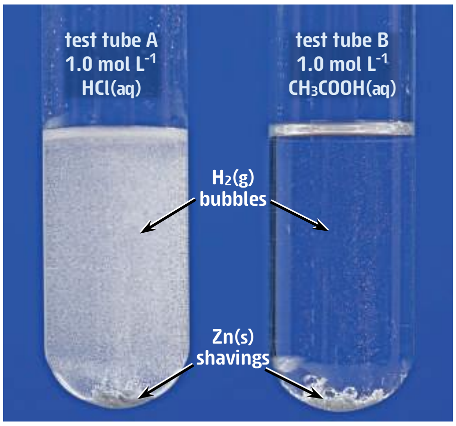
FIGURE 8 In each of these test tubes small **zinc** shavings are reacting with hydrogen ions from two different 1.0 mol L^{-1} acid solutions.

$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

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 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 (→

partial ionisation, ie remaining mostly in the form of unionised molecules. Double arrows (⇄

always produce a higher $H^{+}(aq)$ concentration due to its more complete ionisation and hence show stronger acidic properties than a weak acid. (See Example 1 and Table 1.)

TABLE 1 Strength of some acids and bases

Strong acids	
hydrochloric acid	**HCl**
sulfuric acid.............	**H_2SO_4**
nitric acid	**HNO_3**
Weak acids	
sulfurous acid...........	**H_2SO_3**
phosphoric acid.........	**H_3PO_4**
hydrofluoric acid.......	**HF**
ethanoic acid	**CH_3COOH**
carbonic acid	**H_2CO_3**
ammonium salts	eg **NH_4Cl, NH_4NO_3**
Strong bases	
oxides of group 1	eg **Li_2O, Na_2O, K_2O**
and group 2 metals...	eg **MgO, CaO, BaO**
hydroxides of group 1	eg **LiOH, NaOH, KOH**
and group 2 metals.....	eg **$Mg(OH)_2$, $Ba(OH)_2$**
Weak bases	
metal phosphates	eg **Na_3PO_4, K_3PO_4**
metal carbonates	eg **Na_2CO_3, K_2CO_3**
metal hydrogen-	eg **$NaHCO_3$, $KHCO_3$**
carbonates	**$Ca(HCO_3)_2$**
ammonia.................	ie **NH_3 or NH_4OH**

EXAMPLE 1 Write ionisation equations for the strong acid HNO_3 and the weak acid CH_3COOH (ethanoic acid). Describe the significance of acid strength on the ionisation of these two acids.

$HNO_3(aq) \rightarrow H^{+}(aq) + NO_3^{-}(aq)$ HNO_3 is a strong acid so use a **single** arrow.	HNO_3 is a strong acid (Table 1) so it undergoes **complete ionisation** (single arrow) to produce $H^{+}(aq)$ and $NO_3^{-}(aq)$ ions. Very few (if any) HNO_3 molecules will remain in the solution.
$CH_3COOH(aq) \rightleftarrows H^{+}(aq) + CH_3COO^{-}(aq)$ CH_3COOH is a weak acid so use a **double** arrow.	CH_3COOH is a weak acid (Table 1) so it only **partially ionises** in water (double arrow). It produces some $H^{+}(aq)$ and $CH_3COO^{-}(aq)$ ions but remains mostly in the form of CH_3COOH molecules.

eBook⁺ Quiz 17.4. 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 CO_2 and SO_3 combine with water to form acids. (See border note.) The resulting acids then ionise to form hydrogen ions and an acidic solution.

$CO_2(g) + H_2O(l) \rightleftarrows CO_3(aq)$ *then* $CO_3(aq) \rightleftarrows (aq) + HCO_3^{-}(aq)$

$SO_3(g) + H_2O(l) \rightleftarrows SO_4(aq)$ *then* $SO_4(aq) \rightarrow H^{+}(aq) + HSO_4^{-}(aq)$

Many **metallic oxides** like Na_2O or 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 **O^{2}** . The oxide ion then rapidly combines with water to produce hydroxide ions **OH^{-}**
metal oxide converts into a basic solution of the corresponding **metal hydroxide**.

sodium oxide dissolves .... $Na_2O(s) \rightarrow (aq) + O^{2-}(aq)$

oxide ion reacts with water ..... $O^{2-}(aq) + H_2O(l) \rightarrow (aq)$

overall .... $Na_2O(s) + H_2O(l) \rightarrow (aq) + 2OH^{-}(aq)$

Even many **insoluble** metallic oxides, eg CaO and MgO, will absorb water to produce an hydroxide as shown here.

$CaO(s) + H_2O(l) \rightarrow (s)$ *or* $MgO(s) + H_2O(l) \rightarrow (s)$

Non-metal oxide	**Acid** formed in water
CO_2 .... carbon dioxide	**H_2CO_3** carbonic acid
SO_2 .... sulfur dioxide	**H_2SO_3** sulfurous acid
SO_3 .... sulfur trioxide	**H_2SO_4** sulfuric acid
NO_2 .... nitrogen dioxide	**HNO_3 and HNO_2** nitric and nitrous acid
P_4O_{10} .... phosphorous (v) oxide	**H_3PO_4** phosphoric acid

eBook⁺ Quiz 17.5. 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).

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)					

   a. Estimate the pH range of each solution and complete the table above. (See Fig 9.)
   b. From these solutions choose the one(s) that fit the following descriptions.
      i. The most acidic solution.
      ii. Any neutral solution(s).
      iii. Any solution(s) that will turn blue litmus red.
      iv. The solution with the highest hydrogen ion concentration.
      v. Any solution(s) with the same hydrogen ion and hydroxide ion concentration.
      vi. 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.)

   a. HCl(g)   b. HF(g)   c. NaOH(s)   d. $CH_3COOH(aq)$ e. $Ba(OH)_2(s)$

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 mol L^{-} (aq), a concentrated acid has a high ratio of acid to solution, eg 6.0 mol L^{-} (aq).

Strong and **weak** refer to the degree to which an acid or base produces ions when dissolved in water. A strong acid, eg HCl(aq), completely separates into ions when in solution. Weak acids, eg $H_2CO_3(aq)$, only partially ionise into ions and are mostly present as molecules when dissolved in water.

3. Give an **answer** and a brief **explanation** for each of the following questions. (See border note.)

   a. Which of these solutions has the highest hydrogen ion concentration: 1.0 mol L^{-1} $HNO_3(aq)$ or 1.0 mol L^{-1} $CH_3COOH(aq)$?
   b. Which solution is most basic: 1.0 mol L^{-1} $NH_3(aq)$ or 1.0 mol L^{-1} NaOH(aq) ?
   c. Which solution is most acidic: 1.0 mol L^{-1} HCl(aq) or 0.10 mol L^{-1} HCl(aq) ?
   d. Which solution has the lowest pH: 1.0 mol L^{-1} HCl(aq) or 1.0 mol L^{-1} $H_2SO_4(aq)$?
   e. Which solution gives the most vigorous reaction with calcium carbonate granules: 1.0 mol L^{-1} $H_3PO_4(aq)$ or 1.0 mol L^{-1} $HNO_3(aq)$?

ionises
blue
red
hydroxide ions
hydrogen ions
Na_2CO_3
NaOH
H_2CO_3
HNO_3
reactive metals
dissociate
greater
pungent
sour
fully ionise

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 HCl (j) ____________ producing (k) ____________ hydrogen ion concentrations than do weak acids like CH_3COOH 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 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)**

   a. $SO_3(g)$ b. $NO_2(g)$ c. $Na_2O(s)$ d. BaO(s)   e. $P_4O_{10}(s)$

6. The two oxides K_2O and 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.

   a. 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 (CH_3COOH).
      i. Write a **Arrhenius** equation showing how ethanoic acid produces hydrogen ions in an aqueous vinegar solution.
      ii. What is the effect of ethanoic acid on the **pH** of the vinegar? **Explain**.
      iii. Household vinegar contains around 6% ethanoic acid and is quite safe to consume. This is equivalent to an approximately 1 mol L^{-1} ethanoic acid solution. A 1 mol L^{-1} sulfuric acid solution, however, would not be safe to use as a food acid. **Account** for this difference.

A **vinegar** solution contains the active ingredient **ethanoic acid** (≈ 6% by mass). Such a solution can be safely used as a food acid or around the home to remove scale deposit, such as $MgCO_3$ or $CaCO_3$ from inside a kettle.

   b. Household ammonia based cleaners can contain as much as 10% ammonia by mass. This is equivalent to ≈ 6 mol L^{-1} $NH_3(aq)$. These solutions are excellent floor cleaners as they have the ability to dissolve greasy substances. The active ingredient in these cleaners is ammonia (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.

   $$NH_3(aq) \; + \; H_2O(l) \; \rightleftarrows \qquad {}^{+}(aq) \; + \; OH^{-}(aq)$$

   A 6 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**.

FIGURE 10 Sodium hydroxide, 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 NaOH is a white solid that is very soluble in water. Care should be taken when preparing solutions of 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.

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 (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 $NaHCO_3$)
   drain cleaner (essentially pure NaOH solid)
   spirits of salts (contains concentrated HCl)
   vinegar (contains ≈ 5% CH_3COOH)

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.

   a. Agricultural lime can be added to acidic soils to adjust its pH. The major component of agricultural lime is $CaCO_3(s)$ with varying amounts of $CaO(s)$, $MgCO_3(s)$ and $MgO(s)$ also present. How do these substances react with acid [$H^+(aq)$] present in the soil and how does this alter soil pH? Use suitable equations to support your answer.
   b. In terms of neutralisation, explain how using the nitrogen based **fertiliser** ammonium nitrate (NH_4NO_3) would affect soils with a high pH? Explain with the aid of an equation. (See reactions of ammonium salts p153.)

Acids like HCl and HNO_3 are **monoprotic**. This means one mole of acid can produce one mole of H^+ ions when neutralised with a strong base like NaOH.
Diprotic acids like H_2SO_4 produce two H^+ ions for each molecule of acid. Phosphoric acid (H_3PO_4) is a **triprotic** acid that can ultimately produce three moles of H^+ ions when reacting with a strong base like NaOH.

10. Acids like H_2SO_4 and H_3PO_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 $H_2PO_4^-$ from H_3PO_4. The second equation should show the formation of HPO_4^{2-} from $H_2PO_4^-$ and so on. Use double or single arrows for each equation as appropriate. **(E)**

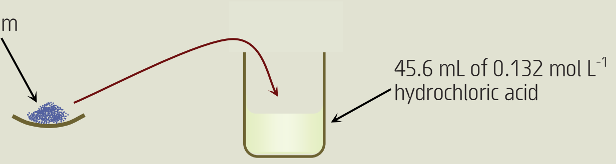
CHAPTER 18 | MORE ON STOICHIOMETRY

Remember, when using **$n = cV$**:
c is concentration (mol L^{-1})
n is moles of solute (mol)
V is the solution volume (L).

18.1 Stoichiometry involving solutions

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.)

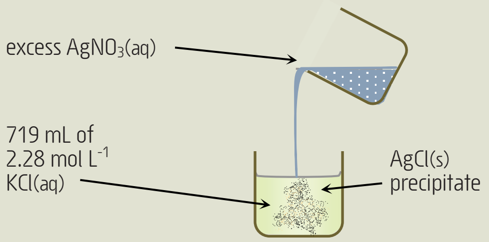
EXAMPLE 1 What mass of aluminium by 45.6 mL of 0.132 mol L^{-1} hydrochloric acid?



$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$	Write an equation for the change described.
$n(HCl) = c\,V = 0.132 \times 45.6 \times 10^{-3} = 6.02 \times 10^{-3}$ mol	Use the concentration equation to find the n(HCl). Volume must be in L, ie 45.6 mL = 45.6×10^{-3} L.
$n(Al) = \frac{2}{6} \times n(HCl) = \frac{2}{6} \times 6.02 \times 10^{-3} = 2.01 \times 10^{-3}$ 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.
$m(Al) = n \times M = 2.01 \times 10^{-3} \times 26.98 = 5.41 \times 10$ g Al (3SF)	Convert the moles of Al to an equivalent mass.

Attempt Set 31 # 1.

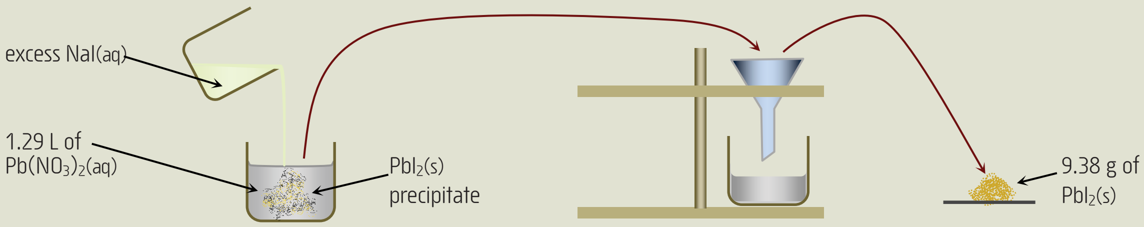
EXAMPLE 2 Determine the mass of silver chloride can be precipitated when excess silver nitrate solution is added to 719 mL of 2.28 mol L^{-1} potassium chloride solution.



$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$	Write an equation for the change described.
$n(KCl) = c\,V = 2.28 \times 0.719 = 1.64$ mol	Volume must be in L, ie 719 mL = 0.719 L.
$n(Cl^-) = n(KCl) = 1.64$ mol	The chloride ion subscript in KCl is 1, thus one mole of KCl contains 1 mole of Cl^-.
$n(AgCl) = n(Cl^-) = 1.64$ mol	Both AgCl and Cl^- have a coefficient of 1 in the equation.
$m(AgCl) = n\,M = 1.64 \times 143.35 = 235$ 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 [$Pb(NO_3)_2(aq)$] involved adding excess sodium iodide solution [NaI(aq)] to 1.29 L of the lead nitrate solution. The resulting precipitate of $PbI_2(s)$ was filtered, washed and dried and found to have a mass of 9.38 g. What was the concentration of lead nitrate



$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$	Write an equation for the change described.
$n(PbI_2) = \frac{m}{M} = \frac{9.38}{461.0} = 2.03 \times 10^{-2}$ mol	Convert the mass of PbI_2 to an equivalent molar amount.
$n(Pb^{2+}) = n(PbI_2) = 2.03 \times 10^{-2}$ mol	Both PbI_2 and Pb^{2+} have a coefficient of 1 in the equation.
$n[Pb(NO_3)_2] = n(Pb^{2+}) = 2.03 \times 10^{-2}$ mol	The lead ion subscript in $Pb(NO_3)_2$ is 1.
$c[Pb(NO_3)_2] = \frac{n}{V} = \frac{2.03 \times 10^{-2}}{1.29} = 1.58 \times 10$ mol L	The moles of $Pb(NO_3)_2$ 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 [Na_2CO_3] to 25.0 mL of sulfuric acid solution SO_4(aq)]. He found the reaction produced 47.2 mL of carbon dioxide gas [CO_2(g)] measured at STP. What was the concentration

$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$	Write an equation for the reaction between sulfuric acid and sodium carbonate.
$n(CO_2) = \frac{V_{(STP)}}{22.71} = \frac{47.2 \times 10^{-3}}{22.71} = 2.08 \times 10^{-3}$ mol	Find the moles of CO_2 using the molar volume of gases relationship, ie $n_{(gas)} = V_{(STP)} \div 22.71$. Gas volume must be in litres (ie 47.2 mL = 47.2×10^{-3} L) measured at STP.
$n(H_2SO_4) = n(CO_2) = 2.08 \times 10^{-3}$ mol	Both H_2SO_4 and CO_2 have a coefficient of 1 in the above equation.
$c(H_2SO_4) = \frac{n}{V} = \frac{2.08 \times 10^{-3}}{25.0 \times 10^{-3}} = 8.31 \times 10$ mol L (3SF)	Use the concentration relationship to determine the concentration of sulfuric acid. Solution volume must be in litres, ie 25.0 mL = 25.0×10^{-3} L.

eBook⁺ Quiz 18.1.

Complete Set 31 and Set 32.

Set 31 Stoichiometry involving solutions

1. What **mass** of magnesium ribbon (**Mg**) will dissolve in 25.5 mL of 6.60 mol L^{-1} HCl(aq)?

2. A chemical investigation involves the precipitation of PbI_2(s) by the reaction of 65.5 mL of 0.750 mol L^{-1} $Pb(NO_3)_2$(aq) with excess sodium iodide solution. What **mass** of **lead iodide** can be expected to form?

3. A tap water sample (Fig 1) is analysed for its chloride ion concentration by adding excess $AgNO_3$(aq) to precipitate the chloride ion as AgCl(s). An analysis of this type used 125 mL of tap water and produced 1.38 g of AgCl(s) precipitate.

   a. Using this information, find the **concentration** of **chloride ions** in the tap water.
   b. Assuming the chloride ions in tap water are due solely to dissolved NaCl, calculate the **sodium chloride** concentration in **mol L^{-1}** and **g L^{-1}** for the tap water sample.

4. In a laboratory exercise Joanne and Verena prepared hydrogen gas by the reaction of zinc with hydrochloric acid. What minimum **volume** of 2.5 mol L^{-1} HCl(aq) should be used if they need to produce at least 1.5 L of H_2(g) measured at STP?

5. The predominant anions in sea water are Cl^-(aq) and SO_4^{2-}(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 $Ba(NO_3)_2$(aq) to 325 mL of sea water causing the precipitation of $BaSO_4$(s). Michelle filtered, washed and dried the $BaSO_4$(s) precipitate and found it had a mass of 2.65 g. To the filtrate Matthew added excess $AgNO_3$(aq) precipitating the chloride ion in the sea water as AgCl(s) and 23.3 g of AgCl(s) was obtained. Using their data, find the **concentration** of **Cl^-**(aq) and **SO_4^{2-}**(aq) in the sea water sample. Express your answer in **mol L^{-1}** and **g L^{-1}.**

6. 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 mol L^{-1} KOH solution to it. She used 15.19 mL of KOH(aq) to completely neutralise the ethanoic acid in her mum's vinegar. Using this information find the **concentration** of **ethanoic acid** (CH_3COOH) in the vinegar sample.

7. Milk of magnesia, a suspension of $Mg(OH)_2$(s) in water, is used to treat indigestion caused by excess stomach acid. (See Fig 2.) One spoonful, equivalent to 880 mg of $Mg(OH)_2$(s) is usually sufficient for this purpose. Assume a person's stomach contained 450 mL of hydrochloric acid [HCl(aq)] with a concentration of 0.075 mol L^{-1}. What is the **concentration** of **HCl** after taking one spoonful of milk of magnesia?

8. What **mass** of **$BaSO_4$**(s) can be expected when 1.12 L of 0.0569 mol L^{-1} $Ba(OH)_2$(aq) is combined with excess K_2SO_4(aq)?

9. Chlorine gas can be produced in the laboratory by the reaction of hydrochloric acid and manganese(IV) oxide (manganese dioxide).

   $MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

   What maximum **volume** of **chlorine gas** can be produced from the reaction of 25 mL of 1.5 mol L^{-1} HCl(aq) with excess MnO_2(s)? Assume STP conditions apply.

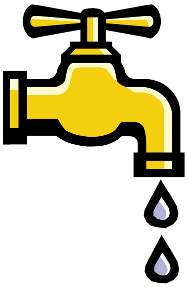


FIGURE 1 In major reticulated Australian water supplies the total dissolved solids (TDS) can range from below 100 mg L^{-1} to more than 750 mg L^{-1}. Water with low TDS can taste flat, while water with high TDS tastes salty and causes scaling in pipes, fittings and household appliances. The 2011 Australian Drinking Water Guidelines provide guidance in the palatability of drinking water according to TDS concentration:

- 0 to 600 mg L^{-1} is considered good.
- 600 to 900 mg L^{-1} is fair.
- 900 to 1200 mg L^{-1} is poor.
- Greater than 1200 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.

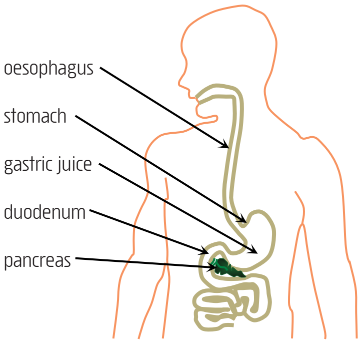


FIGURE 2 **Gastric fluids** in the human stomach are produced by parietal cells in the stomach wall. These fluids contain **hydrochloric acid** with a pH of around 1 to 2.

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.

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^{-1} KOH solution was needed to neutralise this solution.

   a. How can litmus be used to identify the acidic nature of the unknown compound?
   b. 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^- and the salt formula will be KX. Now a balanced equation can be written and the stoichiometric mole ratio found.]
   c. How would your answer to (b) change if the acid was found to be **diprotic**?

Acids like **HCl** and **HNO_3** are **monoprotic**. This means one mole of acid can produce one mole of H^+ ions when neutralised with a strong base like NaOH.
Diprotic acids like **H_2SO_4** produce two H^+ ions for each molecule of acid. Phosphoric acid, **H_3PO_4** is a **triprotic** acid.

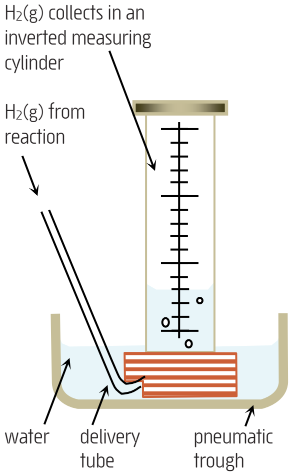
Set 32 Reviewing stoichiometry

1. 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.

   a. Write a balanced **equation** for the reaction between hydrochloric acid and zinc.
   b. Why is the STP volume of hydrogen lower than the actual volume of gas collected?
   c. Determine the **mass** of **zinc** that was present in the 13.5 g sample of brass.
   d. What **hazards** are associated with producing and collecting hydrogen gas?

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.



2. Bubbling **ammonia** gas into a **sulfuric acid** solution produces the fertiliser ammonium sulfate.

   a. Write a **balanced equation** for the reaction of ammonia (NH_3) and pure sulfuric acid, $H_2SO_4(l)$ to produce ammonium sulfate [$(NH_4)_2SO_4$].
   b. What **mass** of H_2SO_4 is needed to form 1.00 tonne of $(NH_4)_2SO_4$ fertiliser?
   c. Determine the **volume** of ammonia gas used if it is measured at STP.

3. 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

   a. Write a **balanced equation** for the reaction between hydrochloric acid and magnesium.
   b. Why is the mass of the flask assembly + HCl solution + Mg after reaction less than before the reaction?
   c. What **mass** of hydrogen was formed in the reaction?
   d. By a suitable calculation, determine the **mass** of **magnesium** that reacted.
   e. 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**.
   f. What **hazards** are posed by the use of 6.0 mol L^{-1} hydrochloric acid and consequently what precautions should the students take in conducting this investigation?

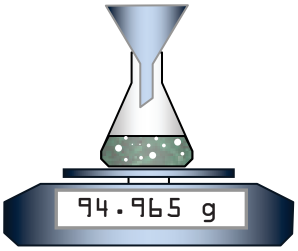


FIGURE 4 **Hydrogen gas** has a very low solubility in aqueous solution. So as the gas H_2 is formed it escapes from the reaction mixture. The loss of mass in the reaction mixture can be assumed to be equal to the mass of H_2 produced.

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_2 can still escape through the opening in the filter funnel.

4. **Ethyne** (commonly known as acetylene) can be produced in the laboratory from the reaction of calcium carbide (CaC_2) with water. A sample of ethyne was produced this way by mixing 2.10 g of CaC_2 with excess water. What **STP volume** of ethyne can be expected from this reaction mixture?

$$CaC_2(s) \quad + \quad 2H_2O(l) \quad \rightarrow \quad C_2H_2(g) \quad + \quad Ca(OH)_2(s)$$

5. **Limestone** is an important building material used for constructing walls for houses and for retaining purposes. It consists of sand grains, essentially $SiO_2(s)$ bound together by the mineral calcium carbonate, $CaCO_3(s)$. A student interested in the percentage of $CaCO_3$ 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 mol L^{-1} hydrochloric acid. The resulting carbon dioxide gas was collected and found to have an STP volume of 549 mL.
   a. Write an **equation** for the reaction between hydrochloric acid and calcium carbonate.
   b. Calculate the **mass** of $CaCO_3$ that was present in the 3.59 g sample of the limestone.
   c. What mass of sand (SiO_2) was present in the limestone sample?

6. **Lime** (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 $CaCO_3$ in the shells producing carbon dioxide gas. The reaction for dissolving the calcium carbonate is shown here.

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

   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 CO_2 gas is bubbled into a potassium hydroxide (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 + KOH solution .... 98.019 g
   mass of conical flask + KOH solution + absorbed $CO_2(g)$ ..... 100.857 g

   a. What **mass** of CO_2 gas was absorbed into the KOH solution and hence what mass of carbon dioxide was liberated from the reaction of the shells with the HCl solution?
   b. Determine the **mass** of $CaCO_3$ in the shell sample.
   c. What is the **percentage** by mass of $CaCO_3$ in this shell sample? **See border note**. **(E)**
   d. 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 % $CaCO_3$ in the shells have been affected? Would this have been a **random** or **systematic** error? **Explain**.

To find the percentage of a component in a mixture:

$$\textbf{\% component} = \frac{\textbf{m(component) x 100}}{\textbf{m(mixture with component)}}$$

7. A Chemistry class investigated the ratio between the **moles of $NaHCO_3$ used** and **moles of Na_2CO_3 produced** when solid sodium hydrogencarbonate, $NaHCO_3(s)$ is decomposed. To do this each group heated a carefully weighed sample of $NaHCO_3(s)$ and weighed the decomposed product, $Na_2CO_3(s)$. (See Fig 5.) A summary of the class results and two incomplete columns are shown.

mass of $NaHCO_3(s)$ decomposed	mass of $Na_2CO_3(s)$ produced	moles of $NaHCO_3$ decomposed	moles of Na_2CO_3 produced
2.56	1.62		
3.80	2.38		
4.11	3.13		
6.34	3.94		
7.07	4.46		

   a. Determine the moles of each compound, $NaHCO_3$ and Na_2CO_3 involved in the reaction for each trial. Enter this into the last two columns of the above table.
   b. Using a suitable scale plot a line graph for n($NaHCO_3$) (**y-axis**) against n(Na_2CO_3) (**x-axis**).
   c. Determine the gradient of your graph.
   d. What does your answer to (c) indicate about the **ratio** of the **coefficients** for $NaHCO_3$ and Na_2CO_3 in the balanced equation for the decomposition of $NaHCO_3$?
   e. One of the data points is clearly in **error**. What type of error is this? **Explain**.

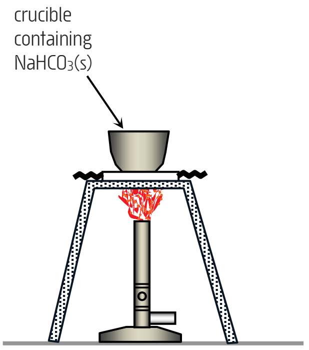


FIGURE 5 As $NaHCO_3(s)$ is heated it decomposes forming $Na_2CO_3(s)$, $H_2O(g)$ and $CO_2(g)$. These gases escape from the crucible leaving only $Na_2CO_3(s)$ in the crucible after heating is complete. Thus the mass of $Na_2CO_3(s)$ formed in the reaction equals the mass of the crucible after heating minus the mass of the empty crucible.

CHAPTER 19 | CHROMATOGRAPHY

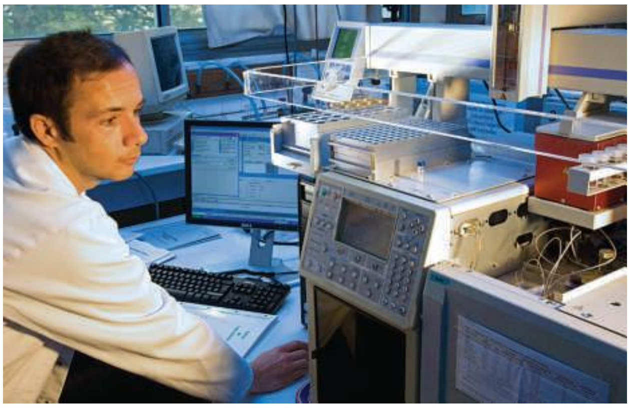


FIGURE 1 This researcher is using **gas chromatography** to analyse samples of wine to determine the aromatic characteristics of different grapes and their suitability for use in winemaking.

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 ($1x10^{-6}$ L) are sufficient. They can also detect picogram amounts ($1x10^{-12}$ 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.

Adsorption is the binding of molecules to a surface, ie molecules become **adsorbed** when they adhere or stick to a surface.

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.

eBook+ Quiz 19.1.

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.

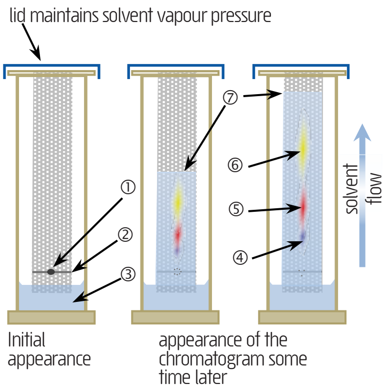


FIGURE 2 **Paper chromatography** for a sample of food dye. A small sample of the dye, ① is placed on a pencil line, ② at the base of a strip of chromatography paper. The chosen solvent, ③ soaks up through the paper chromatography strip by capillary action. Over time the various components of the dye, 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:

$$R_f = \frac{distance\ moved\ by\ solute}{distance\ moved\ by\ solvent}$$

If measured under identical conditions R_f can be used to identify the components in a mixture.

eBook+ Quiz 19.2.

Attempt Set 33 # 1 and 2.

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.)

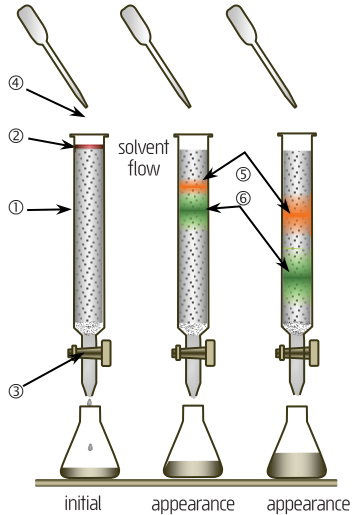
Column chromatography uses a glass tube packed with small beads of silica gel (SiO_2) or alumina (Al_2O_3) as the **stationary phase**. The vertical glass tube is filled with a suitable solvent, the **mobile phase** and a small volume of mixture to be separated is added to the top of the column. Opening 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 C_5-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.



eBook+ Quiz 19.3.

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, Al_2O_3 or silica, 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.

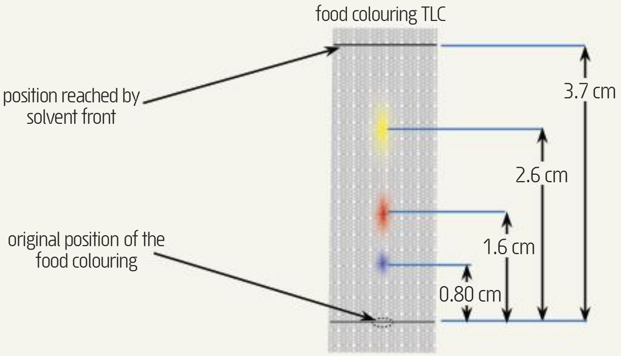
As with paper chromatography the solvent or mobile phase moves up by capillary action through the stationary phase (ie the polar alumina or silica gel layer) carrying the various components of the mixture at different rates depending upon their polarity. This results in the various pure components of 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**, **Rf**. (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.



$$R_f = \frac{distance\ moved\ by\ solute}{distance\ moved\ by\ solvent}$$

$$R_f(yellow\ dye) = \frac{2.6\ cm}{3.7\ cm} = 0.70$$

$$R_f(red\ dye) = \frac{1.6\ cm}{3.7\ cm} = 0.43$$

$$R_f(blue\ dye) = \frac{0.80\ cm}{3.7\ cm} = 0.22$$

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.)

eBook⁺ Quiz 19.4.

Attempt Set 33 # 3 and 4.

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 (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.)

FIGURE 5 Section of a **gas chromatography column** (not to scale) showing the inert 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 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:

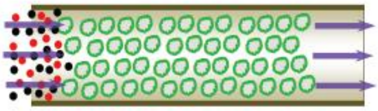
→ direction of carrier gas flow

● SiO_2 particles

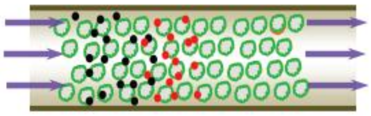
○ liquid stationary phase coating on SiO_2

● vaporised mixture of molecules

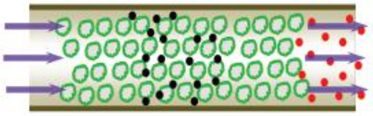
Gas mixture is introduced into the column.



The mixture begins to separate.



The mixture has been separated.



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.

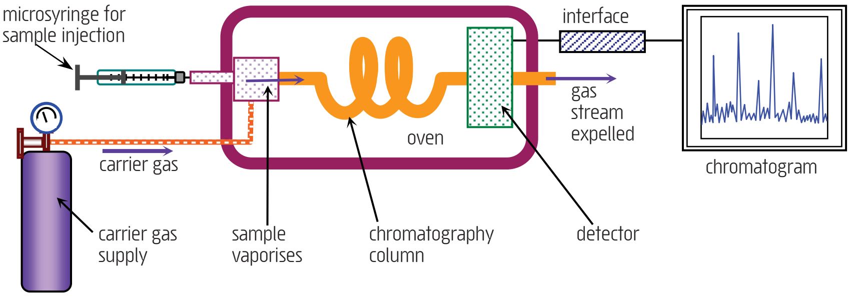
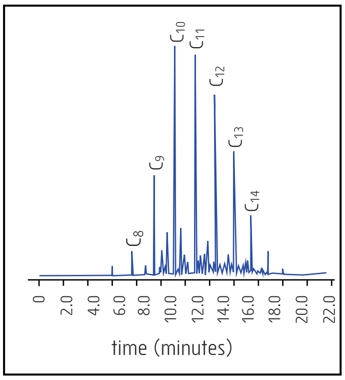


FIGURE 7 Operation of a gas chromatograph (above)
A sample is injected via a silicon rubber seal in the injection port (**A**). The vaporised sample is carried by the carrier gas through the chromatography column (**B**). Various analytes in the sample travel at different rates through the column and 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.



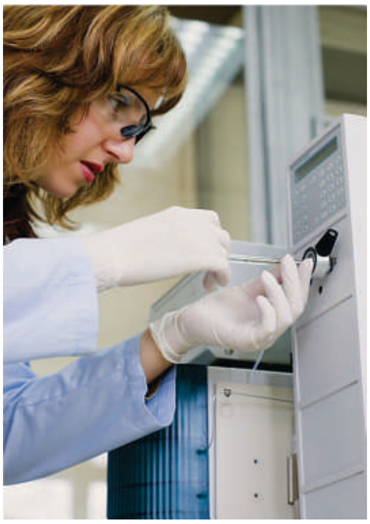
Retention time is an important characteristic of each analyte in the mixture. This primarily depends upon the analyte's **boiling point/volatility**. Low boiling point analytes, ie those with weak intermolecular forces, have a high volatility and tend to remain in the carrier gas. These exit the column 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

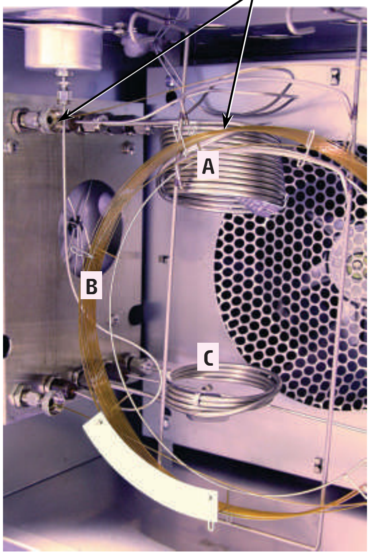


FIGURE 9 Inside a gas chromatograph oven. Several different chromatography columns can be seen. Column **A** and **C** are **packed columns** while column **B** is a **capillary column**. Notice how the columns are coiled so that they conveniently fit inside the oven.

eBook$^+$ Quiz 19.6.

Attempt Set 33 # 5.

Some terms frequently used in instrumental chromatography:

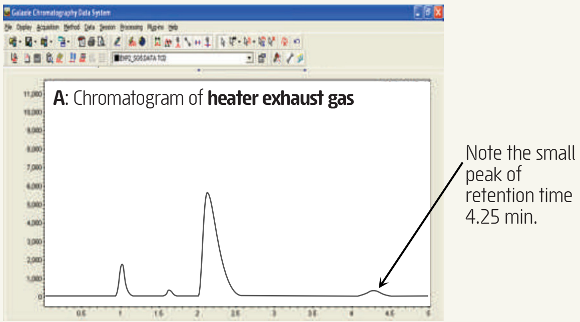
Eluent: The solvent or mobile phase.

Analyte: The substance being analysed or separated.

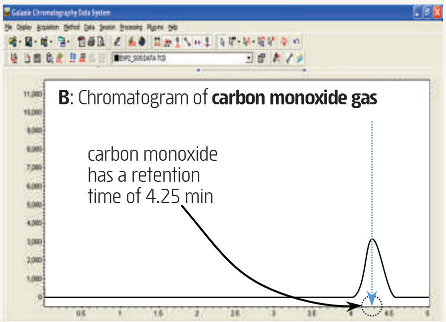
Retention time: The time between injecting a sample and detecting the analyte.

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.



carbon monoxide has a retention time of 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).

eBook+ Quiz 19.7.

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 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 $SiO_2(s)$. 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.

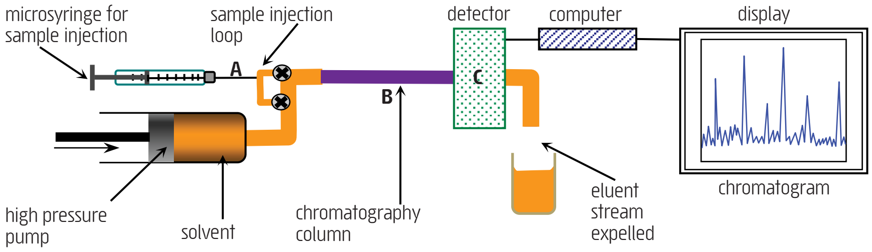


FIGURE 10 Operation of an HPLC
The sample is injected via an injection loop (**A**) into a high pressure column of solvent. The sample passes through the chromatography column (**B**) where the various analytes in the sample travel at different rates through the column and become separated. A detector (**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 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.

eBook+ Quiz 19.8.

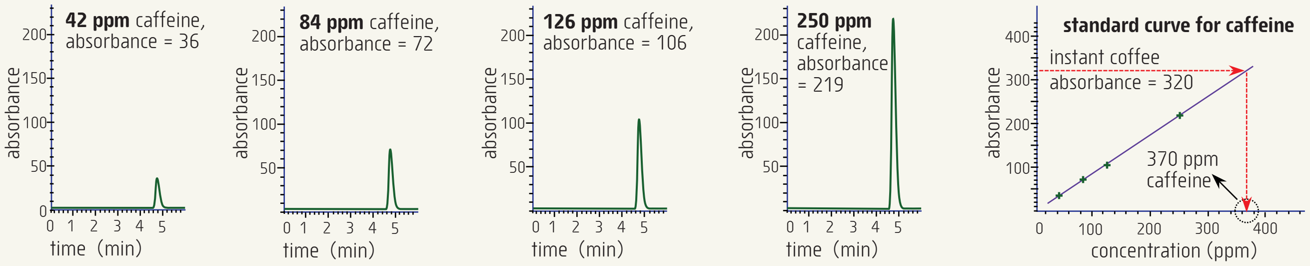
19.9 Concentration analysis from the HPLC chromatograph

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.

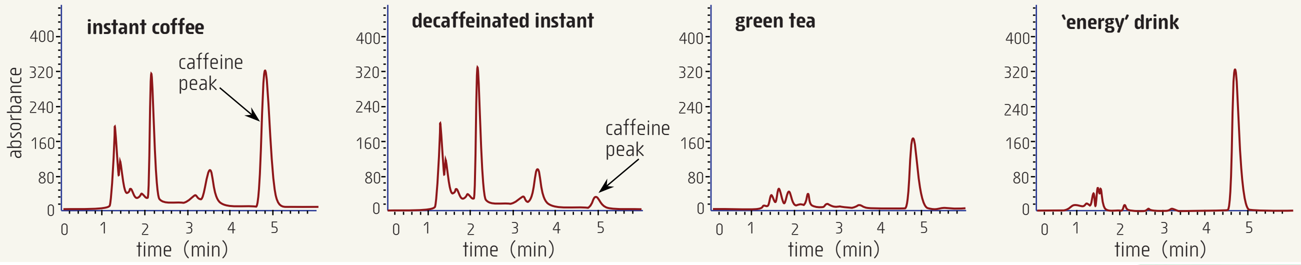
a. Refer to the caffeine chromatograms shown below to produce a standard caffeine curve.
b. Use this curve to determine the caffeine concentration in each of the beverages?

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.



eBook+ Quiz 19.9.

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 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.

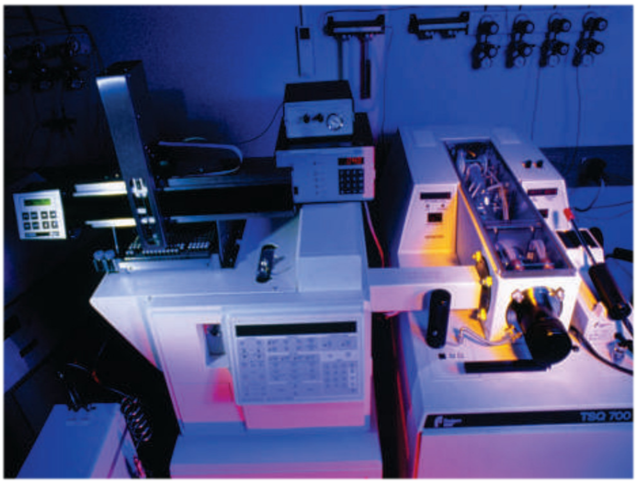


FIGURE 11 **Forensic drug detection apparatus**
A gas chromatograph (centre) connected to a mass spectrometer (right) in a forensic laboratory. This equipment is sensitive enough to detect picogram quantities of illegal drugs in the hair of a suspect, weeks after any drugs were taken.
A sample injection 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.

eBook Quiz 19.10.
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.)

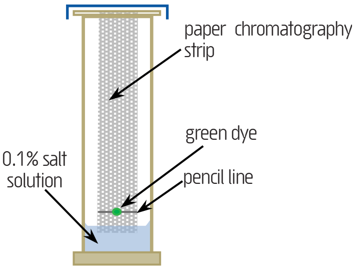
   a. Use the above example to demonstrate your understanding of **stationary phase**, **mobile phase** and **chromatogram** as applied to paper chromatography.

   b. 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?

   c. 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?

   d. 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.

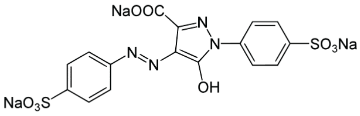


3. The student suspects the **yellow dye** in the green coloured candy (Question 2) may be a dye called yellow #5 (**tartrazine**). (See Fig 13.) This dye causes allergic reactions in some people and so its presence is usually named as an ingredient in products that contain it.

   a. Briefly **describe** how the student can use **TLC** to determine whether the yellow dye in the green coloured candy is indeed tartrazine?

   b. **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.

FIGURE 13 The molecular structure of the food dye **tartrazine** or **yellow #5** (E102).



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.)

   a. Refer to her results (Fig 14) then describe and **compare** the **dye** composition of the three food colourings.

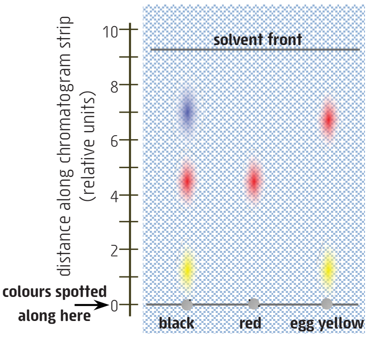
   b. Determine the **retardation factor**, R_f of each of the different dyes.

   c. 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.

   d. 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**.

   e. 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**.



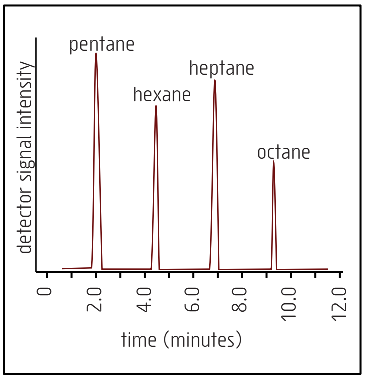
5. The **GC** chromatogram in Fig 15 is for a mixture of four hydrocarbons, C_5H_{12}, C_6H_{14}, C_7H_{16} and C_8H_{18}. The following questions refer to this chromatogram.

   a. Use pentane and heptane to illustrate your understanding of **retention time**.

   b. What **factors** affect the retention time of an analyte in GC and hence **explain** why these hydrocarbons have different retention times.

   c. What is the significance of the **height** and **area** of these peaks?

FIGURE 15 A **GC** chromatogram for a mixture of four hydrocarbons, C_5H_{12}, C_6H_{14}, C_7H_{16} and C_8H_{18}.



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)?

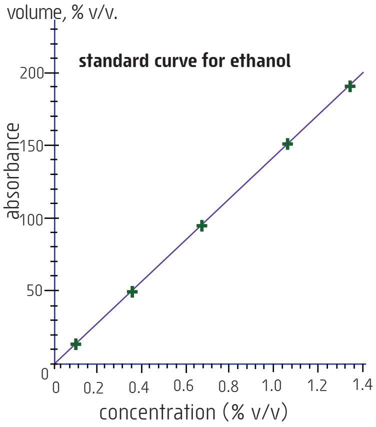
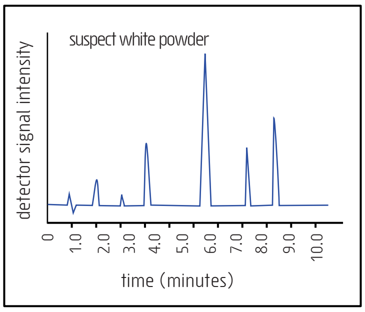
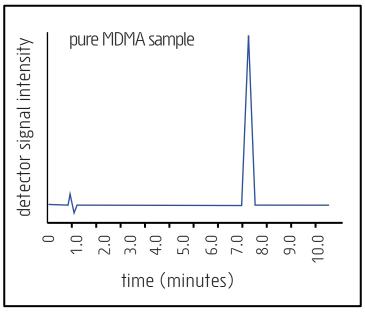


FIGURE 16 Standard curve for ethanol. The alcohol concentration is shown as a percent by volume, % v/v.

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.





   a. On the basis of the HPLC **chromatograms** does the suspected white powder contain the drug MDMA? **Explain**.
   b. Briefly **explain** how the various analytes in the white powder mixture are able to be separated by the process of HPLC.
   c. 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. A technique suitable for analysing **minute** samples (microlitre amounts) of **volatile** fuel residues extracted from the burnt remains at a suspected arson scene.
   b. A technique suitable for separating the components of a plant leaf extract. **Several millilitres** of the extract are available.
   c. A pharmacological analysis of a mixture of **very high molar mass proteins** and **polypeptides** present in a solution of biological fluids.
   d. Analysis of **air** samples for pollutants like sulphur dioxide, nitrogen oxides and various hydrocarbon compounds.
   e. Analysis of the **sugar** content of a fruit juice.

ANSWERS

- **Relative atomic masses** used in all calculations are consistent with data from the periodic table on the back inside cover.
- **Numerical answers** are rounded to the appropriate number of **significant figures** using the rules outlined in Chapter 5. It should be noted that (at the time of writing) the **WACE Chemistry examination** (2016) also requires students to quote their final numerical answers to the **appropriate number of significant figures**.
- Where **partial working** has been evaluated, answers are given with the appropriate number of significant figures, however the **complete number is carried forward** into later parts of a calculation. It is recommended that you also **carry full numerical figures** until completion of a calculation.
- Answers are often accompanied by **extra information** that may be helpful to assist understanding but does not form part of the required answer.

Set 1 Kinetic theory and phases of matter

1. a. physical
   b. particles
   c. random motion
   d. attraction
   e. volume
   f. average kinetic energy
   g. elastically
   h. kinetic energy
   i. temperature
   j. distributed (ie spread)

2. a. The kinetic energy (E_k) of a particle is the energy it has due to its movement and mass, ie E_k(particle) = ½mv^2. At any given temperature the kinetic energies of the particles of a gas will be spread (distributed) over a wide range of values, some high some low. However the average kinetic energy of all the particles of a gas at a given temperature is always the same value for all gases.

   b. The average kinetic energy of the particles of a gas increases with temperature as must the average speed of its particles.

3. a. Diffusion.

   b. The leaking gas and the laboratory air both consist of particles (molecules) that are in constant random motion with plenty of space between the particles. Thus as the particles (molecules) of gas leak into the room they spread out amongst the particles of air already in the room. The motion of the leaking gas particles is only interrupted when they collide with other particles, such as those that make up the laboratory air or with the walls of the laboratory. Hence this process of diffusion continues until the particles of leaking gas and the laboratory air particles are evenly mixed. As a consequence it will soon be possible to notice the smell of the leaking gas throughout the entire laboratory.

   c. The temperature of a gas is a measure of the average kinetic energy of its particles. At a higher temperature the particles of a gas have a higher average kinetic energy and hence they will have a higher average velocity. As the particles move faster on average at the higher temperature so they will spread out through the laboratory air, ie diffuse faster at a higher temperature.

4. Particles in the gas phase have no attraction for one another and move randomly in straight line motion. When they collide with their container walls they exert pressure on the walls. The pressure exerted increases with the **frequency** and force of these **collisions**.

5. a. Pressure increases. This happens as the increased temperature (tyre becomes hot) means an increase in the average kinetic energy of the gas particles inside the tyre. This leads to an increased **force** and **frequency** of gas particle collisions with the tyre walls thus causing the pressure to increase.

   b. The pressure inside the tyre reduces. As gas escapes from the tyre (some air leaks out) there will be fewer gas particles inside the tyre. This leads to a decreased **rate of collisions** between gas particles and the tyre walls, thus the gas pressure reduces.

6. a. The graph shows the ideal gas volume increases with absolute temperature. More precisely, the linear nature of the graph shows that volume is directly proportional to absolute temperature. Also, as the graph passes through the origin it shows the ideal gas has zero volume at absolute zero, ie at 0 kelvin.

b. As temperature decreases so does the average kinetic energy of the particles of an ideal gas. At zero kelvin their particle kinetic energy will be zero, thus their speed will be zero. Thus the particles no longer move in random straight lines and will not fill or take the shape of their container. Also as the particles of an ideal gas have no volume then the gas will not occupy any space inside the container. The ideal gas volume will essentially be zero.

c. Graph B shows the ideal gas pressure decreases with increasing volume. More precisely, the inverse nature of the curve shows that pressure is inversely proportional to volume, ie as volume increases so pressure decreases and vice versa.

According to the kinetic theory, gases exert pressure when their particles collide with their container walls. The pressure increases with the force and frequency of these collisions. As the gas volume increases so the particles have further to travel before striking their container walls and thus the frequency of collisions will decrease and so will the pressure exerted. The force of collisions remains unchanged as the temperature and thus particle Ek is constant.

7. a. One assumption about an ideal gas is that its particles have no (negligible) volume (like a geometric point) whereas the particles of a real gas do occupy space and do have a small and sometimes significant volume. Also it is assumed the particles of an ideal gas have no attraction for one another. The particles of a real gas do have weak and sometimes significant forces of attraction for one another.

b. Two possibilities include: At a temperature of zero kelvin (-273 °C) an ideal gas would have zero volume but a real gas cannot have a zero volume. If a real gas is cooled and/or compressed sufficiently it will condense to form a liquid but an ideal gas would never condense.

8. a. A vapour is the gaseous phase of a material that would normally be a liquid or solid. As wax is normally a solid (at room temperature) then its gaseous phase is referred to as a vapour, ie wax vapour.

b. Physical processes like melting and vaporising are easily reversible. The chemical process of combustion is not easily reversed.

c. As the candle flame raises the temperature of the solid wax it causes the particles of wax to vibrate more vigorously (particles have a higher kinetic energy at higher temperature). At some point the wax particles in the solid phase have sufficient kinetic energy to overcome their mutual attraction and consequently these particles move out of their fixed positions in the solid phase. As these particles are now free to jostle past one another they form a liquid phase, ie the wax has melted.
Some of the melted wax is drawn up the wick (by capillary action) closer to the flame where the temperature is higher. Here the wax particles gain even higher kinetic energy. At some sufficiently high temperature the particles in the liquid phase are moving so energetically that they completely escape from the attraction of other wax particles and form a gas or vapour phase. The wax has now vaporised.

d. Solid wax has the higher density as it has a slightly lower volume for the same mass of wax and *density = mass/volume*. In the liquid phase wax particles are randomly arranged and slightly less tightly packed than in the solid phase. For this reason there is a slight reduction in volume as the liquid phase converts to the more compact and regular particle arrangement of the solid phase. The concave cavity on the wax surface is a result of this shrinkage in volume. [Note: This effect happens for almost all substances except for water. Water is peculiar in this regard as although water particles are packed in an ordered and regular way in ice, the ice structure is less compact than liquid water and hence ice is less dense than liquid water, ie water expands as it freezes, see p133.]

9. a. Liquids like $N_2(l)$ are a condensed phase of matter, ie the particles are very close together and only able to jostle about within the volume of the liquid. When $N_2(l)$ changes to a gas there is a one-off large increase in volume. This happens as in gases the particles have negligible attraction for one another and they move freely in random straight line motion with very large empty spaces between the particles. For this reason the same number of nitrogen particles (molecules) take up much more space when in the gas phase.

b. When a liquid boils there is a one-off rearrangement of its particles. In this example the closely packed nitrogen particles (molecules) must move apart from one another to form a gas phase. There is some attraction between the particles of nitrogen in the liquid phase and this attraction needs to be overcome if the particles are to be spread widely as in the gas phase. Overcoming this attraction requires a considerable amount of energy which must be absorbed from the particles of the surrounding matter. A consequence is surrounding particles lose kinetic energy and their temperature drops, ie a cooling effect. The heat energy lost from the surroundings is stored as potential energy (ie non thermal energy) within the molecules of the gaseous nitrogen.

10. a. The pressure will increase as the particles of nitrogen gas (N_2 molecules) will be closer together and will have less distance on average between themselves and the container walls. This means the particles on average collide with the container walls more frequently (shorter distance to travel). As pressure is due to the collisions of particles with their container walls then if these collisions are more frequent the gas pressure increases.

    b. The average kinetic energy of the particles of a gas (or any substance for that matter) depends upon its temperature. As the gas temperature is **held constant** at -170 °C in both situations then the average kinetic energy of the gas particles in both situations must be the same.

    c. Nitrogen is a real gas and hence there are weak forces of attraction between its particles (molecules). At some point when the nitrogen molecules are sufficiently close, (in this case at 1.50 MPa) the weak forces of attraction are sufficient to cause the particles to clump together (condense) to form a liquid phase. Once in the liquid phase these particles no longer exert pressure and so the pressure inside the cylinder stops increasing.
    In an ideal gas the forces of attraction between its particles are always negligible and so an ideal gas does not condense. Thus for an ideal gas the pressure will continue to rise as the volume of the cylinder is reduced.

11. In an homogeneous mixture the particles (atoms, ions or molecules) of the different substances are uniformly mixed at the particle level, ie there are no clumps of the different components within the mixture. Gas mixtures will always be homogeneous as there are no forces of attraction between the particles of a gas. Attraction would cause clumping of particles that attract more strongly. Also, as the particles are widely spaced and move in random straight line motion they will inevitably diffuse and mix evenly over time to produce a homogeneous mixture.

12. a. The surrounding pressure on a person's body/lungs at sea level is 1 atm, at 20 m depth in the ocean it is approximately 3 atm. (Remember, as stated pressure increases by 1 atm for every 10 m of depth.) Thus the suitable breathing pressure is 1 atm at sea level and 3 atm at an ocean depth of 20 m.

    b. If the inhaled air pressure is less than the surrounding pressure on the body/lungs then it will be very difficult or impossible to inhale air into the lungs. If the inhaled air pressure is greater than the surrounding pressure on the body/lungs then it will be very difficult if at all possible to control the rate of inhaling, the lungs will fill too fast as the high pressure forces air in.

    c. The high pressure inside a scuba tank is achieved by pumping extra air into the tank. (Actually, to achieve this pressure the tank will hold ≈ 180 times the mass of air that it would contain at a normal air pressure of 1 atm.) According to the kinetic theory, gas pressure is a result of particles in the gas phase colliding with their container walls. As extra air has been pumped into the tank (≈180 x normal) then the rate of particle collisions with the tank walls is much greater (≈180 x greater) giving rise to a much greater pressure inside the tank (≈180 x normal, ie 180 atm).

    d. Air inhaled from the scuba tank must be breathed at the same pressure as that being exerted on the body by the surrounding water. At sea level this is 1 atm, at a 10 m depth this is 2 atm and at 20 m depth this is 3 atm. To achieve the higher inhaled air pressure required at greater depth the inhaled air must contain more air particles than the same volume of inhaled air at lower pressure. At 2 atm pressure the inhaled air contains twice as many air particles per litre of air than air inhaled at 1atm pressure. For this reason the air in a scuba tank can be depleted more quickly at greater ocean depth.

e. At a depth of 15 m air pressure in the lungs will be much higher (≈ 2.5 atm) than it would be at sea level. This high pressure matches the external ocean pressure on the body/lungs at this depth. At the ocean surface air pressure exerted on the body is only 1 atm. Exhaling vigorously on the way up ensures air pressure inside the lungs reduces to match the falling external pressure on the body/lungs. If air is not exhaled the higher pressure in the lungs will cause them to expand and possibly rupture.
WARNING! Rapidly ascending from depths of 15 m or more can cause another serious medical problem known as the BENDS. This involves nitrogen gas bubbles forming within the blood stream and other bodily fluids. This condition is extremely painful and can be fatal.

13.a. Increasing the amount of gas will increase the pressure within the balloon. The increased pressure is a result of a greater rate of collisions between gas particles and the walls of the balloon. Consequently the increased collisions with the balloon walls stretch the balloon and its volume increases.

b. Since the mylar does not stretch then increasing the amount of gas inside the balloon **will not** lead to an increased balloon volume. However as more gas enters the balloon this will lead to an increased rate of collisions between gas particles and the mylar walls of the balloon. This then results in an increased pressure inside the balloon.

c. Brought into the sunshine the balloon temperature will increase (heated by sunlight). As a consequence the gas inside heats up and the average kinetic energy of its particles will increase. This increased kinetic energy leads to an increased force and frequency of gas particle collisions with the balloon walls. This causes pressure inside the balloon to increase which leads to an increased balloon volume as latex can easily stretch. The increased buoyancy is a result of the increased balloon volume. (1.2 g of buoyancy for every 1 L of volume.)

Set 2 Composition of matter and atomic structure

1. a. pure
   b. separated
   c. elements
   d. atom
   e. atomic
   f. pure
   g. physical
   h. chemical
   i. physical
   j. homogeneous
   k./l. atomic or
   m. microscopic
   n. heterogeneous

2. a. element b. compound c. mixture*****[1] d. mixture*****[2] e. element f. compound

*****[1] $NaCl_{(aq)}$ consists of two compounds, NaCl and H_2O in a homogeneous liquid mixture known as a solution.

*****[2] Bronze is an alloy consisting of Cu and Sn. The elements form a homogeneous solid mixture called a solution.

3. a. pure and homogeneous
   b. mixture, homogeneous solution
   c. mixture, homogeneous solution
   d. mixture and heterogeneous*****[3]
   e. pure and homogeneous
   mixture, homogeneous solution
   g. mixture, homogeneous solution
   h. mixture and heterogeneous*****[4]

*****[3] The solid pieces of orange pulp will be distributed unevenly throughout the mixture hence the mixture is heterogeneous.

*****[4] Despite the solid powders of $C_6H_8O_{7(s)}$ and $NaHCO_{3(s)}$ being thoroughly mixed it is possible even with a hand lens to identify individual grains of each substance. A homogeneous mixture can only occur if the particles in the mixture are mixed uniformly at the atomic, ionic or molecular level.

4. a. Salt has the chemical formula NaCl. This shows it is a chemical combination of two elements with a definite atomic ratio of one Na atom to one Cl atom. (actually one Na^+ ion to one Cl^- ion.) Thus salt is a compound. Peppercorns are a plant product containing a combination of many different substances in no fixed ratio (peppercorns do not have a chemical formula). Thus peppercorns are a mixture. The fine powder of NaCl and ground peppercorns is also a mixture as the individual components of the powder consist of small granules which are neither chemically combined nor in any definite atomic ratio.

   b. Only the salt is homogeneous. Both peppercorns and the finely ground powder contain a variety of compounds that are unevenly distributed at a microscopic level. The particles in a true homogeneous mixture should be evenly distributed at the atomic, ionic or molecular level.

5. a. Bronze is a mixture as it contains at least two different elements (Cu and Sn) and these elements are combined in **any** proportion. To be a compound these elements would need to be present in a definite proportion which would be shown by a chemical formula.

   b. Solutions are a homogeneous mixture of two or more elements or compounds. Bronze is clearly a mixture (answer 5a) and is also homogeneous. When the metallic components of bronze are melted the individual elements are able to mix thoroughly at the atomic level. This gives rise to a homogeneous mixture. When the liquid freezes the resulting solid alloy remains homogeneous and hence is a solution.

   c. Clearly there are strong forces of attraction between the individual atoms within each of the metals. This is why they form solids at room temperature. As the metals are heated, the average kinetic energy of their atoms increases. At some point their average kinetic energy and hence rate of atomic vibration is high enough for the atoms to partially escape their mutual attraction. At this point the individual atoms are now able to move out of their fixed positions within the solid state and able to jostle past one another in the form of a liquid. This is where the metals are seen to melt and form a liquid.

   Cooling the melted mixture causes a lowering of the average atomic kinetic energies to a point where their attractive forces once again cause the particles to clump together in a solid phase. Now particle motion is again restricted to vibrating about fixed positions and the mixture forms a solid phase.

   d. Once in the liquid phase the atoms of the two different metals are free to move randomly amongst one another (diffuse) and thoroughly mix at the atomic level. This ultimately produces a homogeneous mixture, ie one that is uniform throughout.

6. a. mass number = 14
   atomic number = 7

   b. mass number = 127
   atomic number = 53

   c. mass number = 23
   atomic number = 11

   (Remember, refer to a periodic table for atomic number.)

7. a. N(p) = Z = **3 protons** N(n) = A - Z = 7 - 3 = **4 neutrons** for a neutral atom N(e) = N(p) = **3**
   b. N(p) = Z = **17 protons** N(n) = A - Z = 35 -17 = **18 neutrons** for a neutral atom N(e) = N(p) = **17**
   c. N(p) = Z = **6 protons** N(n) = A - Z = 12 - 6 = **6 neutrons** for a neutral atom N(e) = N(p) = **6**
   d. N(p) = Z = **24 protons** N(n) = A - Z = 52 - 24 = **28 neutrons** for a neutral atom N(e) = N(p) = **24**

8. Isotopes are elements with the same atomic number and having a different mass number. This happens when the isotopes contain a different number of neutrons in their nucleus but have the same number of protons. Isotopes will also have the same number of electrons in their electron cloud. Thus hydrogen atoms contain one proton and no neutrons in their nucleus with one electron in their electron cloud. Deuterium and tritium are identical to hydrogen except they contain one neutron and two neutrons respectively in their nucleus.

9. a. Z(Mg) = 12 ∴ N(p) = **12 protons** also N(e) = N(p) - ion charge = 12 - (+2) = **10 electrons**
   b. Z(S) = 16 ∴ N(p) = **16 protons** also N(e) = N(p) - ion charge = 16 - (-2) = **18 electrons**
   c. Z(Cl) = 17 ∴ N(p) = **17 protons** also N(e) = N(p) - ion charge = 17 - (-1) = **18 electrons**
   d. Z(I) = 53 ∴ N(p) = **53 protons** also N(e) = N(p) - ion charge = 53 - (-1) = **54 electrons**
   e. Z(N) = 7 ∴ N(p) = **7 protons** also N(e) = N(p) - ion charge = 7 - (-3) = **10 electrons**
   f. Z(Fe) = 26 ∴ N(p) = **26 protons** also N(e) = N(p) - ion charge = 26 - (+2) = **24 electrons**
   g. Z(Fe) = 26 ∴ N(p) = **26 protons** also N(e) = N(p) - ion charge = 26 - (+3) = **23 electrons**

10. Since the Ar of carbon is twelve times that of hydrogen, then carbon atoms must be twelve times heavier than hydrogen atoms.

11. As the mass of a He atom is one-third that of a C atom, then the Ar of He is one-third the Ar of C, ie Ar(He) = 12 ÷ 3 = **4**.

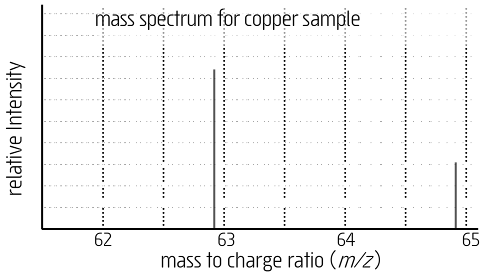
12. a. A copper-65 atom has two more neutrons in its nucleus than does a copper-63 atom. This makes the copper-65 atom heavier.

    b. $$\mathbf{Ar(Cu)} = \frac{\%a \times A_r(a) + \%b \times A_r(b)}{100} = \frac{(69.2 \times 62.9) + (30.8 \times 64.9)}{100} = \mathbf{63.5}$$

    Ar for Cu is 63.5 (3SF).
    (No units as Ar is a ratio.)

13. $$\mathbf{Ar(Cl)} = \frac{\%a \times A_r(a) + \%b \times A_r(b)}{100} = \frac{(75.77 \times 34.97) + (24.23 \times 36.97)}{100} = \mathbf{35.45}\ \text{(4SF)}$$

14. a. The mass spectrum of this copper sample would have two peaks, one with a relative mass of 62.9 and an intensity of 69.2%. The other peak would occur at a relative mass of 64.9 with a peak height of 30.8%.



b. The sample would need to be vaporised to form $Cu_{(g)}$.

c. The vaporised copper atoms need to be ionised. This is achieved when $Cu_{(g)}$ passes through a high energy electron beam. The electron beam is generated across a heating coil and a charged plate. This results in mainly Cu^+ ions. (Some Cu^{2+} ions may also form.)

d. The greatest deviation will occur for the ion of lowest mass, ie the ion of copper-63 of mass 62.9 will have the greatest deviation.

15. The mass spectrum shows rhenium has two isotopes with relative atomic masses of 184.95 and 186.95. (Note the mass readings are to two decimal places. This is reasonable as the smallest grid divisions of relative mass are 0.1 and this can be read to within half the smallest division.) Their respective percentage abundances are 37.5% and 62.5%. Using this data:

$$\mathbf{Ar(Re)} = \frac{\%a \times A_r(a) + \%b \times A_r(b)}{100} = \frac{(37.5 \times 184.95) + (62.5 \times 186.95)}{100} = \mathbf{186} \quad \text{(3 SF)}$$

16. Use the actual mass (kg) of each atomic isotope to determine by what factor the unknown isotope is heavier than carbon-12. Then use the given A_r of carbon-12 (exactly 12) to determine the A_r of the unknown isotope.

$$\mathbf{Ar(unknown\ isotope)} = \frac{\text{mass of unknown isotope (kg)} \times A_r(\text{carbon-12})}{\text{mass of carbon-12 (kg)}} = \frac{4.4804 \times 10^{-27} \times 12.01}{1.9927 \times 10^{-27}}$$

$= \mathbf{26.98}$ (4SF) ie The unknown element is most probably **aluminium**.

Set 3 Discovering the atom's structure

1. a./b. Aristotle/Plato d. Democritus f. nothing
c. could e. could not g./h. philosophies/beliefs

2. a. In a chemical reaction the total mass of the products formed equals **the total mass of the reactants consumed.**

b. The proposal made by Democritus, that matter consisted of indivisible particles called atoms was based on a belief and although later shown to be correct Democritus could not (did not) provide observational evidence to support his claims. Lavoisier however had conducted many experiments (that could be repeated by others) and collected data that supported his proposal for the law of conservation of mass.

c. The product of this reaction is the compound magnesium oxide and thus the reactants are $Mg_{(s)}$ (1.84 g) and $O_{2(g)}$ (1.21 g) giving a total of 3.05 g which is the mass of the reaction product magnesium oxide, $MgO_{(s)}$. Thus there is no increase in mass when both of the reactants are taken into account.

d. The equation for this reaction is: $CuCO_{3(s)} \rightarrow CuO_{(s)} + CO_{2(s)}$. Also, the reaction consumes 7.28 g of $CuCO_{3(s)}$ and produces 4.37 g of the black powder, $CuO_{(s)}$ thus the missing mass = 7.28 – 4.37 = 2.91 g. As mass must be conserved, the missing 2.91 g must be the mass of $CO_{2(g)}$ produced.

3. Proust had demonstrated by careful measurement of mass, that the composition of many compounds, eg $CuCO_3$, had a constant composition by mass. His experimental data was compelling evidence that the previously assumed law was in fact consistent with observation and could be relied upon. Thus Proust had been credited with discovering the law as he was the first to experimentally demonstrate it.

4. a. The mass of MgO will be 3.42 g + 2.25 g = 5.67 g. b. The law of conservation of mass.

c. The mass ratio of Mg:O in magnesium oxide is 3.42:2.25. Dividing both values by the smallest (2.25) simplifies this ratio to 1.52:1.0. Multiply this ratio by 10 (to get 10 g of oxygen), this gives a ratio of 15.2:10.0 thus we can see 15.2 g of Mg will combine with 10.0 g of oxygen.

d. The 'Law of Constant Composition'.

5. When Dalton proposed his atomic theory of matter he was unaware of the structure of the atom. We now understand that all atoms of the same element have the same atomic number, ie same number of protons, but they may have a different numbers of neutrons. Elements like this are known as isotopes. Isotopes have the same chemical properties but may have different properties of mass and radioactivity.

6. a. The cathode rays cause a low pressure gas inside the CRT to glow. Alternatively when the cathode rays strike a phosphor like ZnS they cause it to glow.
   b. Cathode rays are deflected towards a positive charged plate and away from a negative charged plate. Since like charges repel and unlike charges attract then the cathode rays must be negative in charge.
   c. The cathode rays stream away from the high voltage negative plate of the CRT as a wide beam. These rays are attracted towards a positive plate that has a narrow slit in it. The rays passing through the slit form a narrow beam that is attracted to a more distant positive plate.
   d. Thomson used a phosphor coated screen that glowed when struck with cathode rays. This produced a trace showing the path of the cathode rays.
   e. Thomson was able to determine the charge to mass ratio (q_e/m_e) of a cathode ray particle (now known to be an electron). With this value he estimated the mass of a cathode ray particle to be less than one thousandth the mass of the lightest known element. (Now known to be about half this value.)

7. a. Alpha particles are produced by the radioactive decay of some naturally occurring (or artificial) radioisotopes (such as uranium-238 and thorium-234). An alpha particle is a fast moving helium nucleus. It has a +2 charge. (Radium was the actual radioisotope used by Rutherford.)
   b. Gold is a very malleable metal. This means it can be beaten or rolled into very thin sheets. Thin sheets of gold are known as gold leaf.
   c. Based on Thomson's model of the atom, ie with a fairly uniformly spread mass and charge, Rutherford hypothesised the alpha particles should essentially pass through undeflected or at most only slightly deflected.
   d. Rutherford used a zinc sulfide (ZnS) coated screen and a microscope to count flashes produced by alpha particles striking the fluorescent screen.
   e. Rutherford and his co-workers found that most of the alpha particles behaved as expected, ie passed straight through the gold foil with minimum deflection occurring. To their surprise some alpha particles were deflected considerably, some even coming back in the original direction. Rutherford interpreted this to mean there must be a very small, high mass and high charge central nucleus in an atom and that it only makes up a very small percentage of the atom's volume. This nucleus was causing the occasional alpha particle to be deflected through a very wide angle or even back on itself. (Actually Rutherford calculated the positive nucleus must make up less than 0.1 % of the entire atomic volume.)

8. Rutherford suggested the missing mass was attributed to an undetected neutral particle. It was difficult to detect as it had no charge and the detectors used at that time relied upon charged plates to deflect and identify such particles. Sir James Chadwick, in 1932, was able experimentally show the existence of these particles which he later called neutrons.

9. a. The Rutherford model meant electrons would emit energy as they orbited the nucleus. This would cause them to gradually lose energy and speed until finally they would, presumably, spiral into the nucleus. Clearly this is an unstable atom.
   b. Bohr proposed the electrons in an atom could only orbit at certain specific radii that were associated with fixed amounts or quanta of energy. Hence they could not just lose energy and spiral into the nucleus. He also proposed the ground state or lowest electron energy possible was that of the lowest electron radii. Thus electrons would not fall into the nucleus as it is not a lower energy state.
   c. A triangular glass prism (or spectroscope) can be used to observe the spectrum of different coloured light produced from a discharge tube.
   d. The visible part of the emission spectrum of hydrogen gas consists of four distinct lines of light of different colours and wavelength. The colours are red, cyan (green/blue), blue and violet. There is no light (black) between the colours.
   e. The hydrogen emission lines of specific wavelength and colour may occur once the single electron in a hydrogen atom has been excited, eg by electrical discharge. The excited electron is in a higher energy level than normal. When the electron falls back to a lower level it emits a photon of light of a specific energy equal to the energy difference of the higher and lower levels in the electron transition. *Continued next page.*

e. *Continued* This photon of specific energy corresponds to a specific wavelength or colour of light. There are several different visible colours possible for hydrogen depending upon the specific electron transitions involved. The emitted colours are not continuous as only certain quanta of allowable electron energy are possible and hence only certain specific energy photons (colours) can be produced.

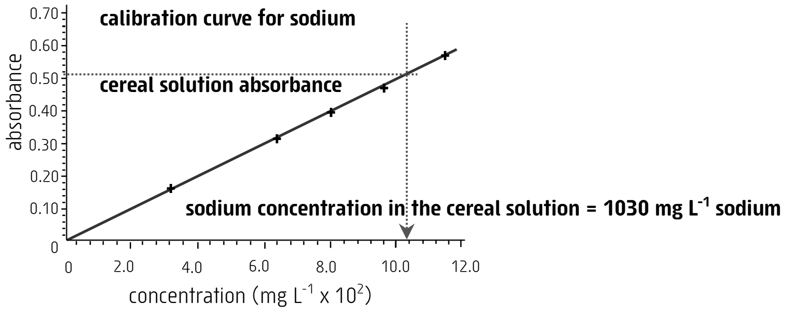
10. a. Obtain a platinum or nichrome wire loop, sometimes called an inoculating loop (ie a loop at the end of 3-4 cm wire with a glass or metal handle). Rinse in hydrochloric acid then distilled water. Dip the loop into a paste or solution of one of the salts. Place this end into a hot almost colourless Bunsen flame. Note the colour produced and record your results. Repeat this for the other salts. Refer to a Flame test colour chart to identify the metal elements present in the test samples and thus identify the sample.

b. Barium chloride produces a green colour, sodium chloride produces a yellow colour and strontium chloride produces a red colour.

c. The heat of the flame excites electrons in the metal ions. When these excited electrons return to their ground state they emit light of specific wavelengths. As every element has its own unique energy values for its different energy levels then the energy of its electron transitions and the light they emit will be unique for each element. This produces a unique emission spectrum for the element and thus a unique flame colour.

11. Distilled water contains pure $H_2O_{(l)}$. It does not contain any metal elements or other elements that will produce a visible emission spectrum when placed into a hot flame. Tap water often contains dissolved salts of metals like sodium or potassium. These metal ions would produce their own emission spectrum when place into the flame thus interfering with the flame colour due to the test salt.

12. a.



b. The hot flame of the AAS ensures any compounds in the aspirated sample are decomposed and atomised. Thus any metal atoms originally present in the test sample are present in the flame as free atoms. Only in this form can the target metal atoms freely absorb light from the light beam directed through it.

c. The actual energy of each electron level in an atom is different for different elements. Thus the energy transitions between these levels are different for different elements. So when the electrons of an atom are excited or return to their ground state the light energy they absorb or release is unique for that element. For this reason an element's absorption spectrum (the wavelengths of light it can absorb) is unique for that element. The AAS uses a light source that produces only the specific wavelengths of light able to be absorbed by the target metal element. In this way the absorbance of light passing through the AAS flame can only be affected by the concentration of the target atoms alone. This allows the AAS to analyse a single element even though many different types may be present in a sample.

Set 4 Mixtures, pure substances and separation techniques

1. a. pure substance c. pure substance e. mixture
b. mixture d. mixture f. pure substance#

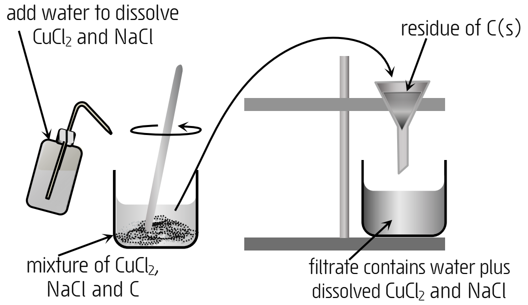
$_2O_{(l)}$ is a pure substance, however, if it contains any dissolved salts or gases then it would be a mixture.

2. A pure substance like water (H_2O) has a distinct and well defined boiling point, in this case 100.0 °C. The boiling point of a mixture however, is not well defined, ie a mixture will boil over a temperature range. Furthermore the composition of a mixture is not constant and can vary and as a result so will its boiling point range. A sea water sample for example has a variable salt concentration that depends on the exact location from where it was collected. Thus it is not possible to quote a consistent boiling point for sea water.

3. a. Physical properties: Yellow in colour, density of 19.3 g mL^{-1}, a hardness of 2.5 on the Moh's scale and has a melting point of 1063 ^oC.
   Chemical properties: Does not dissolve in acids, does not tarnish in air.
   b. A well defined melting point is typical of a pure substance. This implies elemental gold is a pure substance.
   c. A melting point range is typical of a mixture and this implies rose gold is a mixture.
   d. Different chemical properties for rose gold could be its reactivity with acids and its tendency to tarnish in air. Rose gold will have different physical properties such as different boiling point, hardness, electrical conductivity, heat conductivity, density and colour.

4. No the liquid is not pure ethanoic acid. This can be concluded as the boiling point of the liquid does not match that of ethanoic acid. Also the boiling point is not constant, it increased as boiling continued. This behaviour is characteristic of a mixture. A pure substance always has a well defined and constant boiling point. The test liquid might be a solution containing ethanoic acid. This would explain the characteristic pungent odour matching that of ethanoic acid. Remember in a mixture the individual components keep their own physical properties. Furthermore the presence of another component such as water dissolved in the ethanoic acid would alter its boiling point and cause it to boil over a temperature range as was observed.

5. a. Use filtration, ie add water to this mixture, stir and allow the two soluble substances ($CuCl_2$ and NaCl) to dissolve, insoluble C(s) remains undissolved. Filter the mixture using the apparatus shown at right. Use a wash bottle and distilled water to rinse the residue then allow it to dry, this is now pure carbon. The filtrate contains the soluble substances and water.
   b. Both of these compounds are reasonably soluble in water.



6. a. The crystals consist of NaCl(s). These form as sodium chloride is much less soluble in ethanol (0.065 g per 100 g ethanol) than copper chloride (67 g per 100 g ethanol). Thus as ethanol evaporates from the solution it becomes saturated with NaCl well before it becomes saturated in $CuCl_2$.
   b. The SDS for ethanol shows it to be a highly flammable liquid. Heating with an electric mantle avoids an ignition source, ie the flame, for the ethanol vapour.
   c. Washing with ethanol removes any solution adhering to the NaCl crystals. The solution contains dissolved $CuCl_2$ which if not washed off would remain as a contaminant on the dried pure NaCl crystals. Also, as $CuCl_2$ is green and NaCl colourless (white solid), then it is evident when the NaCl crystals have been sufficiently washed as they would change colour from green (coated in solution) to white.
   d. The filtrate contains mainly $CuCl_2$ along with a small amount of dissolved NaCl. Remember NaCl is slightly soluble, 0.065 g NaCl per 100 g of ethanol. Thus evaporating the filtrate produces a residue of mainly $CuCl_2$ along with a small amount NaCl.

7. a. Distillation is used for separating a mixture of volatile and non-volatile components but can also be used to separate a mixture of volatile liquids as long as their boiling points are significantly different. In this example the volatile liquid methyl methanoate, BP = 31.5 ^oC will be separated from the other liquids in the mixture, ie water and methanoic acid with BP's of 100.0 ^oC and 100.8 ^oC respectively.

   When the mixture is heated the lower boiling point component, ie methyl methanoate, boils first and the resulting vapour is essentially composed of methyl methanoate. This vapour then flows into a condenser where it is cooled and condenses back to a liquid called the distillate. The distillate in this case is essentially composed of the lower boiling point liquid methyl methanoate.
   b. No, the distillate is not pure methyl methanoate, it will contain some of the higher boiling point liquids, water and methanoic acid. When the mixture is heated the lower boiling point liquid boils first but the vapour produced will contain some of the higher boiling point components as well, ie water and methanoic acid. The presence of vapour from the higher boiling point liquids becomes more significant as the boiling points of the component liquids are closer. In this case the boiling points are sufficiently close so that a pure distillate of methyl methanoate will not be formed.

c. Pure substances have well defined and measurable physical properties such as melting point, boiling point and density. In this case it would be very easy to check the temperature at which the distillate boils. This can be done by slowly heating a batch of it and using a thermometer to note the temperature at which it boils. If boiling occurs at a constant temperature of 31.5 °C then it can be assumed the distillate is pure methyl methanoate. Alternatively if the boiling point is higher or lower than this or if it rises over time then the distillate is probably a mixture.

d. No it is not possible to use distillation to separate the remaining mixture of methanoic acid and water as their boiling points are too similar. Even though water boils before methanoic acid (very marginally) the resulting vapour would have almost equal proportions of each compound in it.

8. The process of spiral gravity separation is based on separating the components of a mixture according to their density differences. This means if a crushed mixture of components of differing density is gently shaken or agitated then the individual components will settle out in layers according to their density. In a spiral gravity separator the fine mixture of minerals flows along with water, down a spiral channel. The higher density minerals, in this case the valuable 'heavy minerals' such as ilmenite, ($Fe.TiO_3$), rutile, (TiO_2), and zircon ($ZrSiO_4$) become concentrated along the inside of the spiral channel. The heavier density minerals that concentrate on the inside of the channel are siphoned off and hence become separated from the lower density quartz sand.

Set 5 Chemical formula

1. The formula is given second (if this is different to the symbol).
   a. Zn
   b. P, P_4
   c. H, H_2
   d. Fe
   e. C
   f. Ca
   g. Na
   h. O, O_2
   i. N, N_2
   j. Cl, Cl_2

2. a. H_2O
   b. H_2S
   c. H_2SO_4
   d. H_3PO_4
   e. SO_2
   f. N_2O_4
   g. H_2O_2
   h. CO_2
   i. H_2SO_3
   j. CH_3COOH
   k. NCl_3
   l. NO
   m. NH_3
   n. CO
   o. HNO_3
   p. HNO_2
   q. SO_3
   r. N_2O

3. a. one C atom and two O atoms per molecule
   b. one N atom and three H atoms per molecule
   c. one S atom and two H atoms per molecule
   d. three C atoms and eight H atoms per molecule
   e. two H atoms, one S atom and four O atoms per molecule
   f. two C atoms, four H atoms and two O atoms per molecule

4. The formula shows the hydroxide polyatomic ion, OH^- consists of a cluster of one oxygen atom and one hydrogen atom with an overall charge of 1-. The charge arises due to an excess of electrons over protons in the structure. There are a total of 9 protons (ie **9+**) in the ion, 8 from the O atom and 1 from the H atom, and a total of 10 electrons (ie **10-**) in the structure, 8 from the O atom and 1 from the H atom plus 1 extra electron (a gained electron), giving the ion an overall charge of 1-.

   The formula for the ammonium ion, NH_4^+ shows it is a cluster of one nitrogen atom and four hydrogen atoms with an overall charge of 1+. The charge arises due to a shortage of electrons over protons in the structure. There are a total of 11 protons (ie **11+**) in the ion, 7 from the N atom and 1 from each of the four H atoms, and a total of only 10 electrons (ie **10-**) in the structure, 7 from the N atom, 1 each from the four H atoms and minus 1 lost electron to give an overall ion charge of 1+.

5. a. one Li^+ ion for every one Cl^- ion
   b. one K^+ ion for every one MnO_4^-
   c. one Mg^{2+} ion for every one O^{2-} ion
   d. two NH_4^+ ions for every one SO_4^{2-} ion
   e. two Al^{3+} ions for every three S^{2-} ions
   f. one Zn^{2+} ion for every two HSO_4^- ions
   one Fe^{2+} ion for every one O^{2-} ion
   h. two Cr^{3+} ions for every three SO_3^{2-} ions
   i. two Fe^{3+} ions for every three O^{2-} ions
   j. one Au^{3+} ion for every three CN^- ions

6. a. $ZnCl_2$
   b. CuBr
   c. $CaSO_4$
   d. $NaNO_2$
   e. $(NH_4)_2SO_4$
   f. $Al_2(SO_4)_3$
   g. Na_2S
   h. Fe_2O_3
   i. Ag_2CrO_4
   j. $Fe(NO_3)_2$
   k. $Na_2Cr_2O_7$
   l. $Zn_3(PO_4)_2$
   m. CaO
   n. Ag_2SO_4
   o. $Ba(OH)_2$
   p. KOH
   q. $Cu(HSO_4)_2$
   r. $KMnO_4$

7. a. $CuSO_4.5H_2O$
   b. $FeCl_3.6H_2O$
   c. $FeCl_2.2H_2O$
   d. $Zn(NO_3)_2.2H_2O$
   e. $Cr_2(SO_4)_3.5H_2O$ (green form)
   $Cr_2(SO_4)_3.15H_2O$ (violet form)

8. a. HO
   b. O
   c. CH_2O
   d. $C_3H_7N_2O$

9. a. molecular (contains only non-metal elements)
   b. ionic (contains the metal element K and the non-metal element S)
   c. ionic (contains the metal element Na and non-metal elements S, H and O)
   d. covalent network (An exception. See p28 section 4.2.)
   e. ionic (An exception, NH_4^+ forms ionic compounds. See p29.)
   f. molecular (contains only non-metal elements)
   g. molecular
   h. molecular
   i. ionic
   j. molecular
   k. molecular
   l. ionic
   m. ionic
   n. molecular
   o. ionic
   p. ionic
   q. molecular
   r. covalent network

10. a.
$$\textbf{\%C} = \frac{\Sigma A_r(C) \times 100}{A_r(CH_4)} = \frac{12.01 \times 100}{16.04} = \mathbf{74.87\%} \text{ (4SF) and}$$

$$\textbf{\%H} = \frac{\Sigma A_r(H) \times 100}{A_r(CH_4)} = \frac{4 \times 1.008 \times 100}{16.04} = \mathbf{25.13\%} \text{ (4SF)}$$

b.
$$\textbf{\%Ba} = \frac{\Sigma A_r(Ba) \times 100}{A_r[Ba(NO_3)_2]} = \frac{137.3 \times 100}{261.32} = \mathbf{52.54\%} \text{ (4SF) and}$$

$$\textbf{\%N} = \frac{\Sigma A_r(N) \times 100}{A_r[Ba(NO_3)_2]} = \frac{2 \times 14.01 \times 100}{261.32} = \mathbf{10.72\%} \text{ (4SF) and}$$

$$\textbf{\%O} = \frac{\Sigma A_r(O) \times 100}{A_r[Ba(NO_3)_2]} = \frac{6 \times 16.00 \times 100}{261.32} = \mathbf{36.74\%} \text{ (4SF)}$$

c.
$$\textbf{\%N} = \frac{\Sigma A_r(N) \times 100}{A_r[(NH_4)_2SO_4]} = \frac{2 \times 14.01 \times 100}{132.154} = \mathbf{21.20\%} \text{ (4SF) and}$$

$$\textbf{\%H} = \frac{\Sigma A_r(H) \times 100}{A_r[(NH_4)_2SO_4]} = \frac{8 \times 1.008 \times 100}{132.154} = \mathbf{6.102\%} \text{ (4SF) and}$$

$$\textbf{\%S} = \frac{\Sigma A_r(S) \times 100}{A_r[(NH_4)_2SO_4]} = \frac{32.07 \times 100}{132.154} = \mathbf{24.27\%} \text{ (4SF) and}$$

$$\textbf{\%O} = \frac{\Sigma A_r(O) \times 100}{A_r[(NH_4)_2SO_4]} = \frac{4 \times 16.00 \times 100}{132.154} = \mathbf{48.43\%} \text{ (4SF)}$$

d.
$$\textbf{\%Cu} = \frac{\Sigma A_r(Cu) \times 100}{A_r(CuCl_2.2H_2O)} = \frac{63.55 \times 100}{170.48} = \mathbf{37.28\%} \text{ (4SF) and}$$

$$\textbf{\%Cl} = \frac{\Sigma A_r(Cl) \times 100}{A_r(CuCl_2.2H_2O)} = \frac{2 \times 35.45 \times 100}{170.48} = \mathbf{41.59\%} \text{ (4SF) and}$$

$$\textbf{\%H} = \frac{\Sigma A_r(H) \times 100}{A_r(CuCl_2.2H_2O)} = \frac{4 \times 1.008 \times 100}{170.48} = \mathbf{2.365\%} \text{ (4SF) and}$$

$$\textbf{\%O} = \frac{\Sigma A_r(O) \times 100}{A_r(CuCl_2.2H_2O)} = \frac{2 \times 16.00 \times 100}{170.48} = \mathbf{18.77\%} \text{ (4SF)}$$

11. Determine the %N in each of the fertilisers. The one having the highest %N is the fertiliser providing the greatest mass of nitrogen for a given mass of fertiliser.

$$\textbf{\%N[in } \mathbf{(NH_4)_2SO_4}\textbf{]} = \frac{\Sigma A_r(N) \times 100}{A_r[(NH_4)_2SO_4]} = \frac{2 \times 14.01 \times 100}{132.154} = \mathbf{21.20\%} \text{ (4SF)}$$

$$\textbf{\%N[in } \mathbf{NH_4NO_3}\textbf{]} = \frac{\Sigma A_r(N) \times 100}{A_r(NH_4NO_3)} = \frac{2 \times 14.01 \times 100}{80.052} = \mathbf{35.00\%} \text{ (4SF)}$$

$$\textbf{\%N[in } \mathbf{(NH_2)_2CO}\textbf{]} = \frac{\Sigma A_r(N) \times 100}{Ar[(NH_2)_2CO]} = \frac{2 \times 14.01 \times 100}{60.062} = \mathbf{46.65\%} \text{ (4SF)}$$

∴ **Urea, $(NH_2)_2CO$ is the best nitrogen fertiliser.** It has the highest percentage by mass of nitrogen. Thus for a given mass of fertiliser it provides the greatest mass of nitrogen.

12. a.
$$\textbf{\%}\mathbf{H_2O} = \frac{\Sigma A_r(H_2O) \times 100}{A_r[Co(CH_3COO)_2.6H_2O]} = \frac{6 \times 18.016 \times 100}{285.11} = \mathbf{37.914\%} \text{ (5SF)}$$

b. **%H_2O** = $\frac{\Sigma A_r(H_2O) \times 100}{A_r(MgCrO_4.6H_2O)} = \frac{6 \times 18.016 \times 100}{248.41}$ = **43.515%** (5SF)

13. a. The weight loss (1.67 g) is due to the loss of water of crystallisation.

b. **%H_2O** = $\frac{m(H_2O) \times 100}{m(\text{hydrated } CuSO_4)} = \frac{1.67 \times 100}{4.77}$ = **35.0%** (3SF)

c **actual error** = experimental value – theoretical value = 35.0 – 36.1 = -1.1 (2DP)

%error = $\frac{\text{actual error} \times 100}{\text{theoretical value}} = \frac{(-1.1) \times 100}{36.1}$ = -3.0% ie, the experimental value is too low by ≈ **3.0%**

14. a. **m(silver oxide)** = m(crucible + silver oxide) - m(empty crucible) = 37.76 - 22.84 = **14.92 g of silver oxide**

b. The crucible containing silver oxide loses mass as the silver oxide is unstable above 230 °C. As it decomposes, silver and oxygen are produced. Since oxygen is a gas it escapes from the crucible causing it to lose mass. Thus, the mass lost equals the mass of oxygen produced. Silver remains in the crucible.

c. **m(Ag)** = m(crucible + silver residue after heating) - m(empty crucible) = 36.69 - 22.84 = **13.85 g Ag**
m(O) = m(silver oxide) - m(silver) = 14.92 - 13.85 = **1.07 g O**

d. **%Ag** = $\frac{m(Ag) \times 100}{m(\text{silver oxide})} = \frac{13.85 \times 100}{(37.76 - 22.84)}$ = **92.83% Ag** (4SF)

e. **%Ag** (theoretical) = $\frac{\Sigma A_r(Ag) \times 100}{A_r(Ag_2O)} = \frac{2 \times 107.9 \times 100}{231.80}$ = **93.10%** (4SF)

f. **actual error** = experimental value – theoretical value = 92.83 - 93.10 = **-0.27** (2DPs)

%error = $\frac{\text{actual error} \times 100}{\text{theoretical value}} = \frac{(-0.27) \times 100}{93.10}$ = -0.29% ie, the experimental value is too low by ≈ **0.29%**

15. a. The mass of the crucible increases, not because mass is created, but because during the chemical reaction oxygen gas from the atmosphere becomes chemically combined to the magnesium. Thus the total mass present in the crucible increases during the course of the reaction.

b. **%Mg(experimental)** = $\frac{m(Mg) \times 100}{m(\text{the oxide})} = \frac{(26.09 - 25.59) \times 100}{(26.36 - 25.59)} = \frac{0.50 \times 100}{0.77}$ = **65%** (2SF)

c. **%Mg(theoretical)** = $\frac{\Sigma A_r(Mg) \times 100}{A_r(MgO)} = \frac{24.31 \times 100}{24.31 + 16.00}$ = **60.31%** (4SF)

d. **actual error** = experimental value – theoretical value = 65 – 60.31 = 4.69 = **5** (0 DP)

%error = $\frac{\text{actual error} \times 100}{\text{theoretical value}} = \frac{5 \times 100}{60.31}$ = 8% ie, the experimental value is too high by ≈ **8%**

Set 6 Investigating

1. a.

Hypothesis	Independent variable	Dependent variable
1	water temperature	salt solubility
2	mass of dry ice	volume of balloon
3	mass of zinc used	volume of hydrogen produced
4	metal element	hydrogen gas

b. According to hypothesis 4 hydrogen gas will be produced whatever metal reacts with sulfuric acid.

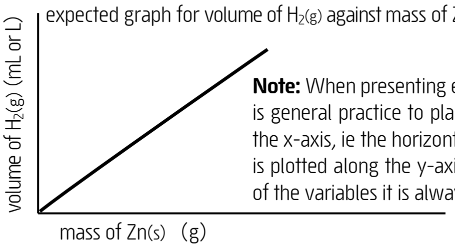
c. The hypothesis suggests the volume of the balloon should double if the mass of dry ice added to it doubles.

d. Hypothesis 1 does not state how the solubility of salt (dependent variable) changes as the water temperature (independent variable) is altered. Possible alternatives to this hypothesis include:
'The solubility of salt in water increases as the temperature of water increases.'
'The solubility of salt in water decreases as the temperature of water increases.'
'The solubility of salt in water is directly proportional to the absolute water temperature.'
'The solubility of salt in water is inversely proportional to the absolute water temperature.'

2. a. Substances involved in the investigation include: Hydrochloric acid solution, zinc granules, zinc chloride solution (a product) and hydrogen gas (a product).
Hydrochloric acid: This is a hazardous substance. It may be corrosive to metals, can cause severe skin burns and eye damage and may cause respiratory irritation. Suitable control measures could include, but are not limited to: use dilute solutions only, avoid breathing its vapours, wash hands thoroughly after handling, use only outdoors or in a well-ventilated area, wear protective gloves, protective clothing and eye protection.
Zinc granules: May be considered non-hazardous.
Zinc chloride: Is a hazardous substance. It is harmful if swallowed, causes severe skin burns and eye damage, is very toxic to aquatic life with long lasting effects. Suitable control measures for this investigation could include, but are not limited to: wash skin thoroughly after the investigation, do not eat or drink during the investigation, avoid releasing it to the environment, wear protective gloves, protective clothing and eye protection.
Hydrogen gas: Is non-toxic but does pose a safety hazard as it is highly flammable thus avoid all ignition sources such as Bunsen flames.

b. They should measure the volume of hydrogen gas produced and the mass of zinc used.

c. Their graph should be linear with a positive gradient as this would indicate a direct relationship between the mass of zinc used and the volume of hydrogen gas produced. The graph should start at the origin as no hydrogen (0 volume) would be expected if no zinc (0 mass) was used.



Note: When presenting experimental data graphically, it is general practice to place the independent variable on the x-axis, ie the horizontal axis. The dependent variable is plotted along the y-axis, ie vertical axis. If time is one of the variables it is always plotted on the x-axis.

3. a. The dependent variable is '**the size of the boiling point elevation**'.

b. The independent variable '**the concentration of solute in the solution**'.

c. Several hypotheses are possible depending on your choice of relationship between the two variables and how specific you are about the relationship. Some possible hypotheses are:

'The boiling point elevation of the solution increases as the solute concentration increases.'

'The boiling point elevation of the solution is directly proportional to the solute concentration.'

'The boiling point elevation of the solution is unaffected by the solute concentration.'

d. Other variables that you think might affect the boiling point of water should be kept constant or monitored. These could include; water purity used to make the solutions (ie use distilled water), room or atmospheric pressure (try to make all boiling point measurements at the same atmospheric pressure), use the same thermometer or temperature probe for all boiling point measurements, use the same volume of test solution for each experiment, use the same beaker and heating apparatus.

e. Your **method** should describe:
- how you will make solutions of different solute concentration
- a method for determining the solution's boiling point
- a list of the data you need to collect
- calculations you perform to find solution concentration and boiling point elevation
- techniques and apparatus you will use.

A summary of a suitable method using salt (NaCl) as the solute is shown here:
Using an electronic balance accurately weigh about 1 g of NaCl. Add this to a 200 mL volumetric flask (a measuring cylinder could be substituted however, it is less precise). *Continued next page.*

Continued Dissolve the salt using distilled water and make the solution volume up to 200.0 mL. Repeat this process for different amounts of salt, ranging up to 20 g NaCl and making at least eight different solutions. The concentration of each solution can be found by dividing the mass of NaCl in grams by the volume of solution in litres, giving salt concentration in g L^{-1}. All data needs to be tabulated.

To find the boiling point of each solution add the 200 mL of solution to a 500 mL beaker and heat this till it boils. Use an electric hot plate or Bunsen burner and tripod assembly. As the solution starts to boil, measure its boiling temperature using a mercury thermometer or a temperature probe. Repeat this process for all of your solutions. In a similar way and using the same apparatus find the boiling point of the distilled water alone. The boiling point elevation of each solution can be calculated by subtracting the boiling temperature of distilled water (100 °C) from the boiling temperature of the solution. Tabulate data. The procedure can be repeated several times to obtain consistent data.

f. You may consider the chemical substances involved, ie salt and water to be non-toxic and in the context of this experiment should not pose a chemical hazard. A safe procedure should be followed when heating with a Bunsen or hot plate. To avoid burns care must be taken not to touch or handle any hot or potentially hot surfaces. This will include but not be limited to the beaker, hot plate surface, tripod, gauze matt and Bunsen. If using a Bunsen assembly take care to ensure its stability and assemble it in a safe position on a bench protective mat where accidental bumping is unlikely. Extra care must be taken when heating salt solutions as these may suddenly boil over, especially if heating the solution quickly. It would be advisable to add boiling chips (small coarse ceramic granules) to the solution as these prevent 'bumping' (ie the unexpected sudden boiling of a solution). Care needs to be used in the proper use of a mercury thermometer. The glass bulb of the thermometer is extremely thin and easily broken if handled roughly or dropped harshly into the beaker. Mercury and its vapours are toxic and if this is released from a broken thermometer then you need to immediately inform your supervisor. Safety glasses should be worn to protect against the unexpected splashing of hot solution.

4. a. The dependent variable is '**the rate of formation of hydrogen gas**'.

b. Some independent variables could be '**the concentration of hydrochloric acid**', '**the temperature of the acid solution**', '**the surface area of magnesium**', '**the mass of magnesium**' or '**the volume of acid used**'. Remember the independent variable is the variable you think is having an effect on the rate of reaction. It may or may not actually turn out to be what is causing the rate change but the purpose of the investigation is to try and find out by testing your hypothesis.

c. Many hypotheses are possible depending on your choice of independent variable. Some possible hypotheses are:
'When magnesium reacts with hydrochloric acid the rate of formation of hydrogen gas increases as the concentration of hydrochloric acid increases.'
'When magnesium reacts with hydrochloric acid the rate of formation of hydrogen gas increases as the temperature of hydrochloric acid increases.'
'When magnesium reacts with hydrochloric acid the rate of formation of hydrogen gas increases as the surface area of magnesium increases.'

d. It would be reasonable to keep many things constant that you think might affect the rate of reaction, eg temperature, concentration, volume of acid used, mass of magnesium, surface area of magnesium. The apparatus, method of gas collection and method of measuring the gas formed should also be kept the same.

e. Natalie and Jayzii need to determine the rate of formation of hydrogen gas. This is best expressed as g s^{-1} or L s^{-1} of hydrogen gas. In either case rate must be calculated (eg Rate = Volume of H_2 produced ÷ time taken) by processing direct measurements of mass or volume of hydrogen produced and the time taken to produce it.

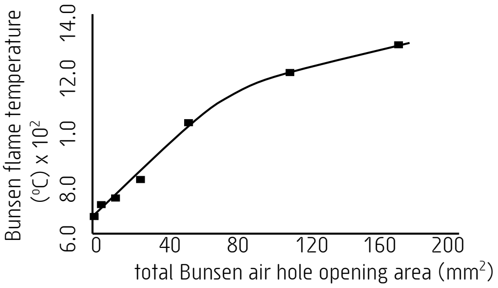
f. The volume of hydrogen can be measured by collecting the gas by the downward displacement of water. This involves collecting the gas in an inverted measuring cylinder. (See Fig 6 p83.) The time taken to collect a fixed volume of the gas can be measured or the volume collected can be progressively monitored over time. Alternatively as the reaction proceeds the contents of the reaction vessel (say conical flask) will progressively lose mass due to escaping hydrogen gas. It is possible to measure the mass of hydrogen produced over time by monitoring the mass of the reaction vessel and its contents. The collected data can then be used to calculate the reaction rate. These ideas are by no means exhaustive, other valid methods are possible.

5. a. The independent variable is the '**molar amount of $NaHCO_3$ used**' while the dependent variable is the '**molar amount of Na_2CO_3 produced**'.
   b. Find the mass of $NaHCO_3$ using: $m(NaHCO_3) = m(crucible + NaHCO_3) - m(empty\ crucible)$
   Find the moles of $NaHCO_3$ (**independent variable**) using: $n(NaHCO_3) = m(NaHCO_3) \div M(NaHCO_3)$
   Find the mass of Na_2CO_3 using: $m(Na_2CO_3) = m(crucible\ and\ residue\ after\ heating) - m(empty\ crucible)$
   The moles of Na_2CO_3 (**dependent variable**) can be found using: $n(Na_2CO_3) = m(Na_2CO_3) \div M(Na_2CO_3)$
   c. Two extra columns have been included to allow space for the processed data.

Mass of empty crucible (g)	**Mass of crucible plus $NaHCO_3$ (g)**	**Mass of crucible plus Na_2CO_3 after heating (g)**	**Mass of $NaHCO_3$ (g)**	**Mass of Na_2CO_3 (g)**	**Moles of $NaHCO_3$ (mol)**	**Moles of Na_2CO_3 (mol)**
		Allow sufficient space for at least 6 entries				

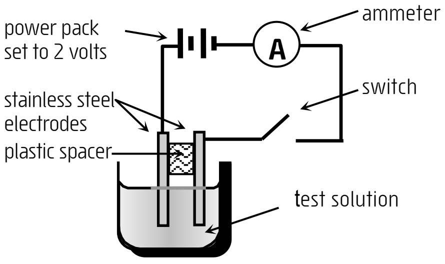
   d. The independent variable, moles of $NaHCO_3$ should be plotted on the horizontal axis with the dependent variable, moles of Na_2CO_3 plotted on the vertical axis.
   e. The graph would be linear (passing through the origin) with a gradient of 0.5. This gradient indicates $n(Na_2CO_3) = \frac{1}{2} n(NaHCO_3)$.

6. a. The independent and dependent variables are respectively, '**the area of the air hole opening at the base of the Bunsen**' and '**the temperature of the Bunsen flame**'.
   b. Other variables that should be kept constant are: the particular Bunsen used, the gas tap should be opened to the same setting, the position of the thermistor (temperature measuring device) in relation to the top of the Bunsen, general laboratory conditions such as drafts and lab temperature, the type of Bunsen gas.
   c. The independent variable (area of air hole opening) can be calculated from the diameter of the air hole using the formula: Total area of four air hole openings = $4 \times \pi \times (d/2)^2$. The areas in order are 0 mm^2, 3.1 mm^2, 7.1 mm^2, 28 mm^2, 64 mm^2, 113 mm^2 and 177 mm^2.
   d. The hypothesis is partially supported by the observations. There is a strong direct relationship between Bunsen flame temperature and the area of air-hole opening for openings from 0 to ≈ 70 mm^2. For larger openings the actual Bunsen temperatures are lower than would be expected if the hypothesis were correct.
   Note: It is often important to construct your graph so that the two axes cross at the point (0, 0). This is especially relevant if the dependent variable is expected to have a value of 0 when the independent variable is made 0. In this graph the origin (0, 0) is of no significance as flame temperature would not be 0 °C when total air hole area is 0 mm^2 and so it is appropriate to use any suitable point for the intersection of the two axes. Here, the point (600, 0) is chosen so that a suitably proportioned graph can be drawn, ie one that highlights the relationship between flame temperature and Bunsen air hole area.



7. a. The dependent variable is **'the degree of electrical conductivity of the salt solution'**. Two independent variables are identified. These are **'the concentration of salt in the solution'** and **'the nature (ie type) of salt used to form the solution'**.
   b. Several examples of hypotheses are shown. The first three examples relate salt concentration to conductivity while the next two look at possible hypotheses relating the nature of the salt to solution conductivity:
      - The conductivity of a salt solution increases in direct proportion to the mass of salt dissolved in it.
      - The conductivity of a salt solution increases in direct proportion to the molar concentration of salt.
      - The conductivity of a salt solution is independent of (ie not affected by) the concentration of salt.
      - The conductivity of the salt solution will be the same for all salts.
      - The conductivity of the salt solution is greater for salts that contain more ions in their formula.

c. Many different methods can be described, however whatever hypothesis you choose you will need to measure solution conductivity. So an apparatus like the one shown here would be suitable for testing solution conductivity. Essentially the conductivity is measured as mA on the milliammeter; the greater this reading the greater is the solution conductivity. Keep the voltage low so that currents are small (ie mA).



When using this apparatus you should be careful to keep a number of variables constant as there is a good chance any one of these will affect the conductivity readings, ie use the same pair of electrodes for each test, keep the electrodes immersed to the same depth for each solution, keep the distance between the electrodes constant, keep temperature constant, only operate the meter for a few seconds for each reading. The solution may need to be kept stirred during each of the measurements; a magnetic stirrer could be used here. Two different independent variables could be investigated. If concentration is the independent variable chosen then you will need to make several solutions of different concentration and test the conductivity for each of these. The solutions can be made by weighing (use a mass balance) a small amount of NaCl (say 9.0 g) and making this up to a known solution volume (eg exactly 100 mL). This can be done by adding the measured NaCl sample to a 100 mL volumetric flask then topping this up to the 100 mL mark. Alternatively a less accurate method would be to add the salt to a 100 mL measuring cylinder and topping this up to 100 mL. Solutions of lower concentration can be obtained by repeating this process using different amounts of salt. Alternatively, dilute the original solution. (eg Take 20 mL of original solution and dilute this to exactly 100 mL. In this case the new salt concentration would be 1.8 g per 100 mL.) Use either a volumetric flask or measuring cylinder for volume measurements. Ensure all solutions are prepared with distilled water and use clean glassware for preparing solutions.

If the nature of the solute was chosen as the independent variable then a variety of different salt solutions (eg NaCl, KCl, $MgCl_2$, $BaCl_2$ $AlCl_3$ and so on) could be prepared. Be sure these all have the same concentration. You may wish to keep the molar concentration (mol L^{-1}) constant or the g L^{-1} concentration constant but you will not be able to keep both types of concentration constant. Whatever measurements you take you should repeat the procedure at least twice for each test solution and average the results obtained. This should include remaking each solution

d. If concentration is your chosen independent variable then you would need to calculate the concentration of each solution in g 100 mL^{-1} or g L^{-1} or mol L^{-1}. Do this using **concentration = mass ÷ volume** (for g L^{-1}) or **moles = mass ÷ molar mass** then **concentration = moles ÷ solution volume** (gives mol L^{-1}) use whichever you prefer. Concentration could then be tabulated along with the respective solution conductivity in mA.

A graph would be an ideal way to display the relationship that exists between these two variables. Concentration should be plotted on the horizontal axis (x-axis) as it is the independent variable. Conductivity would then be plotted on the vertical axis (y-axis). The shape of the line of best fit for this graph would show if the relationship between these two variables is the same as the hypothesis predicts. Remember, your measurements will contain some error so allow for this when drawing the line of best fit and when concluding whether the data supports or refutes the hypothesis.

Alternatively if the nature of the solute is your independent variable then it is best to tabulate the conductivity data against the list of salts used. A bar graph could be used here with conductivity plotted on the vertical axis. The independent variable is shown on the x-axis. No scale can be used here as the independent variable (nature of the salt) is discontinuous, ie has discrete values eg NaCl or KCl, that cannot be related to a scale.

Set 7 Measurement errors and significant figures

1. a. Trial **1**: 24.3 g and 0.972 g mL^{-1} Trial **2**: 24.2 g and 0.968 g mL^{-1} Trial **3**: 24.4 g and 0.976 g mL^{-1}
Trial **4**: 22.1 g and 0.884 g mL^{-1} Trial **5**: 24.1 g and 0.964 g mL^{-1} Trial **6**: 24.3 g and 0.972 g mL^{-1}

b. With the exception of Trial 4, the measurements are precise but not accurate. They are precise as they all fall within a narrow range, ie the results are consistent with each other and the variation is small based on the instruments used. They are inaccurate as the density results are quite a bit less than the expected value

(1.00 g mL^{-1}) especially as the instruments used are capable of being precise to 3 significant figures. (Significant figures discussed later.)

c. All of the measured values give consistently low results for the mass of 25.0 mL of water, ie lower than the expected value of 25.0 g. Consistently high or consistently low results are typical of a systematic error so these measurements show signs of systematic error. Measurements also always contain some degree of random error. This causes some results to be higher while others are lower than expected. In this case, with the exception of Trial 4, the measured values of the mass of 25 mL of water range from 24.1 g to 24.4 g. Thus these measurements are not only consistently lower than the expected 25.00 g; a consequence of systematic error; but they vary quite considerably. This variation in measurement values is due to random errors. Trial 4 (22.1 g) has a particularly large random error and is referred to as an outlier or anomalous result.

d. Averaging can eliminate random errors that cause unexpected up or down fluctuations in the results. Averaging tends to eliminate random errors as the randomly high values average out with the randomly low values. Averaging cannot eliminate systematic errors as this type of error produces results that are consistently high or consistently low. It is justifiable to eliminate Trial 4 from the average as this is an anomalous result, ie it is significantly different to the others. A result like this is sometimes called an outlier. Averaging cannot eliminate the effect of an outlier in the data.

e. A calibration check can be performed by placing a standard mass, eg 10.00 g or 50.00 g and so on, onto the balance pan and checking the reading matches the standard mass. A small error (in the last digit) is acceptable but anything bigger than this means the instrument needs to be recalibrated. (Refer to manufacturer's instructions.)

f. The experimental technique involves measuring 25.0 mL of water in a measuring cylinder then pouring this into a beaker (for weighing) however, it is very likely some water will remain in the cylinder. This could be equivalent to as much as 10 drops of water. A drop of water typically has a mass of 0.05 g, so 10 drops would equate to 0.5 g. This means the results could be consistently low, by around 0.5 g. Another systematic error may occur if the students consistently read the volume in the measuring cylinder from the top of the meniscus rather than the bottom. This is an error in measurement technique and not the fault the measuring cylinder. A consequence of this error is that all of their measurements of volume could be lower by as much as 1 mL. This equates to masses that would be consistently lower than expected by around 1 g.

g. All of these trials, including Trial 4 will contain some degree of random error. This causes some measurements to be a little higher and others a little lower than expected. Trial 4 however is significantly different to the others and this suggests a rather large operator error has occurred. Some possibilities include: misreading the measuring cylinder scale and under filling it, not correctly taring the balance before using it, leaning on the balance table, an occasional strong draft or spilling some of the water while transferring it from the measuring cylinder to the beaker prior to weighing. This type of error should not occur in a well conducted experiment.

2. a. When reading a scale it is appropriate to estimate between the two smallest divisions on the scale. The recorded measurement can include all the figures known with certainty plus one more figure that has some uncertainty. From the scale it is clear the temperature is between 78 ^{o}C and 79 ^{o}C. Estimating between these two scale divisions gives 78.5 ^{o}C which would be the most appropriate reading. The measurement 78.50 ^{o}C is inappropriate as the last two digits, 5 and 0, are both uncertain and only one uncertain figure should be recorded in the measurement. The two readings of 78 and 79 are both inadequate as they do not convey the precision offered by the thermometer.

b. Removing the thermometer from the beaker of hot water would have the effect of lowering the thermometer temperature. This happens as the air temperature is much lower than that of the hot water. This incorrect technique would cause the temperature measurements to be consistently low and causes a systematic error in the measurements.

c. The size of this systematic error depends upon the difference in temperature between the water and the room air. The greater this difference the greater is the error. Thus as the water cools, reaching air temperature, the cooling effect of removing the thermometer from the water would decrease and the size of the error would decrease. Eventually when the water is at room temperature there would be zero error due to this incorrect technique.

d. This describes an anomalous data point also known as an outlier. It is probably the result of a significant single operator error such as misreading the thermometer. When drawing the line of best fit it is reasonable to ignore this data point.

3. a. The mass should be recorded as 23.80 g. This correctly shows the precision offered by the mass balance. It is understood the last digit of the digital display, ie 0 contains some uncertainty. Recording 23.8 g does not adequately reflect the precision offered by this instrument and it incorrectly implies there is some uncertainty in the last recorded digit, ie the 8.
   b. This is a systematic error that is due to poor technique. It will cause the results to be consistently low.
   c. No, repeating this experiment using the same technique, ie with the same systematic error in it, will produce consistently low results. Averaging these consistently low values will not improve the final result.
   d. A desiccator is a container, usually made of glass used for keeping substances dry and free of moisture. It contains a desiccant like silica gel that readily absorbs moisture and so keeps both the air and the material inside the desiccator dry. Also, if a hot or warm object is placed on the pan of an electronic balance it will cause an updraft due to convection currents. The updraft will give a systematic error in the mass measurement making it lower than it should be.

4. a. 4 see rule ①
   b. 3 see rule ① and ②
   c. 3 see rule ① and ②
   d. 1 see rule ① and ⑤
   e. 3 see rule ① and ⑤
   f. 1 see rule ① and ⑤
   g. 2 see rule ①
   h. 5 see rule ① and ②, ④
   i. 4 see rule ①, ②, ③ and ④
   j. 1 see rule ① and ③
   k. 2 see rule ① and ③
   l. 6 see rule ①, ② and ④

5. a. 7.88×10^{-1} or 0.788
   b. 2.58×10^{5} or 258000
   c. 1.25×10^{-2} or 0.0125
   d. 4.0435
   e. 1.1×10^{1} or 11
   f. 6.2506×10^{6} or 6250600
   g. 4×10^{2} or 400
   h. 2.000×10^{-4} or 0.0002000
   i. 6.7×10^{3} or 6700

6. a. 6.59×10^{3} L
   b. 4.990×10^{3} mL
   c. 3.72×10^{3} L
   d. 9.8927×10^{8} Pa
   e. 7.8631×10^{1} kPa
   f. 1.499×10^{-2} g
   g. 2.266×10^{3} kPa
   h. 7.72×10^{2} kPa
   i. 7.25×10^{3} kg
   j. 3.4×10^{6} g
   k. 6.301×10^{2} K
   l. 5.02×10^{2} °C

7. a. 42.448 = **42** 0.16 has the least SF (ie 2SF) so the answer is rounded to 2SF.
   b. 5.277931×10^{1} = **5.278×10^{1}** or 0.07250 has the least SF (ie 4SF) so the answer is rounded to 4SF.
   c. $7.879990661 \times 10^{5}$ = **7.9×10^{5}** or Since 350 has only 2SF then the answer is rounded to 2SF.
   d. 3.218809×10^{2} = **3.22×10^{2}** or **322** Since 3.50 has 3SF then the answer is rounded to 3SF.

8. a. 195.142 = **195.1** 192.1 is precise to 1 decimal place so the answer is given to 1 decimal place only.
   b. 0.08513 = **0.0851** Since 0.0032 is precise to the 4th decimal place the answer is given to the 4th decimal place.
   c. $1.731 \times 10^{2} + 32.96 \times 10^{2}$
   = 34.691×10^{2} = **34.69×10^{2}**
   32.96×10^{2} is precise to the second decimal place (with both numbers expressed to the same powers of ten) so the answer is given to the second decimal place.
   d. 189.058 = **189.1** 192.1 is precise to 1 decimal place so the answer is given to 1 decimal place.
   e. $8.192 \times 10^{5} - 7.791 \times 10^{4}$
   = $81.92 \times 10^{4} - 7.791 \times 10^{4}$
   = 74.1290×10^{4} = **74.13×10^{4}** or **741300**
   81.92×10^{4} is precise to 2 decimal places (when both numbers are expressed to 10^{4}) so the answer is given to 2 decimal places.

9. a.
$$\frac{4.64 \times 10^{3} + 14.592}{0.3766 \times 6.312} = \frac{4.64 \times 10^{3} + 0.014592 \times 10^{3}}{0.3766 \times 6.312} = \frac{\mathbf{4.65}4592 \times 10^{3}}{\mathbf{2.377}0992}$$

$$= \mathbf{1.95}80975 \times 10^{3} = \mathbf{1.96 \times 10^{3}} \text{ or } \mathbf{1960}$$

The numerator is evaluated to **4.65**4592 x 10^{3} however it is only precise to two decimal places (addition rules apply) ie **4.65** x 10^{3}. Thus the numerator has the least number of significant figures (3 SF). The answer is given to 3 SF (multiplication and division rules apply). **Remember to carry all digits then apply rounding to the final answer**.

b. $\dfrac{7.332 \times 10^4 - 21}{9.728 \times 3.4741} = \dfrac{7.332 \times 10^4 - 0.0021 \times 10^4}{9.728 \times 3.4741} = \dfrac{\mathbf{7.329}9 \times 10^4}{\mathbf{33.79}60448}$

$= \mathbf{2.168}863 \times 10^3 = \mathbf{2.169 \times 10^3}$ or **2169**

The numerator is evaluated to 7.3299 x 10^4 however it is only precise to three decimal places (addition rules apply) ie 7.330 x 10^4. Thus as the numerator has 4 SF. The answer is given to 4 SF (multiplication and division rules apply).

10. a. area = 12 x 1 x 10^2 = 12 x 10^2 = 1 x 10^3 mm^2
    b. area = 12 x 1.0 x 10^2 = 12 x 10^2 = 1.2 x 10^3 mm^2

    The number of zinc granules (12) is exact. The area estimates of 1 x 10^2 mm^2 and 1.0 x 10^2 mm^2 limit the answer to 1 SF and 2 SF respectively.

11. Random errors are minimised by using the most precise measuring cylinder that is practical for the task. Typically, larger cylinders have larger scale divisions and hence larger random errors. A 10 mL measuring cylinder has the least random error (± 0.05 mL) so use it for measuring 5.0 mL of acid. For measuring the 95 mL of distilled water use the 100 mL measuring cylinder as this is the smallest cylinder, with the least random error, capable of measuring 95 mL of distilled water.

12. The number of drops (20) is exact and so it has unlimited precision. The number of SF is limited by the mass reading 1.059 g which has 4 SF.

    mass one drop = $\dfrac{\text{mass of 20 drops}}{20} = \dfrac{1.059}{20} = \mathbf{5.295 \times 10^{-}}$

13. a. Since the volume 35 mL is only accurate to the units place, then the answer can only be quoted to the units place, ie Total volume = 35 + 6.55 = 41.55 mL = **42 mL**
    b. Use a more precise measuring cylinder, eg a 50 mL measuring cylinder, to measure the 35 mL volume.

Set 8 Writing chemical equations

1. a. Reactants are zinc [$Zn(s)$] and hydrochloric acid [$HCl(aq)$]. The products are zinc chloride [$ZnCl_2(aq)$] and hydrogen [$H_2(g)$].

   b. Zinc [$Zn(s)$] and hydrochloric acid [$HCl(aq)$] will disappear while zinc chloride [$ZnCl_2(aq)$] and hydrogen [$H_2(g)$] are formed.

   c. This is true for all atoms in all reactions. In a chemical reaction atoms are neither created nor destroyed. Only the way in which atoms are bonded with other atoms changes. Thus the number of each type of atom is conserved.

   d. In a chemical reaction mass is conserved, ie the mass of reactants equals the mass of products. In this investigation the student used 6.48 g of reactants and produced a total of 9.87 g of products (7.32 g of $ZnCl_2$ and 2.55 g of H_2). This data shows a significant increase in mass of reactants over products, a 52% increase in mass. Clearly a significant random error or systematic error has occurred as the mass of products is expected to equal the mass of reactants.

2. a. $3HCl(aq) + Fe(OH)_3(s) \rightarrow FeCl_3(aq) + 3H_2O(l)$
   b. $2HNO_3(aq) + BaO(s) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$
   c. $2NO_2(g) + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$
   d. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   e. $2NaOH(aq) + 2Al(s) + 6H_2O(l) \rightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$

3. a. $CuCO_3(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + CO_2(g) + H_2O(l)$
   b. $H_2SO_4(aq) + Cu(OH)_2(s) \rightarrow CuSO_4(aq) + 2H_2O(l)$
   c. $Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$
   d. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
   e. $SO_2(g) + 2KOH(aq) \rightleftharpoons K_2SO_3(aq) + H_2O(l)$
   f. $2NH_4Cl(aq) + Ca(OH)_2(s) \rightleftharpoons 2NH_3(g) + CaCl_2(aq) + 2H_2O(l)$

4. a. $CH_3COOH(aq) + NaHCO_3(s) \rightarrow H_2O(l) + CO_2(g) + NaCH_3COO(aq)$
   b. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ Using double arrows shows this is a **reversible reaction**.
   c. $H_3C_6H_5O_7(s) + 3NaHCO_3(s) \rightarrow 3H_2O(l) + 3CO_2(g) + Na_3C_6H_5O_7(aq)$
   d. $4Fe(s) + 3O_2(g) + 6H_2O(l) \rightarrow 2Fe_2O_3.3H_2O(s)$
   e. $2NaHSO_4(s) + Na_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g) + 2Na_2SO_4(aq)$ Use **double arrows** as for part b.

5. a. $2Fe^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$
   b. $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$
   c. $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$ (See p47.)
   d. $SO_3^{2-}(aq) + 2H^+(aq) \rightleftharpoons SO_2(aq) + H_2O(l)$

6. a. $Al_2(CO_3)_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3CO_2(g) + 3H_2O(l)$
   b. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
   c. $MgO(s) + 2CH_3COOH(aq) \rightarrow Mg^{2+}(aq) + 2CH_3COO^-(aq) + H_2O(l)$
   d. $Co(s) + 2H^+(aq) \rightarrow Co^{2+}(aq) + H_2(g)$
   e. $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
   f. $3NH_3(g) + H_3PO_4(aq) \rightarrow 3NH_4^+(aq) + PO_4^{3-}(aq)$
   g. $3Pb^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Pb_3(PO_4)_2(s)$
   h. $2Ag^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s)$

7. a. $CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$
   b. $Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$
   c. $MgO(s) + 2H^+(aq) \rightarrow Mg^{2+} + H_2O(l)$
   d. $Ca(s) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) + H_2(g)$
   e. $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
   f. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

8. a. Multiply each equation by a suitable factor in order to equalise the linking reagent. Then add the equations and simplify the result.

① $C(s) + CO_2(g) \rightarrow 2CO(g)$................. *OK as is* .....$C(s) + CO_2(g) \rightarrow 2CO(g)$

② $CO(g) + FeO(s) \rightarrow Fe(l) + CO_2(g)$.... *x 2 gives* $+ 2FeO(s) \rightarrow 2Fe(l) + 2CO_2(g)$

Multiplying the coefficients of equation ② by two equalises the amount of the linking reagent CO.

In total $C(s) + CO_2(g) + \mathbf{2CO}(g) + 2FeO(s) \rightarrow \mathbf{2CO}(g) + 2Fe(l) + 2CO_2(g)$

When simplified: $\mathbf{C}(s) + \mathbf{2FeO}(s) \rightarrow \mathbf{2Fe}(l) + \mathbf{CO_2}(g)$

b. ① $O_2(g) \rightarrow 2O(g)$.................... *OK as is*..........$O_2(g) \rightarrow 2O(g)$

② $O_2(g) + O(g) \rightarrow O_3(g)$ ....*x 2 gives* $(g) + 2O(g) \rightarrow 2O_3(g)$

To equalise the amount of the linking reagent O, multiply the coefficients of equation ② by two.

In total: $O_2(g) + 2O_2(g) + 2O(g) \rightarrow 2O(g) + 2O_3(g)$

When simplified: $\mathbf{3O_2}(g) \rightarrow \mathbf{2O_3}(g)$ Notice that $O_2(g) + 2O_2(g)$ is simplified to $3O_2(g)$ and $2O(g)$ is cancelled from the final equation.

c. ① $CFCl_3(g) \rightarrow CFCl_2(g) + Cl(g)$ .... *OK as is*

② $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ .... *OK as is*

③ $ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$.............. *OK as is*

The linking reagent for ① and ② is Cl(g). This is already equalised. For reactions ② and ③ the linking reagent is ClO(g) and this is also equalised. All three equations can now be added and simplified to produce a single overall equation.

$CFCl_3(g) + Cl(g) + O_3(g) + ClO(g) + O(g) \rightarrow CFCl_2(g) + Cl(g) + ClO(g) + O_2(g) + Cl(g) + O_2(g)$

When simplified: $\mathbf{CFCl_3}(g) + \mathbf{O_3}(g) + \mathbf{O}(g) \rightarrow \mathbf{CFCl_2}(g) + \mathbf{Cl}(g) + \mathbf{2O_2}(g)$

Notice that one Cl(g) is cancelled from both sides of the equation leaving one Cl(g) on the product side. ClO(g) is eliminated from both sides of the equation and two $O_2(g)$ on the product side are written as $2O_2(g)$.

Set 9 Electronic structure and the periodic table

1. a. group 14 and period 2 b. group 2 and period 4 c. group 13 and period 4 d. group 17 and period 5

2. a. fluorine F, bromine Br, iodine I and astatine At b. bromine Br c. strontium Sr

d. scandium Sc, titanium Ti, vanadium V, chromium Cr, manganese Mn, iron Fe, cobalt Co, nickel Ni, copper Cu, zinc Zn

3. a. elements
b. periods
c. atomic number
d. groups
e. properties
f. metallic
g. non-metallic
h. chemical
i. similar
j. atomic number
k. noble gases
l. 8
m. 18
n. 32
o. alkali metals
p. alkali earths

4. a. N and P are both from the same group (group 15) of the periodic table so they would most probably have similar chemical properties.

b. Ar and He are both from the same group (group 18) of the periodic table so they would most probably have similar chemical properties.

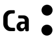
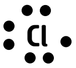
c. C and O would have different chemical properties as they are from different groups.

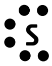
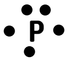
d. O and Se are both from the same group (group 16) of the periodic table so they would most probably have similar chemical properties.

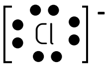
e. K and Br would have very different chemical properties as they occur in the same period and are a great distance apart in that period.

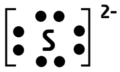
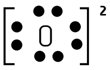
f Mg and S would have very different chemical properties as they occur in the same period and are a great distance apart in that period.

5. a. Ca b. Tl c. Sc d. Ti
From left to right within any period the element's physical properties change from metallic to metalloid to non-metallic. Metallic properties increase towards the bottom of any group.

6. a. **2, 8, 1** 
c. **2, 8, 8, 2** 
e. **2, 8, 7** 

b. **2, 8, 6** 
d. **2, 8, 5** 
f. **2, 8, 18, 3** 

7. a. **2, 8** **Na^+**
c. **2, 8** **Mg^{2+}**
e. **2, 8, 8** 

b. **2, 8, 8** 
d. **2, 8, 8** **Ca^{2+}**
f. **2, 8** 

Metal ions have no dots as they have lost their valence electrons to form positive ions. Core electrons are not shown in the Lewis structure.

8. Isoelectronic atoms or ions have the same number of electrons and the same electron configuration. Each of these species has 10 electrons and has an electron configuration of 2, 8.

9. All three isotopes have six electrons and the same electron configuration, ie 2, 4. As the chemical properties of an element are dependent upon its electron configuration and the carbon isotopes have identical electron configurations then they have identical chemical properties. The same can be said for other isotopes of the same element.

10. a. Li, group 1 period 2 Sr, group 2 period 5 Cl, group 17 period 3 Se, group 16 period 4
Al, group 13 period 3

b. i. The number of valence electrons equals the number of electrons in the highest quantum level of the element's electron configuration.

ii. The element's number of valence electrons equals its periodic group number for groups 1 and 2. For groups 13 to 18 the group number is **10** plus the number of valence electrons.

iii. The element's period number equals the highest quantum level number (valence level) in its electron configuration. (Or number of shells used.)

11.

Periodic table		Number of valence electrons	Valence level number	Electron configuration
Group	Period			
16	3	6	3	2, 8, 6
13	2	3	2	2, 3
15	3	5	3	2, 8, 5
14	3	4	3	2, 8, 4
1	4	1	4	2, 8, 8, 1
17	4	7	4	2, 8, 18, 7

12. a.

Element	Electron configuration	Ion	Electron configuration for the ion	Nearest noble gas	Electron configuration for the noble gas
K	2, 8, 8,1	K^+	2, 8, 8	Ar	2, 8, 8
Mg	2, 8, 2	Mg^{2+}	2, 8	Ne	2,8
S	2, 8, 6	S^{2-}	2, 8, 8	Ar	2, 8, 8
F	2, 7	F^-	2, 8	Ne	2, 8
N	2, 5	N^{3-}	2, 8	Ne	2, 8
Sr	2, 8, 18, 8, 2	Sr^{2+}	2, 8, 18, 8	Kr	2, 8, 18, 8

b. Each element has a partially filled valence level whereas their corresponding ions have eight electrons in their outermost level.

c. The given ions have an electron configuration like that of their nearest noble gas, eg K^+ (2, 8 8) is like Ar (2, 8, 8).

d. When atoms form ions they usually gain or lose sufficient electrons so that their ions have a noble gas electron configuration (ie usually 8 electrons in the outermost level). Clearly there is no need for noble gas elements to form ions as they already have this stable electron configuration.

e. This relationship is consistent for the ions of most elements (especially the main group elements, ie groups 1, 2 and 13 to 18). The elements that do not form ions with a noble gas electron configuration tend to occur amongst the transition metals, especially those further towards the right hand side of the transition metal group of elements.

Set 10 Metallic substances

1. a. valence
   b. metal
   c. electrons
   d. fixed
   e. lattice
   f. move freely
   g. sea of electrons
   h. electrostatic
   i. positive
   j. metallic
   k. non-directional

2. Both sodium and aluminium consist of an array of positive ions surrounded by a mobile sea of electrons. The sodium structure contains metal ions with a positive one charge and has one electron in the sea of electrons for every metal ion. The aluminium structure however, contains aluminium ions with a positive three charge and has three electrons in the sea of electrons for every metal ion.

3. a. For a material to conduct an electric current it must contain mobile charged particles within its structure. As the electrons within the mobile sea of electrons are both free to move and are charged, then they are able to conduct a current. If a voltage is applied to a metal, free electrons (from the mobile sea of electrons) move through the metal structure towards the positive potential. The positive metal ions remain in fixed positions.

   b. The metallic bond is said to be a non-directional bond. Individual ions within the metallic structure are bonded to the mobile sea of electrons (rather than to neighbouring metal ions). If sufficient force is applied to part of the metal then the metallic ions in that region can move relative to one another without disrupting the bond between the metal ions and the mobile sea of electrons. Thus the metal will dent or bend rather than shatter when a force is applied to it.

   c. Electrons within the mobile sea of electrons conduct heat in the form of kinetic energy as they move throughout the solid structure. Vibrating metal ions also contribute to the conduction of heat in metals.

4. The melting points are: Na 98 °C, Mg 650 °C and Al 660 °C. Melting point is an indicator of the strength of the metallic bond, as the strength of the metallic bond increases so the melting point also increases. There is a general increase in melting point (left to right) in the period three metals. This indicates the strength of the metallic bond also increases left to right in the third period metals. The trend however, is not uniform as a much greater increase in melting point is evident from Na to Mg than Mg to Al.

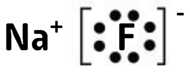
5. **Set A:** The data for Na, Mg and Al does support Harry's hypothesis. As the number of valence electrons increases from Na (one valence electron) to Al (three valence electrons) there is a clear increase in both heat and electrical conductivity. The increase is fairly irregular however, as the increase of one valence electron from sodium to magnesium has a much smaller effect on conductivity than the increase of one valence electron in going from magnesium to aluminium.

   Set B: This data does partially support Harry's hypothesis. As the number of valence electrons increases from K (one valence electron) to V (five valence electrons) there is a general increase in both heat and electrical conductivity. However, there is a significant decrease in both heat and electrical conductivity going from calcium (two valence electrons) to scandium (three valence electrons). Also the increase in conductivity is not uniform with respect to the increase in number of valence electrons.

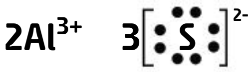
Set 11 Ionic compounds

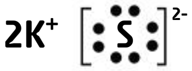
1. a. metal
   b. non-metal
   c. positive
   d. losing
   e. gain
   f. negative
   g. noble gas
   h. three dimensional
   i. unlike
   j. like
   k. attractive
   l. repulsive
   m. stability

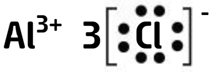
2. When calcium and sulfur atoms collide (touch) a transfer of electrons occurs. Each calcium atom loses two electrons forming a Ca^{2+} ion while each sulfur atom accepts these two electrons to form a S^{2-} ion. The resulting sulfide ions and calcium ions experience strong electrostatic attraction (opposite charges attract) causing them to arrange into a three dimensional array of positive and negative ions. Within the lattice, unlike charged ions are much closer together than like charged ions. This ensures the attractive forces within the lattice exceed the repulsive forces thus resulting in what is referred to as the ionic bond.

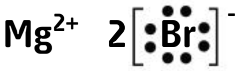
3. a. 

   c. 

   e. 

   b. 

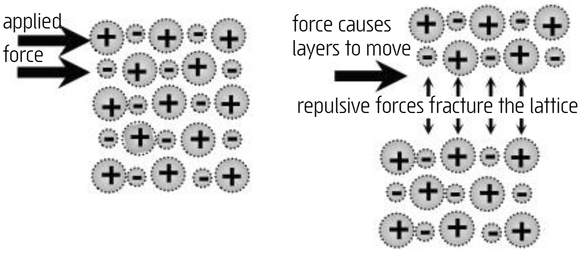
   d. 

   f. 

   Note: The Lewis structures for these **metal ions** have no dots as they have lost their valence electrons to form positive ions. Core electrons are not shown in the Lewis structure.

4. There are two types of forces within the CaO ionic lattice. Attractive forces occur between unlike charged ions, Ca^{2+} and O^{2-} ions, while repulsive forces occur between like charged ions, Ca^{2+} and Ca^{2+} as well as O^{2-} and O^{2-}. On average the distance between like charged ions is significantly **more** than the distance between unlike charged ions. Also the strength of electrostatic forces of attraction and repulsion both diminishes rapidly with increasing distance. As a result the attractive forces within the lattice exceed the repulsive forces so that on balance there is a net attractive force between the ions within an ionic lattice. This net attraction is the ionic bond.

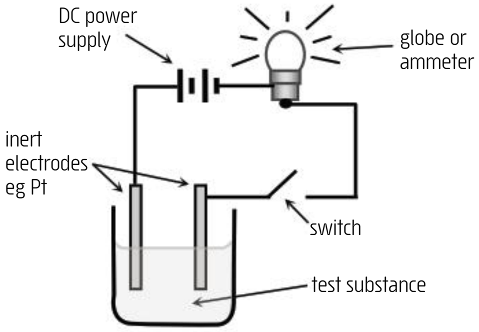
5. When sufficient force is applied to brittle materials they shatter rather than dent or bend. If enough force is applied to part of an ionic lattice the force can cause sections of the lattice to slide in relation to other parts of the lattice. When this happens, like charged ions become closer together than unlike charged ions. In this region of the lattice where slippage occurs the repulsive forces exceed the attractive forces. Consequently the ionic lattice fractures and breaks where the force is applied.



6. a. $AgNO_3$(s) is a **pure** ionic solid consisting of an array of Ag^+ ions and NO_3^- ions occupying fixed positions in a three dimensional ionic lattice.

   $AgNO_3$(l) is a **pure liquid** consisting of Ag^+ ions and NO_3^- ions which can move freely (independently) within the liquid phase.

   $AgNO_3$(aq) is a **solution** consisting of a **mixture** of Ag^+ ions, NO_3^- ions and H_2O molecules. All of these particles can move freely within the solution.

   b. 

   c. They should avoid all contact with skin and eyes as $AgNO_3$ is a corrosive substance. When heating with a Bunsen, wear safety glasses. Provide adequate ventilation as toxic gases may be evolved at either electrode. Take care not to touch hot apparatus.

d. $AgNO_3(s)$ will not conduct. Both $AgNO_3(l)$ and $AgNO_3(aq)$ conduct quite well.

e. For a substance to conduct an electric current it must contain charged particles which are also mobile (able to move freely throughout the material). $AgNO_3(s)$ will not conduct as its charged particles (Ag^+ and NO_3^- are held in fixed positions within the three dimensional lattice structure. $AgNO_3(l)$ will conduct as its charged particles (Ag^+ and NO_3^- (aq) will also conduct an electric current as the charged particles (Ag^+ and NO_3^- When conducting a current, the positive ions move towards the negative electrode while the negative ions move towards the positive electrode.

Set 12 Molecular substances

1. a. non-metal
   b. electrons
   c. covalent
   d. valence
   e. gains
   f. sharing
   g. noble gas
   h. octet
   i. double
   j. six

2. a. covalent molecular
   b. clusters
   c. molecules
   d. covalent
   e. between
   f. van der Waals
   g. intermolecular forces
   h. covalent bonds
   i. unaffected

3. For a substance to conduct an electric current it must contain charged particles which are also mobile, ie are able to move independently through the material. $C_{12}H_{22}O_{11}(s)$ will not conduct as its molecules are neither charged nor free to move. $C_{12}H_{22}O_{11}(l)$ will not conduct as although its molecules are free to move about they are not charged. $C_{12}H_{22}O_{11}(aq)$ will not conduct as although its molecules are free to move about within the solution phase they are not charged.

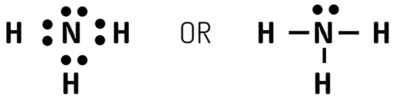
4. Intramolecular forces are the covalent bonds within the cluster of atoms that form a molecule. These are very strong bonds and so the atoms within the molecule are tightly bound together. Intermolecular forces are the forces between neighbouring molecules. These are typically weak forces. When heat is applied to a molecular solid or liquid the weak intermolecular forces are easily overcome (an increase in temperature causes molecular kinetic energy or particle movement to increase) resulting in melting and then boiling. (See Chapter 1.) These weak intermolecular forces explain why many covalent molecular substances are gases or liquids with low boiling points.

5. a.


b.


c.


d.


e.


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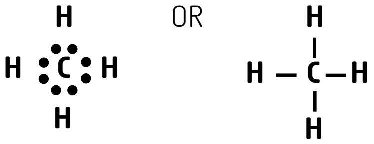

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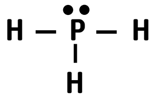

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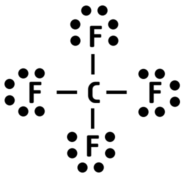

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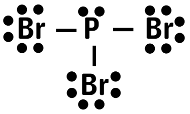

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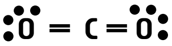

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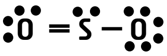

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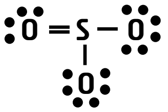

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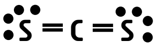

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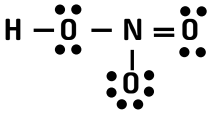

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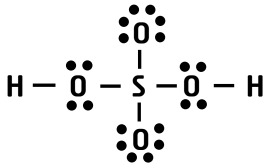

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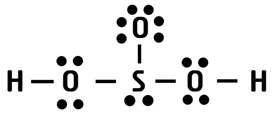

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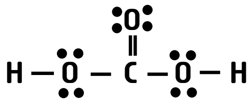

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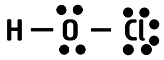

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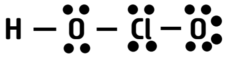

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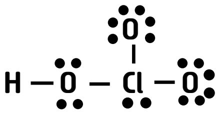

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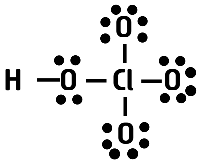


6. A pair of valence electrons that forms a covalent bond is known as a bond pair. A lone pair is a pair of valence electrons not involved in a covalent bond. The ammonia molecule has three bond pairs and one lone pair. (See Fig 1.)

An atom is the smallest particle of an element that has the properties of that element (a nucleus surrounded by electrons). A molecule is a cluster of two or more atoms that are covalently bonded into a single neutral group. (See Fig 2.)

Intramolecular forces are the covalent bonds **within** a molecule. These strong forces bond the atoms into a single cluster known as a molecule. **Intermolecular** forces are the weak forces acting **between** molecules. Intermolecular forces keep the molecular material in a liquid or solid phase depending upon how strong the forces are.

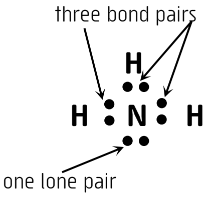


Figure 1 A Lewis structure for the ammonia molecule. Bond pairs form the covalent bonds. These keep the cluster of four atoms together as a single unit called a molecule.

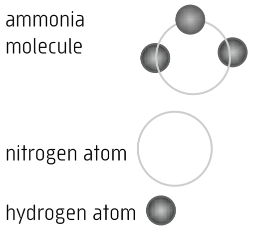


Figure 2 A space filling model of a single ammonia molecule. The molecule consists of three hydrogen atoms covalently bonded to one nitrogen atom.

7. The anomalous behaviour is due to a process of ionisation. When dissolved in water, strong acids like $HCl_{(g)}$, $H_2SO_{4(l)}$, and $HNO_{3(l)}$ interact with water molecules producing ions. An ionisation equation can show this process, $HNO_{3}(aq) \rightleftarrows \quad {}^{-} \qquad {}^{+}(aq)$. The ions formed in this process are free to move throughout the solution and conduct an electric current. The ionisation process only occurs for molecular materials which are acidic or basic in nature.

Set 13 Covalent network substances and carbon allotropes

1. a. covalently
   b. every atom
   c. high
   d, e and f. carbon, silicon,
   g. molecular
   h. structure
   i. molecules
   j. weak
   k. vast array

2. **Covalent bonding** is present in both of these materials. Their different phases, CO_2 being a gas at normal conditions while SiO_2 is a high melting point solid, is due to their different structure. Carbon dioxide has a molecular structure. It consists of molecules of formula CO_2. Each molecule consists of two oxygen atoms covalently bonded by double bonds to a single carbon atom. Strong **intramolecular** forces (covalent bonds) occur within the CO_2 molecule to keep the three atoms strongly bonded as a single cluster known as a molecule. Weak **intermolecular** forces occur **between** the **molecules** making up a sample of CO_2. It is the weak intermolecular forces that result in CO_2 being a gas under normal conditions. Silicon dioxide however consists of a single vast array of Si and O atoms that are covalently bonded to neighbouring Si and O atoms. Each Si atom bonds to four neighbouring O atoms while each O atom is bonded to two neighbouring Si atoms. As the strong bonding extends throughout the SiO_2 structure all atoms are held tightly in their fixed array. Consequently very high temperatures are needed to disrupt (melt) this arrangement and so the substance SiO_2 will be solid at room conditions.

3. Allotropes are different forms of the same element in the same physical state (phase).

   Both diamond and graphite have a covalent network structure. However, their atoms are arranged differently within the two structures. This different arrangement causes their differing properties of hardness and electrical conductivity.

   The diamond structure forms a three dimensional network of carbon atoms with every carbon atom covalently bonded to four adjacent carbon atoms. The bonds are arranged in a tetrahedral formation giving the network its three dimensional structure (Fig 3). This is a very strong arrangement and leads to the high hardness of diamond. The absence of any mobile charged particles within the structure ensures diamond is a non-conductor of electricity. The graphite network structure has each carbon atom covalently bonded to three other carbon atoms forming planar hexagonal rings of six covalently bonded carbon atoms. (See Fig 4.) These planar hexagonal rings interlock with other hexagonal rings to form a two dimensional layer of carbon atoms. Within a sample of graphite many of these two dimensional layers pack on top of each other like sheets of paper in a stack. It is this layered arrangement with weak bonding between the layers which results in graphite being a soft and slippery material.

   Each C atom in the graphite structure shares only three of its four valence electrons forming three covalent bonds with neighbouring C atoms. The fourth unpaired valence electron from each C atom is free to move between the two dimensional layers of C atoms. It is these mobile electrons which enable graphite to conduct an electric current. These electrons also contribute to weak bonding between the layers of carbon atoms.

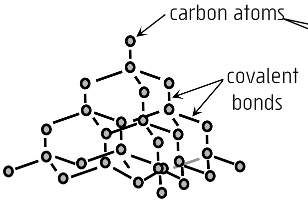


Figure 3 Covalent network structure of diamond. The structure continues in all directions forming a vast three dimensional array of covalently bonded carbon atoms.

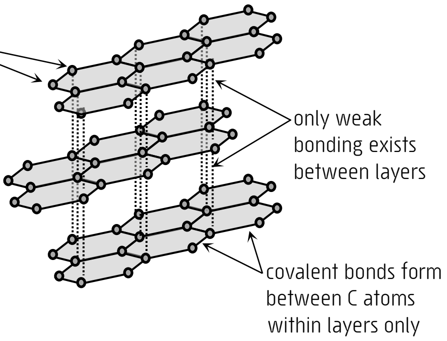
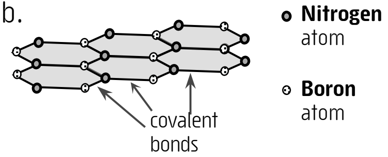


Figure 4 Covalent network structure of graphite. Strong covalent bonding occurs within the two dimensional layers of carbon atoms. Weak forces occur between layers.

4. a. As hexagonal BN has a similar structure to that of graphite it would also be expected to have a high melting point (actually it sublimes at 2600 °C to 2800 °C compared to graphite which sublimes at 3652 °C to 3697 °C) and a soft feel. It could be expected to conduct electricity. (Actually hexagonal BN is a non-conductor of electricity as its structure lacks the mobile valence electrons present in the graphite structure.)

   b.



The covalent network structure of hexagonal BN is similar to that of graphite. Alternating B and N atoms would be consistent with the formula BN. (The layers are aligned differently in hexagonal BN as the hexagons of each layer are located directly above and below each other instead of being staggered as in graphite. Within the structure B and N atoms are directly above and below each other.)

c. This would imply hexagonal BN does not contain mobile charged particles hence all of the valence electrons must remain within bond pairs or lone pairs. So the valence electrons are **not** free to move about within the hexagonal BN structure.

d. Cubic BN would be most suited to this use as it has the diamond structure. This three dimensional arrangement of covalently bonded atoms is known to be responsible for the high hardness of diamond. (Actually cubic BN is used in this way.)

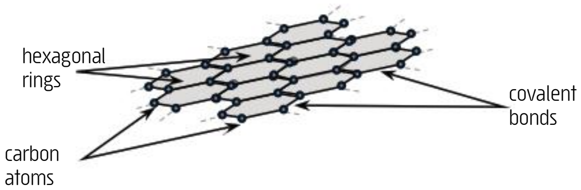
5. a. The 1985 discovery of C_{60} was the result of a collaborative team effort between Harold W. Kroto from the University of Sussex, Richard E. Smalley and Robert F. Curl of Rice University in Houston along with several of their undergraduate students. **Kroto** was attempting to verify the existence of his hypothesised long chain carbon structures that he and other radio astronomers had previously identified as existing in interstellar space. To replicate these conditions and test his idea, Kroto needed the help of Smalley who had invented a piece of equipment called a 'supersonic cluster beam apparatus'. The material they produced using Smalley's apparatus was analysed by **mass spectroscopy** and Kroto was able to verify the presence of the long chain carbon structures he had hypothesised. However, the mass spectrograph also showed an **unexpected** abundance of something they had not been looking for, a previously unknown substance whose mass corresponded to a cluster of 60 carbon atoms. This they later came to know as a C_{60} molecule.

b. 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.

c. A nanometre is a billionth of a meter, 1×10^{-9} m. Buckminsterfullerene, 'buckyballs', C_{60} molecules are referred to as nanoparticles because of their size. A nanoparticle has at least one of its dimensions in the 1-100 nm range. Buckminsterfullerene, C_{60} molecules have a diameter of around one nanometre. A single carbon atom has a diameter of around 0.15 nm and the largest atoms are less than 0.5 nm in diameter.

d. C_{60} has a covalent molecular structure. All 60 carbon atoms within one C_{60} molecule are strongly bonded to one another by covalent bonds. However, only weak attractive forces (van der Waals forces) occur between molecules. As a consequence a bulk sample of C_{60} is most probably soft and weak as its molecules are only weakly attracted to one another.

6. a. Graphite is essentially composed of stacks of graphene sheets loosely bonded together. A graphene sheet consists of a large number of carbon atoms bonded into interlocking hexagonal rings of six carbon atoms.



The graphene sheet is a one atom thick layer but may be many atoms long and wide. It does not have a formula as the number of carbon atoms varies greatly depending upon the overall dimensions of the sheet.

b. The property is known as tensile strength. This measures the ability of a material to resist being stretched. A nanotube resists stretching when pulled along its length as it is very strong in this direction. This strength is due to the continuous covalent bonds between all carbon atoms along the full length of the structure's surface. The strength and arrangement of the covalent bonds also make the nanotube flexible and resistant to breaking when bent or twisted.

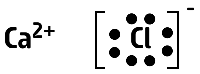
c. Apart from having a high tensile strength and good flexibility (mentioned in Part b), CNTs have a low density compared to metals and depending on their particular structure they may be semiconductors or excellent conductors of electricity. Individual CNTs have a very high surface area for their mass.

Set 14 Review: Bonding, structure and nanotechnology

1. a. ionic
b. metallic
c. covalent molecular
d. ionic
e. covalent network
f. covalent molecular
g. covalent network
h. covalent molecular
i. covalent molecular
j. ionic
k. covalent molecular
l. ionic
m. metallic
n. covalent network
o. covalent network
p. covalent molecular
q. covalent molecular
r. metallic

2. A **covalent bond** is a type of chemical bond where two atoms share one or more pairs of electrons in order to achieve a noble gas electron configuration. The bond results from the electrostatic attraction between the shared pair of **electrons** (**-**) and the two neighbouring **nuclei** (**+**). **Covalent molecular** refers to a type of structure where atoms bond by covalent bonds to form small clusters of two or more atoms. The cluster of covalently bonded atoms is referred to as a molecule. Weak bonding forces may occur between molecules.

3. **a.**



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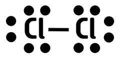
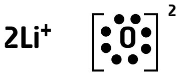
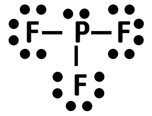


c.

d.



e.



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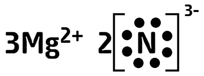

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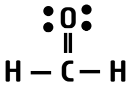

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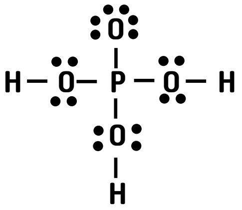
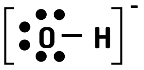


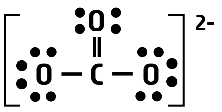
4.

Substance	**Bonding present** covalent, ionic or metallic	**Structure** covalent molecular, metallic, covalent network or ionic lattice	**Phase** solid, liquid, gas or solution	**Physical properties** **Electrical conductivity** yes/no/semi	**Hard and brittle** yes/no	**Malleable and ductile** yes/no
Zn(s)	metallic	metallic	solid	yes	no	yes
$Zn(NO_3)_2$(s)	covalent and ionic	ionic lattice	solid	no	yes	no
$Zn(NO_3)_2$(l)	covalent and ionic		liquid	yes		
$Zn(NO_3)_2$(aq)	covalent and ionic		solution	yes		
$C_{12}H_{22}O_{11}$(s)	covalent	covalent molecular	solid	no	no	no
$C_{12}H_{22}O_{11}$(l)	covalent	covalent molecular	liquid	no		
SiO_2(s)	covalent	covalent network	solid	no	yes	no
C(graphite)(s)	covalent	covalent network	solid	yes	no (brittle but soft)	no
C(diamond)(s)	covalent	covalent network	solid	no	yes	no
C_{60}(s)	covalent	covalent molecular	solid	semi	no	

5. a.



b.



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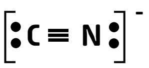

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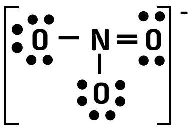

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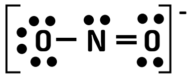

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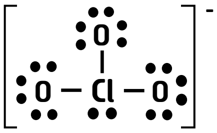


6. a. **Copper**. As copper is a metal it is a good conductor of electricity, malleable and ductile. Its ductility ensures it can flex with the circuit board without cracking. Pure tungsten has similar properties and could be also chosen for the task though copper is a significantly better electrical conductor and tungsten is quite a brittle metal. Woods metal also has the desired properties for this application.

b. **Graphite**. Graphite is a covalent network material which due to its unique structure is both soft and a good conductor of electricity. Being a soft material ensures graphite will wear out rather than the surface over which it slides. None of the other listed materials has this combination of properties. Although metals are good conductors they are generally not soft.

c. **Aluminium oxide**. Aluminium oxide is an ionic solid so it is hard and brittle. This means it would be an abrasive material. As it is brittle the substance can be easily crushed to form the required powder for use in the abrasive cutting compound. Calcium carbonate has similar properties and could be also chosen for the task. While diamond is also hard and brittle it is a relatively rare and expensive material so would not be suitable due to cost.

d. **Woods metal**. Metals typically have moderate to high melting points, however alloys (mixtures of metals) usually have lower melting points than either of the metals from which they are made. So woods alloy is probably the metal with the lowest melting point (actually around 74 °C). Except for candle wax the other materials have high to very high melting points. Candle wax does have a sufficiently low melting point, however being a molecular material it is quite soft and likely to fail due to the water pressure which it must withstand.

e. **CNTs or graphite**. These materials both have high tensile strength, ie resist stretching, and can be incorporated into an epoxy resin to improve its tensile strength characteristics. Both of these are low density solids and so will contribute to the lightweight nature of the resulting composite.

7.

Number of valence electrons		**Formula**	**Bonding**
Element A	**Element B**		
1	7	AB	ionic (A is metallic, group 1, while B is non-metallic, group 17.)
1	5	A_3B	ionic (A is metallic, group 1, while B is non-metallic, group 15.)
2	1	No definite formula as both A and B are metals. These combine in any ratio to form a mixture called an alloy. The bonding between the atoms will be metallic.	
3	6	A_2B_3	ionic (A is metallic, group 3, while B is non-metallic, group 16.)
4	6	AB_2	covalent (A and B are both non-metals as they are from group 14 and 16 respectively.)
6	7	AB_2	covalent (A and B are both non-metals as they are from group 16 and 17 respectively.)
7	7	AB	covalent (A and B are both non-metals from group 17.)

8. A CNT can be described as being a **one dimensional** (ie linear) covalent network structure with no definite formula (ie C_x) as the number of carbon atoms in a single CNT varies depending upon its length and diameter. Each CNT can be described as being like a graphene sheet, ie a single **two dimensional layer** of the **covalent network substance graphite**, rolled into a tube shape. Along the length of the CNT, carbon atoms are covalently bonded into interlocking hexagonal arrangements. There is no theoretical restriction on the length of the CNT. Its length would only depend upon the conditions of manufacture. This explains why the number of carbon atoms in a single CNT is not fixed and hence the formula C_x.
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 (1×10^{-9} m) or more and may be as long as several centimetres. Nanoparticles, like CNTs, are so called as they have one dimension, ie length, width or height, in the nanometre range.

9. a. An amorphous solid is one where the particles are arranged in an irregular way. This is opposite to a crystalline solid where the particles are arranged in a regular lattice. The atoms and ions that make up glass are arranged in an irregular (amorphous) way.

b. A compound contains two or more different elements chemically combined in a definite ratio. As glass does **not** have a definite ratio of elements (its composition varies). It cannot be considered a compound and so is referred to as a mixture.

c. The metal elements like Na, Ca and K will form ionic bonds with oxygen while the non-metal element Si will form covalent bonds with the non-metal oxygen. Hence this substance contains both ionic and covalent bonds.

d. Yes. As described, glass is a mixture of the compounds Na_2O, CaO, K_2O and SiO_2. Three of these compounds are ionic (ie Na_2O, CaO and K_2O) while SiO_2 is a covalent network substance. Both ionic and covalent network materials are hard and brittle. As glass is a mixture it will retain the properties of the compounds of which it is composed.

10.a. The particles of $FeO.Fe_2O_3$ are arranged in a regular lattice.

b. SiO_2 is a covalent network compound and as such it is a hard and brittle material. Its presence in rocks contributes to their hard brittle nature.

c. The compound $FeO.Fe_2O_3$ is an ionic compound. Such compounds are typically quite hard and brittle. Since the chiton uses its teeth to scrape away at the hard rock surface their teeth would wear away very quickly were it not for the hard coating of the ionic compound $FeO.Fe_2O_3$.

11.a. Nanoparticles are particles with at least one dimension in the 1-100 nanometre range (ie 1-100 x 10^{-9} m). Apart from fullerenes (CNTs, C_{60} and so on) many materials can be prepared as nanoparticles, eg quantum dots are nanoparticles typically made from ZnS or ZnSe. Some sunscreens contain nanoparticles of ZnO or TiO_2.

b. 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. These result from their small particle size. Zinc oxide particles, for example, are opaque and white, however, when prepared as nanoparticles they become colourless and invisible. Nanoparticle size samples of ZnS or CdSe, known as quantum dots, exhibit a variety of colours when exposed to UV light. This does not happen to a bulk sample of ZnS or CdSe.

12.a. Nanocomposites 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). Modern nanocomposite applications involve the addition of manufactured nanotubes or graphene to plastics like polypropylene, polystyrene, polycarbonate and epoxy resins.

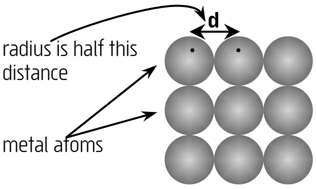
b. Nanocomposites can have enhanced or modified properties such as lower density, improved mechanical strength, electrical and thermal conductivity, catalytic and optical properties that are superior to those of traditional composites like fibreglass or carbon fibre reinforced plastics.

13. A dendrimer is a nanoparticle that can be used as a molecular carrier. In this example the dendrimer will carry four molecules, one that recognizes cancer cells, another that is a therapeutic agent able to kill cancer cells, a third molecule which recognizes when the cancer cell dies and a fourth molecule that signals the cancer cell's death. The resulting dendrimer package is called a nanodevice as it has several components that act together to produce an outcome, ie it is considered a device which has a nanoscale size.

14. Laser ablation involves using high powered laser pulses to vaporise a graphite target in an inert atmosphere. The vaporised carbon atoms collect as CNTs on a water cooled collector surface. A small amount (≈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 sulfide particles. Some other techniques include solution evaporation, chemical vapour deposition, microbial synthesis and chemical precipitation from solution.

Set 15 Periodic trends

1. a. The atomic radius in a metal is half the distance between the centres of two adjacent atoms in the metallic lattice, ie ½d.



b. Periods of elements are represented in the graphed data by elements H to He (1st period), Li to Ne (2nd period) and Na to Ar (3rd period). In each case the atomic radius decreases from left to right in a period (eg from Li to Ne) thus supporting the statement 'left to right in a period of the periodic table the atomic radius decreases as the atomic number increases.'

c. The nuclear charge (+) increases for each consecutive element from left to right in a period (more protons in the nucleus). This means electrons (-) in the electron cloud experience an increasing force of attraction toward the nucleus. Consequently electrons on average are closer to the nucleus in atoms further to the right in a period. Thus the atomic radius decreases for elements further to the right in a period.

d. Atomic radius increases down the groups of the periodic table. This is supported by data for all groups shown on the graph eg group 1 (Li, Na, K) atomic radius increases from Li (≈ 150×10^{-12} m) to K (≈ 230×10^{-12} m).

e. The trend of increasing atomic radius down any group of the periodic table is due to the outer electrons of elements lower in a group occupying higher numbered shells. At the start of each period electrons commence filling higher shells (eg valence shell for Li is 2, for Na is 3 and for K is 4). Electrons in higher shells have a higher total energy and are on average further from the nucleus. This causes the atoms further down a group to have a larger radius. This occurs despite the increasing nuclear charge.

2. a. argon b. F, Cl, Br c. Br, Cu, Ca

3. a. physical
b. minimum
c. most loosely
d. gaseous phase
e. $Na^+_{(g)} + e^-$
f. positive
g. periodic trend
h. atomic number
i. increases
j. decreases
k. nuclear charge
l. further
m. shielding

4. a. These elements occur in group 2 of the periodic table. They are the second, third and fourth element

b. The first ionisation energy for these elements decreases in order from Mg to Ca to Sr. In this same order, Mg to Ca to Sr, the outermost electron being ionised is from a progressively higher shell. Since electrons in higher shells are further from the nucleus they are more weakly attracted to the nucleus. For this reason it takes less energy (lower ionisation energy) to remove the outermost electron from elements lower in a group. This trend occurs despite an increasing nuclear charge which would act to increase the attraction of the outermost electron (-) for the nucleus (+) were it not for the effect of increasing distance (higher shell).

c. The first ionisation energy for Na would be lower than for Mg. In each case the outermost electron occurs in the 3rd shell. However the greater nuclear charge of Mg (12+) compared to Na (11+) causes a stronger electron-nucleus attraction in Mg. This acts to give Mg a higher first ionisation energy than Na.

5. a. (lowest) Mg, P, Ar (highest)
b. (lowest) Br, Cl, F (highest)
c. (lowest) Br, Ga, Ca (highest)
d. (lowest) F, Cl, I (highest)
e. (lowest) C, N, O (highest)
f. (lowest) Mg, Br, O (highest)
g. (lowest) K, Ca, Ga (highest)

The rankings are based on the general periodic trends, ie ionisation energy and electronegativity both increase left to right in a period and decrease top to bottom in a group, atomic radius decreases left to right in a period and increases top to bottom in a group, the number of valence electrons is the same within a group and increases left to right in a period.

6.

Element A	**Element B**	**Formula**	**Covalent, ionic or metallic bonding**
16 (non-metal)	17	AB_2	covalent
13 (not boron)	16 (non-metal)	A_2B_3	ionic
14 (not Sn or Pb)	14 (not Sn or Pb)	AB	covalent
1 (not H)	15 (non-metal)	A_3B	ionic
13 (metallic)	17	AB_3	ionic
2	16(non-metal)	AB	ionic
17	17	AB	covalent

7. a. Metallic physical properties include: good conductors of electricity, good conductors of heat, malleable and ductile, shiny (when scratched) and solid at room temperature (excepting mercury which is a liquid).

b. Most evident in groups 13 to 16, eg for group 13, B is a metalloid and the remaining elements are all metals, in group 14, C is a non-metal, Si and Ge are metalloids while Sn and Pb are metals.

c. Ionisation energy decreases down all groups of the periodic table. Formation of the metallic structure requires metal atoms to form positive ions by releasing their valence electrons. The lower an element's ionisation energy the easier it is to achieve this, as less energy will be required to release valence electrons.

8. a. Metals do not normally form covalent bonds. For the non-metals from groups 14 to 18 the number of covalent bonds is normally; 4 for group 14, 3 for group 15, 2 for group 16, 1 for group 17 and none for group 18. Hence the covalent bonding capacity of non-metal elements is a maximum of 4 for group 14 and decreases as the periodic group number increases, reaching 0 for group 18.

b. For the metals from groups 1, 2, and 13 the ionic charge is normally; 1+ for group 1, 2+ for group 2 and 3+ for group 13. Hence the ionic bonding charge of a metal element is positive and increases as the group number increases.

For the non-metal elements from groups 14, 15, 16, 17 and 18 the ionic charge is normally: 4- for group 14, 3- for group 15, 2- for group 16, 1- for group 17 and 0 for group 18 (these do not form ionic bonds). Hence the ionic bonding charge of a non-metal element is negative with the highest magnitude for group 14 and the magnitude of ionic charge decreasing as the group number increases, reaching 0 for group 18.

9. a. $2K_{(s)} + 2H_2O_{(l)} \rightarrow 2K^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}$ and $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + H_{2(g)}$

b. Ionisation energy decreases down any group of the periodic table. The reaction with water requires the metal element to become oxidised, ie lose one or more electrons. The lower an element's ionisation energy the easier it is to achieve this as less energy will be required to remove valence electrons. Thus this reaction becomes more favourable with elements lower in a group (lower ionisation energy).

c. i Ionisation energy increases left to right in any period of periodic table. The reaction with water requires the metal element to become oxidised, ie lose one or more electrons. The lower an element's ionisation energy the easier it is to achieve this as less energy will be required to remove valence electrons. Hence this reaction becomes more favourable with metals further to the left in a period (lower ionisation energy). Thus as group 1 metals are to the left of group 2 metals then group 1 metals will have the lower ionisation energy and greater tendency to form 1+ ions and thus show the greatest reaction tendency with water.

ii The number of valence electrons per atom increases by one for each consecutive element left to right in a period. The trend starts off with one valence electron for group 1 elements, then two for group two elements and so on (disregarding transition metals). During this reaction the metal element loses all of its valence electrons. Thus Na loses one valence electron to form a Na^+ ion while Ca loses two valence electrons to form a Ca^{2+} ion.

iii Ionisation energy decreases down any group of the periodic table. The reaction with water requires the metal element to become oxidised, ie lose one or more electrons. The lower an element's ionisation energy the easier it is to achieve this as less energy will be required to remove valence electrons. Thus this reaction becomes more favourable with elements lower in a group (lower ionisation energy). Hence for group 2, Be should show the least reactivity with water (does not actually react with water) while radium should show the greatest reactivity (reacts vigorously possibly exploding) with water.

10. **a.** B **b.** C **c.** B **d.** A **e.** None as group 18 elements have 8 valence electrons, or 2 for He. **f.** D (should have a high electronegativity)

11. a. Fluorides with ionic bonding: NaF, MgF_2, AlF_3. Fluorides with covalent bonding: SiF_4, PF_3, SF_2, ClF.

When elements with high electronegativity combine with elements of low ionisation energy (or low electronegativity) they will form an ionic bond. In doing so the element of high electronegativity (has a strong attraction for electrons) gains electrons forming a negative ion while the element of low ionisation energy (can relatively easily lose electrons) loses electrons forming the positive ion. It can also be said that as the difference in electronegativity of two bonded atoms increases so the tendency for them to form an ionic bond also increases.

When two elements of high electronegativity combine they will form a covalent bond. As both elements attract electrons relatively strongly neither is able to form positive ions. Instead both elements share electrons (covalent bond) to achieve a full valence shell.

b. In each case the non-metal element combines with sufficient fluorine to achieve 8 electrons (an octet) in its valence level. Thus for Cl with 7 valence electrons only one F atom can be bonded, S with 6 valence electrons will bond to two F atoms, P with 5 valence electrons will bond to three F atoms and Si with 4 valence electrons will bond to four F atoms.

c. In each case these metal elements combine with sufficient fluorine to remove all of the electrons normally present in their valence shell. Also, each F atom can accept a single electron to form an F^- ion. Thus, Na with one valence shell electron loses this single valence electron resulting in one Na^+ ion and one F^- ion to form NaF.

Ca with 2 valence shell electrons will lose both valence shell electrons resulting in one Ca^{2+} ion and two F^- ions to form CaF_2. Al with three valence shell electrons will lose all three of its valence shell electrons resulting in one Al^{3+} ion and three F^- ions to form AlF_3. Hence the ionic bonding capacity of a metal element increases as the number of valence shell electrons increases.

Set 16 Working with moles

1. a. **6.94 g mol^-** **16.00 g mol^-** **207.2 g mol^-**
   b. **65.38 g mol^-** d. **14.01 g mol^-** f. **55.85 g mol^-**

2. a. **M(O_2)** = 2 x 16.00 = **32.00 g moL^{-1}**
   b. **M(H_2)** = 2 x 1.008 = **2.016 g moL^-**
   c. **M($CaCl_2$)** = 40.08 + 2 x 35.45 = **110.98 g moL^-**
   d. **M($CuSO_4$)** = 63.55 + 32.07 + 4 x 16.00 = **159.62 g moL^-**
   e. **M[$(NH_4)_2SO_4$]** = 2 x 14.01 + 8 x 1.008 + 32.07 + 4 x 16.00 = **132.15 g moL^-**
   f. **M[Cl_2]** = 2 x 35.45 = **70.90 g moL^-**
   g. **M(Fe_2O_3)** = 2 x 55.85 + 3 x 16.00 = **159.70 g moL^-**
   h. **M[$Cu(HSO_4)_2$]** = 63.55 + 2 x 1.008 + 2 x 32.07 + 8 x 16.00 = **257.71 g moL^-**
   i. **M[$Al_2(SO_4)_3$]** = 2 x 26.98 + 3 x 32.07 + 12 x 16.00 = **342.17 g moL^-**
   j. **M[$Ba(OH)_2$]** = 137.3 + 2 x 16.00 + 2 x 1.008 = **171.32 g moL^-**
   k. **M($Na_2CO_3.10H_2O$)** = 2 x 22.99 + 12.01 + 13 x 16.00 + 20 x 1.008 = **286.15 g moL^-**
   l. **M[$Cu(CH_3COO)_2.H_2O$]** = 63.55 + 4 x 12.01 + 5 x 16.00 + 8 x 1.008 = **199.65g moL^-**

3. a. **m($MgBr_2$)** = n x M = 3.15 x (24.31 +2 x 79.90) = **5.80 x 10^2 g** (3 SF)
   b **m(Fe_2O_3)** = n x M = 1.74 x 10^{-3} x (2 x 55.85 + 3 x 16.00) = **0.278 g** (3 SF)
   c. **m[$Cu(HSO_4)_2$]** = n x M = 0.395 x 257.71 = **102 g** (3 SF)
   d **m[$Na_2CO_3.10H_2O$]** = 1.25 x 10^3 x 286.15 = **3.58 x 10^5 g** (3 SF)
   e. **m[H_2SO_4]** = n x M = 7.38 x10^{-2} x 98.09 = **7.24 g** (3 SF)
   f. **m[$H_2C_2O_4.2H_2O$]** = 4.72 x 10^2 x 126.07 = **5.95 x 10^4 g** (3 SF)

4. a. **n(H_2O)** $= \frac{m}{M} = \frac{250}{18.016} =$ **14 mol** (2 SF)

   b. **n[$(NH_4)_2SO_4.2H_2O$]** $= \frac{m}{M} = \frac{1.29 \times 10^{-3}}{168.19} =$ **7.67 x 10^-**

   c. **n[CH_3COOH]** $= \frac{m}{M} = \frac{4.29}{60.05} =$ **7.14 x 10^-**

5. a One NH_3 molecule contains one N atom ∴ **n(N atoms)** =1 x n(NH_3) = 1 x 4.50 = **4.50 mol** of N atoms
   One NH_3 molecule contains three H atoms ∴ **n(H atoms)** =3 x n(NH_3) = 3 x 4.50 = **13.5 mol** of H atoms
   b. One H_2SO_4 molecule contains two H atoms ∴ **n(H atoms)** = 2 x n(H_2SO_4) = 2 x 0.25 = **0.50 mol** of H atoms
   One H_2SO_4 molecule contains one S atom ∴ **n(S atoms)** = 1 x n(H_2SO_4) = 1 x 0.25 = **0.25 mol** of S atoms
   One H_2SO_4 molecule contains four O atoms ∴ **n(O atoms)** = 4 x n(H_2SO_4) = 4 x 0.25 = **1.0 mol** of O atoms

c. One Fe_2O_3 formula unit contains two Fe^{3+} ions ∴ **n(Fe^{3+}** 2 x n(Fe_2O_3) = 2 x 1.7 = **3.4 mol** of Fe^{3+} ions

One Fe_2O_3 formula unit contains three O^{2-} ions ∴ **n(O^2** 3 x n(Fe_2O_3) = 3 x 1.7 = **5.1 mol** of O^{2-} ions

d. One $Ca_3(PO_4)_2$ formula unit contains three Ca^{2+} ions ∴ **n(Ca^{2+}** 3 x n[$Ca_3(PO_4)_2$] = 3 x 0.28
= **0.84 mol** of Ca^{2+} ions

One $Ca_3(PO_4)_2$ formula unit contains two PO_4^{3-} ions ∴ **n(PO_4** 2 x n[$Ca_3(PO_4)_2$] = 2 x 0.28 =
= **0.56 mol** of PO_4^{3-} ions

6. a. **n(CO_2)** $= \frac{V_{(stp)}}{22.71} = \frac{472.0}{22.71} =$ **20.78 mol** (4 SF) Convert the STP volume of carbon dioxide to an equivalent amount in moles using n(gas) = $V_{(stp)} \div 22.71$.

b. **n(H_2)** $= \frac{V_{(stp)}}{22.71} = \frac{3.50 \times 10^3}{22.71} =$ **154 mol** (3 SF) Convert the STP volume of hydrogen to an equivalent amount in moles using n(gas) = $V_{(stp)} \div 22.71$.

c. **n(Cl_2)** $= \frac{V_{(stp)}}{22.71} = \frac{0.1700}{22.71} =$ **7.486 x 10^-** **Note**: 170.0 mL = 0.1700 L.

7. a. **V(CO_2 at STP)** = n x 22.71 = 2.5 x 22.71 = **56.8 L** (3 SF) Rearranging: n(gas) = $V_{(stp)} \div 22.71$ shows that: $V_{(stp)}$ = n(gas) x 22.71.

b. **V(O_2 at STP)** = n x 22.71 = 0.550 x 22.71 = **12.5 L** (3 SF) Procedure as for 7a.

c. n(H_2 gas) $= \frac{m}{M} = \frac{8.32}{2.016} = 4.127$ mol First convert the mass of hydrogen to a molar amount (ie n = m ÷ M) then convert the molar amount of hydrogen to a volume as in part a and b.

V(H_2 at STP) = n x 22.71 = 4.127 x 22.71 = **93.7 L** (3 SF)

d. n(NH_3 gas) $= \frac{m}{M} = \frac{6.50 \times 10^{-2}}{17.034} = 3.816 \times 10^{-3}$ mol Procedure as for 7c.

V(NH_3 at STP) = n x 22.71 = 3.816 x 22.71 = **8.67 x 10^-** The answer only has 3 SF, as the original data, 6.50 x 10^{-2}, only has 3 SF.

8. a. n(O_2 inhaled) $= \frac{V_{(stp)}}{22.71} = \frac{0.50 \times 21}{22.71 \times 100} = 4.62 \times 10^{-3}$ mol Remember only 21 % (ie 21/100) of the 0.50 L breath of air is O_2 gas.

m(O_2 inhaled) = n x M = 4.62 x 10^{-3} x 32.00 = **0.15 g of O_2 gas** (2 SF)
(Note: The final numerical answer to a question involving **estimates** should only be quoted to 1-2 SF.)

b. m(O_2 **absorbed** in one breath) = m(O_2 **inhaled** in one breath) x $\frac{(21-16)}{21} = \frac{0.15 \times 5.0}{21}$

= 3.5 x 10^{-2} g (Note: The fraction of absorbed O_2 in each breath is 5/21.)

m(O_2 absorbed in a week) = number of breaths in a week x mass of oxygen absorbed in one breath
= (14 x 60 x 24 x 7) x 3.52 x 10^{-2} g
= **5.0 x 10^3** **gas ie 5.0 kg** (2 SF)
(Note: The final numerical answer to a question involving **estimates** should only be quoted to 1-2 SF.)

9. a. n(CO_2 $\frac{\quad}{M} = \frac{2.19 \times 10^5}{44.01} = 4.976 \times 10^3$ mol Procedure as for 7c, ie convert m(CO_2) to moles then n(CO_2) to $V_{(STP)}$. Remember to convert 219 kg to 2.19 x 10^5 g.

V(CO_2 = n x 22.71 = 4.976 x 10^3 x 22.71 = **1.13 x 10^5 L** (3 SF)

b. V(O_2 formed) = 1.13 x 10^5 L As given in the question background.

n(O_2 $\frac{(stp)}{22.71} = \frac{1.13 \times 10^5}{22.71} = 4.98 \times 10^3$ mol of O_2 Procedure as for question 6.

m(O_2 = n x M = 4.98 x 10^3 x 32.00 = **1.59 x 10^5 g of O_2 gas consumed ie 159 kg** (3 SF)

10. **n(H_2)** = $\frac{V_{(stp)}}{22.71}$ = $\frac{0.1635}{22.71}$ = **7.199 x 10^{-}**

Remember to convert the STP volume of H_2 (163.5 mL) to an equivalent amount in litres (0.1635 L).

11. a. Convert the given mass of CO_2 (55.0 g) to an equivalent amount in moles. Having found the molar amount convert this to an equivalent STP volume of CO_2.

n(CO_2) = $\frac{m}{M}$ = $\frac{55.0}{44.01}$ = 1.25 mol

V(CO_2 at STP) = n x 22.71 = 1.25 x 22.71 = **28 L** (2 SF) The balloon will inflate to a volume of 28 L not 32 L as expected. This answer of course assumes the balloon is at STP.

12. Since each formula unit of $Al_2O_3.3H_2O$ contains two Al^{3+} ions then:
n(Al) = 2 x n($Al_2O_3.3H_2O$) = 2 x 4.70 x 10^3 = 9.40 x 10^3 mol of Al

Now determine the mass of Al present in 9400 mol of it, ie:
m(Al) = n x M = 9.40 x 10^3 x 26.98 = **2.54 x 10^5 g** of Al can be obtained (2SF)

Set 17 Stoichiometry with mass and moles

1. a. $n(CO_2) = \frac{\mathbf{28}}{\mathbf{4}} \text{ x } n(C_7H_5O_6N_3)$ c. $n(H_2O) = \frac{\mathbf{10}}{\mathbf{21}} \text{ x } n(O_2)$

   b. $n(O_2) = \frac{\mathbf{21}}{\mathbf{4}} \text{ x } n(C_7H_5O_6N_3)$ d. $n(CO_2) = \frac{\mathbf{28}}{\mathbf{6}} \text{ x } n(N_2)$

2. $n(H_2SO_4) = \frac{3}{2} \text{ x } n(Al) = \frac{3 \text{ x } 9.63}{2} = 14.4 \text{ mol}$ (3SF) The coefficients in the equation show the molar amount of H_2SO_4 is 1.5 times (3/2) that of Al.

   $\mathbf{n(Al_2(SO_4)_3)} = \frac{1}{2} \text{ x } n(Al) = \frac{1 \text{ x } 9.63}{2} = \mathbf{4.82 \text{ mol}}$ (3SF) The coefficients in the equation show the molar amount of $Al_2(SO_4)_3$ is half (1/2) that of Al.

3. $\mathbf{n(O_2)} = \frac{6}{2} \text{ x } n(C_2H_5OH) = \frac{6 \text{ x } 3.41}{2} = \mathbf{10.2 \text{ mol}}$ (3SF)

4. $n(C_3H_8) = \frac{m}{M} = \frac{4.5 \text{ x } 10^3}{44.094} = 1.0 \text{ x } 10^2 \text{ mol}$ (2SF) Note: 4.5 kg C_3H_8 = 4500 g C_3H_8.

   and $\mathbf{n(CO_2)} = \frac{3}{1} \text{ x } n(C_3H_8) = \frac{3 \text{ x } 1.0 \text{ x } 10^2}{1} = \mathbf{3.1 \text{ x } 10^2}$

   Also $\mathbf{n(H_2O)} = \frac{4}{1} \text{ x } n(C_3H_8) = \frac{4 \text{ x } 1.0 \text{ x } 10^2}{1} = \mathbf{4.1 \text{ x } 10^2}$

5. a. $n(HF) = \frac{m}{M} = \frac{3.72}{20.008} = 1.86 \text{ x } 10^{-1} \text{ mol}$ (3SF) The molar amount of HF can be used to find the molar amount of Na_2SiO_3 dissolved.

   $\mathbf{n(Na_2SiO_3)} = \frac{1}{8} \text{ x } n(HF) = \frac{1 \text{ x } 1.86 \text{ x } 10^{-1}}{8} = \mathbf{2.32 \text{ x } 10^{-}}$

   b. $n(Na_2SiO_3) = \frac{m}{M} = \frac{16.77}{122.07} = 1.374 \text{ x } 10^{-1} \text{ mol}$

   and $\mathbf{n(NaF)} = \frac{2}{1} \text{ x } n(Na_2SiO_3) = \frac{2 \text{ x } 1.374 \text{ x } 10^{-1}}{1} = \mathbf{2.748 \text{ x } 10^{-}}$

   c. $n(HF) = \frac{m}{M} = \frac{82.59}{20.008} = 4.128 \text{ mol}$

   and $\mathbf{n(H_2SiF_6)} = \frac{1}{8} \text{ x } n(HF) = \frac{4.128}{8} = \mathbf{0.5160 \text{ mol}}$ (4SF)

6. a. $n(H_2) = \frac{m}{M} = \frac{9.25 \times 10^{-2}}{2.016} = 4.59 \times 10^{-2}$ mol (3SF) *and* $n(Zn) = \frac{1}{1} \times n(H_2) = 4.59 \times 10^{-2}$ mol

   m(Zn) $= n \times M = 4.59 \times 10^{-2} \times 65.38 =$ **3.00 g** (3SF)

   b. $n(Zn) = \frac{m}{M} = \frac{7.00 \times 10^{-3}}{65.38} = 1.07 \times 10^{-4}$mol *and* $n(ZnCl_2) = \frac{1}{1} \times n(Zn) = 1.07 \times 10^{-4}$ mol

   so **m(ZnCl$_2$** $= n \times M = 1.07 \times 10^{-4} \times 136.28 =$ **1.46 x 10^{-} g or 14.6 mg** (3SF)

7. a. $n(SO_2) = \frac{m}{M} = \frac{2.95 \times 10^{13}}{64.07} = 4.60 \times 10^{11}$ mol Note: 1 tonne = 1000 kg = 1×10^{6} g

   and **n(S)** $= n(SO_2) =$ **4.60 x 10^{11} mol** (3SF)

   b. $n(SO_2$ from coal fired power stations$) = \frac{75 \times 4.60 \times 10^{11}}{100} = 3.5 \times 10^{11}$ mol

   also $n(CaO) = n(SO_2) = 3.5 \times 10^{11}$ mol
   and **m(CaO)** $= n \times M = 3.5 \times 10^{11} \times 56.08 =$ **1.9 x 10^{13} g of CaO**, ie **19 million tonnes of CaO needed** (2SF)

   c. The formation of lime from calcium carbonate is as follows, $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$. This equation shows the production of one mole of lime, CaO is accompanied by the production of 1 mole of $CO_{2(g)}$, a greenhouse gas. Thus producing significant amounts of lime will be accompanied by the formation of equally significant amounts (in moles) of the greenhouse gas $CO_{2(g)}$. [Also, as kilns operate at high temperatures, then further $CO_{2(g)}$ will be formed as a consequence of the fossil fuel combustion needed to produce the required high kiln temperatures.]

8. a. $n(CO_2) = \frac{m}{M} = \frac{0.4959}{44.01} = 1.127 \times 10^{-2}$mol *and* $n(Na_2CO_3.10H_2O) = n(CO_2) = 1.127 \times 10^{-2}$ mol

   so **m(Na$_2$CO$_3$.10H$_2$O)** $= n \times M = 1.127 \times 10^{-2} \times 286.15 =$ **3.224 g** (4SF)

   b. **% Na$_2$CO$_3$.10H$_2$O** $= \frac{m(Na_2CO_3.10H_2O) \times 100}{m(\text{washing soda } \textbf{mixture})} = \frac{3.224 \times 100}{3.312} =$ **97.35%** (4SF)

9. a. $m(CO_2) = [m(\text{impure } NaHCO_3) + m(\text{flask} + HCl)] - m(\text{flask and contents after reaction})$
   $= (57.982 + 4.362) - 60.373 = 1.971$ g (This is correct to 3DP.)

   As CO_2 has a low solubility in a strongly acidic solution it is reasonable to assume it is totally expelled from the solution as CO_2 gas and thus causes the weight loss noted in the experiment.

   b. $n(CO_2) = \frac{m}{M} = \frac{1.971}{44.01} = 4.479 \times 10^{-2}$ mol *and* $n(NaHCO_3) = \frac{1}{1} \times n(CO_2) = 4.479 \times 10^{-2}$ mol

   m(NaHCO$_3$ $= n \times M = 4.479 \times 10^{-2} \times 84.01 =$ **3.762 g** (4SF)

   c. **%** $NaHCO_3 = \frac{m(NaHCO_3) \times 100}{m(\text{impure sample containing } NaHCO_3)} = \frac{3.762 \times 100}{4.362} =$ **86.25%** (4SF)

   d. Considerable fizzing will occur as this reaction proceeds, thus it is likely that droplets of solution will spray or spatter from the flask. This will increase the weight loss shown by the reaction vessel. A restriction of some sort could be added to the mouth of the flask, eg a one holed stopper with a short length of glass tubing or a filter funnel may be inserted into the opening of the flask. This will reduce the loss of solution by spattering while allowing $CO_{2(g)}$ to escape the flask. Further, if the reaction vessel gets too hot, then a significant amount of water vapour or $HCl_{(g)}$ may be lost from the flask.

   e. An error like this would be a systematic error. Systematic errors produce consistently high or consistently low results. If the experiment were repeated several times, this same error, ie due to the loss of solution by spattering, would cause a consistently high reading for the mass of carbon dioxide evolved.

10. a. $n(O_2) = \frac{m}{M} = \frac{3.47}{32.00} = 0.108$ mol *and* $n(H_2O_2) = \frac{2}{1} \times n(O_2) = \frac{2 \times 0.108}{1} = 0.217$ mol

   m(H$_2$O$_2$) $= n \times M = 0.217 \times 34.016 =$ **7.38 g** (3SF)

   b. $\% H_2O_2 = \frac{m(H_2O_2) \times 100}{m(H_2O_2 \text{ solution})}$ $\therefore$ **m(H$_2$O$_2$ solution)** $= \frac{m(H_2O_2) \times 100}{\% H_2O_2} = \frac{7.38 \times 100}{18.5} =$ **39.9 g** (3SF)

11. a. Multiply each equation by a suitable factor (one that equalises the linking reagent). Then add the three equations and simplify the result.

① $S(s) + O_2(g) \rightarrow SO_2(g)$……………… ***x 2 gives***……….. $2S(s) + 2O_2(g) \rightarrow \mathbf{2SO_2}(g)$

② $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$………. ***OK as is***………… $\mathbf{2SO_2}(g) + O_2(g) \rightarrow \mathbf{2SO_3}(g)$

③ $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$ ….. ***x 2 gives***……….. $\mathbf{2SO_3}(g) + 2H_2SO_4(l) \rightarrow \mathbf{2H_2S_2O_7}(l)$

④ $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$…. ***x 2 gives***……….. $\mathbf{2H_2S_2O_7}(l) + 2H_2O(l) \rightarrow 4H_2SO_4(l)$

Total $2S(s) + 2O_2(g) + 2SO_2(g) + O_2(g) + 2SO_3(g) + 2H_2SO_4(l) + 2H_2S_2O_7(l) + 2H_2O(l) \rightarrow 2SO_2(g) + 2SO_3(g) + 2H_2S_2O_7(l) + 4H_2SO_4(l)$

When simplified: $\mathbf{2S}(s) \mathbf{+ 3O_2}(g) \mathbf{+ 2H_2O}(l) \rightarrow \mathbf{2H_2SO_4}(l)$

b. $n(S) = \frac{m}{M} = \frac{1.250 \times 10^6}{32.07} = 3.898 \times 10^4$ mol *and* $n(H_2SO_4) = \frac{2}{2} \times n(S) = 3.898 \times 10^4$ mol

m(H₂SO₄) $= n \times M = 3.898 \times 10^4 \times 98.09 =$ $\mathbf{3.823 \times 10^6}$ **g** or **3.823 tonne** (4SF)

12. a. Multiply each equation by a suitable factor in order to equalise the $n(CO_2)$ in equation ① & ② and equalise the n(CO) in equation ② & ③. Then add the three equations and simplify the result.

① $C(s) + O_2(g) \rightarrow CO_2(g)$……………………… ***x 3 gives***…….. $3C(s) + 3O_2(g) \rightarrow \mathbf{3CO_2}(g)$

② $C(s) + CO_2(g) \rightarrow 2CO(g)$ ………………….. ***x 3 gives***…….. $3C(s) + \mathbf{3CO_2}(g) \rightarrow \mathbf{6CO}(g)$

③ $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$…… ***x 2 gives***…….. $2Fe_2O_3(s) + \mathbf{6CO}(g) \rightarrow 4Fe(l) + 6CO_2(g)$

Total $3C(s) + 3O_2(g) + 3C(s) + 3CO_2(g) + 2Fe_2O_3(s) + 6CO(g) \rightarrow 3CO_2(g) + 6CO(g) + 4Fe(l) + 6CO_2(g)$

When simplified: $\mathbf{6C}(s) \mathbf{+ 3O_2}(g) \mathbf{+ 2Fe_2O_3}(s) \rightarrow \mathbf{6CO_2}(g) \mathbf{+ 4Fe}(l)$

b. **%** $Fe_2O_3 = \frac{m(Fe_2O_3) \times 100}{m(\text{ore containing } Fe_2O_3)}$ $\therefore m(Fe_2O_3) = \frac{\%(Fe_2O_3) \times m(\text{ore})}{100} = \frac{97 \times 1 \times 10^6}{100} = 9.7 \times 10^5$

$n(Fe_2O_3) = \frac{m}{M} = \frac{9.7 \times 10^5}{159.7} = 6.1 \times 10^3$ mol *and* $n(C) = \frac{6}{2} \times n(Fe_2O_3) = \frac{6 \times 6.1 \times 10^3}{2} = 1.8 \times 10^4$ mol

. **m(C)** $= n \times M = 1.8 \times 10^4 \times 12.01 =$ $\mathbf{2.2 \times 10^5}$ **g** *or* **220 kg** (2SF)

Set 18 Stoichiometry with mass and gas volumes

1. $n(NaN_3) = \frac{m}{M} = \frac{12}{65.02} = 0.19$ mol *and* $n(N_2) = \frac{3}{2} \times n(NaN_3) = \frac{3 \times 0.19}{2} = 0.28$ mol

(remember to carry the full number into later parts of a calculation)

then **V(N**$_2$ **6.3 L** (2SF)

2. a. $n(C_6H_{12}O_6) = \frac{m}{M} = \frac{8.5}{180.156} = 4.7 \times 10^{-2}$ mol *and* $n(O_2) = \frac{6}{1} \times n(C_6H_{12}O_6) = 0.28$ mol

then $V(O_2) = n \times 22.71 = 0.28 \times 22.71 =$ **6.4 L** measured at STP (2SF)

b. $V(\text{air needed}) = \frac{V(O_2)}{0.21 \times 0.25} = \frac{6.4}{0.21 \times 0.25} = 122$ L air needed

number of breaths $= \frac{\text{volume of air needed}}{0.50} = \frac{122}{0.5} =$ **240 breaths** (2SF)

3. a. $n(H_2O) = \frac{m}{M} = \frac{150}{18.016} = 8.3$ mol *and* $n(H_2) = \frac{2}{2} \times n(H_2O) = 8.3$ mol

then **V(H**$_2$ $= n \times 22.71 = 8.3 \times 22.71 =$ **190 L** measured at STP (2SF)

$n(O_2) = \frac{1}{2} \times n(H_2O) = \frac{8.3}{2} = 4.2$ mol *and* **V(O**$_2$ **95 L** at STP (2SF)

b. Liquid water is a condensed phase of matter where the molecules of water attract strongly and pack closely while still being able to randomly jostle past one another. The reaction products, H_2 and O_2, are both gases. In the gas phase molecules of H_2 and O_2 have negligible attraction for one another and so spread out to fill the volume of their container. When confined at 100 kPa and at a temperature of 273 K each mole of gas will spread to occupy a volume of 22.71 L. Hence the large increase in volume when 8.3 mole of water in the liquid phase is converted to 12.5 moles of gaseous products.

4. $n(CO_2) = \frac{V_{(STP)}}{22.71} = \frac{155}{22.71} = 6.83$ mol *and* $n(Na_2CO_3) = \frac{1}{1} \times n(CO_2) = 6.83$ mol

then **m(Na$_2$ $_3$** = n x M = 6.83 x 105.99 = **7.23 x 10^2 g** (3SF)

5. $n(CO_2) = \frac{V_{(stp)}}{22.71} = \frac{1.17}{22.71} = 5.15 \times 10^{-2}$ mol *and* $n(NaHCO_3) = \frac{2}{1} \times n(CO_2) = 0.103$ mol

then **m(NaHCO$_3$** = n x M = 0.103 x 84.008 = **8.66 g** (3SF)

6. $n(NH_3) = \frac{V_{(stp)}}{22.71} = \frac{5.00 \times 10^3}{22.71} = 220$ mol

$n[(NH_2)_2CO] = \frac{1}{2} \times n(NH_3) = 110$ mol *and* **m[(NH$_2$ $_2$** **6.61 x 10^3**

7. $n(C_4H_{10}) = \frac{V_{(stp)}}{22.71} = \frac{6.03}{22.71} = 0.266$ mol

n(O$_2$ $\frac{13}{2} \times n(C_4H_{10}) = \frac{13 \times 0.266}{2} = 1.73$ mol *and* **V$_{STP}$(O$_2$** **39.2 L** (3SF)

Set 19 Limiting reagent calculations

1. a. actual mole ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{0.600}{0.251} = 2.39$ *and* stoichiometric ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{4}{1} = 4$

As the actual ratio (2.39) is **less than** the required stoichiometric ratio (4) then there is **insufficient HCl** for a complete reaction, ie **HCl is the LR**.

b. actual mole ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{7.08 \times 10^{-2}}{1.92 \times 10^{-2}} = 3.69$ *and* stoichiometric ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{4}{1} = 4$

As the actual ratio (3.69) is **less than** the required stoichiometric ratio (4) then there is **insufficient HCl** for a complete reaction, ie **HCl is the LR.**

c. actual mole ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{6.55 \times 10^{-1}}{1.42 \times 10^{-1}} = 4.61$ *and* stoichiometric ratio = $\frac{n(HCl)}{n(MnO_2)} = \frac{4}{1} = 4$

As the actual ratio (4.61) is **greater than** the required stoichiometric ratio (4) then the denominator **MnO$_2$ is the LR.**

2. a. $n(Na_2CO_3) = \frac{m}{M} = \frac{5.00}{105.99} = 4.72 \times 10^{-2}$ mol *and* $n(HCl) = \frac{m}{M} = \frac{4.00}{36.46} = 0.110$ mol

Let Na_2CO_3 be the limiting reagent, then: n(HCl required) = $\frac{2}{1} \times n(Na_2CO_3) = 2 \times 4.72 \times 10^{-2} = 9.43 \times 10^{-2}$ mol

The actual amount of HCl (0.110 mol) exceeds what is required (9.43×10^{-2} mol) ∴ there is excess HCl so **Na$_2$ $_3$ is the LR.**

n(NaCl formed) = $\frac{2}{1} \times n(Na_2CO_3) = 9.43 \times 10^{-2}$ mol

m(NaCl) = n x M = $9.43 \times 10^{-2} \times 58.44$ = **5.51 g (3SF)**

b. $n(Na_2CO_3) = \frac{m}{M} = \frac{1.926}{105.99} = 1.817 \times 10^{-2}$ mol *and* $n(HCl) = \frac{m}{M} = \frac{1.205}{36.46} = 3.305 \times 10^{-2}$ mol

Let Na_2CO_3 be the limiting reagent, then:

$n(HCl \text{ required}) = \frac{2}{1} \times n(Na_2CO_3) = 2 \times 1.817 \times 10^{-2} = 3.634 \times 10^{-2}$ mol

The actual amount of HCl (3.305×10^{-2}mol) is less than what is required (3.634×10^{-2} mol) for a complete reaction $\therefore$ **HCl is the LR.**

$n(NaCl \text{ formed}) = \frac{2}{2} \times n(HCl) = 3.305 \times 10^{-2}$ mol and **m(NaCl)** $= n \times M = 3.305 \times 10^{-2} \times 58.44 =$ **1.931 g** (4SF)

3. $n[NaOH] = \frac{m}{M} = \frac{5.240}{40.00} = 0.1310$ mol

actual mole ratio $= \frac{n(H_2SO_4)}{n[NaOH]} = \frac{0.1640}{0.1310} = 1.252$ *and* stoichiometric ratio $= \frac{n(H_2SO_4)}{n[NaOH]} = \frac{1}{2} = 0.500$

The actual ratio (1.252) is greater than the required stoichiometric ratio (0.5) $\therefore$ **NaOH is the LR**. Thus NaOH determines the quantity of other reagents involved in the reaction.

$n(Na_2SO_4 \text{ formed}) = \frac{1}{2} \times n(NaOH) = 6.550 \times 10^{-2}$ mol

and **m(Na**$_2$ $_4$ $= n \times M = 6.550 \times 10^{-2} \times 142.05 =$ **9.304 g** (4SF)

4. $n[Ba(NO_3)_2] = \frac{m}{M} = \frac{1.740 \times 10^{-1}}{261.32} = 6.659 \times 10^{-4}$ mol $n(Na_2SO_4) = \frac{m}{M} = \frac{9.260 \times 10^{-2}}{142.05} = 6.519 \times 10^{-4}$ mol

actual mole ratio $= \frac{n(Na_2SO_4)}{n[Ba(NO_3)_2]} = \frac{6.519 \times 10^{-4}}{6.659 \times 10^{-4}} = 0.9790$ stoichiometric ratio $= \frac{n(Na_2SO_4)}{n[Ba(NO_3)_2]} = \frac{1}{1} = 1$

The actual ratio (0.979) is less than the required stoichiometric ratio (1) $\therefore$ **Na**$_2$ $_4$ **is the LR.** Thus Na_2SO_4 determines the quantity of other reagents involved in the reaction.

$n(BaSO_4 \text{ formed}) = \frac{1}{1} \times n(Na_2SO_4) = 6.519 \times 10^{-4}$ mol

m(BaSO$_4$ $= n \times M = 6.519 \times 10^{-4} \times 233.37 =$ **0.1521 g** (4SF)

$n[Ba(NO_3)_2 \text{ used}] = \frac{1}{1} \times n(Na_2SO_4) = 6.519 \times 10^{-4}$ mol

also $m[Ba(NO_3)_2 \text{ used}] = n\ M = 6.519 \times 10^{-4} \times 261.32 = 0.1704$ g

m[Ba(NO$_3$ $_2$ **remaining]** $= m[Ba(NO_3)_2 \text{ added}] - m[Ba(NO_3)_2 \text{ used}]$
$= 0.1740 - 0.1704 =$ **0.0036 g** (4 DP, ie 2SF)

5. a. $n(K_2CO_3) = \frac{m}{M} = \frac{9.50}{138.21} = 6.87 \times 10^{-2}$ mol *and* $n[Cu(NO_3)_2] = \frac{m}{M} = \frac{14.00}{187.57} = 7.46 \times 10^{-2}$ mol

actual mole ratio $= \frac{n(K_2CO_3)}{n[Cu(NO_3)_2]} = \frac{6.87 \times 10^{-2}}{7.46 \times 10^{-2}} = 0.921$ *and* stoichiometric ratio $= \frac{n(K_2CO_3)}{n[Cu(NO_3)_2]} = \frac{1}{1} = 1$

The actual ratio (0.921) is less than the required stoichiometric ratio (1) $\therefore$ there is insufficient K_2CO_3 for complete reaction, ie **K**$_2$ $_3$ **is the LR.**

$n[Cu(NO_3)_2 \text{ used}] = \frac{1}{1} \times n(K_2CO_3) = 6.87 \times 10^{-2}$ mol

also $m[Cu(NO_3)_2 \text{ used}] = n \times M = 6.87 \times 10^{-2} \times 187.57 = 12.9$ g

m[Cu(NO$_3$ $_2$ $= m[Cu(NO_3)_2 \text{ added}] - m[Cu(NO_3)_2 \text{ used}] = 14.0 - 12.9 =$ **1.1 g** (1 DP, ie 2SF)

b. $n(K_2CO_3) = \frac{m}{M} = \frac{3.380 \times 10^{-2}}{138.21} = 2.446 \times 10^{-4}$ mol *and* $n[Cu(NO_3)_2] = \frac{m}{M} = \frac{5.980 \times 10^{-2}}{187.57} = 3.188 \times 10^{-4}$ mol

actual mole ratio = $\frac{n(K_2CO_3)}{n[Cu(NO_3)_2]} = \frac{2.446 \times 10^{-4}}{3.188 \times 10^{-4}} = 0.767$ *and* stoichiometric ratio = $\frac{n(K_2CO_3)}{n[Cu(NO_3)_2]} = \frac{1}{1} = 1$

The actual ratio (0.767) is less than the required stoichiometric ratio ∴ there is insufficient K_2CO_3 for a complete reaction, ie **K**$_2$ $_3$ **is the LR.**

$n[Cu(NO_3)_2 \text{ used}] = \frac{1}{1} \times n(K_2CO_3) = 2.446 \times 10^{-4}$ mol

also $m[Cu(NO_3)_2 \text{ used}] = n \times M = 2.446 \times 10^{-4} \times 187.57 = 0.04587$ g

m[Cu(NO$_3$ $_2$ **remaining]** = $m[Cu(NO_3)_2 \text{ added}] - m[Cu(NO_3)_2 \text{ used}]$
= 0.05980 - 0.04587 = **0.01393 g** (5DP, ie 4SF)

6. a. $n[Ca_3(PO_4)_2] = \frac{m}{M} = \frac{4.92 \times 10^6}{310.18} = 1.59 \times 10^4$ mol *and* $n(H_3PO_4) = \frac{m}{M} = \frac{6.67 \times 10^6}{97.994} = 6.81 \times 10^4$ mol

actual mole ratio = $\frac{n(H_3PO_4)}{n[Ca_3(PO_4)_2]} = \frac{6.81 \times 10^4}{1.59 \times 10^4} = 4.29$ *and* stoichiometric ratio = $\frac{n(H_3PO_4)}{n[Ca_3(PO_4)_2]} = \frac{4}{1} = 4$

The actual ratio (4.29) is greater than the stoichiometric ratio (4) ∴ Ca is the LR $(PO_4)_2$ needs to be added for a complete reaction.

Using the excess reagent gives the amount of limiting reagent that would be needed for a complete reaction. Thus:

$n[Ca_3(PO_4)_2$ for a complete reaction$] = \frac{1}{4} \times n(H_3PO_4) = \frac{6.81 \times 10^4}{4} = 1.70 \times 10^4$ mol

$n[Ca_3(PO_4)_2$ extra for complete reaction$] = n[Ca_3(PO_4)_2$ for complete reaction$] - n[Ca_3(PO_4)_2$ already added$]$

$= 1.70 \times 10^4 - 1.59 \times 10^4 = 0.12 \times 10^4$ mol or 1.2×10^3 mol (2DP, ie 2SF)

m[Ca$_3$ $_4$ $_2$ **extra for complete reaction]** = n x M = $1.2 \times 10^3 \times 310.18$ = **3.6 x 10^5 g** (2SF)

b. $n[Ca(H_2PO_4)_2$ produced for a complete reaction$] = \frac{3}{4} \times n(H_3PO_4) = \frac{3 \times 6.81 \times 10^4}{4} = 5.10 \times 10^4$ mol

m[Ca(H$_2$ $_4$ $_2$ **formed]** = n x M = 5.10 $10^4 \times 234.05$ = **1.19 x 10^7 g or 11.9 tonne** (3SF)

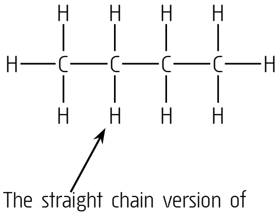
Set 20 Hydrocarbons: Nomenclature and structure

1. a./b. carbon/hydrogen
   c/d. natural gas/petroleum
   e. methane
   f. ethane
   g. molar mass
   h. mixtures
   i. molecule
   j. carbon atoms
   k. cracking
   l. fuels
   m./n. fibres/plastics

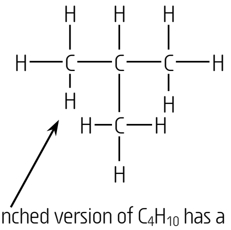
2. a. ethane b. butane c. hexane d. octane

3. $C_{20}H_{42}$, $C_{24}H_{50}$, $C_{28}H_{58}$

4. In a straight chain hydrocarbon the carbon atoms are bonded into a single chain of consecutive carbon atoms. Terminal carbon atoms have three attached hydrogen atoms and all other carbon atoms are bonded to two hydrogen atoms. In a branched hydrocarbon structure some carbon atoms may be bonded to three or four carbons. This means there will be side chains to the main chain of carbon atoms.

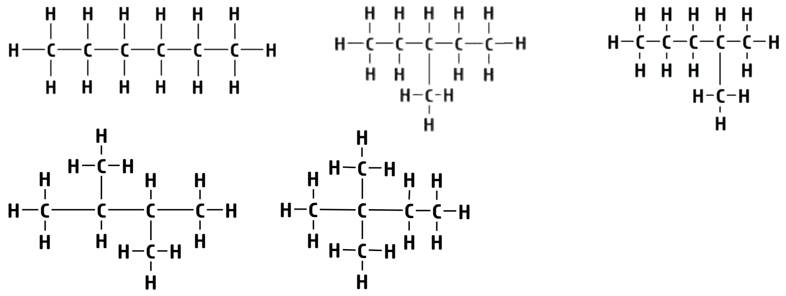


The straight chain version of C_4H_{10} has a single chain of four consecutive carbon atoms.



The branched version of C_4H_{10} has a chain of three consecutive carbon atoms with a single carbon atom forming a side chain.

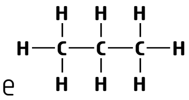
5. a.



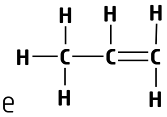
b. These are the structural isomers of C_6H_{14}.

6. Alkanes are saturated hydrocarbons, ie their molecules do not contain double bonds. Their general formula is C_nH_{2n+2}. Alkenes are hydrocarbons with molecules that contain one double bond. They are said to be unsaturated, their general formula is C_nH_{2n}. Thus an alkene molecule has two less hydrogen atoms than a corresponding alkane with the same number of carbon atoms.

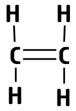
propane



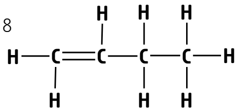
propene



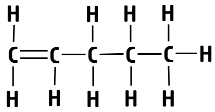
7. a. C_2H_4



b. C_4H_8

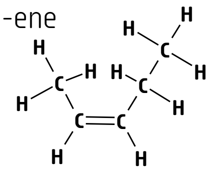


c. C_5H_{10}

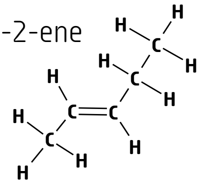


8. *Cis-trans* isomers are possible for pent-2-ene but not for pent-1-ene. The *cis-trans* isomers for pent-2-ene are shown here.

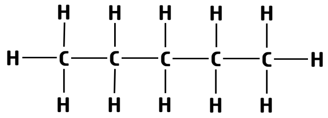
cis-pent-2-ene



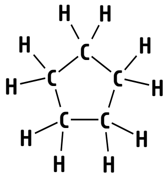
trans-pent-2-ene



9. The structural formula of cyclopentane shows each C atom is bonded to two other C atoms and is attached to two H atoms. This is also the case for most of the C atoms in pentane. The terminal C atoms of pentane however have three attached H atoms and are only attached to a single C atom. For this reason, the molecular formula and structural formula show cyclopentane has two less hydrogen atoms per molecule than pentane.



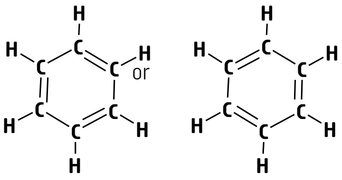
pentane C_5H_{12}



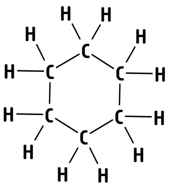
cyclopentane C_5H_{10}

10. Both cyclohexane and benzene consist of a cyclic ring of six carbon atoms. In cyclohexane each C atom is bonded to two H atoms and has a single bond to each adjacent C atom in the ring. By contrast, each C atom in a benzene ring is bonded to only one H atom and the bonds to adjacent C atoms are intermediate in nature between a single bond and a double bond. (Although they are shown as alternating single and double bonds.) For this reason the benzene structure is said to be aromatic. Also, benzene molecules form a flat structure while cyclohexane molecules are not. (See Table 5 and Fig 6 p94.) This however, is **not** evident from the structural formula as shown at right.

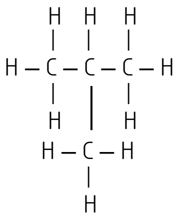
benzene C_6H_6



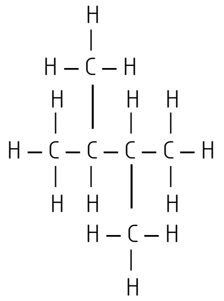
cyclohexane C_6H_{12}



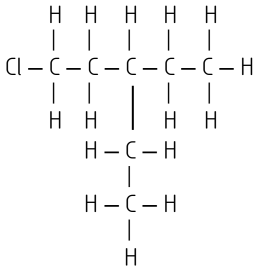
11. a.



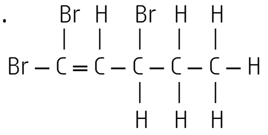
b.



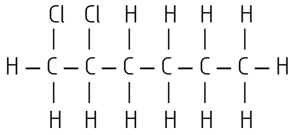
c.



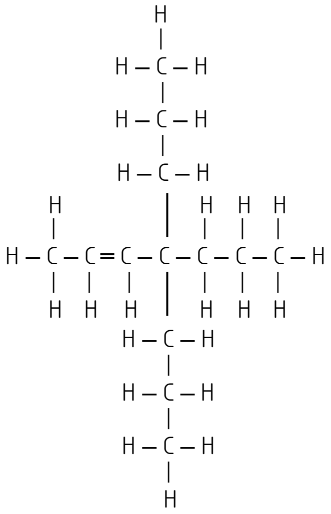
d.



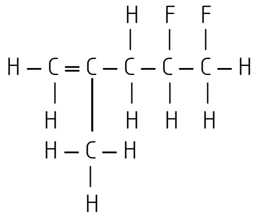
e.



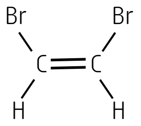
f.



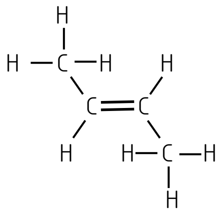
g.



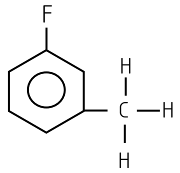
h.



i.

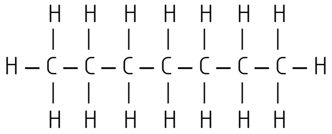


j.

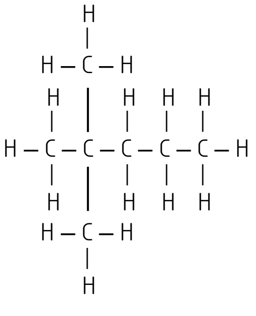


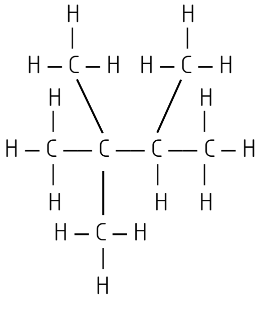
12. a. methylbutane
    b. 2,5-dimethylheptane (note longest chain)
    c. 1,2,2-tribromo-4,4-dimethylpentane
    d. 3-iodoprop-1-ene
    e. 4-methylhex-2-ene (*cis* or *trans*)
    f. 4,4-dimethylpent-1-ene
    g. 4-bromo-1,1-dichloro-3-methylpentane
    h. *cis*-1,2-diiodoethene
    i. 1-bromo-2-ethylcyclopentane
    j. 1-ethyl-2-methylbenzene
    k. 4-methylcyclohexene
    l. *trans*-pent-2-ene

13. a.



As can be seen, these three hydrocarbon compounds have the same molecular formula, C_7H_{16} but have different structural formula. [Compounds like this are known as structural isomers.]





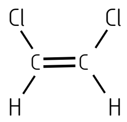
b. From the data given it can be seen that the octane rating is higher for molecules with branching. Thus for different hydrocarbons with the same molecular formula (ie structural isomers) octane rating is higher as the molecular branching increases.

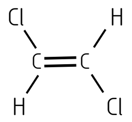
14. a.	same	both are butane
b.	different (ie isomers)	3-methylpentane and 2-methylpentane
c.	same	both are 2-methylpentane
d.	same	both are 1,2-dichloroethane
e.	same	both are 2-methylhexane
f.	different	trans-1-bromoprop-1-ene and cis-1-bromoprop-1-ene (ie cis-trans isomers)
g.	different	trans-1,2-dibromoethene and 1,1-dibromoethene (ie isomers)
h.	same	both are 1-bromo-3-methylbenzene

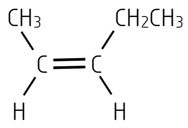
15. a. 2-methylpentane
    b. 3-methylbut-1-ene
    c. butane
    d. 3-ethyl-3-methylpentane
    e. 1-bromo-3-methylbenzene
    f. *cis*-1,2-dichloroethene or *trans*-1,2-dichloroethene

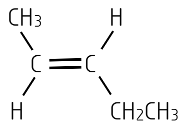
16. *Cis-trans* isomers are possible for c and e a b d and f do not show *cis* and *trans* isomerism. Remember, if either two two identical groups attached to it then *cis-trans* isomerism will not be possible.

c. *cis*-1,2-dichloroethene or *trans*-1,2-dichloroethene **e.** *cis*-pent-2-ene or *trans*-pent-2-ene









17. The carbon chain of stearic acid is saturated as it does not contain double bonds. Linoleic acid is polyunsaturated as it contains two double bonds. These double bonds are located in each of the two hydrocarbon sections, $(CH)_2$ [ie $CH = CH$]. Oleic acid contains one double bond. This is located in the hydrocarbon section $(CH)_2$. Thus oleic acid is a monounsaturated acid.

18. a. propene
    b. methylpropane
    c. 2,2-dimethylbutane *or* 2,3-dimethylbutane
    d. methylbenzene (toluene)

Set 21 Reactions of hydrocarbons

1. a. $CH_2 = CH_2(g) + Cl_2(g) \rightarrow CH_2ClCH_2Cl(l)$
   b. $CH_2 = CH_2(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$
   c. $CH_2 = CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$
   d. $CH_2 = CHCH_3(g) + Br_2(g) \rightarrow CH_2BrCHBrCH_3(l)$
   e. $C_5H_8(l) + Cl_2(aq) \rightarrow C_5H_8Cl_2(l)$
   f. $CH_2 = CHCH_3(g) + HBr(g) \rightarrow CH_3CHBrCH_3(l)$

2. a. $CH_3CH_3(g) + Cl_2(g) \xrightarrow{UV} CH_3CH_2Cl(g) + HCl(g)$
   b. $CH_4(g) + 4Br_2(g) \xrightarrow{UV} CBr_4(l) + 4HBr(g)$
   c. $CH_3CH_2CH_2CH_2CH_2CH_3(l) + Br_2(g) \xrightarrow{UV} CH_3CH_2CH_2CH_2CH_2CH_2Br(l) + HBr(g)$
   [The added Br may attach to any of the carbon atoms.]
   d. $C_6H_6(l) + \overset{UV}{Br_2}(aq) \rightarrow C_6H_5Br(l) + HBr(g)$
   e. $CH_3CH_3(g) + 6Cl_2(g) \xrightarrow{UV} CCl_3CCl_3(s) + 6HCl(g)$

3. a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
   b. $2C_3H_8(l) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(g)$
   c. $2C_{24}H_{50}(s) + 49O_2(g) \rightarrow 48CO(g) + 50H_2O(g)$
   d. $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$
   e. $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$
   f. $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$

4. a. $CH_3CH_3(g) \rightarrow CH_2 = CH_2(g) + H_2(g)$
   This reaction is essentially the reverse of the addition of hydrogen to the alkene ethene.
   b. Increasing temperature increases the rate of all chemical reactions. The high temperature means ethene will be produced at an economic rate.
   c. Ethene is an important raw material in the petrochemical industry. It is used mainly for the production of plastics and synthetic fibres as well as for the production of other valuable organic compounds.

5. a. Aromatic compounds are those containing a benzene ring (C_6H_6). These may be formed from the catalytic reforming of straight chain alkanes like hexane (6C atoms). Hydrogen gas will be a by-product of this reaction. Other aromatic compounds like methylbenzene could be produced from the reforming of hydrocarbons like heptane (7C atoms). Branched hydrocarbons like 2,2-dimethylpentane (C_7H_{16}) can be produced by the rearrangement of the carbon atoms in its hydrocarbon counterpart heptane (C_7H_{16}).
   b. $C_7H_{16}(g) \rightarrow C_6H_5CH_3(g) + 4H_2(g)$ Hydrogen gas is the by-product of this reaction.
   c. The bulk of the products formed in the reforming process are aromatic and branched chain hydrocarbons. These compounds have a much higher octane rating than the starting materials (ie straight chain hydrocarbon compounds). Thus reforming produces valuable high octane hydrocarbons useful as fuel additives.

6. a. i substitution ii HBr and bromoethane iii The bromine water slowly changes from orange to colourless.
b. i combustion ii CO_2 and H_2O iii The gas burns producing heat and light.
c. i substitution ii chlorobenzene and HCl iii The chlorine water slowly changes from pale yellow to colourless.
d. i addition ii 2-chloropentane iii A colourless gas dissolves, little else is observed.

7. a. $CH_4(g)$ and $Cl_2(aq)$, substitution
b. but-1-ene and $Br_2(aq)$, addition
c. but-1-ene (or but-2-ene) and $HCl(g)$, addition
d. benzene and $Br_2(aq)$, substitution

8. a. Yes. Ethene will rapidly decolourise bromine water (orange to colourless). Ethane does this much more slowly.
b. No. An addition reaction occurs in both cases so they both rapidly decolourise bromine water.
c. No. A substitution reaction occurs in both cases so they both slowly decolourise bromine water.
d. Yes. An addition reaction occurs with 3-methylcyclopentene rapidly decolourising the bromine water (orange to colourless). Methylcyclopentane decolourises bromine water much more slowly (substitution).
e. Yes. Hexene undergoes addition (rapidly decolourises bromine), while benzene undergoes substitution (slowly decolourises bromine water).
f. Yes. The two isomers are cyclopropane and propene. Cyclopropane undergoes substitution (slowly decolourising bromine water). Propene undergoes addition (rapidly decolourising bromine water).

Set 22 Fuels and energy in chemical systems

1.

	Enthalpy	**Heat**		**Enthalpy**	**Heat**
a.	Yes	Yes	e.	Yes	Yes
b.	Yes	Yes	f.	No *[2]	No*[2]
c.	Yes	No	g.	Yes	No
d.	No	Yes *[1]	h.	Yes	No

*[1] Heat flows from regions of high temperature to regions of lower temperature.

*[2] Only the total energy in a closed system is conserved. Individual forms of energy may disappear, however this means an equal amount (joules) of some other form(s) of energy will appear in place of the lost energy form. Thus total energy is conserved while individual forms of energy may increase or decrease.

2. The energy stored within chemical bonds contributes to the enthalpy (H) of a substance. During a chemical change chemical bonds within the reactants are broken and new chemical bonds within the products are formed. In an exothermic reaction this results in an overall decrease in the energy stored within chemical bonds. This decrease in stored energy is balanced by an increase in heat energy of the reaction mixture, ie an increase in its temperature. However, as the reaction mixture becomes hotter than the surroundings, heat then flows out of the reaction mixture and into the surroundings, ie heat is now lost. This loss of heat from the reaction mixture equates to a reduction of its enthalpy (H) and is signified by the NEGATIVE value of ΔH (a negative ΔH means a reduction in enthalpy). Total energy is conserved as the lost enthalpy reappears as an equivalent amount of heat energy (or some other form of energy) in the surroundings.

3. The reaction of $Ba(OH)_2(s)$ with $NH_4Cl(s)$ must be an endothermic reaction. In an endothermic reaction the enthalpy present within products is greater than the enthalpy present within reactants. This means there is an INCREASE in the energy stored within the chemical bonds. As total energy must be conserved this increased bond energy comes at the expense of a decrease in the kinetic energy of the particles in the system. The decreased particle kinetic energy is expressed as a reduced temperature, ie loss of heat, in the reaction mixture.

4. a. This reaction causes a temperature rise. This happens when enthalpy decreases and the reaction releases an equivalent amount of heat to the surroundings. Thus the reaction is exothermic.

b. $2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g)$

c. $2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g) + 2.510 \times 10^6$ J

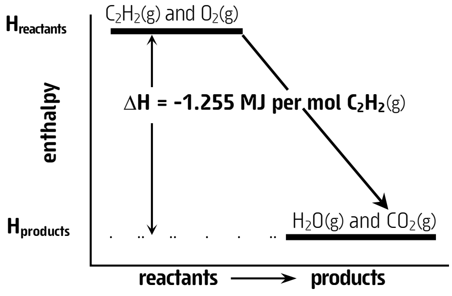
There are two moles of $C_2H_2(g)$ involved in the reaction so the heat produced is: 2 x 1.255 MJ = 2.510 M J = 2.510×10^6 J.

d. $2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g) \quad \Delta H = -2.51 \times 10^6$ J

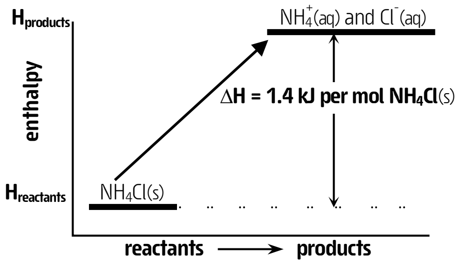
or $2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g) \quad \Delta H = -1.255 \times 10^6$ J mol^{-1} C_2H_2

As this reaction is exothermic (heat produced) then enthalpy must be lost. Thus ΔH has a negative value to show this.

e.



5. a. Endothermic. This reaction causes temperature to fall. This happens when a reaction converts heat from within the system into enthalpy in the form of increased bond energy. Heat then flows into the system from the surroundings.
   b. $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$
   c. $NH_4Cl(s) + 1.4\ kJ \rightarrow NH_4^+(aq) + Cl^-(aq)$
   d. $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq) \qquad \Delta H = 1.4\ kJ$
   e.



6. a. Endothermic, as bonds between water molecules in the liquid phase (ie IMFs) are broken to form individual un-bonded water molecules in the gas phase.
   b. Exothermic, as bonds are formed between CO_2 molecules (ie inter molecular forces, IMFs) when the gas phase condenses to form the solid phase.
   c. Endothermic, as bonds between individual sulfur atoms in the S_8 molecules (ie covalent bonds) are broken to form individual un-bonded sulfur atoms.

7. a. $H_2O(g)$ b. $CO_2(g)$ c. $H_2O(l)$ d. $H_2O(l)$ at 80 °C
   The enthalpy of a given substance depends upon its phase. It will have its greatest enthalpy as a gas (weakest bonds between molecules) and its lowest as a solid
   liquid phase is somewhere in between the two. Remember, bond making releases energy and decreases enthalpy while bond breaking absorbs energy and increases enthalpy. Also, the enthalpy of a substance increases with increasing temperature.

8. Water in the gas phase, $H_2O(g)$ has a higher enthalpy than water in the liquid phase, $H_2O(l)$. Thus in reaction ① there is a greater drop in enthalpy (ΔH = -890 kJ) as the product, water is present as a liquid, $H_2O(l)$. In reaction ② the product water is present as a gas, $H_2O(g)$.

9.

	Gas oven	**The glass cleaner**	**Ice melting**	**Respiration**	**Photosynthesis**
Endothermic or exothermic?	exothermic	endothermic	endothermic	exothermic	endothermic
Enthalpy increased or decreased?	decreased	increased	increased	decreased	increased
Increase or decrease in temperature?	increase	decrease	decrease	increase	decrease
Increase or decrease in the heat energy present?	increase	decrease	decrease	increase	decrease
Total energy increased decreased or unchanged?	unchanged	unchanged	unchanged	unchanged	unchanged
Overall stronger bonds, reactants or products?	products	reactants	reactants	products	reactants

Note: An exothermic reaction is one that releases heat energy to the surroundings at the expense of reduced enthalpy in the form of reduced chemical bond energy. The presence of extra heat energy causes the reaction mixture and surrounding temperature to rise. An endothermic reaction has the reverse effect as it converts heat into increased enthalpy in the form of increased chemical bond energy. In either case total energy is conserved or unchanged.

10. a. Note: For a fuel value in MJ kg^{-1} use energy in MJ, ie 0.394 MJ instead of 394 kJ and mass in kg, ie 12.01×10^{-3} kg instead of 12.01 g.

$$\text{fuel value} = \frac{\Delta H_c}{M} = \frac{0.394}{12.01 \times 10^{-3}} = 32.8\ \text{MJ kg}^{-1}$$

   b. Note: For an emission value in $g(CO_2)\ MJ^{-1}$, use mass of CO_2 formed in grams, ie the equation shows 44.01 g of CO_2 is formed (ie 1 mole of CO_2). Energy produced must be in MJ, ie the equation shows 0.394 MJ of heat is produced (394 kJ). The answer is obtained by dividing $m(CO_2)$ by energy released.

$$CO_2 \text{ emission value} = \frac{m(CO_2)}{\text{energy}} = \frac{44.01}{0.394} = 112\ g(CO_2)\ MJ^{-1}$$

   b. The tabulated values for coal are; fuel value 24-30 MJ kg^{-1}, rate of carbon emission 90-95 $g(CO_2)\ MJ^{-1}$. These values are similar to but not the same as those calculated above for pure carbon. This is to be expected as coal is a complex mixture of carbon and carbon compounds with a very high carbon content, ie 50% to 98% carbon.

11. a. The tabulated values for rate of emission of carbon dioxide when burning coal are 90-95 g(CO_2) MJ^{-1} ie an average of 93 g(CO_2) MJ^{-1} (2SF).
    b. From Table 1, natural gas produces 51 g(CO_2) MJ^{-1} while coal produces 90-95 g(CO_2) MJ^{-1}, ie the carbon emissions would be significantly less with NG.
    c. CO_2 emission comparison: using NG = $\frac{(CO_2)\text{ emission rate due to NG}}{(CO_2)\text{ emission rate due to coal}} \times 100 = \frac{51 \times 100}{93} = 55\%$
    ie Emissions with NG are reduced to 55% of those with coal.

12. a. The tabulated values for rate of emission of carbon dioxide when burning CNG (or NG) are 51 g(CO_2) MJ^{-1} and for LPG 59 g(CO_2) MJ^{-1}. Thus CNG is better in terms of having lower greenhouse gas (CO_2) emissions.
    b. CNG is essentially methane, CH_4 and this gas does not easily liquefy under pressure (BP of CH_4 = -152 °C). For vehicles to carry a reasonable amount of CNG the gas must be stored in cylinders at a very high pressure, ie ≈ 200 - 250 times normal atmospheric pressure. Such high pressures are a problem for transport vehicles. Potential safety concerns are associated with tank leakage, refuelling and traffic accidents. LPG by comparison consists of a mixture of propane, C_3H_8 and butane, C_4H_{10} and liquefies at moderate pressures. (The BP of C_3H_8 = -42.1 °C and BP of C_4H_{10} = -0.5 °C). For this reason LPG does not pose the same safety risks in transportation as does CNG. Furthermore, engines using CNG require higher rates of maintenance due to their higher operating temperatures and faster rates of wear.
    c. The energy density for LPG is 26 MJ L^{-1} and for petrol 34 MJ L^{-1}. Thus LPG has a lower energy density, around 76% that of petrol. This is a problem when replacing petrol with LPG as the fuel tank will need to be significantly larger (by ≈1.3 times) in order to provide an equivalent amount of energy.

13. a. Biofuels include fuels like bioethanol (ethanol), biogas and biodiesel. These fuels are produced from biomass (organic matter) like sugar, molasses, starch, bagasse (sugar cane waste), straw and even biowaste.
    b. Bioethanol can be produced by the fermentation of sugars or other forms of biomass. Since biomass can be regrown, then these fuels are a renewable resource. Petrol is produced from petroleum (crude oil) refining. As petroleum is a non-renewable resource then petrol is also a non-renewable resource. Once depleted it cannot be replaced.
    c. Note: For a fuel value in MJ g^{-1} use enthalpy change (ΔH) in MJ, ie 1.367 MJ instead of 1367 kJ and molar mass (M) of ethanol in g, ie 46.06 g.
    fuel value = $\frac{\Delta H_c}{M} = \frac{1.367}{46.07} = 0.02967$ MJ g^{-1} (4SF)
    d. As the density of ethanol is 789 g L^{-1} then a litre of ethanol represents 789 g of it. The fuel value from part (c) shows 0.02967 MJ of heat are produced for every 1.0 g of ethanol burnt, so the energy produced by 1.0 L (789 g) will be 0.02967 x 789 = 23.4 MJ. Thus ethanol has an energy density of 23.4 MJ L^{-1}. Since petrol has an energy density of 34 MJ L^{-1} (Table 1 p108) then the much lower energy density of ethanol does present an issue for the replacement of petrol with ethanol. For the same energy output, vehicles using pure ethanol will need a significantly larger fuel tank than petrol vehicles. (An ethanol fuel tank would need to be ≈1.5 times bigger than a petrol fuel tank for an equivalent energy output.)

14. a. The chemical process of photosynthesis produces sugar by absorbing $CO_2(g)$ from the atmosphere. Conversion of sugar to bioethanol followed by its combustion releases exactly the same amount of $CO_2(g)$ as was originally absorbed during photosynthesis. Thus combustion of ethanol does not contribute to the presence of $CO_2(g)$ in the atmosphere. Combustion of fossil based fuels like petrol does contribute to elevated atmospheric CO_2 as it releases carbon [as $CO_2(g)$] that has not been part of the Earth's biosphere for around 300 million years. (Carbon present in fossil fuels was absorbed from the atmosphere by plant photosynthesis around 300 million years ago.)
    b. Producing a biofuel like bioethanol involves various activities that may generate carbon emissions not balanced by plant photosynthesis. Fossil fuels for example may be used in activities such as farming to grow biomass (eg sugarcane), manufacturing fertilisers for crops, transporting biomass or for transporting the resulting biofuel. Thus if fossil fuels are used in the production of biofuels then the resulting biofuel cannot be considered completely carbon neutral.
    c. E10 is a petrol/ethanol blend consisting of 90% petrol (fossil fuel) and 10% ethanol. **E85** consists of **85% ethanol** and 15% petrol (fossil fuel). However, due to vehicle manufacturer warranties on locally available cars, the Australian government has legislated to restrict the use of higher ethanol blends. Only E85 flexible vehicles are able to operate on E85 fuel.

d. The 'Ethanol Production Grants (EPG) program' grants ethanol producers 38.1 cents per litre of ethanol produced, if the ethanol is to be used as a fuel in transportation. The Australian Government does this because it is committed through the Kyoto Protocol to achieve set targets for reductions in carbon emissions. One way to achieve this is to move to fuels with lower rates of carbon emissions such as biofuels.

15. a. $C_{46}H_{92}O_2(s) + 68O_2(g) \rightarrow 46H_2O(g) + 46CO_2(g)$

b. **Heat per mol ($C_{46}H_{92}O_2$)** $= \dfrac{\text{heat released}}{\text{moles of wax burnt}} = \dfrac{\text{heat released}}{[\text{m(wax burnt)} \div \text{M(wax)}]}$

$= \dfrac{625}{[(85.59 - 63.04) / 677.196]}$ = **18800 kJ mol^{-} $H_{92}O_2$** (3SF)

c. $C_{46}H_{92}O_2(s) + 68O_2(g) \rightarrow 46H_2O(g) + 46CO_2(g) \quad \Delta H = -18800$ kJ

$C_{46}H_{92}O_2(s) + 68O_2(g) \rightarrow 46H_2O(g) + 46CO_2(g) + 18800$ kJ

The negative value of ΔH shows enthalpy is lost. Since heat is released (exothermic) it appears on the right hand side of the equation.

d. i Matt and Erin's investigation assumes all of the heat released from the burning candle was absorbed by the water. However, the beaker itself, surrounding air and the exhaust gases will all receive some of the heat released from combustion of the candle.

ii As a consequence of the lost heat the water temperature rise will be less than it should be. This means the candle would appear to be producing less heat than it is and would result in consistently lower values for ΔH_c. The consistently low values for ΔH_c indicate this is a systematic error.

iii This source of error could be partially avoided by using a copper calorimeter so that heat transfer to both the water and its container (calorimeter) can be taken into account. Using a larger mass of water would also reduce heat loss to the environment. More effective insulation surrounding the candle and beaker can also help minimise heat loss to the room.

iv The black residue is soot, which is unburnt carbon. This shows that incomplete combustion of the wax has occurred. A consequence of this is less heat will be produced from the burning wax than if complete combustion had taken place. This will result in consistently lower temperature rises for the water and give rise to a lower calculated value for ΔH_c.

Set 23 Reaction rate

1. a. The altered factor is the higher concentration of hydrochloric acid. This leads to an increased rate of reaction between zinc and hydrochloric acid.

b. The altered factor is the lower temperature inside the refrigerator. This leads to a decreased rate of reaction involving the spoilage of milk.

c. The altered factor is the higher surface area of the coal dust. This leads to an increased reaction rate between coal (C) and air (O_2).

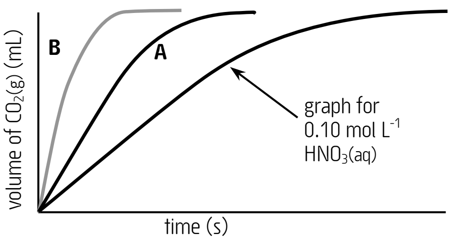
d. The altered factor is the addition of a catalyst, ie copper sulfate solution, which increases the reaction rate. (Remember the blue colour of the $CuSO_4$ solution showed no change over time, ie copper sulfate is not consumed, yet its presence caused the reaction rate to increase.)

e. Two altered factors are the higher temperature and higher surface area of the iron particles. This leads to an increased rate of reaction between iron (Fe) and air (O_2), ie combustion of iron.

2. The rate of this reaction can be increased by raising the temperature of the reaction mixture, using a higher concentration of sulfuric acid, using a suitable catalyst (if one can be found), or by using more finely powdered solid copper oxide (higher surface area).

3. a. At any given time during the reaction, graph B has a higher gradient (steeper slope) than graph A. This means there is a higher rate of formation of carbon dioxide gas in reaction B than in reaction A. Thus the reaction rate for B is greater than the reaction rate for A. This can happen if the temperature of the reaction mixture in B is higher than in A.

b. The concentration of nitric acid is reduced from 0.50 mol L^{-1} to 0.10 mol L^{-1}. The lower acid concentration results in a lower reaction rate. Thus the gradient of the graph for the production of carbon dioxide will be lower than in A. Also the final volume of carbon dioxide produced will be the same as the overall moles of nitric acid is the same in both experiments.



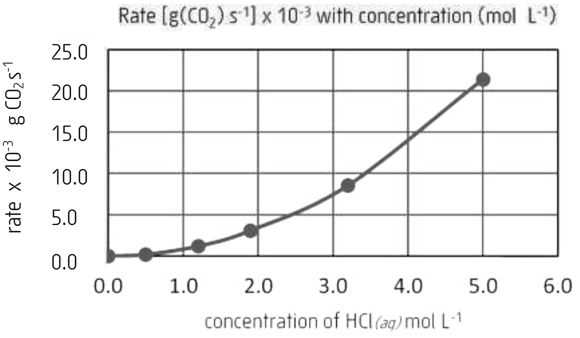
4. a. The mass loss is due to the loss of $CO_2(g)$. At any point in the experiment the mass loss equals the mass of $CO_2(g)$ formed.

   b. Rate for 0.50 mol L^{-1} HCl: $\text{rate} = \dfrac{\text{amount produced}}{\text{time taken}} = \dfrac{0.30}{1490} = 2.0 \times 10^{-4}\ \text{g}\ CO_2\ \text{s}^{-1}$ (2SF)

   Rate for 1.2 mol L^{-1} HCl: $\text{rate} = \dfrac{\text{amount produced}}{\text{time taken}} = \dfrac{0.30}{231} = 1.3 \times 10^{-3}\ \text{g}\ CO_2\ \text{s}^{-1}$ (2SF)

   Similarly, rates for the other hydrochloric acid solutions are: 2.9×10^{-3} g CO_2 s^{-1}, 8.6×10^{-3} g CO_2 s^{-1} and 2.1×10^{-2} g CO_2 s^{-1}.

   c. If spattering occurred then the mass loss of the flask and its contents would be due to the loss of $CO_2(g)$ plus the loss of solution. The assumption that the mass loss equals the mass of $CO_2(g)$ formed would be incorrect. The true mass of $CO_2(g)$ formed would be somewhat less than the mass loss. As a consequence the mass of $CO_2(g)$ produced would appear higher than it actually was and the resulting rate would also appear higher than it actually was. Consistent errors like this are systematic errors.



   e. The results do show an increase in rate with increasing concentration. However, the rate is not seen to increase in direct proportion to concentration. A direct proportion would be shown if the graph was straight, instead the graph is upward curving as in an exponential relationship. Thus the hypothesis is not exactly supported. (In fact this graph shows the rate quadruples when the concentration doubles. Thus the rate of this reaction increases with the square of the concentration.)

   f. As given, $CO_2(g)$ is denser than air so as it forms it will fill the flask from the solution level upwards. Thus initially it will be the air in the flask that is expelled rather than $CO_2(g)$. For the same volume, the air expelled weighs less than the $CO_2(g)$ formed. Once the flask is filled with $CO_2(g)$ (ie after ≈ 200 mL of it is produced) then the weight loss of the flask will be due to lost $CO_2(g)$. Now the weight loss is equal to the weight of $CO_2(g)$ being produced.

5. The rate of a reaction can be found by measuring the rate of formation of any one product or by measuring the rate of consumption of any one reactant. For the given reaction it would be convenient to measure the rate of formation of hydrogen gas or to measure the rate of consumption of zinc solid.

   Using the downward displacement of water technique (illustrated in Example 1 p116) allows hydrogen to be collected as it is produced and its volume to be monitored. Graphing the volume of $H_2(g)$ formed against the time taken reveals the rate of reaction over time. This is shown by the graph's gradient. Alternatively the rate of the reaction can be calculated for any given time interval using; **rate = volume of H_2 formed (mL) ÷ time taken (s)**.

   Another option is to measure the mass of hydrogen produced over time. This can be achieved by placing the reaction flask onto an electronic balance. (See Fig 19 p123) The reaction flask will show a steadily reducing mass as hydrogen gas is formed and escapes from the flask. The flask's mass loss at any given time gives the mass of hydrogen produced up to that time. Graphing the mass of hydrogen formed against time shows the rate of reaction.

Continued next page.

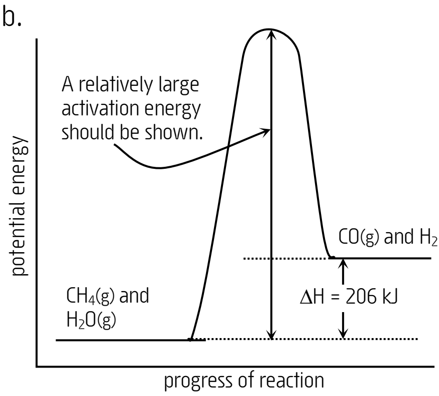
Alternatively the reaction rate over a chosen time interval can be calculated using: **rate = mass H_2 formed (g) ÷ time taken (s)**. An inherent problem with this technique is due to the low molar mass of hydrogen. This means the mass of hydrogen produced will be quite small. Thus even with a precise balance there is likely to be a large random error in the mass measurements for the mass of hydrogen gas formed.

A third technique could be to measure the mass of zinc consumed over time. This would be the least convenient of the three techniques. It involves using a single piece of zinc in the reaction mixture and removing it from the reaction flask at given time intervals. The zinc is then washed, dried and weighed to give the mass of zinc remaining and enabling the mass of zinc consumed to be calculated. Returning the zinc to the reaction flask allows further readings to be taken. Once again the mass of zinc consumed can be plotted against time to graphically show reaction rate. Alternatively, the reaction rate can be calculated for any given time interval using: **rate = mass Zn used (g) ÷ time taken (s)**.

6. a. molecules
   b. randomly
   c. collide
   d. electron clouds
   e. repel
   f. kinetic energy
   g. activation energy
   h. orientation
   i. activated complex
   j. breaking
   k. forming
   l. decompose
   m.reactants
   n. water

7. a. Crude oil (petroleum) is used to produce liquid fuels like kerosene, diesel and petrol. It is a non-renewable resource and is now in short supply worldwide. Natural gas is also a non-renewable resource, however it is much more abundant. Vehicles designed to use liquid fuels can be converted to use compressed natural gas (CNG), however there is a considerable cost involved. There are storage problems associated with using CH_4 in the form of CNG as it is a gas at room temperature. Very high pressures must be used to store it and this presents safety and cost issues. Converting gaseous CH_4 to a liquid hydrocarbon like petrol would help solve these problems.

   b.



   c. The high activation energy implies the bonds in the reactants that must be broken or rearranged are strong and possibly numerous.

   d. The high activation energy means the reaction will probably be quite slow. This adds costs to the industrial synthesis as conditions like high temperature and pressure may need to be used to achieve a reasonable rate for this endothermic reaction.

8. For a reaction to occur, the reacting particles must collide with a suitable orientation and have at least a minimum amount of energy known as the activation energy. As temperature increases so the average kinetic energy of particles also increases. Thus at a higher temperature a greater percentage of the collisions between reacting particles will have a collision energy greater than or equal to the activation energy. This results in an increased rate of reaction. (The increased temperature does cause a slight increase in the rate of collisions, due to the faster moving particles, but this has a **very minor** effect on increasing the reaction rate.)

9. Use a high pressure. This increases the rate of collisions between reacting particles, CH_4(g) and H_2O(g) thus increasing the reaction rate.
   Use a catalyst. This lowers the activation energy thus allowing a greater percentage of collisions to have energy ≥ activation energy.

10. a. decrease — This is a lower temperature than originally used. Thus the particles will have lower kinetic energy and the percentage of collisions with energy ≥ activation energy decreases. Consequently the rate of reaction reduces. [Note: A decrease in temperature does produce a small decrease in rates of collision. This is a minor unable to the large decrease in rate that happens with small decreases in temperature.]
    b. unchanged — More acid of the same concentration does not affect rates of collisions, energy of collisions or their orientation. So this has no effect on the initial reaction rate.
    c. increase — Using a higher concentration of HCl increases the concentration of reacting species (hydrogen ions, H^+). This leads to an increase in the rate of collisions between the reacting particles (H^+ ions and Ni atoms) and the subsequent increase in reaction rate.

d. decrease — Adding distilled water will reduce the concentration of the aqueous species H^+(aq). This leads to a reduction in the rate of collisions between H^+(aq) and Ni(s). Consequently reaction rate will decrease.

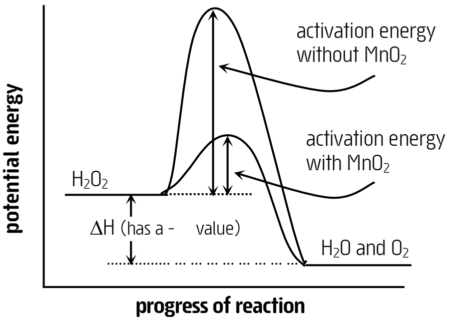
e. increase — Smaller pieces of nickel (same total mass) means an increase in the surface area of nickel. This increases the rate of collisions between hydrogen ions (liquid phase) and nickel atoms (solid phase). Thus reaction rate increases.

f. increase — This higher temperature means particles will on average have a higher kinetic energy. Upon collision the particles are more likely to have a collision energy exceeding the activation energy. Thus the rate of reaction increases due to an increase in the percentage of collisions with energy ≥ activation energy. (See Fig 5 p118.)

11. a. There may have been a very small difference in mass which could have been explained by expected random or systematic errors in the experimental procedures used, such as filtering, drying or weighing.

b. In the presence of MnO_2 the rate of decomposition of H_2O_2 increased. Also the MnO_2 appeared not to be consumed. This can happen if MnO_2 is acting as a catalyst. A catalyst allows a reaction to occur by a different pathway of lower activation energy without the catalyst being consumed*****. Thus with MnO_2 present, a greater percentage of collisions have energy ≥ activation energy and are successful in forming products. The MnO_2 increases the reaction rate without appearing to be consumed in the reaction. [*****Actually, the catalyst is consumed in one step of the reaction however, an equal amount of it is produced in another step so that overall it is not consumed.]

c.



d. Catalase is a biological catalyst. Such catalysts are known as enzymes. Catalase also catalyses the decomposition of hydrogen peroxide. Its effect on increasing rate is much greater than MnO_2 and is one of the fastest acting enzymes (catalysts) known.

12. a. The enzyme is a biological catalyst for this reaction. It speeds up the reaction by providing an alternative reaction pathway of lower activation energy.

b. An enzyme does not appear as a reactant or product of the reaction as it is neither produced nor consumed over the course of the reaction. (This is despite the enzyme still being involved in the reaction.)

c. Enzymes have a complex molecular structure, are specific to a single reaction only and are often extremely effective in increasing reaction rate. Inorganic catalysts are often effective for a range of reactions (ie not specific to a single reaction) and their effect on rate is usually not as great.

13. a. A thistle funnel allows acid to be added to the reaction flask without removing the stopper. It ensures all of the hydrogen gas is able to be collected as soon as it starts to form. For proper use, the end of the thistle funnel must be below the surface of the solution.

b. When 65 mL of acid solution is added to the flask (via the thistle funnel) it will displace 65 mL of air from within the flask. The displaced air will bubble directly into the measuring cylinder and as a result all of the measurements for the volume of hydrogen produced will be greater by 65 mL. Such an error is a systematic error in the procedure. (Alternatively the student could allow for this by subtracting this volume, 65 mL, from each reading.)

c. During the first two minutes the gradient of the graph increases showing reaction rate also increases. As the equation shows, this is an exothermic reaction and as the reaction proceeds heat is released causing the temperature of the reaction mixture to rise. Reaction rates rise with temperature and consequently the reaction rate increases during the first few minutes.

During the last two minutes the gradient of the graph decreases, showing rate decreases. As the reaction progresses HCl(aq) will be consumed causing its concentration to fall. This explains the reduction in reaction rate towards the end of the experiment. Similarly as the reaction progresses the aluminium foil is consumed and its total surface area decreases. This further reduces the reaction rate towards the end of the experiment.

14. a. $2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$

As can be seen, Pt does not appear in the overall equation for the catalytic conversion of NO_2 to N_2 and O_2 thus Pt is neither consumed nor produced in the overall reaction. Pt does however, speed up this reaction as without it NO_2 remains unchanged in the exhaust gas. Thus Pt is acting as a catalyst, ie Pt is neither consumed nor produced but speeds up the rate of the reaction for NO_2 changing to N_2 and O_2.

b. Arranging the catalyst this way provides it with a high surface area. This is important as in the first step of the overall reaction (see Question 14 (a) part i) NO_x molecules react with Pt atoms. A greater Pt surface area gives a greater rate of collisions between NO_x molecules and Pt atoms. This increases the rate of the first step of the catalysed reaction for the decomposition of NO_x.

c. If Pb atoms become adsorbed to the platinum surface then fewer Pt atoms will be exposed to the NO_x molecules in the exhaust. This leads to a lower rate of collisions between NO_x molecules and Pt atoms and thus reduces the rate of the catalysed reaction for NO_x decomposing to N_2 and O_2.

Set 24 Molecular shape and polarity

1. a. molecule
b. central
c. VSEPR
d. groups
e. valence shell
f. lone pairs
g. six
h. linear
i. triangular planar
j. three
k. bent
l. tetrahedral

2. a. linear b. pyramidal c. bent d. triangular planar e. tetrahedral

3. According to the VSEPR theory the shape of a molecule results from the repulsion between groups of electrons (both bonding and non-bonding) in the valence shell of the central atom in a molecule. The central atom of CO_2 is carbon and it has two groups of electrons (4 electrons in each group). The optimum shape for this is linear. This shape allows the maximum angular separation of the two groups of electrons in the valence shell of the carbon atom.

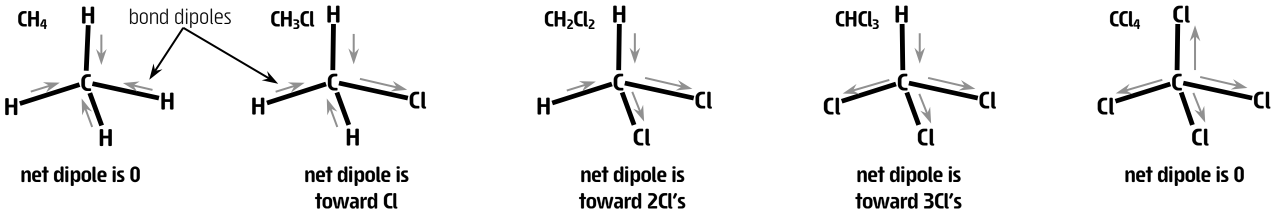
The central atom of a H_2O molecule is oxygen and it has 4 groups of electrons (2 groups of bonding electrons and 2 lone pairs). The optimum shape for this configuration is bent. This shape allows the maximum angular separation of the 4 groups of electrons in the valence shell of the oxygen atom.

4. If two atoms of different electronegativity form a covalent bond then an uneven sharing of the bonding electrons will occur. When this happens the **more** electronegative atom attracts the electrons more strongly and gains a small negative charge (δ^-) and the **less** electronegative atom gains a small positive charge (δ^+). This happens as the bonding electrons spend more time near the more electronegative element. Covalent bonds like this are said to have a bond dipole.

In HF the single covalent bond has a bond dipole as fluorine is more electronegative than hydrogen (4.0 and 2.1 respectively). Thus the fluorine end of the bond has a slight negative charge (δ^-) and the hydrogen end has a slight positive charge (δ^+).

In F_2 the single covalent bond has a zero bond dipole as both fluorine atoms have the same electronegativity. The shared pair of electrons in the covalent bond is **on average** midway between the two bonded fluorine atoms.

5.

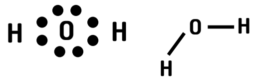


Even though all of the bonds in these structures have a bond dipole (ie polar bonds), the molecules are not necessarily polar. Molecular polarity depends on the sum of the bond dipoles within the molecule. In CH_4 and CCl_4 the bond dipoles are of equal size with symmetrically opposing directions. As a result the net dipole in these molecules is zero and they are non-polar. In CH_3Cl, CH_2Cl_2 and $CHCl_3$ the bond dipoles are not symmetrically opposing (see diagrams above) and so do not cancel out. Consequently these molecules have a net dipole and they are polar.

6\. a.

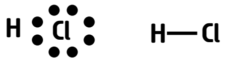
linear and non-polar

b.



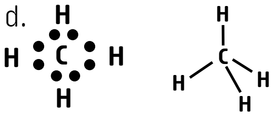
bent and polar

c.



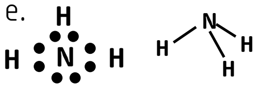
linear and polar

d.



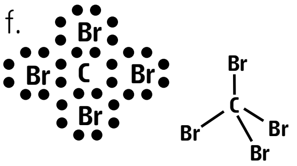
tetrahedral and non-polar

e.



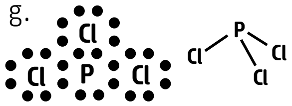
pyramidal and polar

f.



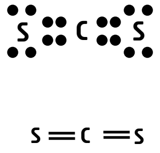
tetrahedral and non-polar

g.



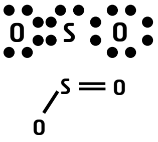
pyramidal and polar

h.



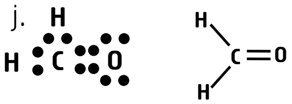
linear and non-polar

i.



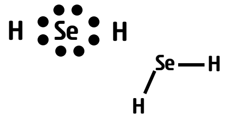
bent and polar

j.



triangular planar and polar

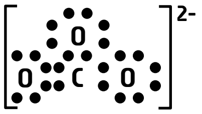
k.



bent and polar

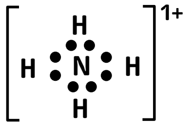
Note: These **molecular shapes** have been drawn without showing lone pairs. Showing these is optional and depends upon the particular situation.

7\. a.



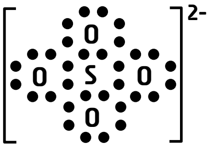
triangular planar

b.



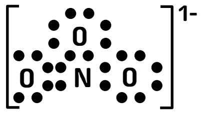
tetrahedral

c.



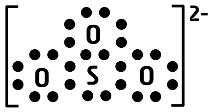
tetrahedral

d.



triangular planar

e.



pyramidal

8\. In each case the molecular polarity is ordered from least (left) to most (right). Consider both the bond dipole strength, which depends upon electronegativity differences and the molecular symmetry.

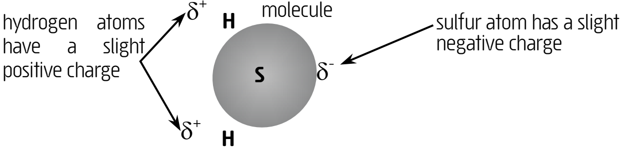
a. HI < HBr < HF b. $H_2Te < H_2Se < H_2S < H_2O$ c. $CF_4 = CH_4 < CH_3F$ d. $CH_2I_2 < CH_2Cl_2 < CH_2F_2$

Set 25 Intermolecular forces

1\.
a. covalent bonds, strong
b. intermolecular forces, weak
c. ionic bonds, strong
d. covalent bonds, strong
e. intermolecular forces, weak
f. covalent bonds, strong
g. metallic bonds, strong
h. intermolecular forces, weak

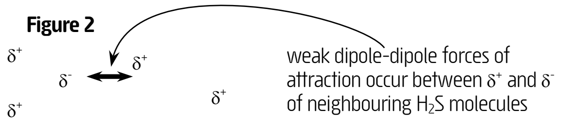
2\. When a molecular substance like galactose or glucose melts, the intermolecular forces between the molecules have been partly overcome. This allows the molecules to move freely amongst one another in the liquid phase. A high melting point indicates the molecules need a high kinetic energy in order to partially overcome their mutual attraction (intermolecular forces) and change from the solid phase to the liquid phase. Thus the intermolecular forces in galactose are stronger than the intermolecular forces in glucose.

3\. **Figure 1**



The H_2S molecule is polar and thus has an uneven distribution of charge. In these molecules the hydrogen atoms have a slight positive charge (δ^+) while the sulfur atom has a slight negative charge (δ^-). (Fig 1.)

Figure 2



Adjacent molecules in a sample of H_2S will attract (weakly) by aligning the opposite charges of their dipoles. (Fig 2.) Although this is a weak force it contributes to the ability of H_2S to condense to a liquid at -60 °C.

4\. a. Dispersion forces originate from the random motion of electrons within a molecule. This random electron motion produces short lived dipoles (temporary dipoles) to form within the molecule. This effect induces similar dipoles in nearby molecules (induced dipoles). The molecule with the temporary dipole and the one with the induced dipole then experience overall 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 once again. As dispersion forces are due to the random motion of electrons, then the strength of this force increases as the number of electrons in the molecule increases.

b. i Cl_2 has greater dispersion forces (higher BP). This is due to its greater number of electrons per molecule and dispersion forces increase in strength with increasing number of molecular electrons.

ii CH_3CH_3 has greater dispersion forces (higher BP). This is due to its greater number of electrons per molecule and dispersion forces increase in strength with increasing number of molecular electrons.

iii Butane has greater dispersion forces (higher BP). Both substances have the same number of electrons per molecule. However, dispersion forces are greater for linear molecules rather than spherical molecules. This is due to the higher surface area of the linear shape. Since butane molecules are more linear than methyl propane molecules, which are more spherical, then the dispersion forces and BP are greater for butane.

5. a. covalent bonds
b. weak
c. intermolecular forces
d. liquid and solid
e. melting and boiling points
f. all
g. electrons
h. molar mass
i. dipole-dipole
j. electrostatic
k. HF
l. —OH or —NH
m. —OH or —NH
n. an F, O or N atom
o. lone pair
p. soluble
q. insoluble
r. extremely soluble

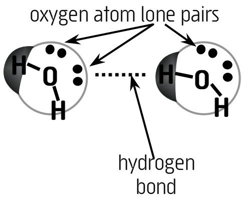
6. a. Dispersion forces and dipole-dipole forces are present in both substances. Water has an extreme form of dipole-dipole interaction more correctly described as hydrogen bonding.

b. Dipole-dipole forces are stronger in water as the dipole is stronger in water. The stronger dipole is a result of the greater electronegativity difference between H and O (2.1 and 3.5 respectively) compared to that for H and S (2.1 and 2.5 respectively).

c. Dispersion forces are stronger in H_2S as H_2S has a greater number of electrons per molecule compared to H_2O.

d. Hydrogen bonding occurs between water molecules. This is the strongest form of intermolecular force occurring in **small** molecules. H_2S does not have hydrogen bonding.

e.



Each water molecule can be involved in up to 4 hydrogen bonds with four neighbouring water molecules. This can happen as each lone pair and each hydrogen of a water molecule is capable of being involved in a hydrogen bond.

7. a. dispersion forces
b. dispersion forces and dipole-dipole forces
c. dispersion forces, dipole-dipole forces (*****see note) and hydrogen bonding
d. dispersion forces and dipole-dipole forces

***Hydrogen bonding** is often described as an extreme or unique form of dipole-dipole attraction. For this reason the attraction between polar water molecules are described as hydrogen bonding rather than dipole-dipole forces. However, it must be noted that water molecules can attract by dipole-dipole forces. This is especially evident if water is mixed with a polar substance that is unable to attract by hydrogen bonding.

8. a. dispersion forces
b. dispersion forces and dipole-dipole forces
c. dispersion forces, dipole-dipole forces* (*as for Q 7) and hydrogen bonding
d. dispersion forces
e. dispersion forces, dipole-dipole forces* (as for Q 7) and hydrogen bonding
f. dispersion forces and dipole-dipole forces
g. dispersion forces
h. dispersion forces
i. dispersion forces, dipole-dipole forces* (see Q 7) and hydrogen bonding
j. dispersion forces and dipole-dipole forces
k. dispersion forces, dipole-dipole forces* (see Q 7) and hydrogen bonding
l. dispersion forces, dipole-dipole forces* (see Q 7) and hydrogen bonding

9. a. Cl_2 has a greater number of molecular electrons so its dispersion forces are stronger than those in F_2. Therefore Cl_2 has the higher boiling point.

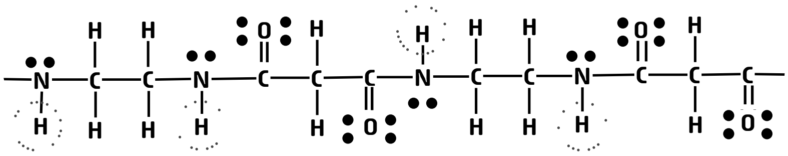
b. Both molecules have similar dispersion forces, however as ethanol has the ability to hydrogen bond then ethanol will have the higher boiling point.

c. C_4H_{10} has a greater number of molecular electrons so its dispersion forces are stronger than those in CH_4. Therefore C_4H_{10} has the higher boiling point.

10. The intermolecular forces present in water include dispersion forces, dipole-dipole forces and hydrogen bonding. None of the other compounds (H_2S, H_2Se or H_2Te) exhibit hydrogen bonding. The lack of hydrogen bonding in these compounds arises as the elements S, Se and Te are not sufficiently electronegative and thus cannot produce the dipole strength required for hydrogen bonding to occur. The presence of hydrogen bonding in water and lack of it in the other compounds is the major factor contributing to the much higher boiling point of water.
Of the remaining three compounds that do not hydrogen bond (H_2S, H_2Se and H_2Te) the variation in boiling point is due to the different strength of dispersion forces. Dispersion forces increase in the order ($H_2S < H_2Se < H_2Te$). Their boiling points follow this same trend with H_2S having the lowest boiling point and H_2Te having the highest. This trend in boiling points occurs despite the molecular polarity increasing in the opposite order (H_2S is most polar with H_2Te least polar). This shows dispersion forces have a greater influence on boiling points than dipole-dipole forces.

11. a. Glycerol molecules are polar and can hydrogen bond (each glycerol molecule contains three -OH groups). Hence glycerol molecules attract strongly by hydrogen bonding or dipole-dipole forces. Water molecules are also polar and can attract by hydrogen bonding or dipole-dipole forces. Thus water is the best solvent for glycerol as water molecules and glycerol molecules will be able to mix and attract one another by similar intermolecular forces.
    b. Octane molecules attract other octane molecules by dispersion forces only. Decane molecules also attract one another by dispersion forces only. For this reason decane would be the best solvent for octane as the two types of molecules can attract one another by dispersion forces and therefore the two substances will readily mix to form a solution.
    c. Diesel fuel is a mixture of non-polar compounds hence the molecules in this mixture attract one another only by dispersion forces. Decane is also non-polar and its molecules are able to attract by dispersion forces only. For this reason decane would be the best solvent for diesel fuel as the molecules in the two different substances can attract one another by dispersion forces and so will readily mix to form a solution.
    d. Glucose molecules are polar and can hydrogen bond (each glucose molecule contains five -OH groups). Hence glucose molecules attract strongly by hydrogen bonding and dipole-dipole forces. Water molecules are also polar and can attract by hydrogen bonding and dipole-dipole forces. Thus water is the best solvent for glucose as water molecules and glucose molecules will be able to mix and attract one another either by dipole-dipole forces or by hydrogen bonding.

12. a.



    b. These hydrogen atoms are covalently bonded to a N atom. The high electronegativity of the N atom results in a strong dipole with H. Consequently the hydrogen atom has a strong positive charge (δ^+). These hydrogen atoms can then interact quite strongly with the strong negative dipole (δ^-) and lone pair of a N or O atom from the same molecule. This strong interaction is the basis of hydrogen bonding in a protein molecule.
    c. Lone pairs involved in hydrogen bonding are the ones from the oxygen atoms.

13. a. The dispersion forces in methanol are slightly greater than those in methane as methanol has slightly more electrons per molecule than does methane. This difference, however, is far too small to account for the great difference in boiling points. The presence of hydrogen bonding in methanol and its absence in methane is the main reason for the much higher boiling point of methanol.
    b. Strength of dispersion forces increase with the number of molecular electrons (molecular size). As octane is a significantly larger molecule with a much greater number of electrons per molecule than methanol then the dispersion forces in octane are much greater than those in methanol. This difference explains the higher boiling point of octane. This occurs despite the presence of strong hydrogen bonding amongst the much smaller methanol molecules.

14. a. The solid would be expected to sink if placed into a container of its liquid phase, ie wax has the 'normal' behaviour. This is to be expected as in the solid phase the particles are usually packed more closely together, ie have a higher density and the higher density substance will sink if placed into a lower density liquid.
    b. When water freezes the resulting crystal lattice of water molecules (ie, ice) is arranged in such a way that it allows each water molecule to have four hydrogen bonds with four neighbouring water molecules. This regular ordered arrangement maximises hydrogen bonding but takes up more space than the random arrangement in liquid water. As a result, the less compact ice, has a lower density than liquid water.

15. a. Alcohols like methanol are polar and can hydrogen bond as each methanol molecule contains one -OH group. Hence methanol molecules attract most strongly by hydrogen bonding. Water molecules are also polar and attract most strongly by hydrogen bonding. Thus water is a good solvent for methanol as water molecules and methanol molecules will be able to mix and attract one another strongly by hydrogen bonding with each other.
    b. Solubility of the alcohols decreases with increasing molar mass of the alcohol.
    c. As the molar mass of the alcohols increases so does its molecular size and hence the number of electrons per molecule also increases. This increase in molecular electrons means a corresponding increase in the size of the dispersion forces between the alcohol molecules. For larger alcohol molecules the strength of the dispersion forces is so great it far exceeds the strength of the hydrogen bonding with water molecules. As a result the larger alcohol molecules do not mix and hydrogen bond with water molecules. Instead, the higher molar mass alcohols remain undissolved as a separate layer, where the alcohol molecules strongly attract one another by dispersion forces.

16. Short chain carboxylic acids like methanoic acid are polar and can hydrogen bond as each methanoic acid molecule contains one -OH group. Hence methanoic acid molecules attract most strongly by hydrogen bonding. Water molecules are also polar and attract most strongly by hydrogen bonding. Thus water is a good solvent for methanoic acid and other short chain carboxylic acids, as water molecules and these carboxylic acid molecules will be able to mix and their molecules can attract one another strongly hydrogen bonding.
    Long chain carboxylic acids like palmitic acid are also polar and can hydrogen bond as each acid molecule contains one -OH group. However, these larger carboxylic acid molecules are attracted most strongly to one another by dispersion forces. For this reason water is a poor solvent for long chain carboxylic acids (fatty acids) as water molecules attract most strongly by hydrogen bonding while fatty acid molecules attract most strongly by dispersion forces. Thus fatty acids and water do not mix as their different molecules cannot attract one another strongly enough.

17. a. Surface tension.
    b. The surface tension of a liquid is a result of its intermolecular forces. At the surface of a liquid there is an imbalance of these forces causing surface molecules to be pulled inwards towards the bulk of the liquid. As a consequence the surface is trying to contract to achieve a minimum area. This puts the surface in compression and gives rise to surface tension. Usually, the stronger the intermolecular forces the greater the resulting surface tension.
    c. The surface tension of non-polar benzene would be less than that of water. Surface tension is a consequence of an imbalance in intermolecular forces occurring at the surface of a liquid. Generally, the stronger the intermolecular forces the greater the resulting surface tension.
    d. Since the detergents improve wetting ability they must reduce surface tension.

Set 26 Electrolytes in solution

1. a. solute and solvent b. homogeneous c. unsaturated d. supersaturated (temporarily) e. solubility

2. a. The solubility of gases typically decreases as temperature increases. Thus the graph for substance B has the typical shape of a solubility curve for a gas.

   b. Cerium(III) sulfate is a solid and the solubility of most solids increases with temperature. In the case of $Ce_2(SO_4)_3$ its solubility decreases with increasing temperature.

   c. The solubility of substance A at 40 °C is 52 g per 100 mL of water. Thus a minimum of 52 g of A is required to be added to the 100 mL of water to prepare a saturated solution of it at 40 °C. When cooled to 20 °C the solubility of A reduces to 28 g per 100 mL of water. For this reason the solution is now supersaturated. At some point in time crystals of A will begin to form and continue forming until the solution is once again saturated but no longer supersaturated. This will require about 24 g of crystals to form.

3. a. $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$ NaOH is ionic and $\therefore$ a strong electrolyte. The single arrow shows dissociation goes to completion.
   b. $CH_3COOH(l) \rightleftarrows CH_3COO^-(aq) + H^+(aq)$ CH_3COOH is a weak acid and $\therefore$ a weak electrolyte. The double arrows show partial ionisation.
   c. $Cu(CH_3COO)_2(s) \rightarrow Cu^{2+}(aq) + 2CH_3COO^-(aq)$ $Cu(CH_3COO)_2$ is ionic and $\therefore$ a strong electrolyte.
   d. NR C_2H_5OH is a non-electrolyte.
   e. $FeCl_3(s) \rightarrow Fe^{3+}(aq) + 3Cl^-(aq)$ $FeCl_3$ is ionic and $\therefore$ a strong electrolyte.
   f. NR $C_{12}H_{22}O_{11}$ is a non-electrolyte.
   g. $(NH_4)_2SO_4(s) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$ $(NH_4)_2SO_4$ is ionic and $\therefore$ a strong electrolyte.
   h. $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$ HCl is a strong acid and $\therefore$ a strong electrolyte.
   i. $H_2S(g) \rightleftarrows H^+(aq) + HS^-(aq)$ H_2S is a weak acid and $\therefore$ a weak electrolyte. [Note: As H_2S is a weak electrolyte only show its single ionisation.]
   j. NR $CHCl_3$ is a non-electrolyte.
   k. $K_2Cr_2O_7(s) \rightarrow 2K^+(aq) + Cr_2O_7^{2-}(aq)$ $K_2Cr_2O_7$ is ionic and $\therefore$ a strong electrolyte.
   l. $HNO_3(l) \rightarrow H^+(aq) + NO_3^-(aq)$ HNO_3 is a strong acid and $\therefore$ a strong electrolyte.

4. a. Conductivity in an aqueous solution is due to the presence of mobile ions. Thus the greater the concentration of ions in solution the greater its conductivity. Since 1.0 mol L^{-1} KCl(aq) has a greater concentration of ions, ten times that of 0.1 mol L^{-1} KCl(aq), then 1.0 mol L^{-1} KCl(aq) has a greater conductivity than 0.1 mol L^{-1} KCl(aq).

   b. As one mole of $FeCl_3$ produces four moles of ions then the total concentration of ions in 1 mol L^{-1} $FeCl_3(aq)$ is 4 mol L^{-1}. However, one mole of $FeCl_2$ produces only three moles of ions so in 1 mol L^{-1} $FeCl_2(aq)$ the total ion concentration is only 3 mol L^{-1}. As solution conductivity increases with increasing ion concentration then 1.0 mol L^{-1} $FeCl_3(aq)$ will have the greater conductivity.

   c. Both solutions have the same concentration, however HCl is a stronger electrolyte than CH_3COOH. In solution a greater percentage of HCl molecules are ionised. Thus 1.0 mol L^{-1} HCl(aq) has a greater concentration of ions and is a better conductor of electricity than 1.0 mol L^{-1} $CH_3COOH(aq)$.

5. a. As HCl is a strong electrolyte all of the dissolved molecules of hydrogen chloride [HCl(aq)] become ionised to form $H^+(aq)$ and $Cl^-(aq)$ ions. Thus no molecules of HCl remain.

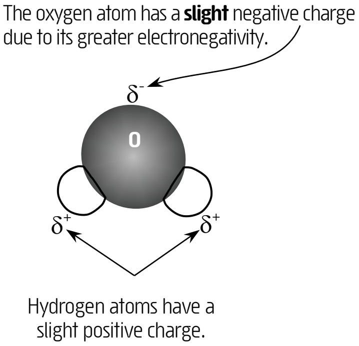
   b. Solid NaCl consists of a lattice of Na^+ and Cl^- ions held in fixed positions (**not mobile**) and hence cannot conduct electricity. Since NaCl is a strong electrolyte, its solution will produce **mobile** $Na^+(aq)$ and $Cl^-(aq)$ ions. Mobile ions allow electrical conductivity to occur.

   c. An ionic compound such as AgCl, can only dissociate into ions once it has dissolved. AgCl has a very low solubility, hence very little of it dissolves and so very little of it can dissociate into ions. Thus the concentration of ions in AgCl(aq) is always low.

   d. Upon dissolving, $Cu(NO_3)_2(s)$ completely dissociates into independent separate ions, $Cu^{2+}(aq)$ and $NO_3^-(aq)$. Thus no particles of formula $Cu(NO_3)_2$ exist.

6. a. dissolves
   b. aqueous
   c. polar
   d electrons
   e. slight negative charge (δ^-
   f. electrostatically
   g. hydrated
   h. ion-dipole
   i. dissociation
   j. $Na^+(aq) + Cl^-(aq)$

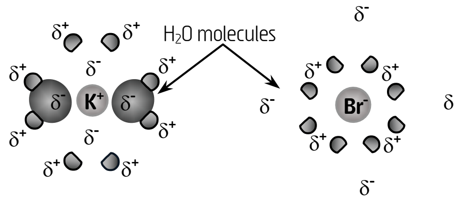
7. a.


The oxygen atom has a **slight** negative charge due to its greater electronegativity.

Hydrogen atoms have a slight positive charge.

b. Polar molecules have an uneven distribution of charge. These molecules have slightly positively charged regions and slightly negatively charged regions. In water molecules the oxygen atom has a slight negative charge (δ^-) while each of the hydrogen atoms has a slight positive charge (δ^+).

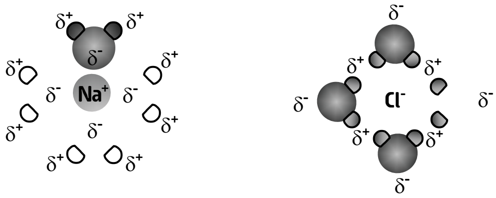
c.



Note: The oxygen atoms (large spheres) are closest to the positive ion (K^+). Hydrogen atoms (small spheres) are closest to the negative ions (Br^-).

8. a. In the ionic solid NaCl, the positive Na^+ ions and negative Cl^- ions are strongly attracted to one another. This keeps the ions in fixed positions within the ionic lattice. When NaCl is placed into water, the attraction of the Na^+ ions for the negative dipole of the water molecule and the attraction of the Cl^- ions for the positive dipole of the water molecule help to overcome the mutual attraction of Na^+ ions for Cl^- ions in the ionic lattice. These ion-dipole forces, where both Na^+ and Cl^- ions attract water molecules (Fig 1), help to explain the solubility of NaCl in water.

Figure 1



Note: The oxygen atoms (large spheres are closest to the positive ion (Na^+). Hydrogen atoms (small spheres) are closest to the negative ions (Cl^-).

b. Solvent polarity increases in the order: hexane (least polar), methanol then water (most polar). The data shows salt solubility increases in the same order. Thus salt is least soluble in hexane and most soluble in water. This trend is to be expected as the solubility of an ionic solute depends upon the ability of its ions to form ion-dipole bonds with the solute molecules. The more polar the solvent molecules, the greater the strength of the ion-dipole forces. Thus salt solubility should be greatest in the most polar solute (water) and least soluble in the least polar solvent (hexane).

Set 27 Precipitation reactions

1. a. $ZnCO_3(s)$, white b. $Fe(OH)_2(s)$, pale green c. NR d. $PbCl_2(s)$, white
   e. $CaSO_4(s)$, white [As $CaSO_4$ is slightly soluble only a faint milkiness may be seen.] f. $BaSO_4(s)$, white

2. a. $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$ b. $Zn^{2+}(aq) + \mathbf{2}OH^-(aq) \rightarrow Zn(OH)_2(s)$ c. $\mathbf{2}Fe^{3+}(aq) + \mathbf{3}CO_3^{2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$
   d. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$ *and* $Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$

3. a. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$ Two colourless solutions produce a white precipitate.
   b. NR
   c. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ Two colourless solutions produce a white precipitate.
   d. $Ca^{2+}(aq) + \mathbf{2}OH^-(aq) \rightarrow Ca(OH)_2(s)$ Two colourless solutions produce a faint white precipitate [$Ca(OH)_2$ is slightly soluble].
   e. $Cr^{3+}(aq) + \mathbf{3}OH^-(aq) \rightarrow Cr(OH)_3(s)$ A green and colourless solution produce a grey-green precipitate.
   f. $Cu^{2+}(aq) + \mathbf{2}OH^-(aq) \rightarrow Cu(OH)_2(s)$ A blue and colourless solution produce a blue (gelatinous) precipitate.
   g. $Sn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SnCO_3$ Two colourless solutions produce a white precipitate.
   h. $Co^{2+}(aq) + \mathbf{2}OH^-(aq) \rightarrow Co(OH)_2(s)$ A pink and a colourless solution produce a red precipitate.
   i. $Pb^{2+}(aq) + \mathbf{2}Cl^-(aq) \rightarrow PbCl_2(s)$ Two colourless solutions produce a faint white precipitate [$PbCl_2$ is slightly soluble].
   j. $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$ Two colourless solutions produce a faint white precipitate [$CaSO_4$ is slightly soluble].
   k. NR
   l. $Al^{3+}(aq) + \mathbf{3}OH^-(aq) \rightarrow Al(OH)_3(s)$ Two colourless solutions produce a white precipitate.

4. The colours of the listed reagents are: $CoCl_2$(aq) [pink], $CuSO_4$(aq) [blue], $Pb(NO_3)_2$(aq) [colourless], $Cr_2(SO_4)_3$(aq) [green], $FeCl_3$(aq) [pale brown], Na_2CO_3(aq) [colourless], MgI_2(aq) [colourless] and $FeSO_4$(aq) [pale green].
   a. $FeCl_3$(aq) (pale brown solution) and Na_2CO_3(aq) (colourless solution) will produce a brown precipitate of $Fe_2(CO_3)_3$.
   b. $Pb(NO_3)_2$(aq) [colourless] and Na_2CO_3(aq) [colourless] will produce a white precipitate of $PbCO_3$ **or** Na_2CO_3(aq) (colourless) and MgI_2(aq) (colourless) forms $MgCO_3$(s). The precipitate $PbSO_4$ is also white, however neither of the sulfate solutions is colourless.
   c. $FeSO_4$(aq) [pale green] and Na_2CO_3(aq) [colourless] will produce a pale green precipitate of $FeCO_3$. The precipitate $Cr_2(CO_3)_2$ is also a grey-green colour, however $Cr_2(SO_4)_3$(aq) has a dark green colour.
   d. $CuSO_4$(aq) [blue] and Na_2CO_3(aq) [colourless] will produce the green precipitate $CuCO_3$.
   e. $Pb(NO_3)_2$(aq) [colourless] and MgI_2(aq) [colourless] will produce the yellow precipitate PbI_2.
   f. $CoCl_2$(aq) [pink] and Na_2CO_3(aq) [colourless] will produce the red precipitate $CoCO_3$.

5. a. Mix together a solution of any soluble cobalt salt with a solution of a soluble carbonate, eg $Co(NO_3)_2$(aq) with Na_2CO_3(aq). Note the other salt produced ($NaNO_3$) is soluble. Avoid a combination producing two insoluble salts.
   b. Mix together a solution of any soluble nickel(II) salt with the solution of a soluble hydroxide, eg $Ni(NO_3)_2$(aq) with NaOH(aq). Note: The other salt produced ($NaNO_3$) is soluble. Avoid a combination producing two insoluble salts.
   c. Mix $Cr(NO_3)_3$(aq) and NaOH (aq) or any other suitable solutions of a soluble chromium(III) salt and a soluble hydroxide.
   d. Mix together $BaCl_2$(aq) and $MgSO_4$(aq) or any other suitable solutions of soluble barium and sulfate salts.

6. Yes. Adding a few drops of $Ba(NO_3)_2$(aq) will produce a white precipitate with Na_2CO_3(aq) while no change is observed with NaOH(aq). The white precipitate forms as $BaCO_3$ is insoluble while $Ba(OH)_2$ is soluble, so no precipitate forms with NaOH(aq).

7. These solutions contain the different cations Mg^{2+}(aq) and Pb^{2+}(aq). These cations have a different pattern of solubility with Cl^-(aq), Br^-(aq), I^-(aq) and SO_4^{2-}(aq). In each case the lead salts: $PbCl_2$, $PbBr_2$, PbI_2 and $PbSO_4$ are insoluble while the magnesium salts are soluble. Hence adding a solution containing one of these anions will produce a noticeably different result with the two solutions. To do this choose any soluble salt containing one of these anions, eg NaCl(s) and produce a solution of it by dissolving the salt in water. Add a few drops of the chosen reagent, eg NaCl(aq) to each of the two solutions. The solution producing a white precipitate contains the Pb^{2+}(aq) ions, ie this is the $Pb(NO_3)_2$(aq) solution.

8. a. Add some NaBr(aq) to both. A white precipitate is observed with lead nitrate solution, while no change occurs with calcium nitrate solution. [Na_2CO_3(aq) and $MgSO_4$(aq) produce the same result (a white precipitate) with both solutions. $Pb(NO_3)_2$(aq) produces no reaction in both cases.]
   b. Add some NaBr(aq) to both. A cream precipitate is observed with silver nitrate, while no change is seen with calcium nitrate.
   c. Not possible. The only difference between these solutions is the Na^+(aq) and K^+(aq) ions and these ions have the same pattern of solubility.
   d. Add some Na_2CO_3(aq) to both solutions. A grey-green precipitate [$FeCO_3$(s)] is observed with iron(II) nitrate, while a brown precipitate [$Fe_2(CO_3)_3$(s)] is observed with iron(III) nitrate.

9. Both of these solids are soluble so add water to a small sample of each solid to form a solution of each in separate test tubes. These solutions contain the same cation K^+(aq) but different anions Cl^-(aq) and I^-(aq). The anions have the same pattern of solubility but produce different coloured precipitates with Pb^{2+}(aq) and Ag^+(aq). The precipitates PbI_2(s) and AgI(s) are yellow and pale yellow respectively while $PbCl_2$(s) and AgCl(s) are white. Hence adding a solution containing either of these cations, Pb^{2+}(aq) or Ag^+(aq) will produce a noticeably different result with the each solution. To do this choose a soluble salt containing one of these cations, eg $Pb(NO_3)_2$ (aq) and add a few drops of it to each of the unknowns. The solution producing a white precipitate contains the Cl^-(aq) ions, ie is KCl(aq) while the solution with the yellow precipitate is KI(aq).

10. a. All three solids are soluble. First add water and dissolve a small sample of each into three separate test tubes. Now add some $Ba(NO_3)_{2(aq)}$ to all three. A white precipitate identifies potassium sulfate, while no change is seen for potassium hydroxide or potassium chloride solution. To the remaining two unidentified solutions add a few drops of $Mg(NO_3)_{2(aq)}$. The KOH solution will produce a white precipitate $[Mg(OH)_{2(s)}]$ while the KCl solution has no reaction.

    b. Dissolve a little of each solid into three separate test tubes. Add a few drops of $Pb(NO_3)_{2(aq)}$ to all three solutions. The NaI solution is identified by a yellow precipitate. A white precipitate is observed with both $NaCl_{(aq)}$ and $Na_2CO_{3(aq)}$ solutions. To a fresh sample of the remaining two unidentified solutions $[NaCl_{(aq)}$ and $Na_2CO_{3(aq)}]$ add a little $Ca(NO_3)_{2(aq)}$ solution. A white precipitate identifies $Na_2CO_{3(aq)}$, no reaction occurs with $NaCl_{(aq)}$.

    c. Dissolve a little of each solid into three separate test tubes. Add a few drops of $Na_2SO_{4(aq)}$ to all three solutions. No precipitate is observed with magnesium chloride, the other two both produce a white precipitate. To a fresh sample of the two unidentified solutions $[CaCl_{2(aq)}$ and $BaCl_{2(aq)}]$ add a little $NaOH_{(aq)}$ solution. A white precipitate identifies $CaCl_{2(aq)}$ while $BaCl_{2(aq)}$ shows no reaction.

Set 28 Solution concentration and drinking water

1. a. **c(NaOH)** $= \frac{n}{} = \frac{1.41}{2.40} =$ **0.588 mol L^{-}**

   b. **c(CH_3** $\frac{n}{} = \frac{0.71}{0.561} =$ **1.3 mol L^{-}**

2. a. **n($CuSO_4$** $\frac{m}{} = \frac{16.2}{159.62} =$ **0.101 mol** *and* **c($CuSO_4$** $\frac{n}{V} = \frac{0.101}{1.94} =$ **$5.23 \times 10^{-}$** -

   b. n(NaCl) $= \frac{m}{} = \frac{0.139}{58.44} = 2.38 \times 10^{-}$

   and **c(NaCl)** $= \frac{n}{V} = \frac{2.38 \times 10^{-3}}{0.494} =$ **$4.81 \times 10^{-}$** - Mass must be in g, ie 139 mg = 0.139 g.

   c. **n[$Fe_2(SO_4)_3.9H_2O$]** $= \frac{m}{} = \frac{129}{562.05} =$ **0.230 mol** *and* **c[$Fe_2(SO_4)_3$]** $= \frac{n}{V} = \frac{0.230}{11.77} =$ **$1.95 \times 10^{-}$** -

3. a. **c(CO_2) gL^{-1}** $= \frac{m}{} = \frac{1.90}{0.375} =$ **5.07 g L^{-}**

   b. **c(sucrose) gL^{-1}** $= \frac{m}{V} = \frac{112}{0.375} =$ **299 g L^{-}** Note: 375 mL = 0.375 L

4. a. n[$Ca(NO_3)_2$] = cV = 1.5 x 15 = 23 mol *and* **m[$Ca(NO_3)_2$]** = nM = 23 x 164.10 = **3.7×10^3 g** (2SF)

   b. n(Na_2CO_3) = cV = 4.59 x 0.750 = 3.44 mol *and* **m(Na_2CO_3)** = nM = 3.44 x 105.99 = **365 g** (3SF)

5. a. **$c_{ppm}(Na_2CO_3)$ =** $\frac{m_{(solute)}}{m_{(solution)}} \times 1 \times 10^6 = \frac{122.0 \times 1 \times 10^6}{4460} =$ **2.735×10^4** Use the same units for both masses, ie 4.460 kg = 4460 g.

   b. **c_{ppm}[of dissolved salt]** $= \frac{m_{(solute)}}{m_{(solution)}} \times 1 \times 10^6 = \frac{0.75 \times 1 \times 10^6}{562} =$ **1.3×10^3**

6. n[C_{12} $_{22}$ $_{11}$ $^{-3}$ = 0.088 mol *and* m[C_{12} $_{22}$ $_{11}$)

   Number of teaspoon of sugar $= \frac{m(sugar)}{6} = \frac{30}{6} =$ **5 teaspoons of sugar!** (1SF)

7. a. **c(O_2)g L^{-}** $\frac{m(O_2)}{} = \frac{4.97}{16.6} =$ **0.299 g L^{-}** **c(CO_2** - $\frac{m(CO_2)}{V(air)} = \frac{0.0102}{16.6} =$ **$6.14 \times 10^{-}$** -

   b. **V(air)** $= \frac{m(O_2)}{c(O_2)} = \frac{1.0 \times 10^3}{0.299} =$ **3300 L** (2SF)

   c. **$c(CO_2)_{ppm}$** $\frac{m(CO_2) \times 1 \times 10^6}{m(air)} = \frac{0.0102 \times 1.0 \times 10^6}{(16.2 + 4.97 + 0.275 + 0.0102)} =$ **4.75×10^2**

8. $n[Ca(ClO)_2$ $^{-6} \times 81 \times 10^3 = 0.43$ mol   Note: one kilolitre (1 kL) = 1000 L

$m(Ca(ClO)_2)$ = $n \times M = 0.43 \times 142.98$ = **61 g** (2SF) Note: Calcium hypochlorite is consumed as it decomposes bacteria. It also slowly degrades to free chlorine which is lost from the pool by evaporation. Thus the actual daily dose of calcium hypochlorite for a pool of this size is considerably more than 61 g.

9. $c(Au)_{ppm} \quad \frac{(Au)}{m_{(sea\ water)}} \times 1 \times 10^6$

thus **m(Au)** $= \frac{c(Au)_{ppm} \times m_{(sea\ water)}}{1 \times 10^6} = \frac{1.4 \times 10^{-3} \times 1.4 \times 10^{24}}{1 \times 10^6} = 1.96 \times 10^{15}$ g = $\mathbf{1.96 \times 10^{12}}$ **kg**

10. a. **$c(H^+)$** = $c(HCl)$ = **4.5 mol L^{-1}** *and* **$c(Cl^-)$** = $c(HCl)$ = **4.5 mol L^{-1}**
    b. **$c(Ca^{2+})$** = $c[Ca(NO_3)_2]$ = **1.4 mol L^{-1}** *and* **$c(NO_3^-)$** = $2 \times c[Ca(NO_3)_2]$ = **2.8 mol L^{-1}**
    c. **$c(Cr^{3+})$** = $2 \times c[Cr_2(SO_4)_3]$ = **1.5 mol L^{-1}** *and* **$c(SO_4^{2-})$** = $3 \times c[Cr_2(SO_4)_3]$ = **2.25 mol L^{-1}**

11. $n[Al_2(SO_4)_3] = \frac{m}{M} = \frac{22.5}{342.17} = 0.0658$ mol *and* $c[Al_2(SO_4)_3] = \frac{n}{V} = \frac{0.0658}{1.00} = 6.58 \times 10^{-2}$ mol L^{-1} (3SF)

$c(Al^{3+}$ = $2 \times c[Al_2(SO_4)_3]$ = **0.132 mol L^-** *and* **$c(SO_4^{2-})$** = $3 \times c[Al_2(SO_4)_3]$ = **0.197 mol L^-**

12. Water sources on Earth include the ocean (97.3%), glaciers and polar ice caps (2.1%) with rivers, lakes and groundwater comprising only 0.6%. Of these, sea water contains high concentrations of dissolved salts and is unsuitable for consumption while water in polar ices caps and glaciers is inaccessible. The small amount of 'fresh' water in rivers, lakes and groundwater may also be unsuitable for direct consumption due to varying salt concentrations, presence of toxic heavy metal ions, suspended material or pathogenic organisms.

13. TDS refers to the total dissolved solids present in drinking water. Dissolved solids are typically in the form of various non-toxic ions, eg Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and so on as well as various dissolved organic compounds. As these are non-toxic there is no upper limit on their maximum concentration. There are, however, guidelines based on palatability and aesthetics which suggest 900-1200 mg L^{-1} is poor and greater than 1200 mg L^{-1} is unacceptable.

14. a. Potable water is water that is safe to drink and cook with. It should be clear, colourless and odourless, contain no pathogens or toxic substances and be pleasant to taste.
    b. Increased population and changing rainfall patterns means the recharge of dams and groundwater is no longer able to meet demand.
    c. A semi permeable membrane (SPM) is a membrane that allows water molecules to pass through but not larger molecules or salt ions. Osmosis occurring in plant cells uses the natural tendency of water to diffuse through a cellular SPM, from water in the soil that has a low salt concentration, into the plant root cells where the salt concentration is higher.
    d. In both cases a semi permeable membrane (SPM) is involved. In reverse osmosis however, pressure is applied to salty water forcing water to pass through the SPM in an opposite direction to what happens naturally in osmosis. Thus in RO water is forced to diffuse through an SPM from a solution of high salt concentration (eg sea water) into very low salt (zero salt) concentration 'solution' called permeate (fresh water).

15. a. In an aqueous solution sodium ions will be strongly attracted to polar water molecules by ion-dipole forces. Typically each ion (positive or negative) will be surrounded by and simultaneously attracted to the oppositely charged dipole of several water molecules. Thus separating water molecules from the salt solution involves bond breaking, an endothermic process. This explains why desalination requires so much energy.
    b. Desalination by distillation involves evaporation of water followed by its condensation to produce pure (distilled) water. Converting $H_2O_{(l)}$ to $H_2O_{(g)}$ requires a large input of energy that is not required in the RO technique of desalination. The extra energy needed for evaporation is a result of the strong intermolecular forces (mainly hydrogen bonding) acting between neighbouring water molecules in the liquid phase. This extra bond breaking is not required in RO and explains why more energy is involved in desalination by distillation. Modern distillation plants do use a heat exchanger to recover most of this energy when the water vapour recondenses (bond forming). The recovered energy is then used to assist in the distillation of further salty water.

16. a. $\mathbf{c}_{ppm}\ ^{-} \quad \frac{m(F^-)}{m(solution)} \times 10^6$ *ie* $m(F^-) = \frac{\mathbf{c}_{ppm}\ ^{-} \times m(solution)}{1 \times 10^6} = \frac{1.0 \times 4.5 \times 10^7}{1 \times 10^6} = \mathbf{45\ g}$ (2SF)

Note: 45 000 L of water has a mass of 45 000 kg, ie 45 000 000 g.

b. $n(\mathbf{F}^- \quad \frac{}{M} = \frac{45}{19.00} = 2.4$ mol of F^-

also $n(NaF) = n(F^-)$ *so* **m(NaF)** = n x M = 2.4 x 41.99 = 99.45 or **99 g NaF** (2SF)

c. Concentration in ppm is a **mass** ratio of solute to solution while concentration in mol L^{-1} relates the **moles** of solute to the solution volume. While the moles of F^- and NaF in a given volume of $NaF_{(aq)}$ will be the same, the mass of F^- and mass of NaF in the same volume of solution will not be the same (as F^- and NaF have different molar masses, ie 19.0 g mol^{-1} and 42 g mol^{-1}respectively). For example, a 1.0 L solution of 1 mol L^{-1} $NaF_{(aq)}$ will contain 1 mole of NaF (42 g of it) in the form of 1 mole of F^- (19 g of it) and 1 mole of Na^+ (23 g of it). Thus the molar concentration of F^- in a solution of NaF are the same value but the concentration in ppm, ie grams of each per million grams of solution, will not be the same.

d. n(NaF in 100 g of solution) = $\frac{m}{M} = \frac{4.1}{41.99} = 0.098$ mol

and $n(F^-$ in 100 g of solution) = n(NaF in 100 g of solution) = 0.098 mol

$m(F^-$ in 100 g of solution) = n x M = 0.098 x 19.00 = 1.9 g (showing 2SF)

$\mathbf{c(}F \quad = \frac{m(F^-)}{m(solution)} = \frac{1.9}{100} \times 1 \times 10^6 = \mathbf{19000\ ppm}$ (2SF)

17. a. Chlorine is added at this stage of drinking water treatment for the purpose of disinfection. Chlorine is a bactericide, it destroys various cellular pathogens.

b. $\mathbf{c(Cl}_2\ _{ppm} \quad \frac{_2)}{m_{(tap\ water)}} \times 1 \times 10^6$

thus $\mathbf{m(Cl_2)} = \frac{c(Cl_2)_{ppm} \times m_{(tap\ water)}}{1 \times 10^6} = \frac{1.0 \times 9.79 \times 10^{11}}{1 \times 10^6} = \mathbf{9.8 \times 10^5} \qquad _2$ (2SF)

c. Chlorine will be consumed in the process of destroying various cellular pathogens that may be present in tap water. This will decrease its concentration so more will need to be added to maintain 1 ppm Cl_2 concentration at the consumer outlet.

Set 29 Acid base properties and reactions

1. solution A **Acidic**. Any solution that turns blue litmus red is an acidic solution.

solution B Neutral
solutions have no effect on litmus colour.

solution C **Acidic**. All acids produce hydrogen with magnesium metal. Bases and neutral salts do not liberate hydrogen gas from magnesium.

solution D **Inconclusive**. Solution conductivity is a property of acidic, basic and neutral salt solutions. Further, as the litmus did not change colour but only remained blue then the solution could be neutral or basic.

solution E **Acidic**. Solutions with a pH lower than 7 are acidic solutions. Also, copper metal has a low reactivity and does not liberate hydrogen from acid solutions.

solution F **Neutral**. The solution cannot be acidic as all acidic solutions react with sodium carbonate to produce the colourless gas, carbon dioxide. Also since the solution does not turn red litmus blue it cannot be basic. The solution must be neutral.

solution G **Basic.** Basic solutions produce the pungent odour of ammonia gas when added to an ammonium salts.

solution H Neutral Any solution that turns universal indicator green is neutral (or very close to neutral).

2. a. $MgSO_4(aq)$, $CO_2(g)$ and $H_2O(l)$
   b. $CaCl_2(aq)$, and $H_2(g)$
   c. $H_2O(l)$, $CO_2(g)$ and $NaNO_3(aq)$
   d. $ZnSO_4(aq)$, $CO_2(g)$ and $H_2O(l)$
   e. $Mg(CH_3COO)_2(aq)$ and $H_2O(l)$
   f. $ZnSO_4(aq)$ and $H_2(g)$
   g. $CaCl_2(aq)$ and $H_2O(l)$
   h. $NH_3(g)$, $NaCl(aq)$ and $H_2O(l)$
   i. $BaSO_4(s)$ and $H_2O(l)$
   j. $Na_2CO_3(aq)$ and $H_2O(l)$

3. a. $6HNO_3(aq) + Al_2(CO_3)_3(s) \rightarrow 2Al(NO_3)_3(aq) + 3CO_2(g) + 3H_2O(l)$
   b. $3HCl(aq) + Fe(OH)_3(s) \rightarrow FeCl_3(aq) + 3H_2O(l)$
   c. $2HNO_3(aq) + BaO(s) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$
   d. $KOH(aq) + NH_4Cl(aq) \rightarrow NH_3(g) + KCl(aq) + H_2O(l)$
   e. $2HCl(aq) + Fe(s) \rightarrow FeCl_2(aq) + H_2(g)$
   f. $2CH_3COOH(aq) + ZnCO_3(s) \rightarrow Zn(CH_3COO)_2(aq) + CO_2(g) + H_2O(l)$
   g. $3H_2SO_4(aq) + 2Al(s) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$
   h. $2H_3PO_4(aq) + 3Ba(OH)_2(s) \rightarrow Ba_3(PO_4)_2(s) + 6H_2O(l)$
   i. $CO_2(g) + Ba(OH)_2(s) \rightarrow BaCO_3(s) + H_2O(l)$
   j. $SO_3(g) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$
   k. $K_2SO_3(aq) + 2HCl(aq) \rightarrow SO_2(g) + 2KCl(aq) + H_2O(l)$
   l. $SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$

4. a. $CuCO_3(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + CO_2(g) + H_2O(l)$
   A green solid dissolves and a colourless, odourless gas is formed as the solution changes from colourless to blue.
   b. $CuO(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l)$
   A black solid dissolves forming a clear blue solution.
   c. No reaction as both $Mg(OH)_2$ and $NaOH$ are basic.
   d. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   A grey solid dissolves producing a clear colourless solution and a colourless, odourless gas.
   e. $MgCO_3(s) + 2CH_3COOH(aq) \rightarrow 2CH_3COO^-(aq) + Mg^{2+}(aq) + CO_2(g) + H_2O(l)$
   A colourless odourless gas is evolved as the white solid dissolves.
   f. $Cu(OH)_2(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$
   A blue solid dissolves resulting in a clear blue solution.
   g. $Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$
   A white solid dissolves producing a clear colourless solution.
   h. $2CH_3COOH(aq) + Mg(s) \rightarrow 2CH_3COO^-(aq) + Mg^{2+}(aq) + H_2$
   A grey solid dissolves producing a clear colourless solution and a colourless, odourless gas.
   i. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$
   A strong pungent odour is evolved, no bubbles seen as ammonia is very soluble in water.
   j. NR [Cu is not a sufficiently reactive metal. It is unable to displace hydrogen from an acidic solution.]
   k. $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
   A colourless, odourless gas dissolves producing a clear colourless solution.
   l. $SO_2(g) + 2OH^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O(l)$
   The colourless pungent gas dissolves resulting in no odour and a colourless solution.
   m. $SO_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l)$
   A colourless solution produces a pungent, choking odour.

5.

i	CuO	CuO is a basic oxide and so will dissolve in nitric acid. It produces a blue solution containing $Cu^{2+}(aq)$.
ii	$Ca(OH)_2$	$Ca(OH)_2$ is a basic hydroxide that dissolves in acid producing a colourless solution. The other compounds that react with an acid solution either produce coloured solutions (CuO gives a blue solution, $Cr_2(CO_3)_3$ gives a green solution) or a colourless gas is evolved ($Cr_2(CO_3)_3$ and $MgCO_3$).
iii	$Cr_2(CO_3)_3$	Of the substances listed, only $Cr_2(CO_3)_3$ will dissolve in an acid to produce a green solution. This is due to formation of $CrCl_3(aq)$. This reaction also produces a colourless gas [CO_2] but this is not mentioned in the question.
iv	$MgCO_3$	$MgCO_3$ dissolves in sulfuric acid producing the colourless gas, carbon dioxide gas. The other carbonate compound [$Cr_2(CO_3)_3$] also produces a colourless gas but its solution is green.
v	NH_4Cl	NH_4Cl dissovles in a basic solution like sodium hydroxide to yield the strongly pungent gas ammonia, $NH_3(g)$.

6. **A variety of correct answers are possible. The following are some suggested answers.**
   a. Add some 1 mol L^{-1} hydrochloric acid (or other strong acid but not nitric acid) to each solid. With zinc a colourless gas is produced. No reaction is observed with silver. (Silver is not a sufficiently reactive metal, ie it does not produce hydrogen gas with acidic solutions.)
   b. Add some 1 mol L^{-1} hydrochloric acid (or other strong acid but not nitric acid) to each solid. With magnesium a vigorous reaction produces a colourless gas and a colourless solution. A similar but much slower reaction is observed with iron (iron is a much less reactive metal, lower down the activity series than magnesium) and the resulting solution will be pale green.
   c. Add some acid solution to both, eg nitric acid or any other acid solution. Both solids will dissolve as they are both basic. Only copper carbonate will produce a colourless gas. Both compounds produce a coloured (blue) solution.
   d. Add some acid solution to all three solids, eg nitric acid or any other acid solution. Zinc carbonate will fizz quite strongly producing an odourless colourless gas and a colourless solution. (The gas formed is carbon dioxide gas.) The other two solids will dissolve producing colourless solutions. To a second sample of the unidentified solids add some sodium hydroxide, or any other strong soluble base. Ammonium chloride will dissolve and produce a strongly pungent odour. (The odour is due to the formation of ammonia gas.) The remaining solid is calcium chloride which might dissolve due to its solubility in water, but no other changes would be observed.

7. a. Sulfur dioxide gas reacts with calcium oxide as shown here: $SO_2(g) + CaO(s) \rightarrow CaSO_3(s)$.
   Alternatively this process may be viewed as two consecutive reactions:
   $SO_2(g) + H_2O(l) \rightleftarrows H_2SO_3(aq)$ then $H_2SO_3(aq) + CaO(s) \rightarrow CaSO_3(s) + H_2O(l)$.
   In either case the same overall reaction can be seen to occur.
   b. The major component in structures made of iron is the element Fe. This metal reacts with acidic oxides in the presence of water to produce hydrogen gas and an iron(II) salt as shown:
   $Fe(s) + SO_3(g) + H_2O(l) \rightarrow FeSO_4(s) + H_2(g)$ This process may be seen as two consecutive reactions:
   $SO_3(g) + H_2O(l) \rightleftarrows H_2SO_4(aq)$ then $H_2SO_4(aq) + Fe(s) \rightarrow FeSO_4(s) + H_2(g)$
   In either case the same overall reaction can be seen to occur. Consequently acid rain will corrode or dissolve these structures over time. As acid rain has quite a low hydrogen ion concentration the process will be quite slow, its effects being noticed over months or years rather than days.
   c. Limestone and marble both contain significant amounts of $CaCO_3(s)$. This substance readily reacts with acidic oxides producing a calcium salt and carbon dioxide as shown here:
   $2CaCO_3(s) + 4NO_2(g) \rightarrow Ca(NO_3)_2(s) + Ca(NO_2)_2(s) + 2CO_2(g)$ This reaction may be better understood as three consecutive reactions:
   initially ....$2NO_2(g) + H_2O(l) \rightleftarrows HNO_3(aq) + HNO_2(aq)$
   then ....$2HNO_3(aq) + CaCO_3(s) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$
   and.....................$2HNO_2(aq) + CaCO_3(s) \rightarrow Ca(NO_2)_2(aq) + CO_2(g) + H_2O(l)$
   This effectively means the insoluble limestone or marble dissolves as it converts to water soluble calcium nitrate or calcium nitrite. Consequently the structures become seriously eroded and damaged.

Set 30 Understanding acids and bases

1. a. Note these pH values are **estimates only**: A pH ≈ 4-5, B pH ≈ 8-10, C pH ≈ 7, D pH ≈ 0-3, E pH ≈ 11-14.
   b. i. D [ie the lowest pH.]
   ii. C [Neutral solutions have a pH of 7.]
   iii. D and A [Solutions of pH<7 are acidic.]
   iv. D [The lowest pH gives the highest $c(H^+)$.]
   v. C [Only neutral solutions have $c(H^+) = c(OH^-)$.]
   vi. B and E [Solutions of pH>7 are basic.]

2. a. HCl is a strong acid that ionises in water to produce $H^+(aq)$ and thus its solutions are acidic, ie $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$.
   b. As stated, HF is a weak acid so it partially ionises in water to produce $H^+(aq)$ thus making its solutions acidic, ie $HF(g) \rightleftarrows H^+(aq) + F^-(aq)$.
   c. Sodium hydroxide is a strong base that dissociates in water to produce $OH^-(aq)$ and thus its solutions are basic, ie $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$.

d. As ethanoic acid produces $H^+(aq)$, its solutions are acidic, ie $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$.

e. As barium hydroxide dissociates in water to produce $OH^-(aq)$, its solutions are basic, ie $Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$.

3. a. 1.0 mol L^{-1} HNO_3 has the highest hydrogen ion concentration. Ethanoic acid is a weak acid (see Table 1 p157) and only partially ionises in aqueous solution. By comparison nitric acid is a strong acid and is completely ionised in aqueous solution thus producing a higher hydrogen ion concentration.

b. Both 1.0 mol L^{-1} $NH_3(aq)$ and 1.0 mol L^{-1} $NaOH(aq)$ form basic solutions. Ammonia is a weak base (see Table 1 p157) and so it produces a lower concentration of hydroxide ions than the stronger base $NaOH(s)$.

c. 1.0 mol L^{-1} $HCl(aq)$ produces the most acidic solution as its solution has a $H^+(aq)$ concentration of 1.0 mol L^{-1}. The 0.10 mol L^{-1} $HCl(aq)$ solution forms an acidic solution having an $H^+(aq)$ concentration of only 0.10 mol L^{-1}.

d. Both $HCl(aq)$ and $H_2SO_4(aq)$ are strong acids. HCl is a monoprotic acid producing 1 mol of $H^+(aq)$ per mol of $HCl(aq)$. By comparison H_2SO_4 is a diprotic acid producing up to 2 mole of $H^+(aq)$ per mol of acid. [See additional note below.] Hence the $H^+(aq)$ concentration for 1.0 mol L^{-1} $H_2SO_4(aq)$ is greater than for 1.0 mol L^{-1} $HCl(aq)$ and thus 1.0 mol L^{-1} H_2SO_4 has a lower pH.

[**Additional note**: The ionisation of the strong diprotic acid H_2SO_4 occurs in two stages. The first ionisation is essentially complete producing 1 mole of $H^+(aq)$ and 1 mole of $HSO_4^-(aq)$ per mol of H_2SO_4 molecules.

The subsequent ionisation of the weak acid HSO_4^- is incomplete producing a little less than 1 mol of $H^+(aq)$ per mol of $HSO_4^-(aq)$. Thus overall the ionisation of a 1 mol L^{-1} H_2SO_4 solution produces an $H^+(aq)$ concentration slightly less than 2 mol L^{-1} but considerably greater than the 1 mol L^{-1} for $HCl(aq)$.]

e. 1.0 mol L^{-1} $HNO_3(aq)$ has the most vigorous reaction with calcium carbonate granules.

The rate of this reaction depends upon the concentration of hydrogen ions. Since nitric acid is a strong acid and H_3PO_4 is a weak acid then 1.0 mol L^{-1} $HNO_3(aq)$ has a higher concentration of $H^+(aq)$ than 1.0 mol L^{-1} $H_3PO_4(aq)$. This is despite phosphoric acid being a triprotic acid and nitric acid a monoprotic acid.

4. a. sour
b. reactive metals
c. red
d blue
e. pungent
f. hydrogen ions
g. hydroxide ions
h. ionises
i. HNO_3
j. fully ionise
k. greater
l. H_2CO_3
m. NaOH
n. dissociate
o. Na_2CO_3

5. a. acidic b. acidic c. basic d. basic e. acidic

6. K_2O dissociates in water, initially forming O^{2-} ions. These O^{2-} ions then react with water to form hydroxide ions. This raises the solutions pH.

$K_2O(s) \rightarrow 2K^+(aq) + O^{2-}(aq)$ *then* $O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$ *overall* $K_2O(s) + H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq)$

When added to water, SO_2 initially dissolves to form $H_2SO_3(aq)$ which then partially ionises forming hydrogen ions. This lowers the solutions pH.

$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$ *then* $H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$

overall $SO_2(g) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$

7. a. i. $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ The formation of $H^+(aq)$ causes the solution to become acidic.

ii. The partial ionisation of $CH_3COOH(aq)$ produces some hydrogen ions. This raises the hydrogen ion concentration and consequently lowers pH.

iii. Sulfuric acid is a strong acid that undergoes complete ionisation in aqueous solution. Thus sulfuric acid produces a much higher hydrogen ion concentration than the same concentration of ethanoic acid (CH_3COOH). This higher hydrogen ion concentration may cause skin irritation or skin burns. For this reason a 1 mol L^{-1} ethanoic acid solution is safe for human consumption but a 1 mol L^{-1} sulfuric acid solution is not.

b. Sodium hydroxide is a strong base while ammonia is a weak base. The weakly basic nature of ammonia is evident from the double arrows in its ionisation equation (as given). Although both produce hydroxide ions when dissolved in water, for a given concentration, sodium hydroxide produces a much higher hydroxide ion concentration. This is due to the complete dissociation of sodium hydroxide in aqueous solution compared with the partial ionisation of ammonia. The higher hydroxide ion concentration in 6 mol L^{-1} $NaOH(aq)$ can result in skin irritation and burns. For this reason using a 6 mol L^{-1} sodium hydroxide solution around the home should be avoided, or at least used very carefully, ie with gloves, eye protection and good ventilation.

8. Tile grout is an insoluble basic oxide. An acid would be a suitable substance for dissolving the insoluble grout as acids react with basic oxides to produce water and a salt (most salts are soluble). Care should be exercised when handling strong acids or bases as both substances can be quite corrosive and cause skin burns or irritation. These substances are especially harmful to moist sensitive areas such as lungs and eyes. Avoid inhaling vapours of strong acids.

   Baking soda contains the weak base $NaHCO_3$ and so will be of no use as it will not dissolve CaO. Otherwise $NaHCO_3$ is not a particularly hazardous substance.

   Drain cleaner contains the strong base NaOH and so will be of no use as it will not dissolve CaO. Exercise great care (as outlined above) when handling a strong base like $NaOH_{(s)}$.

   Spirits of salts contains the strong acid HCl and so will dissolve CaO to produce water and soluble $CaCl_2$. This is a possible choice for removing the grout. However, as spirits of salts is a concentrated solution of the strong acid HCl then great care needs to be taken with its use. Wear gloves, eye protection and ensure plenty of ventilation (open doors and windows). It would be advisable to dilute the spirits of salts before using it. If diluting the acid ensure you add acid to water rather than water to the concentrated acid.

   Vinegar contains the weak acid CH_3COOH and so will dissolve CaO to produce water and soluble $Ca(CH_3COO)_2$. This is a good choice for removing the grout. As vinegar contains only a weak acid (ethanoic acid) and the acid is quite dilute then it is safe to handle without any special precautions.

9. a. Metallic carbonates and oxides like $CaCO_{3(s)}$ and $CaO_{(s)}$ will react with and hence neutralise any acid [$H^+_{(aq)}$] that may be present in the soil. Some reactions which may occur to raise the soil pH, ie consume $H^+_{(aq)}$, are shown here:

   $CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$ *and* $CaO_{(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)}$

   [Note: Alternatively, the substance $CaO_{(s)}$ can react with water in the soil producing insoluble $Ca(OH)_{2(s)}$. As this base has a low solubility it will not cause soil pH to rise significantly, rather its presence would maintain a slightly alkaline soil pH while acting to neutralise excess acid present in the soil.]

   b. High pH soils are basic, ie they have a high hydroxide ion concentration. The ammonium ion from ammonium nitrate will react with (neutralise) hydroxide ions to raise the soil pH, ie

   $NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)} + NH_{3(aq)}$ *alternatively* $NH_4NO_{3(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)} + NH_{3(aq)} + NO_3^-{}_{(aq)}$

10. first ionisation: $H_3PO_{4(aq)} \rightleftarrows H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$ [A double arrow is used as H_3PO_4 is a weak acid that undergoes partial ionisation.]
    second ionisation: $H_2PO_4^-{}_{(aq)} \rightleftarrows H^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$
    third ionisation: $HPO_4^{2-}{}_{(aq)} \rightleftarrows H^+_{(aq)} + PO_4^{3-}{}_{(aq)}$

Set 31 Stoichiometry involving solutions

1. $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

   $n(HCl) = cV = 6.60 \times 25.5 \times 10^{-3} = 0.168$ mol

   and $n(Mg) = \frac{1}{2} \times n(HCl) = \frac{1}{2} \times 0.168$ mol $= 8.42 \times 10^{-2}$ mol

   also **m(Mg)** $= n \times M = 8.42 \times 10^{-2} \times 24.31 =$ **2.05 g Mg** (3SF)

2. $Pb^{2+}_{(aq)} + 2I^-_{(aq)} \rightarrow PbI_{2(s)}$

   $n[Pb(NO_3)_2] = cV = 0.750 \times 65.5 \times 10^{-3} = 4.91 \times 10^{-2}$ mol*and* $n(Pb^{2+}) = n[Pb(NO_3)_2] = 4.91 \times 10^{-2}$ mol
   also $n(PbI_2) = n(Pb^{2+}) = 4.91 \times 10^{-2}$ mol *so* **m(PbI₂)** $= n\,M = 4.91 \times 10^{-2} \times 461.0 =$ **22.6 g PbI₂** (3SF)

3. a. $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$

   $n(AgCl) = \frac{m}{M} = \frac{1.38}{143.35} = 9.63 \times 10^{-3}$ mol *and* $n(Cl^-) = n(AgCl) = 9.63 \times 10^{-3}$ mol

   thus $\mathbf{c(Cl^-)} = \frac{n}{V} = \frac{9.63 \times 10^{-3}}{0.125} = \mathbf{7.70 \times 10^{-}}$ - **(aq)** (3SF)

   b. $n(NaCl) = n(Cl^-) = 9.63 \times 10^{-3}$ *and* $\mathbf{c(NaCl)mol\ L^{-1}} = \frac{n}{V} = \frac{9.63 \times 10^{-3}}{0.125} = \mathbf{7.70 \times 10^{-}}$ -

Alternatively: As NaCl is the only source of Cl^-(aq) and as one mole of NaCl contains one mole of Cl^- then:
$c(NaCl) = c(Cl^-) = 7.70\ x10^{-}$ $\quad ^{-}$

For the concentration of NaCl(aq) in g L^{-1} $\quad$ $m(NaCl) = nM = 9.63\ x10^{-3} \times 58.44 = 0.563$ g NaCl

and $\quad \mathbf{c(NaCl)g\ L^{-1}} = \frac{m}{V} = \frac{0.563}{0.125} = \mathbf{4.50\ g\ L^{-}}$ $\quad$ (3SF)

4. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

   $n(H_2) = \frac{Vstp}{22.71} = \frac{1.5}{22.71} = 6.6\ x10^{-2}$ mol $\quad$ *and* $\quad$ $n[HCl] = 2 \times n(H_2) = 2 \times 6.6\ x10^{-2} = 0.13$ mol HCl

   and $\mathbf{V[HCl]} = \frac{n}{c} = \frac{0.13}{2.5} = \mathbf{5.3\ x10^{-}}$ $\quad$ (2SF)

5. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

   $n(BaSO_4) = \frac{m}{M} = \frac{2.65}{233.37} = 1.14\ x10^{-2}$ mol $\quad$ *and* $\quad$ $n(SO_4^{2-}) = n(BaSO_4) = 1.14\ x10^{-2}$ mol

   $\mathbf{c(SO_4^{2-})mol\ L^{-1}} = \frac{n}{V} = \frac{1.14\ x10^{-2}}{0.325} = \mathbf{3.49\ x\ 10^{-2}\ mol\ L^{-1}\ SO_4^{2-}(aq)}$ $\quad$ (3SF)

   $m(SO_4^{2-}) = n\ M = 1.14\ x10^{-2} \times 96.07 = 1.09$ g $\quad$ *and* $\quad$ $\mathbf{c(SO_4^{2-})gL^{-1}} = \frac{m}{V} = \frac{1.09}{0.325} = \mathbf{3.36\ g\ L^{-1}\ SO_4^{2-}\ (aq)}$ $\quad$ (3SF)

   $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

   $n(AgCl) = \frac{m}{M} = \frac{23.3}{143.35} = 0.163$ mol $\quad$ *and* $\quad$ $n(Cl^-) = n(AgCl) = 0.163$ mol

   $\mathbf{c(Cl^-)mol\ L^{-1}} = \frac{n}{V} = \frac{0.163}{0.325} = \mathbf{0.500\ mol\ L^{-}}$ $\quad$ **(aq)** $\quad$ (3SF)

   $m(Cl^-) = n\ M = 0.163 \times 35.45 = 5.76$ g $\quad$ *and* $\quad$ $\mathbf{c(Cl^-)gL^{-1}} = \frac{m}{V} = \frac{5.76}{0.325} = \mathbf{17.7\ g\ L^{-}}$ $\quad$ **(aq)** $\quad$ (3SF)

6. $CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$
   $n(KOH) = c\ V = 0.1520 \times 15.19 \times 10^{-3} = 2.309 \times 10^{-3}$ mol $\quad$ *and* $\quad$ $n(CH_3COOH) = n(KOH) = 2.309 \times 10^{-3}$ mol

   $\mathbf{c(CH_3COOH\ in\ vinegar)} = \frac{n}{V} = \frac{2.309 \times 10^{-3}}{20.00 \times 10^{-3}} = \mathbf{0.1154\ mol\ L^{-}}$ $\quad _{3}$ $\quad$ (4SF)

7. $2HCl(aq) + Mg(OH)_2(aq) \rightarrow MgCl_2(s) + 2H_2O(l)$

   $n[Mg(OH)_2] = \frac{m}{M} = \frac{880 \times 10^{-3}}{58.326} = 1.5088\ x10^{-2}$ mol

   and $\quad$ $n(HCl\ reacted) = \frac{2}{1} \times n[Mg(OH)_2] = \frac{2 \times 1.5088 \times 10^{-2}}{1} = 3.018 \times 10^{-2}$ mol $\quad$ (1DP or 2SF)

   $n[HCl\ initially\ present] = c\ V = 0.075 \times 0.45 = 3.375\ x10^{-2}$ mol $\quad$ (2SF)
   $n[HCl\ remaining] = n[HCl\ initially\ present] - n[HCl\ consumed\ by\ Mg(OH)_2] = 3.375 \times 10^{-2} - 3.018 \times 10^{-2}$
   $= 0.357 \times 10^{-2}$ mol ie 4×10^{-3} mol $\quad$ (1DP)

Assume the spoonful of milk of magnesia has negligible effect on the volume of solution in the stomach. [Note: The faint digits seen below are carried digits but not significant digits.]

$\mathbf{c(HCl)} = \frac{n}{V} = \frac{\mathbf{0.3}57 \times 10^{-3}}{\mathbf{0.45}} = \mathbf{8 \times 10^{-3}\ mol\ L^{-1}\ HCl(aq)}$ (1SF)

8. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

   $n[Ba(OH)_2] = c\ V = 5.69 \times 10^{-2} \times 1.12 = 6.37 \times 10^{-2}$ mol $\quad$ *and* $\quad$ $n(Ba^{2+}) = n[Ba(OH)_2] = 6.37 \times 10^{-2}$ mol

   $n(BaSO_4\ formed) = n(Ba^{2+}) = 6.37 \times 10^{-2}$ mol *and* $\mathbf{m(BaSO_4)} = n\ M = 6.37 \times 10^{-2} \times 233.37 = \mathbf{14.9\ g\ BaSO_4}$ (3SF)

9. $n(HCl) = c\,V = 1.5 \times 25 \times 10^{-3} = 3.8 \times 10^{-2}$ mol

$n(Cl_2 \text{ formed}) = \frac{1}{4} \times n(HCl) = \frac{1 \times 3.8 \times 10^{-2}}{4} = 9.4 \times 10^{-3}$ mol

and **$V(Cl_2$ stp)** = $n \times 22.71 = 9.4 \times 10^{-3} \times 22.71 =$ **0.21 L Cl_2 (2SF)**

10.a. Litmus contains a plant dye whose colour turns red in acid solutions and turns blue in basic solutions. Adding a piece of blue litmus to the solution of the unknown compound will confirm its acidic properties if it turns a red colour.

b. $HX(aq) + KOH(aq) \rightarrow KX(aq) + H_2O(l)$

Note: If HX represents the general formula for the monoprotic acid then its ion has a valence of 1-, ie X^{1-} and so the potassium salt is KX.

$n(KOH) = c\,V = 0.1578 \times 25.74 \times 10^{-3} = 4.062 \times 10^{-3}$ mol *and* $n(HX) = n(KOH) = 4.062 \times 10^{-3}$ mol

also $n(HX) = \frac{m}{M}$ *Rearranging this shows* **M(HX)** $= \frac{m}{n} = \frac{0.4652}{4.062 \times 10^{-3}} =$ **114.5 g mol^{-}**

c. Had the acid been diprotic then one mole of acid would react with two moles of KOH, ie

$H_2X(aq) + 2KOH(aq) \rightarrow K_2X(aq) + 2H_2O(l)$

In this case the molar amount of H_2X would be half that originally calculated (ie 2.031×10^{-3} mol). This would give rise to it having a molar mass twice that originally found (ie M = 229.1 g mol^{-1}).

Set 32 Reviewing stoichiometry

1. a. **$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2 + H_2$**

b. The hydrogen gas is collected at room temperature and pressure. Room pressure is usually close to 101.3 kPa rather than STP pressure of 100.0 kPa. This would cause the measured volume to be slightly less than if collected at STP. However, as room temperature is normally well above the STP value of 0 °C (273 K), typically around 25 °C (298 K) or more, then the higher temperature means the collected volume of gas would be higher than if collected at STP.

c. $n(H_2) = \frac{V_{(stp)}}{22.71} = \frac{2.07}{22.71} = 9.11 \times 10^{-2}$ mol

$n(Zn) = n(H_2) = 9.11 \times 10^{-2}$ mol *and* **m(Zn)** $= n \times M = 9.11 \times 10^{-2} \times 65.38 =$ **5.96 g** (3SF)

d. Hydrogen gas is non-toxic however, it is flammable and poses a potential fire and explosion hazard. Avoid any ignition source and wear safety glasses. The quantities produced in this experiment would not pose a serious safety hazard. Hydrochloric acid however, is corrosive, can cause severe skin burns and eye damage and may cause respiratory irritation. As a precaution do not breathe any acid mist or vapour, wash hands thoroughly after handling, use only in a well-ventilated area and wear eye protection. Depending upon the acid concentration you may consider face protection, gloves and protective clothing.

2. a. **$2NH_3$ + H_2 $_4$ → $(NH_4$ $_2$ $_4$**

b. $n[(NH_4)_2SO_4] = \frac{m}{M} = \frac{1.00 \times 10^6}{132.15} = 7.57 \times 10^3$ mol *and* $n(H_2SO_4) = \frac{1}{1} \times n[(NH_4)_2SO_4] = 7.57 \times 10^3$ mol

then **$m(H_2SO_4)$** $= n \times M = 7.57 \times 10^3 \times 98.09 =$ **7.42×10^5 g of H_2 $_4$ or 0.742 tonne** (3SF)

c. $n(NH_3) = 2 \times n[(NH_4)_2SO_4] = 1.51 \times 10^4$ mol

and **V_{stp}** $_3$ $= n \times 22.71 = 1.51 \times 10^4 \times 22.71 =$ **3.44×10^5 L** (at STP) (3SF)

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

b. The mass loss represents the mass of $H_2(g)$ that was produced during the reaction and then escaped from the flask.

c. **$m(H_2$ formed)** $= [m_{(\text{conical flask})} + m_{(\text{HCl solution})} + m_{(Mg)}]$ **before reaction** - $[m_{(\text{conical flask + HCl solution + Mg})}]$ **after reaction**

$= 94.965 - 94.816 =$ **0.149 g** (3SF: As addition and subtraction rules apply.)

d. Determine the mass of Mg that would be used according to the mass of hydrogen produced.

$n(H_2) = \frac{m}{M} = \frac{0.149}{2.016} = 7.39 \times 10^{-2}$ mol *and* $n(Mg) = \frac{1}{1} \times n(H_2) = 7.39 \times 10^{-2}$ mol

m(Mg) = n x M = $7.39 \times 10^{-2} \times 24.31$ = **1.80 g of Mg** (3SF) was consumed in the reaction with hydrochloric acid.

e. Using a balance that measures only to tenths of a gram would reduce their **precision**. This is especially relevant as the weight loss being determined is of the order of a few tenths of a gram, ie 0.149 g. Using a balance that is precise to tenths of a gram would give a weight loss of either 0.1 g or 0.2 g. This result is much less precise and has only one significant figure in the measurement instead of 3 significant figures obtained by using a balance measuring to milligram amounts.

f. Hydrochloric acid is corrosive to many metals, can cause severe skin burns and eye damage and may cause respiratory irritation. As a precaution they should not breathe any acid mist or vapour and should wash hands thoroughly after handling. They should work in a well-ventilated area and wear eye protection. As 6 mol L^{-1} $HCl_{(aq)}$ is quite concentrated they should consider using face protection, gloves and protective clothing.

4. $n(CaC_2) = \frac{m}{M} = \frac{2.10}{64.10} = 3.28 \times 10^{-2}$ mol

$n(C_2H_2 \text{ formed}) = \frac{1}{1} \times n(CaC_2) = 3.28 \times 10^{-2}$ mol

and **V(C**$_2$ $_2$ = n x 22.71 = $3.28 \times 10^{-2} \times 22.71$ = **0.744 L of C**$_2$ $_2$ **gas** (3SF)

5. a. $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

b. $n(CO_2) = \frac{V_{(stp)}}{22.71} = \frac{0.549}{22.71} = 2.42 \times 10^{-2}$ mol *and* $n(CaCO_3 \text{ reacting}) = \frac{1}{1} \times n(CO_2) = 2.42 \times 10^{-2}$ mol

m(CaCO$_3$ = n x M = $2.42 \times 10^{-2} \times 100.09$ = **2.42 g** (3SF)

c. **m(SiO**$_2$ = m(limestone sample) – m($CaCO_3$) = 3.59 – 2.42 = **1.17 g** (3SF)

6. a. The increase in mass of the potassium hydroxide solution is due to the absorbed CO_2. Thus:
m(CO$_2$ = 100.857 - 98.019 = **2.838 g** (4SF)

b. $n(CO_2) = \frac{m}{M} = \frac{2.838}{44.01} = 6.449 \times 10^{-2}$ mol *and* $n(CaCO_3) = \frac{1}{1} \times n(CO_2) = 6.449 \times 10^{-2}$ mol

also **m(CaCO**$_3$ = n x M = $6.449 \times 10^{-2} \times 100.09$ = **6.454 g (4SF)**

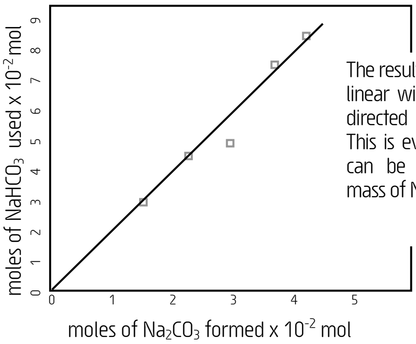
c. **% CaCO**$_3$ $\frac{m(CaCO_3) \times 100}{m(\text{shells})} = \frac{6.454 \times 100}{8.765}$ = **73.64% (4SF)**

d. Since CO_2 has a low but significant solubility in water then some of it will dissolve in the water over which it is collected. A lower volume of carbon dioxide gas will be collected than is produced. Hence the calculated value for the moles of CO_2 will be less than it actually is and as a consequence the moles and mass of $CaCO_3$ contained in the shells will appear lower. This poor technique will give **consistently** low values for the percentage composition of $CaCO_3$ in the shells and is therefore a systematic error.

7. a.

mass of NaHCO$_3$	**mass of Na$_2$ $_3$**	**moles of NaHCO$_3$**	**moles of Na$_2$ $_3$**
2.56	1.62	0.0305	0.0153
3.80	2.38	0.0452	0.0225
4.11	3.13	0.0489	0.0295
6.34	3.94	0.0755	0.0372
7.07	4.46	0.0842	0.0421

b.



The resulting graph should be linear with a line of best fit directed at the point (0, 0). This is evident as no Na_2CO_3 can be formed when the mass of $NaHCO_3$ is zero.

c. The graph has a gradient of 2.02.
Remember gradient = rise/run.

d. The graph gradient (≈ 2) shows that the molar amount of $NaHCO_3$ used is double the molar amount of Na_2CO_3 produced. This tells us that the coefficient of $NaHCO_3$ in the balanced equation will be twice that of Na_2CO_3.

e. The data point n($NaHCO_3$) = 0.0489, n(Na_2CO_3) = 0.0295 looks like it contains a large random error as it does not readily fit the graphical trend shown by the other data points. Random errors are present in all measurements causing measured values to be either a little higher or lower than the expected result. When the random error is exceptionally large, as in this case, it is referred to as an anomaly or outlier.

Set 33 Chromatography

1. a. pure substances
   b. identify
   c. concentration
   d. paper
   e. TLC
   f. stationary solid
   g. mobile liquid
   h. dissolve in
   i. adsorbed onto
   j/k. GC or HPLC
   l. sensitive
   m. microlitre
   n. picogram
   o. food and beverage
   p. blood and urine

2. a. The stationary phase is the paper. Components from the mixture that strongly adsorb onto this paper move slowly during the chromatographic process. The mobile phase is the 0.1% salt solution. Components from the mixture that readily dissolve in the mobile phase will move quickly along the stationary phase during the chromatographic process. The chromatogram is the resulting strip of chromatography paper with the adsorbed and separated components along its length.

   b. The purpose of the line is to provide a reference point from which to measure the distance travelled by the mobile phase and each of the separated components. This allows the retardation factor of each component to be calculated. Inks such as used those used in pens contain dyes that will also undergo separation during the chromatographic process. Their presence will thus interfere with the results of the investigation.

   c. The components of the mixture are spotted on the end of the chromatography paper strip. If the spotted mixture is dipping into the mobile phase then the components in it will dissolve in the surrounding solution in the beaker. As time goes by these dissolved components along with the solution (mobile phase) will continually move back into the chromatography paper strip and a meaningful separation of components cannot be achieved.

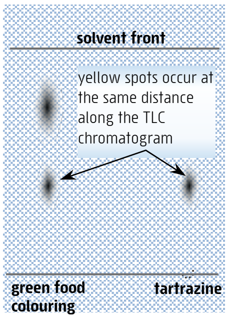
   d. In paper chromatography, the extent to which a component in a mixture dissolves in the mobile phase or remains adsorbed onto the paper strip depends upon the polarity of the mobile phase and the nature of the paper strip. In this case the blue dye has moved much further than the yellow dye thus the yellow dye is more strongly adsorbed onto the paper (polar) while the blue dye dissolves better in the mobile phase. Thus the polarity of the blue dye better matches the polarity of the mobile phase.

3. a. The student will need to perform a TLC of both the food colouring with the suspected tartrazine as well as a pure sample of tartrazine. Both chromatograms should be produced with the same solvent and using a similar (or the same) TLC plate. Any other conditions that may affect the outcome should also be kept constant.

   The distance travelled by each of the yellow dyes and the overall distance travelled by the solvent are measured. This data is used to calculate the R_f for each of the yellow dyes. If the R_f values are the same then the compounds can be assumed to be the same.

   Alternatively, if the two dyes are both tested on the same TLC plate then by visually comparing the distance travelled by the yellow dye in the food colouring and the pure tartrazine sample it is possible to decide if the compounds are the same.

   b. The blue dye and the yellow dye should have separated. (As stated in the background.) Since the blue dye has a greater Rf it should have travelled further. Also as the two yellow dyes are the same they should have travelled the same distance.



4. a. The black food colouring contains three dyes, a yellow dye, a red dye and a blue dye. The red food colouring contains a single compound, a red dye. The egg yellow food colouring contains two dyes, a yellow dye and a red dye. The yellow dyes appear to be the same compound while the red dye in black and red food colouring is the same but a different red dye is present in the egg yellow food colouring.

b. **Black food colouring:**

$R_f(\text{yellow}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{1.2}{9.2} = 0.13$ $R_f(\text{red}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{4.4}{9.2} = 0.48$

$R_f(\text{blue}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{7.0}{9.2} = 0.76$

Red food colouring:

$R_f(\text{red}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{4.4}{9.2} = 0.48$

egg yellow food colouring:

$R_f(\text{yellow}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{1.2}{9.2} = 0.13$ $R_f(\text{red*}) = \dfrac{\text{distance moved by solute}}{\text{distance moved by solvent}} = \dfrac{6.7}{9.2} = 0.73$

c. These two red dyes do not appear to be the same compound as they have different R_f values. The R_f values for the red dye from the black food colouring and egg yellow colouring respectively are 0.48 and 0.73.

d. $R_f(\text{amaranth, E123}) = \dfrac{\text{distance moved by E123}}{\text{distance moved by solvent}} = \dfrac{3.3}{6.9} = 0.48$

This is the same R_f value for the red dye from the black and red food colouring (both 0.48) but different to that from the egg yellow. Thus the black and red food colourings contain E123 but not the egg yellow food colouring.

e. Most polar to least is: yellow (most polar), red then blue (least polar). The most polar component will have the greatest tendency to adsorb onto the more polar stationary phase.

5. a. Pentane and heptane have retention times of 2.0 minutes and 6.8 minutes respectively. The retention time of an analyte is the time it takes from entering the GC to exiting the column and entering the detector.

b. Retention time of an analyte in a GC depends upon several factors.

- Volatility: the more volatile the analyte (lower boiling point) the more likely it will be in the vapour phase and hence the lower its retention time.
- Column temperature: the higher this is, the more likely the analyte is present as a vapour and hence present in the mobile gas phase. Thus retention time decreases with increasing column temperature.
- Carrier gas flow rate: the greater this is, the shorter the retention time for all analytes.

This series of hydrocarbons are analysed at the same temperature with the same column and gas flow rate. For this reason the retention times depend only upon the individual analyte's volatility or boiling point. As their boiling points increase with increasing dispersion forces, ie with increasing molar mass or number of carbon atoms per molecule, then their retention time should also increase with the number of carbon atoms per molecule. This is the same as the trend in retention times that is seen in the chromatogram.

c. The peak height or more specifically the area of each peak is proportional to the amount of each analyte responsible for the peak. Hence the height or area of each peak is proportional to the concentration of the analyte in the original solution injected into the GC.

6. One method is to run individual chromatograms of pure samples (solutions) of the drugs that are suspected of being present, eg methylphenidate (Ritalin). The chromatograms must be run at the same temperature with the same column and gas flow rate as for the original urine samples. By comparing the retention time of the pure samples with the retention times for the various peaks in the urine sample, it is possible to determine if the drugs in question are present. This is indicated where peaks in the urine sample have the same retention time as the pure drug samples. [Another technique is to add the suspected drug to one urine sample and compare its chromatogram with that of another urine sample without the added drug.]

7. Using the standard curve for ethanol and interpolating the absorbance values of the different beers shows: Beer X: 0.96% ethanol, Beer Y: 0.32% ethanol and Beer Z: 1.39% ethanol (all by volume). Beer X and Y are suitable for unregulated sale but the alcohol content of Beer Z classifies it as a liquor.

8. a. On the basis of the HPLC chromatograms the white powder does contain the drug MDMA. Under the same conditions MDMA produces a peak with a retention time of 7.2 minutes. The analysis of the white powder also shows a peak, although smaller, at 7.2 minutes.

   b. Retention time of an analyte in HPLC depends upon the polarity of the mobile and stationary phases as well as the polarity of the analyte. The analyte will tend to reside (dissolve in) in the phase of similar polarity. Thus if the stationary phase polarity closely matches the analyte's polarity then its retention time will be great as it will tend to remain dissolved in the stationary phase. Conversely if the mobile phase polarity more closely matches the analyte's polarity then its retention time will be small as the analyte tends to spend more time dissolved in the mobile phase. The pressure used and the length of the HPLC column will also affect retention time. Overall, analytes will elute faster in shorter columns and with higher pressure.

   c. Several standard solutions with a suitable range of concentrations are prepared for the analyte in question, eg MDMA. These solutions are analysed using the HPLC and the results graphed in the form of a calibration curve, ie a graph of detector signal intensity against analyte concentration. The unknown solution is then prepared and also analysed with the HPLC using the same chromatography column and mobile phase. The detector intensity at the retention time for the unknown is then used in conjunction with the standard curve to determine the concentration of the analyte in the unknown.

9. GC is only suitable for analysing substances that are easily vaporised and do not decompose when heated sufficiently to make them vaporise. Enzymes and blood proteins have high molar masses and hence are unlikely to be volatile and if heated will be broken down chemically. For this reason GC is not suited to their analysis. HPLC can be used instead as it does not rely on vaporising the compound. The compounds only need to be prepared as a solution.

10. a. Use GC. The sample size is very small and GC is readily able to analyse these small amounts. The substances are volatile and this is essential for GC analysis. It would also be possible to use HPLC for this analysis.

    b. Since there is a large sample available, ie several millilitres then thin-layer chromatography would be suitable. HPLC would also work though it clearly is more involved and expensive while TLC is simple, quick and low cost. GC may be suitable but this would depend on the volatility of the components in the leaf extract. Paper chromatography would not be ideal as component separation with this technique is rather poor.

    c. Use HPLC. The sample size is very small and HPLC is readily able to analyse these small amounts. The substances are not readily volatile (very high molar mass) and hence GC analysis is not suitable.

    d. Use GC. The sample is already in a gaseous form so it can be readily analysed by GC. HPLC could be used but it would require the pollutants to be extracted and put into a solution form. This would be problematic as the different pollutants would have different solubilities in various solvents.

    e. Use HPLC. The sugars are in solution and thus suitable for HPLC analysis. Since sugars are not volatile they cannot be directly analysed by GC. TLC may also be an inexpensive method that could be used instead of HPLC.

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APPENDICES

Appendix 1: Common ions

TABLE 1 Name and formula of common positive ions

hydrogen	H^+	magnesium	Mg^{2+}	copper(II)	Cu^{2+}	aluminium	Al^{3+}
lithium	Li^+	calcium	Ca^{2+}	zinc	Zn^{2+}	iron(III)	Fe^{3+}
sodium	Na^+	strontium	Sr^{2+}	lead(II)	Pb^{2+}	chromium(III)	Cr^{3+}
potassium	K^+	barium	Ba^{2+}	mercury(I)	Hg_2^{2+}	gold(III)	Au^{3+}
silver	Ag^+	manganese(II)	Mn^{2+}				
caesium	Cs^+	iron(II)	Fe^{2+}				
rubidium	Rb^+	cobalt(II)	Co^{2+}				
ammonium	NH_4^+	nickel(II)	Ni^{2+}				

TABLE 2 Name and formula of common negative ions

hydride	H^-	dihydrogenphosphate	$H_2PO_4^-$	sulfide	S^{2-}
fluoride	F^-	ethanoate	CH_3COO^-	carbonate	CO_3^{2-}
chloride	Cl^-	perchlorate	ClO_4^-	sulfate	SO_4^{2-}
bromide	Br^-	chlorate	ClO_3^-	sulfite	SO_3^{2-}
iodide	I^-	chlorite	ClO_2^-	hydrogenphosphate	HPO_4^{2-}
hydroxide	OH^-	hypochlorite	ClO^-	dichromate	$Cr_2O_7^{2-}$
nitrate	NO_3^-	cyanide	CN^-	chromate	CrO_4^{2-}
nitrite	NO_2^-	permanganate	MnO_4^-	oxalate	$C_2O_4^{2-}$
hydrogencarbonate	HCO_3^-				
hydrogensulfate	HSO_4^-	oxide	O^{2-}	phosphate	PO_4^{3-}
hydrogensulfide	HS^-	peroxide	O_2^{2-}	nitride	N^{3-}

Appendix 2: Appearance of common species

TABLE 3 Colour of selected ions in aqueous solution

Ion	Colour	Ion	Colour	Ion	Colour
Cu^{2+}	blue	Fe^{2+}	pale green	MnO_4^-	purple
$[Cu(NH_3)_4]^{2+}$	deep blue	$FeCl_2^+$	yellow	Cr^{3+}	dark green
$[CuCl_4]^{2-}$	green	Fe^{3+}	pale brown	$Cr_2O_7^{2-}$	orange
Ni^{2+}	green	$[Fe(CN)_6]^{3-}$	red	CrO_4^{2-}	yellow
Co^{2+}	pink	Mn^{2+}	pale pink (may appear colourless)		

Note: The colour of ions in solution will vary due to concentration ligands solvent colourless , Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, Al^{3+}, Sn^{2+}, Sn^{4+}, S^{2-}, F^-, Br^-, I^-, CH_3COO^-, CO_3^{2-}, HCO_3^-, CN^-, $C_2O_4^{2-}$, $HC_2O_4^-$, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, OH^-, SO_3^{2-}, HSO_3^-, SO_4^{2-}, HSO_4^-.

TABLE 4 Appearance of common elements and their solutions at standard conditions

Substance	Formula	Appearance	Substance	Formula	Appearance
chlorine	$Cl_2(g)$	yellow-green gas	silicon	$Si(s)$	grey solid
chlorine (in) water	$Cl_2(aq)$	pale yellow solution	sodium	$Na(s)$	silvery metallic
bromine	$Br_2(l)$	red liquid	potassium	$K(s)$	silvery metallic
bromine (in) water	$Br_2(aq)$	orange solution	magnesium	$Mg(s)$	silvery metallic
bromine in CH_2Cl_2	$Br_2(CH_2Cl_2)$	red solution	calcium	$Ca(s)$	silvery metallic
iodine	$I_2(s)$	purple solid	iron	$Fe(s)$	silvery metallic
iodine (in) water	$I_2(aq)$	brown solution	copper	$Cu(s)$	salmon pink metallic
iodine in CH_2Cl_2	$I_2(CH_2Cl_2)$	purple solution	zinc	$Zn(s)$	silvery-grey metallic
carbon (graphite)	$C(s)$	black solid	aluminium	$Al(s)$	silvery metallic
nitrogen	$N_2(g)$	colourless gas	silver	$Ag(s)$	silvery metallic
oxygen	$O_2(g)$	colourless gas	gold	$Au(s)$	yellow metallic
sulfur	$S_8(s)$	yellow solid	lead	$Pb(s)$	silvery-grey metallic

TABLE 5 Appearance of common compounds and their solutions at standard conditions

Substance	Formula	Appearance	Substance	Formula	Appearance
carbon monoxide	$CO(g)$	colourless gas	hydrochloric acid	$HCl(aq)$	colourless solution
carbon dioxide	$CO_2(g)$	colourless gas	hydrogen bromide	$HBr(g)$	colourless gas
sulfur dioxide	$SO_2(g)$	colourless gas	hydrogen iodide	$HI(g)$	colourless gas
sulfur trioxide	$SO_3(g)$	colourless gas	nitrogen monoxide	$NO(g)$	colourless gas*
ammonia	$NH_3(g)$	colourless gas	nitrogen dioxide	$NO_2(g)$	brown gas
hydrogen sulfide	$H_2S(g)$	colourless gas	dinitrogen tetroxide	$N_2O_4(g)$	colourless gas#
hydrogen peroxide	$H_2O_2(l)$	pale blue liquid	nitric acid	$HNO_3(aq)$	colourless solution
hydrogen peroxide	$H_2O_2(aq)$	colourless solution	phosphoric acid	$H_3PO_4(aq)$	colourless solution
hydrogen fluoride	$HF(g)$	colourless gas	sulfuric acid	$H_2SO_4(aq)$	colourless solution
hydrogen chloride	$HCl(g)$	colourless gas	sulfurous acid	$H_2SO_3(aq)$	colourless solution

* Nitrogen monoxide readily forms the brown gas NO_2 on exposure to air.

\# Dinitrogen tetroxide exists in equilibrium with brown NO_2 gas.

Appendix 3: Physical constants and formulas

Physical constants

Standard temperature and pressure (S.T.P.) ....100.0 kPa and 0.0 °C
Ionisation constant of water (K_w) ....1.00 x 10^{-14} at 25 °C
Universal gas constant (R) ....8.3145 J K^{-} -
Number of particles in a mole (Avogadro's constant) ....6.022 x 10^{23} mol^{-}
°C (S.T.P) ....22.71 L
Absolute zero...0 K or -273.15 °C

Relating common units

Temperature	0.0 °C = 273.15 K
Pressure	101.3 kPa = 1 atm = 760 mmHg
Concentration	1 mol L^{-1} = 1 M
Volume	1 L = 1 x 10^3 mL = 1 x 10^3 cm^3 = 1 dm^3 = 1 x 10^{-3} m^3

SI prefixes

P	**T**	**G**	**M**	**k**	**d**	**c**	**m**	**μ**	**n**	**p**	**f**
peta	tera	giga	mega	kilo	deci	centi	milli	micro	nano	pico	femto
10^{15}	10^{12}	10^9	10^6	10^3	10^{-}	-	-	-	-	-	-15

Formulas

$$n(gas) = \frac{V_{STP}}{22.71}$$

where: **n(gas)** = the moles of gas (mol)
V_{STP} = the volume of gas in litres (L) at STP

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

where: **c** = the concentration of solute in moles per litre (mol L^{-1})
n = the amount of solute in moles (mol)
V = the volume of solution (solvent + solute) in litres (L)

$$pH = -\log[H^+]$$

where: **pH** = minus the logarithmic value of the hydrogen ion concentration
[H⁺] = the concentration of hydrogen ions in moles per litre (mol L^{-1})

$$c_{ppm} = \frac{m_s \times 10^6}{m_t}$$

where: **c_{ppm}** = the concentration of solute in parts per million by mass (ppm)
m_s = the mass of solute in grams (g)
m_t = the mass of solution (solvent + solute) in grams (g)

$$m = n \times M \quad \text{also expressed as} \quad n = \frac{m}{M}$$

where: **n** = the amount of substance in moles (mol)
m = the mass of the substance in grams (g)
M = the molar mass of the substance in grams per mole (g mol^{-1})

$$density = \frac{m}{V}$$

where: **density** = the density of the substance in grams per litre (g L^{-1})
m = the mass of a substance in grams (g)
V = the volume of the substance in litres (L)

$$PV = nRT \quad \text{also expressed as} \quad n = \frac{PV}{RT}$$

where: **n** = the amount of gas in moles (mol)
P = the gas pressure in kilopascals (kPa)
V = the volume of gas in litres (L)
R = Universal gas constant, ie 8.3145 J K^{-} -
T = the gas temperature in kelvin units (K)

Appendix 4: Solubility and precipitate colours

TABLE 6 Solubility rules for ionic compounds in water

Soluble*^{1}	**Exceptions**	
	Insoluble*^{2}	**Slightly soluble*^{3}**
All nitrates and ethanoates (acetates)	Nil	Nil
Most chlorides, iodides and bromides	AgCl, AgBr, AgI, PbI_2.	$PbCl_2$, $PbBr_2$.
Most sulfates	$SrSO_4$, $BaSO_4$, $PbSO_4$.	$CaSO_4$, Ag_2SO_4.

Insoluble*^{2}	**Exceptions**	
	Soluble*^{1}	**Slightly soluble*^{3}**
Most hydroxides	NaOH, KOH, $Ba(OH)_2$. [Note: AgOH and $NH_4OH(s)$	$_2$, $Sr(OH)_2$.
Most carbonates	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$.	Nil
Most phosphates	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$.	Nil
Most sulfides	Na_2S, K_2S, $(NH_4)_2S$.	Nil

*^{1} Soluble means more than 0.1 mole dissolves per litre.

*^{2} Insoluble means less than 0.01 mole dissolves per litre.

*^{3} Slightly soluble means between 0.1 and 0.01 moles dissolve per litre.

TABLE 7 Colour and formula of common precipitates

Ions	**Cl^-**	**Br^-**	**I^-**	**SO_4^{2-}**	**OH^-**	**CO_3^{2-}**	**PO_4^{3-}**	**S^{2-}**
Na^+								
K^+								
NH_4^+								
Mg^{2+}					$Mg(OH)_2$ white	$MgCO_3$ white	$Mg_3(PO_4)_2$ white	decomposes
Ca^{2+}				$CaSO_4$ white	$Ca(OH)_2$ white	$CaCO_3$ white	$Ca_3(PO_4)_2$ white	CaS white
Sr^{2+}				$SrSO_4$ white	$Sr(OH)_2$ white	$SrCO_3$ white	$Sr_3(PO_4)_2$ white	SrS grey
Ba^{2+}				$BaSO_4$ white		$BaCO_3$ white	$Ba_3(PO_4)_2$ white	BaS white
Cr^{3+}		$CrBr_3$ grey-green			# $Cr(OH)_3$ blue-gy-green	* $Cr(OH)_3$ blue-gy-green	$CrPO_4$ blue-grey	decomposes
Mn^{2+}					$Mn(OH)_2$ pale pink	$MnCO_3$ pale pink	$Mn_3(PO_4)_2$ white	MnS pink
Fe^{2+}					$Fe(OH)_2$ green	$FeCO_3$ grey/green	$Fe_3(PO_4)_2$ grey-green	FeS black
Fe^{3+}					$Fe(OH)_3$ brown	$Fe_2(CO_3)_3$ brown	$FePO_4$ grey-brown	Fe_2S_3 green-black
Co^{2+}					$Co(OH)_2$ red	$CoCO_3$ red	$Co_3(PO_4)_2$ blue-purple	CoS black
Ni^{2+}					$Ni(OH)_2$ green	$NiCO_3$ green	$Ni_3(PO_4)_2$ green	NiS black
Cu^{2+}					$Cu(OH)_2$ blue	$CuCO_3$ green	$Cu_3(PO_4)_2$ blue	CuS black
Ag^+	AgCl white	AgBr cream	AgI pale yellow	Ag_2SO_4 white	* Ag_2O brown	Ag_2CO_3 yellow	Ag_3PO_4 yellow	Ag_2S black
Zn^{2+}					# $Zn(OH)_2$ white	$ZnCO_3$ white	$Zn_3(PO_4)_2$ white	ZnS grey-white
Cd^{2+}					# $Cd(OH)_2$ white	$CdCO_3$ white	$Cd_3(PO_4)_2$ colourless	CdS yellow
Al^{3+}					# $Al(OH)_3$ white	$Al_2(CO_3)_3$ white	$AlPO_4$ white	decomposes
Sn^{2+}					# $Sn(OH)_2$ white	$SnCO_3$ white	$Sn_3(PO_4)_2$ white	SnS black
Pb^{2+}	$PbCl_2$ white	$PbBr_2$ white	PbI_2 yellow	$PbSO_4$ white	# $Pb(OH)_2$ white	$PbCO_3$ white	$Pb_3(PO_4)_2$ white	PbS grey

\# These compounds are amphoteric and will redissolve in excess OH^-.

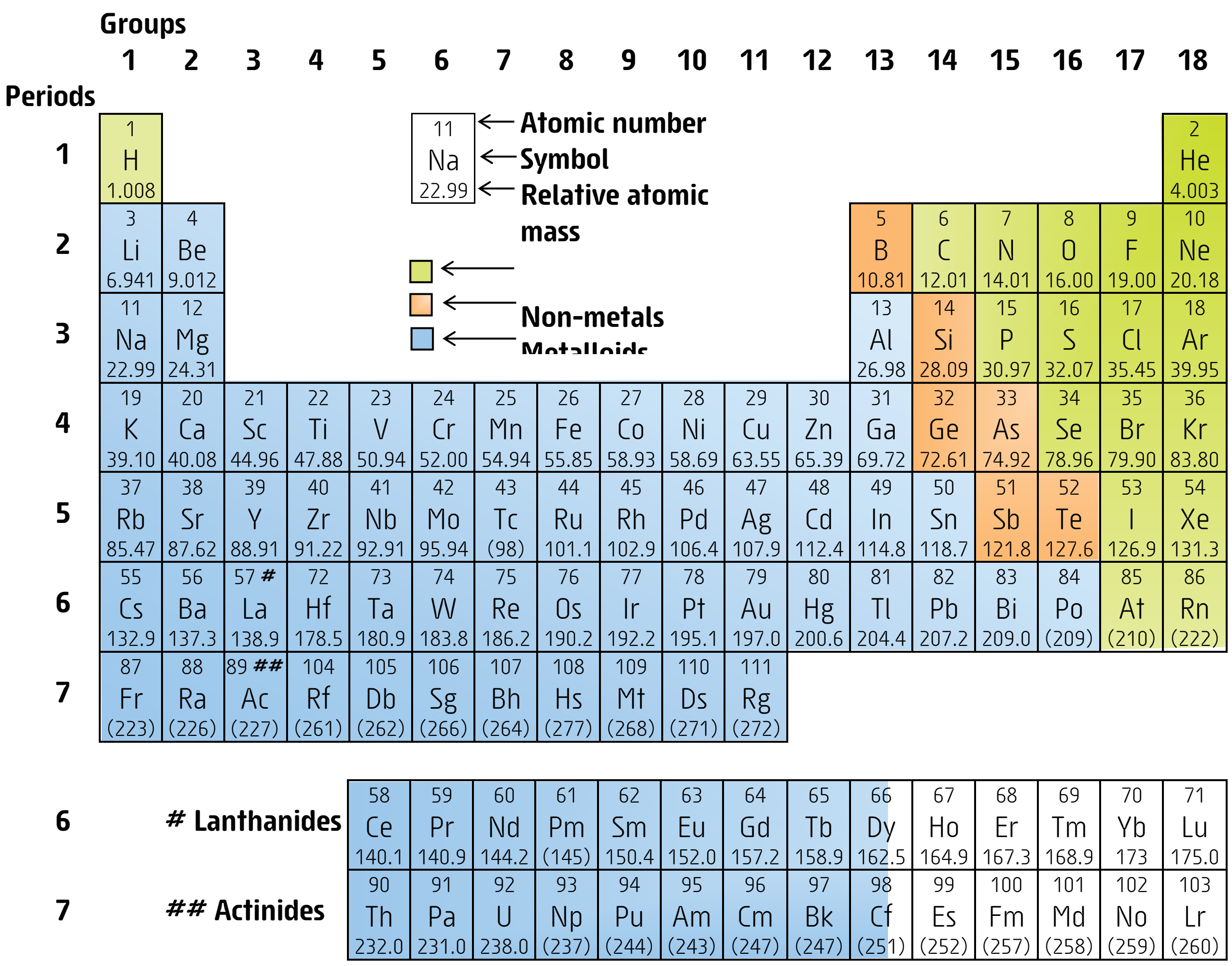
* Note: $Ag_2O(s)$ forms instead of $AgOH(s)$, $Cr(OH)_3(s)$ forms instead of $Cr_2(CO_3)_3(s)$.

Appendix 5: Standard Reduction Potentials

Half-reaction	**E^o (volts)**
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.76
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^- + H_2O(l)$	+1.49
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.70
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.17
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.24
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	-0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2C_2O_4(aq)$	-0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-$	
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.68
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.36
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.90
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.94
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04

Reduction potentials are for standard conditions, ie solution concentrations of 1 mol L^- ^{5} kPa and temperatures of 25 ^oC.
Data has been sourced from G. Aylward & T. Findlay, *SI Chemical Data* (2008, 6th Edition) John Wiley & Sons Australia, LTD.

Appendix 6: The periodic table of the elements



11 Na 22.99	← Atomic number ← Symbol ← Relative atomic mass

🟩 ←

🟧 ← Non-metals

🟦 ← Metalloids

Periods \ Groups	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 # La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 ## Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

6	# Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175.0
7	## Actinides	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)