YEAR 11 ATAR COURSE REVISED EDITION

ACADEMIC
TASK FORCE

REVISION SERIES

CHEMISTRY

UNITS 1 & 2

ANDREW DEAN
ROY SKINNER

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CHEMISTRY

Year 11 ATAR COURSE

Units 1 and 2

WACE Revision Series

Revised Edition

Andrew Dean and Roy Skinner

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Website: www.academictaskforce.com.au

National Library of Australia ISBN 978-1-74098-205-4

First published 2017

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Printed in Singapore.

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Dr Skinner has taught physics and chemistry in three different countries and has been the Head of Science in 5 schools. In 1993 he was appointed Lecturer in Science Education at Edith Cowan University and in 1999 was awarded the De Laeter Medal as most outstanding science teacher in Western Australia. He has marked TEE and WACE examinations for 15 years.

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How to Use this Study Guide

This book should be used in conjunction with a class textbook to reinforce the most important principles and understandings. The essentials are presented so students can teach themselves the concepts. Students then work through the many example questions. Answers should be entered in this workbook to produce a progressive learning in a student friendly manner.

An active learning style is supported through the use of simple pictures and diagrams within the text.

Sets of example questions are supplied throughout on concepts which reflect those used for class tests and examinations (these are titled Set 1, Set 2, etc.).

Dr Roy Skinner and Andrew Dean

Chapter

1

Materials and their Makeup

1.1 WHAT IS CHEMISTRY?

Chemistry is part of everything in our lives today. It is the study of all the materials in the Universe, their properties and how they can be combined or separated by having energy inputs and outputs.

The use of chemical knowledge is important and widespread in our society – utilised by pharmacists and research chemists to doctors, engineers, biologists, winemakers, forensic police, geologists, miners, metallurgists, food scientists, nuclear medics, toxicologists and perfume makers.

Every material in existence is made up from chemicals of some kind - even our skin and bones. Everything we do involves a chemical process of some kind, from growing and cooking food to cleaning our homes or bodies and driving a car. Chemistry is one of the physical sciences that helps us to describe, explain and improve our world.

1.2 CHEMISTS

There are five main branches of chemistry, with specialist chemists in each of them.

Biochemistry is the study of the chemical processes that occur in plants and animals.

Organic chemistry, sometimes called the Chemistry of Life, specifically studies compounds of carbon that may be found in living things. Because of its ability to form many bonds, carbon can form compounds that are very intricate and can produce molecules that can perform complex functions, such as carrying oxygen around the body or stimulating an enzyme.

Inorganic chemistry studies materials derived from the ground (e.g. metals, gases, ores and salts) that do not have carbon as part of their makeup.

Analytical chemistry uses measurements and calculations to observe and explain the physical and chemical properties of substances.

Physical chemistry uses physics principles of forces and energy to study and explain how matter and energy interact. Quantum mechanics and thermodynamics are branches of physical chemistry where theoretical explanations and predictions can produce further understanding.

Within these five broad areas there are also important specialist jobs for chemists. Below are some of these.

Food Chemists

A food chemist analyses all that we eat to see whether there are any harmful substances present and whether the true content written on the label is actually present. Food chemists are mainly concerned with the food components: carbohydrates, lipids and proteins. Food chemists improve the quality, safety, storage and taste of our food. Specialists such as Flavorists study various chemicals that can change the taste of food or enhance its colour, odour or texture.

Environmental chemists

Environmental chemists observe and analyse natural systems of soil and water to see how chemicals interact with the surrounding environment. Environmental chemists must first understand the chemicals and chemical reactions present in natural processes for soil water and air. This study can determine the extent to which human activities have harmed the ecosystem in any way.

This would include testing rivers, lakes and studying the aftermath of mining operations for pollution.

Agricultural chemists

Agricultural chemists investigate the effect of chemicals used in plant production and develop new compounds such as fertilizers, insecticides and herbicides necessary for large-scale crop production.

Chemical engineering

Chemical engineers have a university background in chemistry, engineering and economics. They research and develop new materials or production processes that involve chemical manufacturing methods associated with processes such as metal extraction, acid, bases and fertilizer manufacture, pharmaceuticals, fuels, food additives and even chocolate making. Chemical engineering jobs fall into two main groups: industrial applications and development of new products.

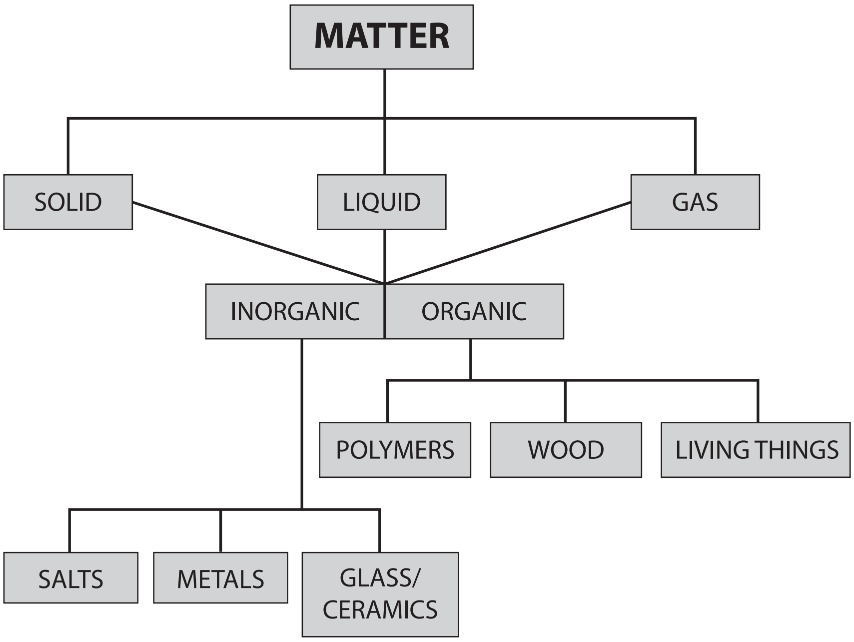
Industries require chemical engineers to devise new ways to make the manufacturing of their products easier and more cost effective. Chemical engineers also design and operate important processing plants.

Geochemistry

Geochemists combine the study of chemistry and geology to assess such things as the viability of mining and petrochemical operations. They can make geological surveys in the field and offer advice on economical undertakings as well as locating new chemical and ore-body resources, and experimenting with new alloys.

1.3 MATERIALS SCIENCE

All the matter around us can be classified thus:



Ancient humans have always used different materials in the environment for different purposes, depending on their particular properties. Properties such as weight, strength, flexibility, heat resistance, conductivity, corrosion resistance and ductility make some common materials ideal for specific jobs.

Wood and bones had useful properties in their strength and ability to be easily shaped and thus became used to make ancient peoples' first implements. Later, ancient Egyptians produced copper chisels to cut stones for the pyramids because of the hardness of a metal that was easy to extract from its ores. As early as 5000 BC ancient people were able to locate copper ores (mainly copper sulfide), roast it to release the sulfur as sulfur dioxide and melt the liquid copper to cast it into tools and weapons. Later it was discovered that the addition of a small amount of tin made an alloy (mixture of metals) called bronze which had improved physical properties over copper. Tin, being a fairly unreactive metal, was easy to extract from its ore but was not found near the sites of copper mines.

Hence international trade became important for the production of bronze implements - the Bronze Age arrived. From about 3000 BC bronze became an important alloy for the production of swords, coins, medals, statues, ships' fittings and nails. Its melting point of 950^{o}C made it a viable product for nations with less technological capability than we have today. In fact, bronze is still used today to make coins, bells and ships propellers, due to strength, hardness and resistance to corrosion in sea water.

Timeline for some important chemical processes

10,000 BC Pottery and ceramic plates produced

8000 BC Glass first produced in Egypt

2800 BC Soap is produced from animal fat

1000 BC The Iron Age, when iron could be extracted and small implements forged from steel

1808 Aluminium isolated for first time by Davy to become a precious metal. Later developed commercially in 1889 for the Beyer Process

1850 Bessemer process for the mass production of steel

1866 First polymer produced (polystyrene) which became common by the 1920s. Polymers mimic some naturally-occurring long-chain molecules found in nature, such as bone, hair, skin silk and ivory

1933 First detergent produced in USA ("Dreft")

1947 First electric "Chemical switch" produced from silicon, called the Transistor

1960 First artificial diamond produced

1986 First high temperature superconductors produced

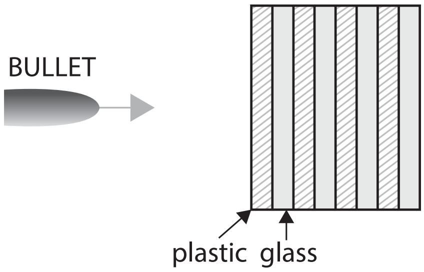
1.4 COMPOSITE MATERIALS

A composite material is one made by combining two or more constituent materials to produce improved physical or chemical properties. The new composite may be an enhancement on the individual materials used because it is stronger, lighter, more flexible or less expensive compared to the separate homogeneous materials.

An ancient example of a composite material is that by adding straw to mud, a brick can be produced which is stronger and more resilient. Another example is plywood, where opposing grain in thin layers of wood are glued together to make the material stronger and lighter compared with just a plank of wood. The first known use of plywood was actually over 5000 years ago. Papier maché, concrete and fibreglass are all composite materials in use today with superior properties.

The new Boeing 787 Dreamliner has a body made from carbon fibre so it can be pressurised to a higher extent and have less weight.

Bulletproof glass is a composite comprising alternate layers of polycarbonate plastic and tempered glass which can resist bullets aimed at it from quite close range.



1.5 NANO CHEMISTRY

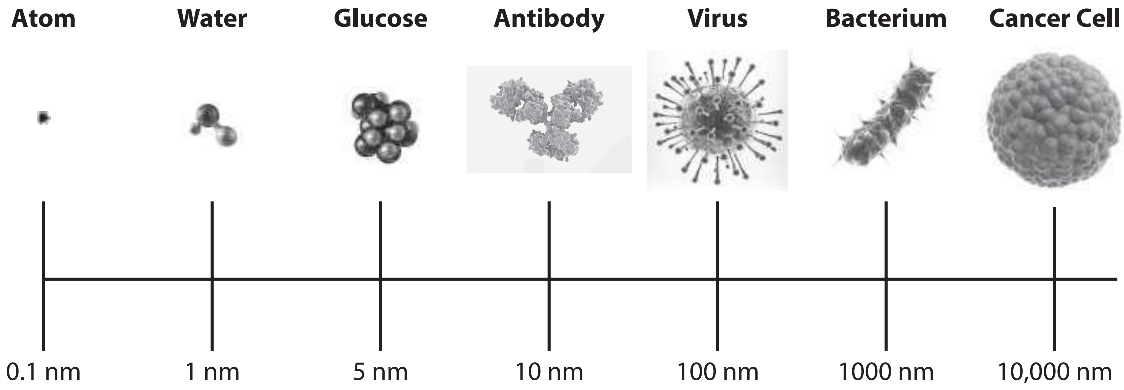
The word "Nano" in Latin indicates the number 9. Nano particles therefore have a very small size of several nanometres. One nanometre = 10^{-9} metres. The word Nanotechnology has emerged in the last decade to mean the science of manipulating and using atoms in that size range because of their beneficial properties.

Nanoparticles of a material show different properties compared to larger particles of the same material. For example, forces of attraction between surfaces may be weak for macromolecules (larger size), but strong when the particles are nanoscale. This is because the surface area to volume ratio becomes greater as the subdivision of a material increases. For example, petrol liquid will just burn when lit but finely vaporised petrol will react much faster and explode.

Nanoparticles exist in nature with things like soot, dust, sea spray, river silt and even occur on insects like butterflies. The wing of a butterfly is made of a pattern of intertwining and curved nanoparticles producing what is known as a Gyroid structure. This surface interacts with light to give the wing its characteristic iridescent sheen.

Below is a table showing the comparative particle sizes of some common molecular structures.

Particle sizes in nanometres



Nano-technology involves the ability to see and to control individual atoms and molecules. Since these particles are extremely small, scientific tools such as Scanning Tunnelling Microscope (STM) and Atomic Force microscope have ushered in the age of nanotechnology.

1.6 USES OF NANO PARTICLES

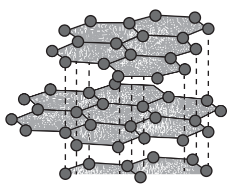
Global sales in the nanomedicine area alone reached $1 trillion in 2013 and in the USA close to $4 billion is spent on research in nanotechnology each year. Because of the large surface area to volume ratio of nanoparticles, drugs in this form can react with their target much faster and can even be used in self-cleaning oven and window products.

Another use for nanoparticles is in paints and sun creams which use titanium dioxide nanoparticles. TiO_2 is a white solid, but the particles used are so small they do not reflect visible light and cannot be seen, so they can block harmful ultraviolet light without appearing white on the skin. The “Butterfly Wing” effect is also made use of in women’s make-up, giving the skin an iridescent sheen. Catalysts in the form of nanoparticles are also more efficient due to the increased area of contact.

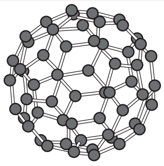
Nanoparticles can also be added to sports implements to make them stronger, whilst often being lighter. They have been used in tennis rackets, golf clubs and shoes and silver nanoparticles have also been added to sports socks and tee-shirts. This addition stops them from absorbing the odours from exercise as well as imbuing antibacterial properties. A company is even selling clothing which is coated with nanoparticles that repel water.

Carbon Matrices

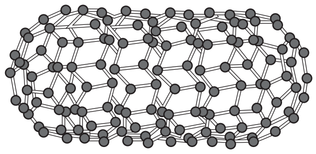
Carbon atoms can be linked up either into balls, called Buckyballs (real name Buckminsterfullerene, containing 60 carbon atoms), or graphene sheets and nanotubes. The tubes and balls can be used to store nutrients for agriculture or slow-release drugs in the body and also have good lubricating properties. Boron nitride is another compound that can be formed into sheets and tubes. Nanowires made from Hexagonal Boron Nitride (HBN) are used in hip replacement operations, where they can be implanted and encourage bone growth to hold the ball and socket in place due to their large surface area. HBN nanowires are also used in dental surgery for implants into the jaw bone.



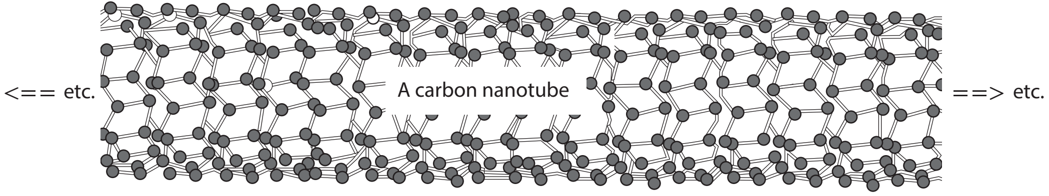
A section of multi-layered graphite



One of the simplest 'buckyballs' C_{60}

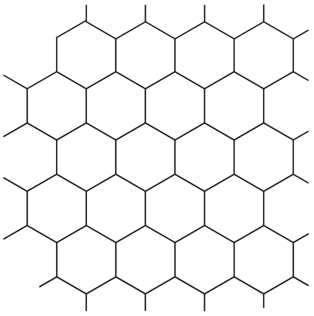


A longer buckminsterfullerene which is 'rugby ball' or 'sausage' shaped, C_{72} etc.



A section of a carbon nanotube e.g. 6 x 100 nm, the ends would be like those of the 'sausage' above right.

Graphene sheets are becoming more and more useful as their production methods become more efficient. Hence their cost has decreased significantly from a price of $100 a square centimetre in 2009.



Graphene sheet

Graphene nanoribbons have been produced that are only 0.34 nm thick by Chemical Vapour Deposition which are now used in a variety of highly efficient devices, such as the OLED flexible television screen we see advertised. Graphene transistors only 10 atoms wide can switch much faster than normal transistors at up to 100 billion times per second, which will make computing more efficient.

Graphene is 90% transparent to light and has been used to make solar cells with a much higher efficiency, as well as batteries and supercapacitors with a super storage power. These batteries are only ⅕ of the thickness of paper! The large surface area of graphene sheets can be utilised to store hydrogen gas for fuel cells and has even been used to produce an “Invisibility Cloak” by the electrical heating of air to bend light to pass round an object. Graphene is rapidly becoming the nanomaterial of the future.

An American university has produced “Smart Dust” whose particles are smaller than a grain of sand which can be used to create tiny cameras and listening devices. One university has even produced a miniature guitar made from nanoparticles which is only 10 micrometres long (10,000 nm) - the size of red blood cell - which has strings and can produce notes, albeit 17 octaves above normal guitars. This was just to demonstrate the technique of etching devices from small grains of crystalline silicon called Electrobeam Lithography.

1.7 PROBLEMS WITH NANOPARTICLES

Being as the particles used in make-up and sunscreen are so small, there has been concern lately that nanoparticles might get into the bloodstream through the pores of the skin and cause medical problems. Over 300 different sunscreens in use in Australia now contain these minute particles. Indeed, there are reports that these creams do cause inflammation, which may lead to more serious problems because nanoparticles have been detected in blood and urine samples. It is not certain whether these particles residing within the body can cause long-term effects.

5000 tonnes of carbon nanotubes are produced each year and these have been shown to cause cancer in animals. There is a call for greater regulation of the addition of very small particles or beads in food and pharmacological products. Another product called Microbeads is used as an abrasive in facial cleanser. These tiny balls of polyethene polymer micrometres in size cause abrasion to the skin and cleanse it. The problem with microbeads is that they are so small that they cannot be filtered out of the water system and end up in the environment. Recently it was found that the Great Lakes in USA contained as much as 19 tonnes of these beads in the beds of the lakes– 1.1 million per square kilometre! These microbeads become lodged in the digestive tracts of wildlife, such as fish and birds and can cause death. Not only that, but the problem is magnified by the fact that these beads actually absorb pollutants, such as heavy metals and industrial chemicals, like PCBs phthalates and oestrogen disruptors which can affect humans further up the food chain.

1.8 PURIFYING MATERIALS

Mixtures or solutions often have a component that is useful to us and one that is not – or maybe several components may be useful, so a process of separation of one component from another is needed. The separation process used always relies on the different physical or chemical properties for each component e.g. particle size, density, magnetic attraction, adhesion, boiling point, solubility etc. Flotation is a simple way of separating very low density particles of, say, sawdust or leaves from drinking water in a stream.

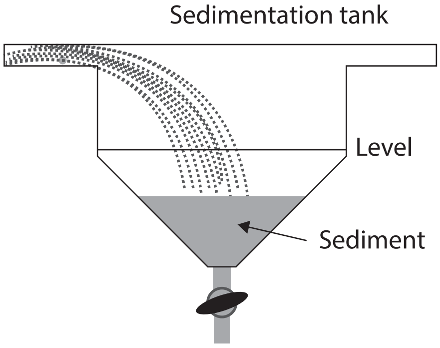
1.9 SEPARATION BY PARTICLE SIZE

Panning for gold is an example of where separation occurs because the density of gold is greater than that of water or sand and so, by swilling in a pan, the gold is left behind. Muddy water can be left to settle and clear water could be siphoned off from the top in an emergency.

1.9.1 Sedimentation

Sedimentation tanks allow small particles such as silt or mud to settle from a liquid in order to separate the two components. This process is used in industry where recycled water is to be used in a chemical process.

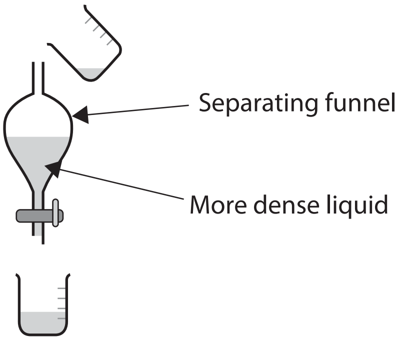
A centrifuge is far more efficient but more complicated. Centrifuges act like spin-dryers where rotation spins the water off leaving the particles behind.



1.9.2 Decantation

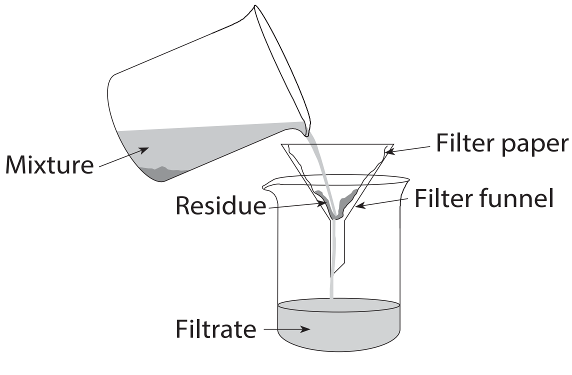
Decantation is used in the laboratory to separate mixtures.

A mixture of solid and liquid or two immiscible liquids is allowed to settle and separate by gravity. Once the mixture components have separated, the less dense liquid is poured off leaving the heavier liquid or solid behind. In the separating funnel it is the lower liquid that is required sometimes, so this is drawn off via the tap at the bottom.



1.9.3 Filtration

When very fine particles are required to be separated from a liquid, the process of filtration is an easy way to achieve this. For instance, if a precipitate is needed from an aqueous solution and then it is poured through a filter paper folded into a filter funnel the fine holes in the paper trap the larger solid particles. Filter papers can be used with different sized pores for smaller particle sizes. The Filtrate is the liquid passing through the paper and the Residue is the solid left on the paper. This can be dried and preserved.

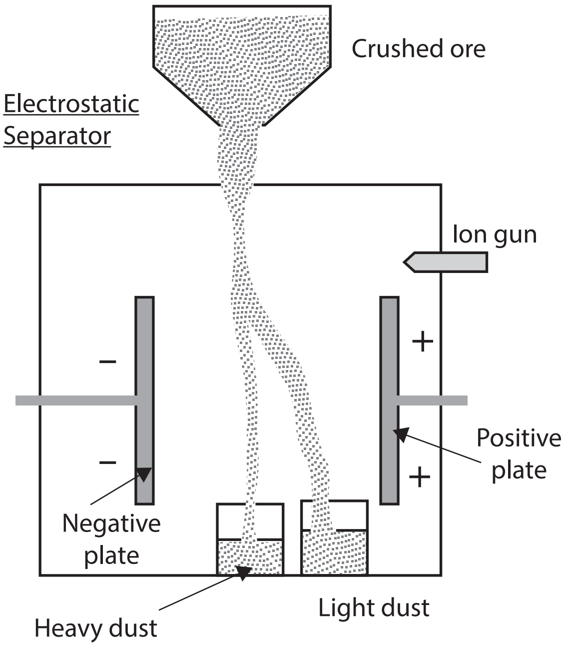


Other examples of separation based on filtration outside the laboratory are air and oil filters in automobiles, air filters in air-conditioners, paper filters in coffee makers etc.

1.9.4 Electrostatic separation

To remove dust from flue gases in a coal-burning furnace two electric plates are used which attract the small dust particles so that they do not go out into the atmosphere. This method is refined in the Mining industry to separate out and concentrate a useful metal ore from the sand and dust it is mixed with by use of an Electrostatic Separator.

The ore would be crushed into a powder and allowed to fall through a tower whilst being bombarded with an ion beam (e.g. negative electrons) This would give a charge to all the particles but the heavier ones would be less attracted to a positively-charged electrode. Thus, the heavier (e.g. gold-bearing) particles would land in a different positions to the lighter dust.



1.9.5 Magnetic separation

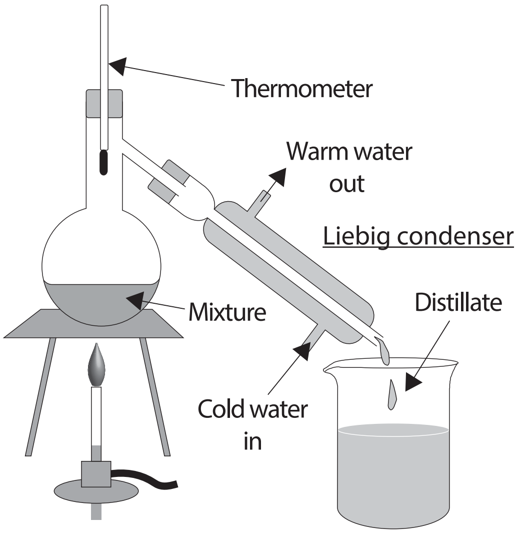
Some metal ores are magnetic (e.g Fe, Co, Ni) and so, to separate the metal compound from the rocks and sand the ore is crushed and passed through a magnetic field. The magnetic ore would be attracted and the inert sand and rocks would pass straight through, thus separating and concentrating the important compounds.

1.10 PURIFYING BY BOILING POINT DIFFERENCE

Distillation is another familiar procedure for separating mixtures of liquids, based on the differences in their boiling points or volatility. It is the procedure with which large petrochemical plants achieve the separation of petroleum into gasoline, diesel and lubricating oils.

The diagram shows a simple laboratory distillation apparatus that would be used to obtain pure water from sea water. Water boils at a much lower temperature than salt, so the water boils off as steam, leaving the salt in the distillation flask. Distillation is also used to produce alcohol spirits (whisky, vodka, brandy, etc) from a low alcohol mixture.

For instance, wine has around 12% alcohol which, when distilled, produces brandy with an alcohol content of around 40%.



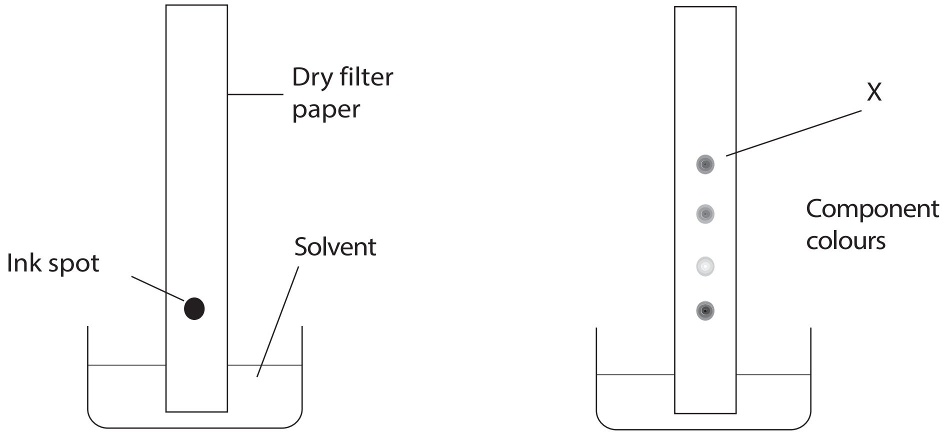
Oxygen can also be isolated from air by liquefying it and then separating it from liquid nitrogen by Fractional Distillation. Air is first filtered to remove dust, and then cooled in stages until it reaches -200°C. At this temperature all air has been liquefied. The temperature is then raised to just above -196°C, the boiling point of nitrogen, so nitrogen boils off, leaving the liquid oxygen behind as its boiling point is -183°C.

1.11 PURIFYING BY ADSORPTION

Chromatography is a separation process that relies on the fact that different chemicals adhere, or stick to an inert or Stationary layer more than others due to their different intermolecular forces. If the stationary layer is paper and we want to separate out the component colours of black ink, for instance, we could use water or ethanol as the solvent. Separating out colours is what gives this technique the name Chromatography as Chromo is the Latin name for Colour and this particular arrangement is called Paper Chromatography.

Paper Chromatography

As the solvent moves upward on the paper, it carries the components of the mixture that are attracted to it along. The components which adhere or are adsorbed strongly by the paper move most slowly.



From the diagram we can see that the coloured ink X with the greatest attraction to the Mobile Phase (solvent) and the least for the Stationary Phase (paper) has moved the furthest from the solvent reservoir.

The stationary phase is in the form of a thin film of a non-reacting solid. The mobile phase here is a liquid but it can also be a gas, as with a gas chromatography apparatus.

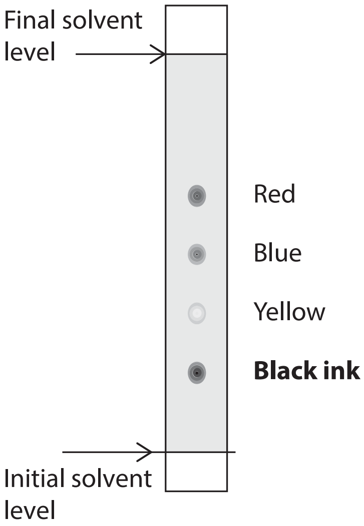
A particular soluble component can be identified by what is called its Retention Factor, R_f. The value of this factor is unique for any compound.

An example is shown in the diagram where a black ink sample has been spotted onto some filter paper immersed in a solvent and left for some time so the coloured components of the ink can be separated by paper chromatography.

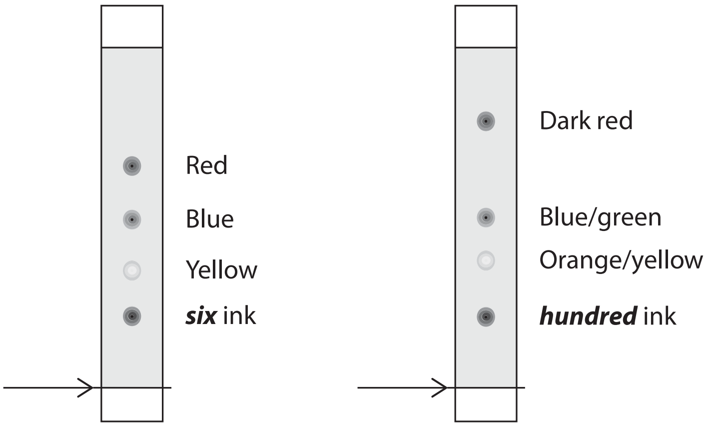
We can see that what we see as black ink is actually composed of 3 component colours – yellow, blue and red. In the diagram we can see that the red ink is attracted more to the mobile phase than the other colours are and hence it has travelled further up the stationary, paper phase than the others.

If this particular colour were to be used in another make of ink we could identify it from component colours separated out by chromatography.

This process could be used in forensic analysis of inks to determine whether one ink was the same as another.

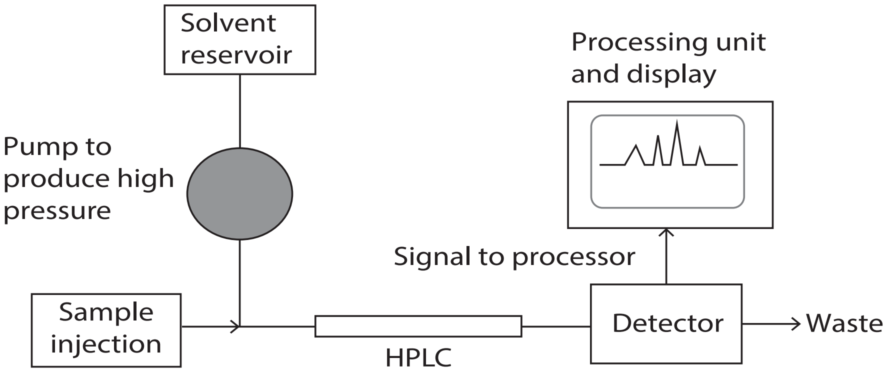


For instance, suppose it was suspected that a cheque for six dollars had been forged by adding the word "hundred" onto the end of it. ***Six hundred dollars***. By sampling the inks from the words "six" and "hundred' from the cheque the following results might be obtained:



It is apparent from the chromatography traces produced by the ***six*** ink and the ***hundred*** ink that these two words were written with different inks, although both inks look an identical black colour. The ***hundred*** was written after the ***six*** was written and hence the cheque was forged.

1.12 GAS/LIQUID CHROMATOGRAPHY



The High Performance Liquid Chromatography (HPLC) system is much more sophisticated than the simple paper system as it can analyse substances in either the liquid or gas phases to a high degree of accuracy. It is designed to separate compounds which are dissolved in solution using a gas as the mobile phase, a pump, an injector, a separation column and a detector.

The sample mixture is injected into the separating column consisting of a polymer as the Stationary Phase and is carried through the column by a helium gas mobile phase. The different components in the mixture pass through the material in the column at different rates – again depending on their strength of attachment to the mobile and stationary phases. The time to reach the detector would be unique for different components. Hence, by measuring this time against known times for each chemical, the component chemicals could be identified.

HPLC is used for medical, legal, research and manufacturing purposes. For instance, doctors can detect the amount of vitamin D or alcohol in blood samples or performance-enhancing drugs or poisons in urine. In chemical research HPLC is used to separate the components of complex biological samples or pharmaceutical products, including amino acids.

Law enforcement agencies can detect drugs such as heroin, cocaine and cannabis, as well as traces of other liquids from a crime scene.

Environmental agencies use HPLC to determine the level of pollutants in a water sample or minute quantities of contaminants in oil or gases.

More details on chromatographic analysis is given in Unit 2 of this book.

Set 1 Questions

1. A chemist is trying to find out the percentage of iodine contained in seawater.
   (a) What main branch of chemistry would this involve? ____________________
   (b) How could we extract dry salt from seawater? Explain.
   (c) 25 grams of seawater was boiled away to dryness in a beaker. When it was reweighed it was found that 0.88 grams of salt remained. Calculate the percentage of salt in seawater.

2. How was the hardness of copper tools increased by ancient people and how did this innovation improve their lives?

3. There was a Bronze Age and an Iron Age many centuries ago, but no Aluminium Age. Why was this?

4. Circle the homogeneous materials in this list:
   (a) Iron ore (b) Tap water (c) Composites
   (d) Leather (e) Sulfur

5. (a) Convert 107 nanometres to centimetres. __________________________
   (b) Why do wood chips burn faster than a plank of wood?
   (c) Estimate the thickness of a page of this book – in nanometres. ___________
   (d) Why are nanoparticles of carbon (e.g. Buckyballs) so efficient at absorbing odours in socks?

6. (a) Carbon nanotubes can be used to store nutrients inside their structure. Why do Agricultural scientists recommend nanotube-based fertilizers for farmers?

___

___

(b) Why is it that carbon can be made into 3 dimensional sheets but sulfur cannot?

___

(c) Why are graphene sheets so strong?

___

___

7. Do you think there should be a government regulating department for the overseeing of the addition of nanoparticles into domestic products? Give your reasons.

___

___

8. Name and briefly describe the technique you would use to separate each of the following mixtures in to two components.

(a) Table salt and pepper ___

(b) Sugar and sand ___

(c) Drinking water contaminated with fuel oil ___

(d) Vegetable oil and vinegar ___

(e) Iron filings and grit ___

9. Which separating technique is operating in each of the following?

(a) Pouring a mixture of cooked pasta and boiling water into a colander.

___

(b) Removing coloured impurities from raw sugar to make refined sugar.

___

(c) Producing whisky from a fermented solution of alcohol.

___

10. (a) A cube of metal measuring 1.00 cm x 1.00 cm x 1.00 cm is melted down and poured into a spherical mould.

What would be the radius of this sphere (volume of a sphere is $\frac{4}{3}\pi r^3$).

___

(b) Which has the largest surface area, the cube or the sphere? (area of a sphere is $4\pi r^2$). Show your calculations.

___

(c) If the cube had been cut into 8 smaller cubes measuring 0.50 cm x 0,50 cm x 0.50 cm. what would the total surface area of all the cubes be?

(d) From these results, can you explain why granular sugar dissolves in tea quicker than sugar cubes?

11. The holes punched into the surface of a CD to turn music into a digital code are 800 nm long, with gaps of 800 nm between.

If the CD music outer track has a radius of 5.50 cm, how many holes and spaces 800 nm long can be fitted around this track?

12. Some of the best tomatoes are called "Vine-ripened" tomatoes which are grown in special conditions and cost a lot more than ordinary tomatoes. It is suspected that an Asian company is selling their tomatoes as Vine-Ripened but are actually just grown in the ground using inferior human waste fertilizer.

How could chromatography be used to detect the difference between the Asian tomatoes and the genuine Vine-Ripened ones? Outline the techniques to be used.

13. In both World Wars gas masks were distributed to the population in case of poisonous gas attacks. These contained a mixture of activated carbon and zeolites which have high adsorption rates and large surface area-to-volume ratios. For instance, 1 gram of activated carbon has an adsorption area of 3000 m^2.

(a) Explain why carbon and zeolites were effective in saving soldiers and other people in a gas attack.

____

____

____

(b) New gas masks are now produced using nanoparticles of carbon. Explain why these are likely to be more effective than the older type of gas masks.

____

____

Notes

Chapter

2

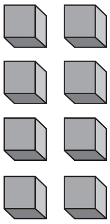
Atomic Structure

2.1 RESEARCH HISTORY

It may surprise you to know that the idea that all matter is made up of small, indivisible particles dates back over 2000 years to the Greek philosophers. They were great thinkers but did not use experiments to check that their ideas made sense – just logic.

Democritus 460 BC

This great philosopher was the first to propose the idea that all matter was made of small, indivisible "building block" particles which made up everything in the Universe. Democritus called these particles "atoms" from the Greek word "Atmos", meaning Indivisible. Another Greek philosopher disagreed with these ideas and declared that everything was made up from earth, air, fire and water and this alternative idea prevailed for hundreds of years.



Lavoisier 1780

This French scientist also accepted the "earth, air, fire and water" model but actually performed experiments to discover how elements combined where he discovered the principle of Conservation of mass. He also discovered the element oxygen and drew up the first crude table of elements.

Dalton 1803

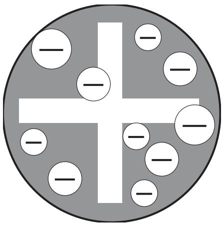
This great English experimental scientist believed that the make-up of matter was due to small atoms which joined up to form compounds in a fixed ratio and that these atoms were unique for every element i.e. elements only contain one kind of atom.

Mendeleev 1869

This Russian scientist arranged all the known elements into the first periodic table in order of atomic masses, which had some discrepancies, but he then forecast an element to exist below aluminium called eka-magnesium and predicted its mass and properties. When technetium was discovered later its properties were exactly as predicted for the eka-magnesium, validating his theories.

Thompson 1897

Knowing that atoms contained positive and negative particles, Thompson proposed the Plum Pudding model of the atom, where the "pudding" was completely charged positively with the negative particles (which are now known as electrons) stuck into interior structure. We can imagine the distribution of negative charges as chocolate pieces in a chocolate-chip biscuit.



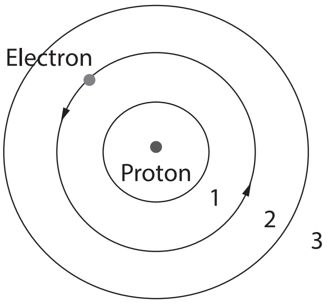
Planck 1900

From his Photoelectric experiment, Max Planck completely revolutionised scientists' ideas of energy when he showed that energy is not continuous, but exists in "Packets" called Quanta. This later explained why electrons moving in circular orbits could not spiral downwards, but could only lose energy by dropping a whole step, or level in the atom.

Milliken 1908

Milliken determined a value for the charge on an electron as 1.6×10^{-19} of a coulomb.

Rutherford 1912



By firing alpha particles at gold nuclei, Rutherford realised that the Plum Pudding Model of the atom was wrong and that the positive charges resided in the central nucleus with electrons orbiting them at quite a large distance.

His reasoning was that if the + and – charges were close then the deflections of the α-particles would be small, but the actual observations showed massive deflections, as if the atom was made entirely of + charges.

Later, Bohr linked the quantisation principle to produce the atomic model, where electrons exist in orbitals with set, quantised energy levels: An electron can only exist in one level or another, but not between levels, so when it loses energy it can only emit specific, discrete wavelengths.

Mosely 1913

In his experiments with the x-ray spectra of elements, Mosely derived the idea of the atomic number of an element as the number of protons in its nucleus, which led to the modern version of the Periodic Table based on atomic number, rather than mass number.

De Broglie 1924

Experimenters had found that fast-moving electrons fired at a thin sheet of metal produced a diffraction pattern, showing that they were behaving like waves of light. This led to De Broglie formulating the idea that electron orbitals were in fact standing wave patterns of electrons produced by the interference of electron waves around the nucleus.

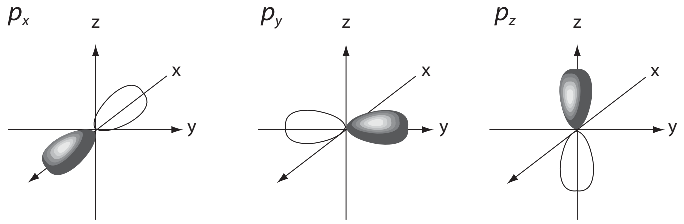
Electron orbital "cloud"

Schrodinger 1926

Electrons having wave-like properties led to a whole new view of electron behaviour, where an electron can be in many places at once, just as a wave on the sea can be. This new view of electron orbitals as wave patterns led Schrodinger to describe paths in terms of **probability densities** for finding the electron in a particular position by using a wave equation.

This led to our present idea of orbitals and sub-orbitals as probability density maps and to the structure of the Periodic Table.

This diagram shows the predicted shape of the three different p sub-orbitals.



Chadwick 1932

Measuring the mass of the nucleus, Chadwick realised that there must be a heavier particle present, apart from a proton. From this he went on to discover the neutron. Thus he showed that there were three elementary particles.

Gell-Mann and Zweig 1964

By the 1960s, many other sub-atomic particles had been discovered with various masses, so it was proposed that all fermions (in the nucleus) were composed of smaller particles called Quarks. This Standard Model is the accepted structure of all matter today. Protons and neutrons are thought to be made up from three of these quarks.

2.2 ATOMIC MODELS

The Quark model has no real bearing on the reactions and larger structure of atoms, so explanations of atoms, molecules and their interactions are largely explained by reference to the model of an atom where a positive nucleus is surrounded by orbiting electrons. The positive charge of the nucleus will attract an electron but, due to its orbital speed and inertia, the electron can remain in a stable orbital. The Quantum understanding of energy (energy can only be lost in "packets") dictates that these electrons can only exist in discrete orbitals, but cannot exist between orbitals.

Where there is more than one proton in a nucleus the electrostatic repulsive force would be massive as the protons are so close together. However the Strong Nuclear Force causes attraction to "switch on" between any particles in the nucleus once the distance between them becomes less that 10^{-15} metres.

The electrostatic repulsive force would cause a nucleus consisting solely of protons to break apart but the addition of neutrons allows the Strong Nuclear Force to hold nucleons together in a stable configuration. Apart from hydrogen, atoms need roughly the same number of neutrons as protons in any nucleus to allow isotopes of an element to be stable. However, this ratio of neutrons to protons becomes greater as the elements become heavier. So with uranium, for instance, there are 143 neutrons in the nucleus for only 92 protons. Past uranium, the repulsive force cannot be overcome by the Strong Force and instability arises. Hence uranium is the heaviest naturally-occurring element on Earth.

2.3 ATOMIC NUMBERS AND MASSES

The modern Periodic table arranges each known element in order of the number of protons in its nucleus. This number is called the Atomic Number and has the symbol Z. For instance, sodium is the 11th element and hence has an atomic number of 11. As mentioned, the number of neutrons needed to make it a stable nucleus is about 11, but the most common isotope of sodium has 12 in its nucleus. The proton number plus the neutron number is called the Mass Number, symbol A (atomic mass), so, in this case, sodium would have a mass number of 23. There are, however, other isotopes of sodium that exist. Isotopes are elements with the same atomic number but with a different mass number due to different numbers of neutrons in the nucleus. More than 20 different isotopes of sodium have been produced artificially by bombardment with neutrons but the main stable isotope is Na-23, with some others being unstable, so they decay emitting radiation.

We designate particular isotopes by showing the Z value at bottom left and A at top left e.g. Sodium 23 would have the symbol ${}^{23}_{11}\mathrm{Na}$.

The Relative Atomic Mass (M_r) is defined as the mass of an atom in atomic mass units (amu). 1 amu is defined as the mass of $^1/_{12}$ of a carbon atom, which is roughly the mass of one proton.

The Abundance of an isotope is the percentage of that isotope found in nature compared with all its other isotopes. Chlorine, for instance, occurs on Earth as two main isotopes – chlorine-35 and chlorine-37. The abundances of these are roughly 77.5% and 22.5% respectively. The mass number quoted in the Periodic Table is 35.45 – but how can it have a fractional number? This is because the Mass Numbers quoted are the Weighted Averages of all the isotopes of the elements. To calculate the value of a weighted average we multiply the value of the mass of each isotope by its abundance and add these values.

Example

Weighted average M_r of chlorine is $M_r = \frac{35 \times 77.5 + 37 \times 22.5}{100} = 35.45$ amu.

The actual atomic mass of an element can be determined by an instrument called the Mass Spectrometer which uses the fact that ionised elements fired into a magnetic field will be deflected into a circle of specific radius. An ion is a charged atom of an element with either an additional positive or negative charge.

For instance, a chlorine atom, which has 17 protons and 18 electrons would be a chloride ion, written Cl^-. A sodium atom with 11 protons and only 10 electrons would be designated as Na^+ - a sodium ion.

2.4 THE MASS SPECTROMETER

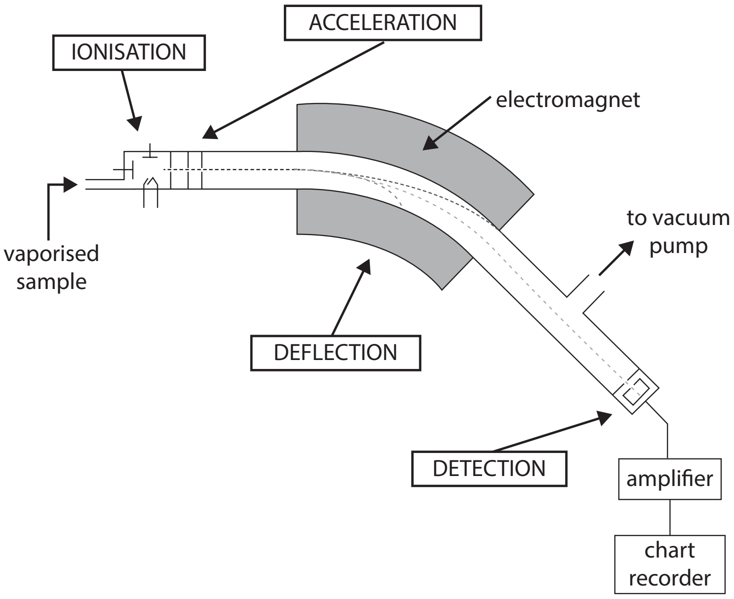
The atomic weights of all the elements can be found by using a mass spectrometer.

This instrument has an accurately controlled magnetic field intensity and a velocity selector through which ionised atoms pass to ensure all particle velocities are fixed at the same value.

The sample is first vaporised into single atoms or molecules and then bombarded with electrons to ionise the vapour.

The ions (positive ions are shown here) are then accelerated by an electric field to a high speed then pass through a strong magnetic field which bends them into a circular path.

A full diagram of a mass spectrometer



They then strike the detector at the correct radius if they have a particular mass and charge.

The radius of the beam depends on the magnetic field strength (B), the velocity of the ions (v), the charge on the ions (q) and the mass of the element (m).

The formula for the radius of the path of an ion is given by: $m = \frac{Brq}{v}$.

By measuring the radius and knowing values of B (magnetic field), q (charge) and v (velocity), the mass of an ion can be determined. The values of the atomic masses of all known elements is laid out in the Periodic Table.

2.5 THE PERIODIC TABLE OF ELEMENTS

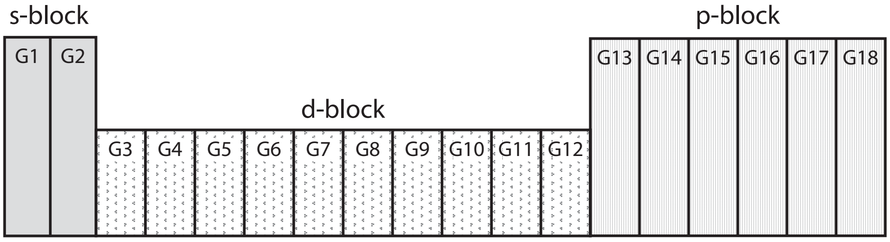
The modern Periodic Table shows all the elements in order of increasing Atomic Number and Group Number arranged in rows called Periods. Upon investigation, it was found that electrons existed in shells. Each electron shell is shown horizontally as a Period in the table. Each shell has a fixed number of electrons that it can accommodate.

For the 1st Period the shell is full when it has reached 2 electrons but the 2nd shell must accommodate 8 electrons to achieve a stable configuration. Elements arranged vertically in columns show similar properties and so are placed in the same group. E.g. all elements in Group 1 are shiny and soft and react with water to produce a basic solution. Elements in Group 17 are coloured and form acids with hydrogen, and so on. The group structure also shows the arrangement of Valence electrons i.e. electrons in the outer shell. These are the ones that give the elements their characteristic properties and reaction types. As a full shell denotes stability, elements will react to achieve a full shell and thereby move from higher energy to lower energy states.

Elements that already have a full shell do not need to react and are said to be Inert. This group of gases is called the Noble Gases (group 18). Some other groups also have names given to them e.g. Group 1 is called the Alkali Metals, Group 2 is called the Alkaline Earth Metals and Group 17 is called the Halogens.

2.6 SHELLS AND SUB-SHELLS

Looking at the periodic table structure we can see that there appear to be rectangular blocks linking elements vertically. This is because, each shell is arranged in sub-shells called s, p and d sub-shells, as shown below.



Each member of a group (G_1, G_2, …etc has the same number of electrons in its outer shell and so has similar properties.

Each electron cloud area of a sub-shell (an orbital) can only hold 2 electrons. One of these electrons is said to have Spin up and the other Spin down. Once a particular orbital has a spin up electron, the next electron must be spin down and then no more can enter as 2 is the stable number for each orbital.

S subshells only have one orbital which contains 2 electrons

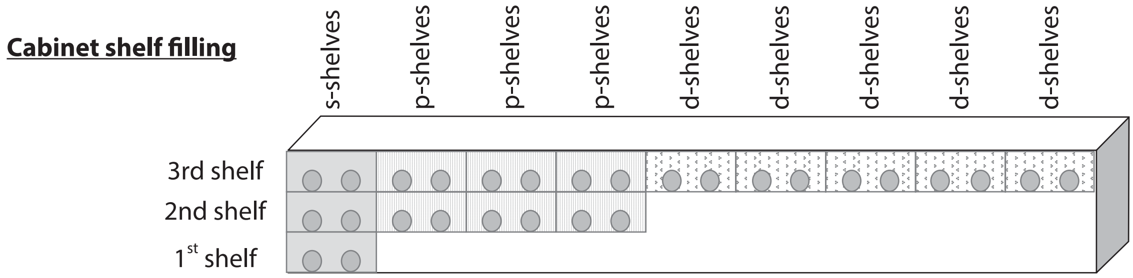
P subshells have 3 orbitals, each containing 2 electrons. Total capacity = 6 electrons

D sub-shells have 5 orbitals, each containing 2 electrons. Total capacity = 10 electrons.

F subshells have 7 orbitals, each containing 2 electrons. Total capacity = 14 electrons.

There is also another f subshell for the very heavy elements which has 7 orbitals and can take 14 electrons.

We can think of the filling of shells as similar to the filling of shelves in a cabinet with different numbers of shelves in each level.



2.7 ELECTRON SHELLS

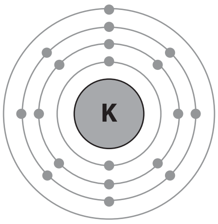
Electrons are located in shells, or distinct energy levels around the nucleus. They are denoted by the numbers 1,2,3,4,… which are called principal quantum numbers. Simple electron configurations just show the number of electrons in each shell, or energy level. The first shell can hold 2 electrons. The second shell can hold 8 electrons. The third shell can hold 18 electrons*. The fourth shell can hold 32 electrons and so on.

*In this course you will only be required to provide simple electron configurations for the first 20 elements up to and including calcium. For these elements the third shell holds 8 electrons. Beyond these elements, some of the fourth shell fills before completely filling the third shell. This is discussed briefly below.

The number of electrons that each element has can be shown in the various shells or energy levels as numbers in each shell. For instance, neon is number 10 in the Periodic Table so it must have a full 1st shell and a full 2nd shell. It would be denoted as Ne 2, 8. Aluminium has

13 electrons and its electron configuration would be: 2, 8, 3 as it has full 1st and 2nd shells but 3 electrons in its outer shell - its Valence Shell. This means that these 3 electrons only will take part in a reaction.

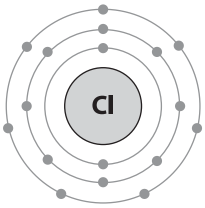
e.g. potassium has 19 electrons



Its electron configuration is 2,8,8,1

It has one electron in its valance shell and is in group 1 of the periodic table.

e.g. chlorine has 17 electrons



Its electron configuration is 2,8,7

It has seven electrons in its valence shell and is in group 17 of the periodic table.

2.8 ELECTRON CONFIGURATIONS, SUBSHELLS AND ORBITALS (EXTENSION)

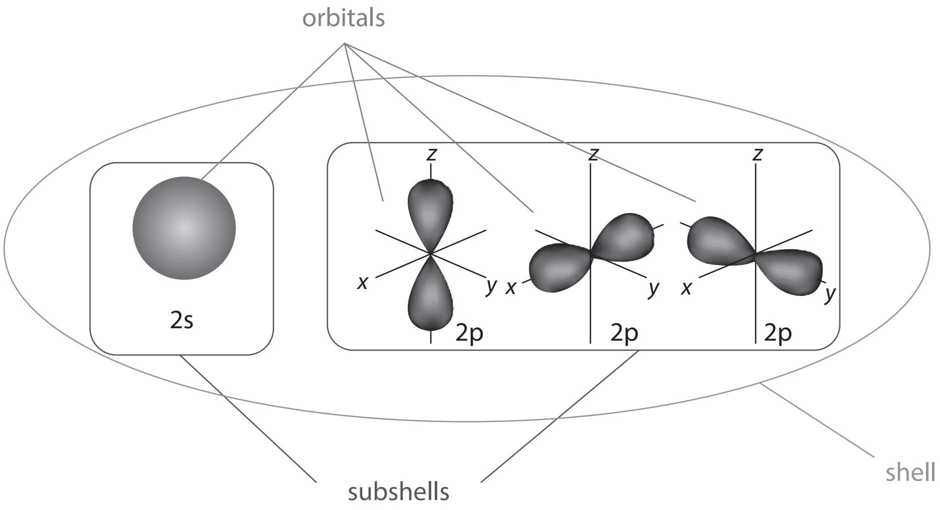
Shells consist of **subshells** with different shapes, called s, p, d and f subshells. The subshells consist of **orbitals** that can each hold 2 electrons.

S subshells are spherical in shape and have one orbital that can hold 2 electrons.

P subshells have three dumbbell shaped orbitals that can hold 2 electrons each, so a total capacity of 6 electrons.

D subshells are quite complex in shape and have five orbitals that can hold 2 electrons each, so a total capacity of 10 electrons.

F subshells are also complex in shape and have seven orbitals that can hold 2 electrons each, so a total capacity of 14 electrons.



The first shell can hold only 2 electrons and these are found in an s subshell (1s).

The second shell can hold up to 8 electrons in an s subshell (2s) and three p subshells (2p).

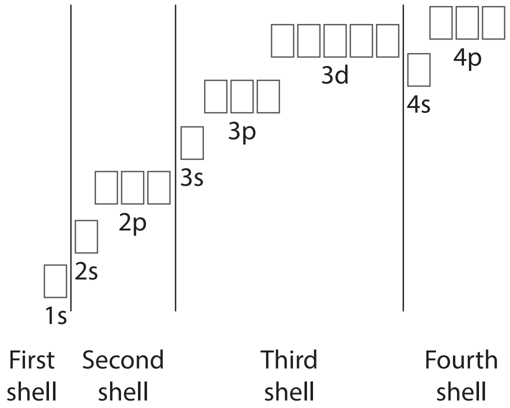
The third shell can hold up to 18 electrons in an s subshell (3s), three p subshells (3p) and five d subshells (3d).

The fourth shell can hold up to 32 electrons in an s subshell (4s), three p subshells (4p), five d subshells (4d) and seven f subshells (4f).

To determine the electron configuration of an atom in its lowest energy or ground state using s, p, d, f notation:

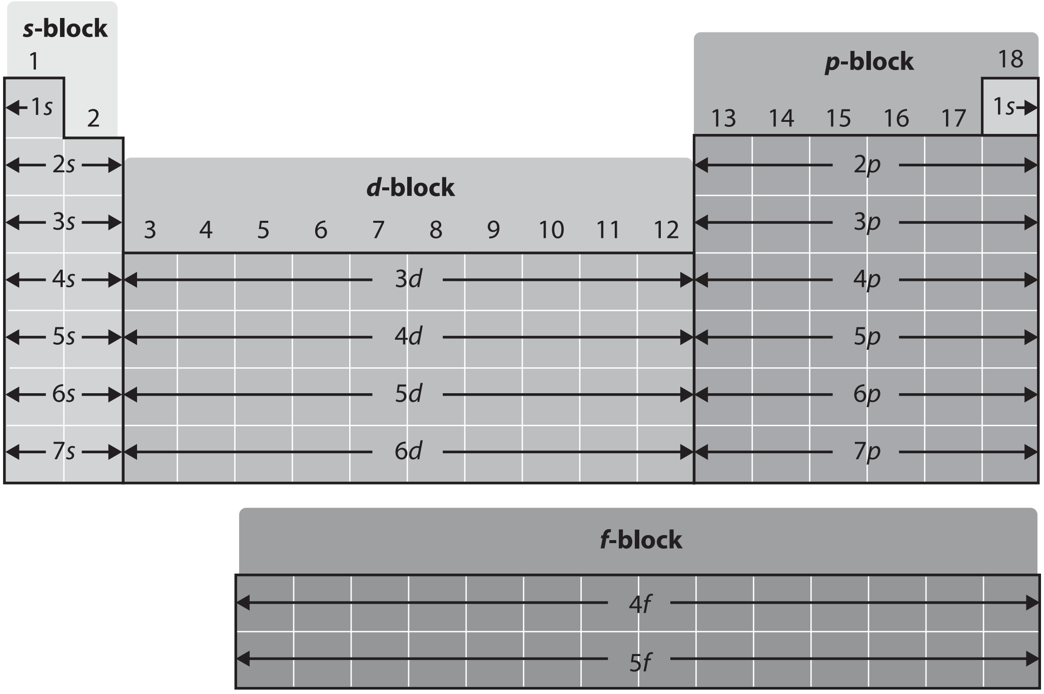
1. Place the electrons into orbitals starting with the lowest energy orbitals first.
2. Place a maximum of 2 electrons into each orbital

   N.B. the 4s subshell fills before the 3d subshell.



Examples

1. Sodium	${}^{11}_{23}\text{Na}$	
	Simple arrangement	(2, 8, 1)
	Electron configuration	$1s^2\ 2s^2\ 2p^6\ 3s^1$
2. Oxygen	${}^{16}_{8}\text{O}$	
	Simple arrangement	(2, 6)
	Electron configuration	$1s^2\ 2s^2\ 2p^4$
3. Calcium	${}^{40}_{20}\text{Ca}$	
	Simple arrangement	(2, 8, 8, 2)
	Electron configuration	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$



Periodic Table, spdf blocks

The position of an element on the periodic table gives information about the number of electrons in its valence shell, and the subshell that these outer electrons are in.

Elements in groups 1 and 2 are called the s-block elements and their outer electrons are in an s subshell. Elements in groups 13 to 18 are called the p-block elements and their outer electrons are in a p subshell. Elements in groups 3 – 12 are called the d-block elements, or transition metals and their outer electrons are in a d subshell. The lanthanide and actinide elements are called the f-block elements and their outer electrons are in an f subshell.

2.9 ATOMIC SYMBOLS

There is an agreed way of representing isotopes in chemical symbolism. The element symbol is always written with the atomic number Z at bottom left and the atomic weight (or mass number) on the top left to denote that isotope. E.g. sodium-23 would be shown as $^{23}_{11}\text{Na}$ which distinguishes it from the other isotopes $^{22}_{11}\text{Na}$ and $^{24}_{11}\text{Na}$. These two isotopes would all react in that same way with water as they have the same number of valence electrons and they would both produce hydrogen but their **physical** properties, like melting point, hardness, density and melting point would be slightly different.

Periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.968	4 Be beryllium 9.012											5 B boron 10.82	6 C carbon 12.01	7 N nitrogen 14.01	8 O oxygen 16.00	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31											13 Aℓ aluminium 26.98	14 Si silicon 28.09	15 P phosphorus 30.97	16 S sulfur 32.07	17 Cℓ chlorine 35.45	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.88	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38	31 Ga gallium 69.72	32 Ge germanium 72.59	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 *La lanthanum 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.9	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tℓ thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium 226.0	89–103 **Ac actinium	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Uut ununtrium	114 Fℓ flerovium	115 Uup ununpentium	116 Lv livermorium	117 Uus ununseptium	118 Uuo ununoctium

* Lanthanide series	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
** Actinide series	90 Th thorium 232.0	91 Pa protactinium	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

Key:

Atomic number
Symbol
Name
Standard
atomic weight

[Data source: The International Union of Pure and Applied Chemistry Periodic Table of the Elements (2016)]

2.10 VALENCIES

Valency is the combining power of an element. Elements in the same group of the periodic table have the same valency. The valency of an element is related to how many electrons are in the outer shell which it can either gain or lose electrons to obtain a full shell. Group 1 elements have 1 valence electron in their outer shell so if they can lose this electron they will achieve a stable configuration. E.g. sodium has an electron configuration of 2, 8, 1, so if it loses a valence electron it will become isoelectronic with neon, a noble gas with the lowest energy in the period. "Isoelectronic with neon" means it has the same electron configuration of 2, 8. Group 1 elements will always give away 1 electron in reactions to become a 1+ ion e.g. Na^+. Group 2 elements will always give away 2 valence electrons when reacting to become isoelectronic with a noble gas e.g. Magnesium (2, 8, 2) will become Mg^{2+} which is 2, 8. Likewise aluminium (Z = 2, 8, 3) can gain a noble gas structure of 2, 8 by losing 3 electrons and becoming Al^{3+}.

By contrast, at the other end of the 2nd Period, fluorine, in group 17, would need to **gain** an electron to reach a noble gas structure, so its valence electron structure would move from 2, 7 to 2, 8 (a stable structure) and thus become the ion F^-. Oxygen (2,6) in Group 16, similarly, would need to gain 2 electrons to achieve stability and thus become an oxygen ion O^{2-}. Hence we say that magnesium has a valency of +2 and oxygen has a valency of -2.

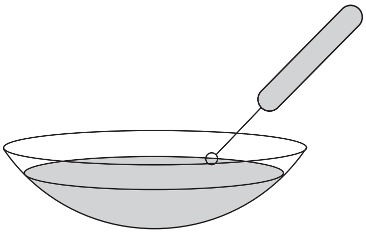
Groups 14 and 15 can either gain or lose electrons in their reactions to become isoelectronic with a noble gas structure and hence can have a variable valency in their compounds.

2.11 FLAME TESTS

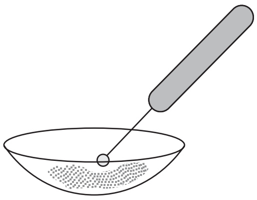
A flame test is used in chemistry laboratories to identify metal ions (cations) present in a sample of salts. The colour turned by the flame is characteristic of individual metals and is due to the metal ions emitting light when heated. For instance, if copper is present the flame turns blue/green, potassium gives a lilac flame and sodium a yellow flame. Barium gives a pale green flame and calcium gives brick-red flashes in the flame.

The way to perform flame tests is as follows: Take a mounted nichrome wire and dip it into hydrochloric acid to clean it then dip it into the sample and place the wire loop into the flame to note the colour.

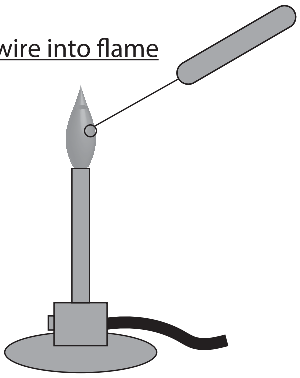
Clean wire in HCl



Dip wire into sample

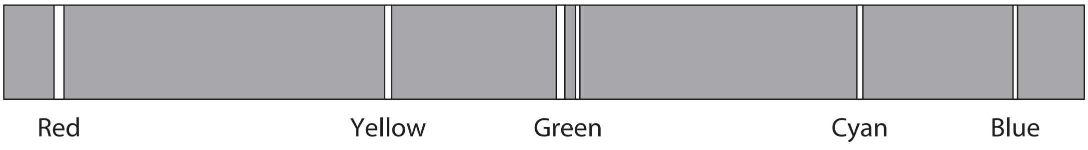


Place wire into flame



If the light from a metal flame is analysed by passing it through a prism individual component colours are seen as a series of lines. The pattern seen is called a Line Emission Spectrum, an example of which is shown below as coloured lines on a black background.

Line emission spectrum of a metal



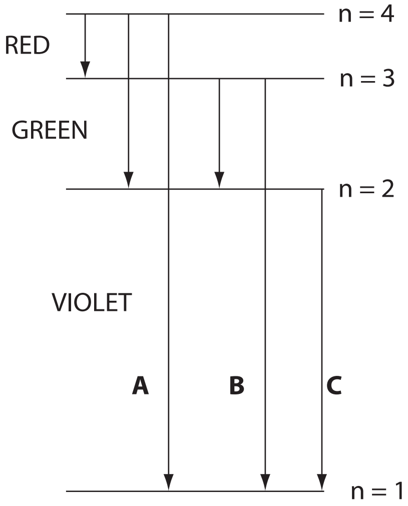
The fact that metal ions emit a series of specific colours, rather than a continuous (rainbow) spectrum puzzled scientists until the Quantum Model for energy was accepted.

This model proposed that energy is not absorbed or emitted in a continuum, but in "packets", called Quanta. The size of each packet depended directly on the frequency of the light – the higher the frequency, the more energy that is contained in the packet. Blue light, therefore contains more energy than red light, according to the formula **E = hf**, where h is a constant.

Hence, the electrons in an atom can only occupy specific energy levels, rather than being able to orbit at any distance from the nucleus.

When an atom absorbs energy from a flame this promotes the electrons into higher energy levels. When they fall down again to their original energy level, the electrons emit the energy in the form of electromagnetic waves. The greater the energy jump the shorter the wavelength emitted.

Hence a large loss of energy might give a violet line whilst a small energy jump would give rise to the emission of a red line, according to the Quantum Theory because red light has a lower frequency.



Possible energy transitions for an electron falling from the 4th energy level

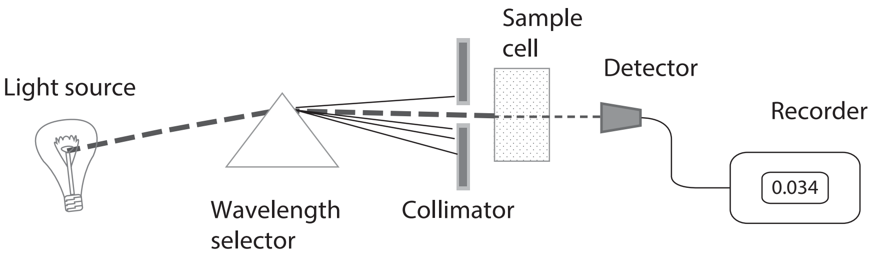
2.12 ATOMIC ABSORPTION SPECTROSCOPY

White light contains all possible wavelengths and wave energies, so if white light is shone through a vaporised metal in a flame the vapour will absorb specific energies corresponding to the emission lines of the metal - shown above as lines A, B and C. An electron normally in the lowest level 1 will be promoted up to level 2, 3 or 4 and absorb that specific colour. Hence, if we look at the Absorption Spectrum we will see a continuous spectrum (rainbow) **minus** the colours associated with that metal.

If a sample of an unknown metal ore, for instance, is vaporised in a very hot flame (e.g. acetylene at 2300°C) and white light is shone through it, from the absorption spectrum all the elements present in the ore can be identified. An atomic absorption spectrometer is used extensively by mining companies to discover the metallic contents and their concentrations.

2.13 SPECTROPHOTOMETRY

Spectrophotometry is an experimental technique used to find the concentrations of small amounts of substances in solution by recording how much light they absorb. The Photometer apparatus is shown below.



Spectrophotometer apparatus

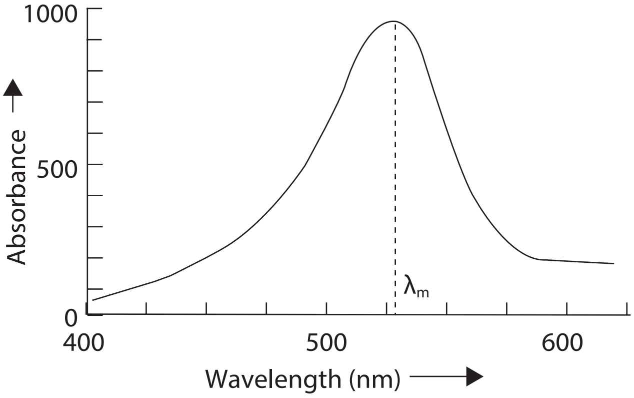
Particular wavelengths can be selected by shining light through a prism and rotating it until the correct colour passes through the slit (collimator). The wavelength is then selected which gives the maximum absorbance by the sample (λ_m) and then when it passes through it the brightness of the transmitted light is detected by a photodiode sensor. The transmitted values are displayed on the recorder instrument display. The photometer must first be calibrated by recording the amount of the key wavelength λ_m detected for known concentrations of the compound used.

Example – To determine the concentration of an unknown sample of potassium permanganate ($KMnO_4$)

First, the specific wavelength absorbed by $KMnO_4$ must be found by passing different wavelengths through a solution of the compound and finding the wavelength that is absorbed most (λ_m).

In this case we can see that the manganese ion present absorbs most light at a wavelength of about 530 nanometres.

This is the wavelength, then, that will be chosen for the rest of the experiment.

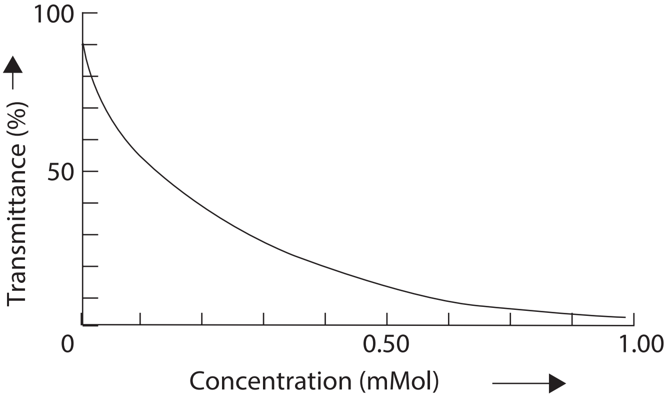


Calibration

The baseline value for transmitted light is determined with just the solvent in the cell, so the concentration is zero. The instrument is now calibrated by the following procedure:

Sample solutions of $KMnO_4$ are prepared with known concentrations and transmitted light levels are found for each concentration measured in millimoles (mmol L^{-1}).

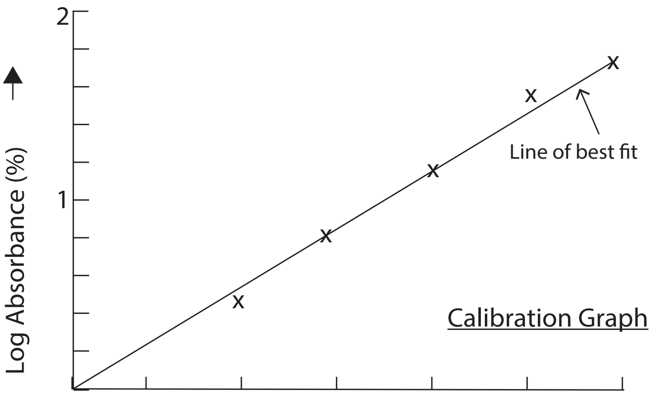
Now the instrument is calibrated so we know how the transmittance recorded corresponds to each concentration. Transmittance T_λ is given by:



$$T_\lambda = \frac{\text{Brightness measured through the solution}}{\text{Brightness measured through the solvent only}} \times 100\%$$

From the graph we can see that, as the solution of $KMnO_4$ becomes more concentrated, the amount of light transmitted becomes reduced exponentially, therefore the amount of light absorbed becomes greater exponentially.

e.g. if Transmittance = 30%, then Absorbance A = 70%. This is also an exponential graph so if we plot the logarithm of A we will get a rising straight line graph from which it is much easier to predict unknown concentrations. Note: the log of 100% = 2, which will be the maximum value.



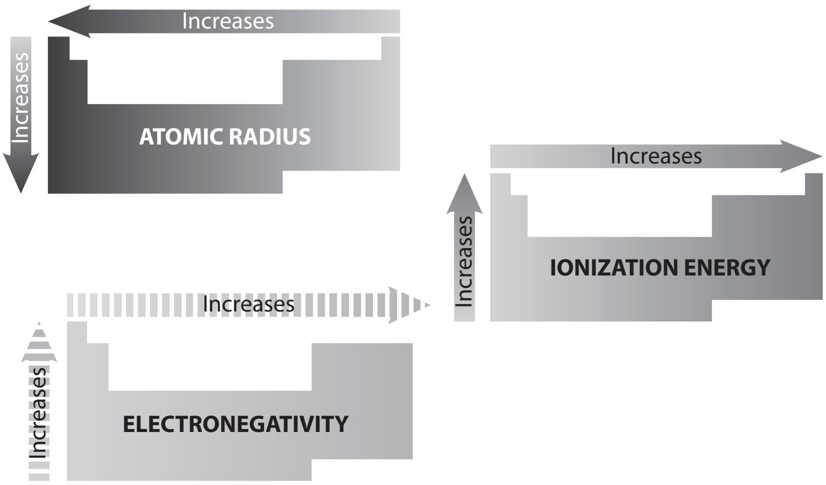
A line of best fit is plotted of log A versus concentration to use as a calibration graph and determine the concentration of an unknown solution.

Suppose we wanted to find the concentration of manganese in spinach. A solution would be made with crushed spinach and then placed in the photometer to obtain a reading of Absorbance and its logarithm. From this graph we could now determine the concentration of manganese at a wavelength of $\lambda_m = 530$ nm. For instance, if the log of A value was found to be 1.2, then, from the graph, the concentration of manganese could be predicted to be about 0.4 mmol L^{-1}.

2.14 DIFFERENT ATOMS

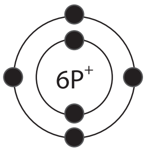
We have seen in section 2.5 how all the elements on Earth came to be classified according to their atomic numbers into groups and periods. We now know that the period number is the same as the shell number and that different shells can accommodate different numbers of electrons to fill them to make one of the noble gas structures, which is particularly stable. The first shell can hold 2 electrons maximum, the second shell 8 electrons maximum, the 3rd shell 18 electrons maximum etcetera. Within each shell there are s, p, d or f sub-shells which are also filled in a certain order. The modern Periodic Table then has 18 Groups and 7 Periods with elements past period 7 that have only been man-made in a laboratory. Let us now look at the trends in properties brought about by the electron configuration of each atom.

2.15 TRENDS IN THE PERIODIC TABLE



Core Charge

The Core Charge of an atom shows the attraction of the outer electrons (valence electrons) towards the nucleus. The protons will attract the outer electrons but the shells below them will produce repulsion and so the attractive force on electrons will change depending on the core charge.



For example Carbon has a configuration of 2, 4.

In a carbon nucleus there are 6 protons with a positive charge and 2 electrons in the inner shell with negative charge, so the core charge is +6 – 2 = +4.

Chlorine has an electron configuration of 2, 8, 7 with 17 protons in the nucleus.
As it has 10 electrons in the shells below the valence shell, its core charge will be 17 – 10 = +7.

As we go across the elements of the 2nd period of the table, from sodium to neon the core charge becomes greater (Note that neon has a zero core charge).

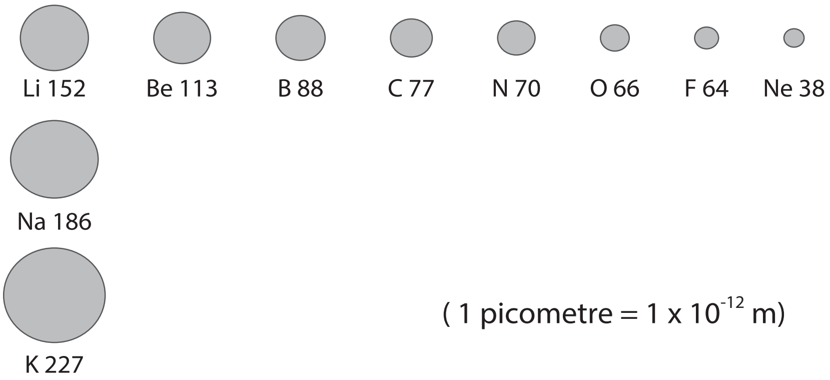
Element	Li	Be	B	C	N	O	F	Ne
e Arrangement	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8
Core charge	+1	+2	+3	+4	+5	+6	+7	0

NB Core charge **down** group 1 would be +1.

Atomic Radius

The size of an atom depends on how much the outer shell of electrons is attracted to the nucleus. As the core charge becomes larger across a period then the atomic radius (distance from the nucleus to the outer shell) will become smaller. The trend in the table above therefore will be for a lithium atom to have a larger size than neon. Going downwards in a group, there will be additional shells of electrons which take up more space but the core charge remains the same and so the atomic radius will increase down a group.

Atomic radius of atoms in picometres (pm)



(1 picometre = 1 x 10^{-12} m)

Melting Points

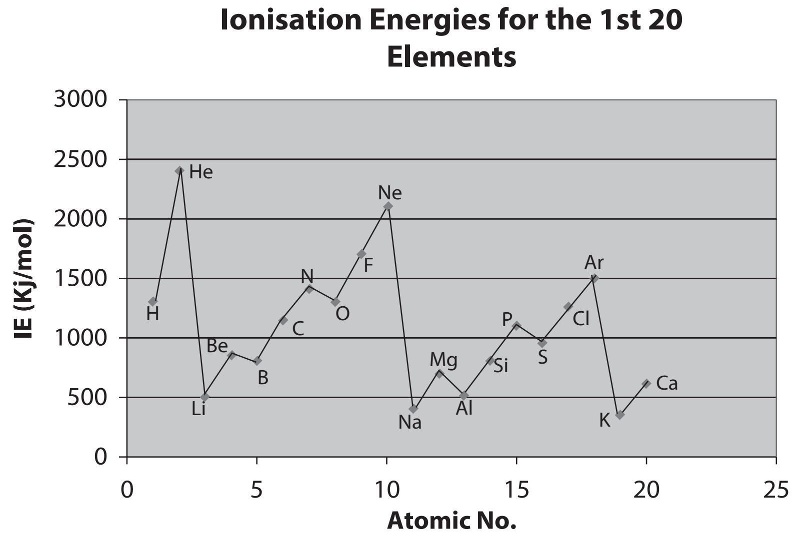
The melting point of an element is indicative of the forces holding the solid together: If the forces are large, then the heat energy needed to separate the particles will be large and hence the melting point would be higher. Going down Group 1, the atoms become larger from lithium to potassium and hence solid lithium would have its particles more tightly bonded therefore the melting points of Group 1 metals would become lower as we go down the group.

Going from left to right of a period, the melting points tend to increase due to the core charge getting greater and the atomic radius getting smaller. This increase occurs only up to Group 14 where giant, strong networks are formed, then the melting point falls, as Group 15 onwards are gases.

First Ionisation Energy

We have seen in Chapter 2 that when two elements react electrons become exchanged to form a bond. Which element donates and which one accepts an electron will depend on which loses its electrons easier. The energy needed to take an electron from an element is called its Ionisation Energy. To be exact, the first Ionisation Energy of an element (IE) is the energy needed to extract a single electron from the outer shell of a gaseous element and is measured in kilojoules per mole of the element.

Obviously, the larger the core charge, the larger the attraction to the outer electrons so, looking at the table above, we would see a gradual increase in 1st ionisation energy of these elements going from left to right. Being as the noble gases have a full shell and are particularly stable, they have the highest of all ionisation energies in the period. In fact the IE is so high that these gases were originally known as the Inert Gases because they were not known to react with any other element until, in 1961, a compound (XeF_6) was made with Xenon and PtF_6.


Ionisation Energies for the 1st 20 Elements

A rise in IE can be seen in the 1st period from Lithium to Neon due to the increase in core charge i.e. more protons in the nucleus will exert a greater attractive force on the valence electrons, so more energy will be needed to extract them. The small dip between Be and B is apparent because the s-subshell has been filled, giving a slightly more stable configuration.

There is another trend to be noted when we compare elements in the same group e.g. He, Ne, Ar. Here we can see a decrease in IE down the group (He > Ne > Ar) due to the outer shell of valence electrons in Ar being a greater distance away from the protons' attractive force in the nucleus and a charge "shielding" effect from the shells below. Here we see that the atomic radius has a greater effect on the IE than the fact that there are more protons as we go down any group. The same trend is visible with the Alkali Metals lithium, sodium and potassium (See table below)

Alkali metal	Li	Na	K
Ionisation energy (kJ mol^{-1})	520	496	419

The lower the IE value for a metal, the more easily it can donate its electrons and hence the more reactive it is. Caesium is therefore the most reactive metal in Group 1. Non-metals, such as fluorine react differently by **accepting** electrons from a metal and hence the greater their IE, the more likely they are to react with a donor atom. And so fluorine is the most reactive element of the halogens in Group 17.

Metallic Character

Characteristics of metals are that they are shiny, good conductors, malleable and ductile. These properties are all due to the fact that the IEs of metals are low. At room temperature, there is enough heat energy to ionise their valency electrons and so valence electrons are "floating around" and not attached to the nucleus, or Delocalised. This non-directional attraction to the metal nuclei gives rise to Metallic Bonding, where the electron cloud is attracted inwards and can be distorted without breaking the bonds. It is the free electrons that make metals good conductors and easy to bend without snapping.

In general, the metals in the Periodic Table occur on the left side and non-metals on the right, with the exception of hydrogen. However, as the period number increases downwards the IEs become smaller and elements become more metallic in character due to their freer electrons. A non-metal group like Group 14 has 4 electrons in the valence shell and a fairly high attraction for electrons, so the upper elements have non-metallic properties - like being non-shiny and brittle. As we go down the group however, the IE becomes lower and outer electrons become more able to be released, as with metals. As we pass from carbon to silicon this element takes on some metallic properties and is classified as a metalloid. Metalloids are brittle but shiny and do conduct a small amount of electricity. Below silicon in Group 14 is Germanium which has metallic properties and below that is lead which is definitely a metal.

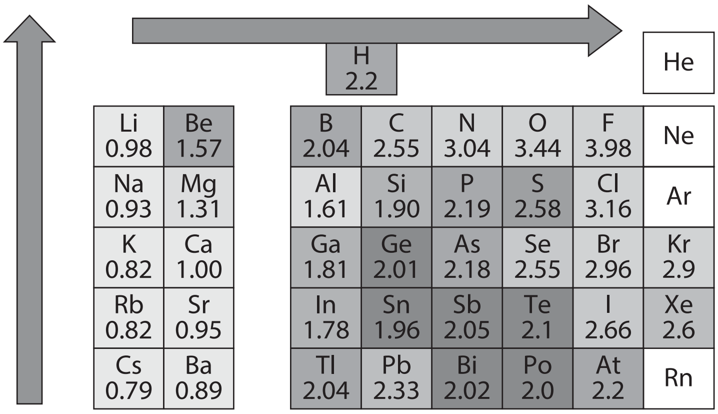
Valency Trend

The valency of an element in a compound is determined from the number of bonds it can form. Group 1 elements always give away a single electron to form an ionic bond and therefore have a valency of 1. The Octet Rule states that elements will always form bonds to allow each of them to have a full shell – either by donating or sharing electrons. Group 1 always donates 1 electron to achieve zero electrons in the outer shell but has a full shell below it. Group 2 always forms 2 bonds and Group 13, with 3 valence electrons always forms 3 bonds and so has a valency of 3. The trend, therefore, going across a period, is for the valency and Bonding Capacity, to increase up to Group 14 and then to decrease due to elements accepting rather than donating electrons. For instance, nitrogen has 5 electrons in the outer shell, but it will accept 3 electrons to establish a full shell of 8. Thus nitrogen has a valency of 3, not 5. Oxygen, with 6 electrons in the valence shell, usually gains 2 to reach 8 and has a valency of 2. Fluorine would usually have a valency of 1.

Electronegativity Trend

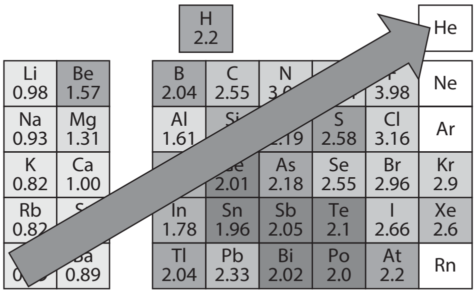
The electronegativity of an element is a measure of its <u>attraction</u> to electrons. Obviously this will be directly linked to its ionisation energy, as the harder it is to extract an electron the higher must be the ability to pull electrons towards the nucleus because of its core charge.

Below are some electronegativity values for the 3rd shell (arrows show increase):



			H 2.2				He
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 2.9
Rb 0.82	Sr 0.95	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
Cs 0.79	Ba 0.89	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn

Note overall trend



We can see that the electronegativity rises across the period but that noble gases have a zero value – no attraction at all for electrons - hence their ability to react is zero.

Another trend shows electronegativity decreasing down any group.

It can be seen that, going down any group, the trend is that the attraction for electrons decreases due to the larger distances of the outer shells from the nucleus. If there is a difference in electronegativities with any two elements bonding together, then the bond becomes a Polar bond where the electrons are pulled closer to one of the elements than the other. The only time a bond would not be polar is if the two atoms joining are of the same element, e.g. O_2, Cl_2.

An electronegativity difference results in the element with the higher electronegativity gaining a slight negative charge. E.g. in a sulfur-chlorine bond the chlorine pulls the electrons in the covalent bond closer towards it.

Electrons not shared equally like this S $\overset{\times}{\cdot}$ Cl but like this: $\overset{\delta+}{S}\ \overset{\times}{\cdot}\ Cl^{\delta-}$

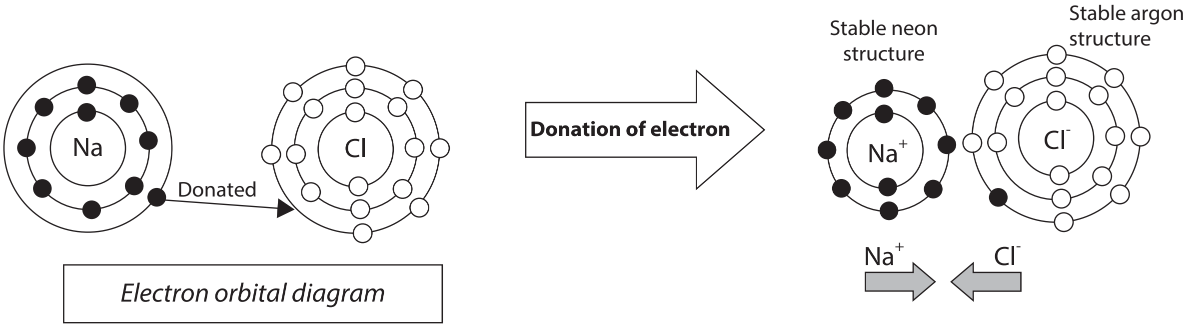
The S-Cl bond thus will be polar, with the chlorine atom being the more negative.

2.16 IONIC COMPOUNDS

A compound consists of several atoms or ions joined together with bonds. The reason that ions or atoms do join together is because, by doing so they produce a lower energy state. i.e. if sodium loses and electron to, say, chlorine we have seen that both elements can then achieve a full shell, which is lowest in energy. All systems in the Universe tend to lose energy and move to a state of lowest energy. E.g a ball on a hill will roll down spontaneously to end up at the bottom and thereby lose potential energy.

With sodium, it will always tend to lose an electron it its reactions to become a sodium ion Na^+ which has a full shell configuration 2, 8. Chlorine, likewise will always tend to gain an electron to become a Cl^- ion with a full shell configuration 2, 8, 8.

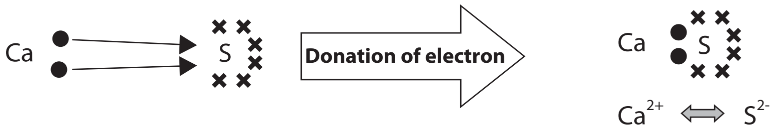
Hence sodium will react spontaneously with chlorine to form sodium chloride NaCl. The positive sodium ion is attracted to the negative chloride ion.



This kind of bonding between a metal and a non-metal is called **Ionic Bonding.**

More than one electron needs to be donated in some cases and we can show this by an electron dot diagram below:

The formation of calcium sulfide occurs between a Group 2 metal and a Group 16 non-metal shown as Electron-Dot Diagrams.



Calcium has 2 electrons in its valence shell which it donates to the valence shell of the sulfur. Both atoms now have a full shell and have achieved stability. The calcium 2+ ion as held by strong electrostatic attraction to the sulfur 2- ion.

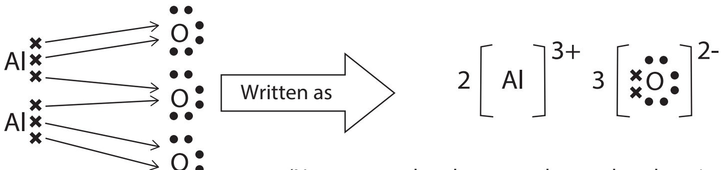
Example

Give the formula and electron dot diagram for the compound aluminium oxide.

Answer

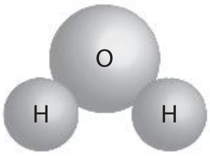
Aluminium has 3 electrons in its valence shell and oxygen has 2 electrons. 2 aluminium atoms can donate 6 electrons and 3 oxygen atoms can receive these 6 electrons, so the formula of the compound will be Al_2O_3.

The Electron-dot Diagram is shown on the right.

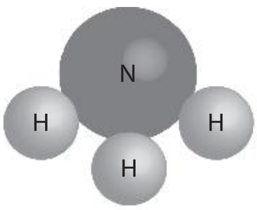


(Note: square brackets must be used to show ions)

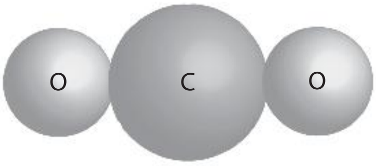
2.17 COVALENT COMPOUNDS



H_2O



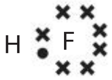
NH_3



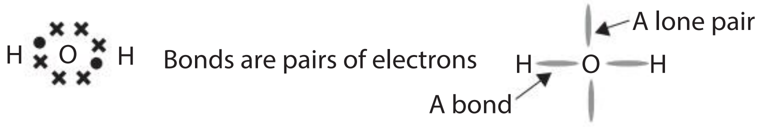
CO_2

Covalent bonds occur between 2 non-metals because they both need to accept electrons in order to achieve stability. They compromise by sharing of electrons in a covalent bond so each can achieve a noble gas configuration. For example, non-metals always donate electrons and the gas HF contains two non-metals hydrogen and fluorine. Hydrogen needs to gain 1 electron to achieve a full 1st shell and fluorine needs to gain an electron to achieve a full 2nd shell. Hence a pair of electrons is shared between them to make a Covalent Bond – hydrogen now has 2 electrons and fluorine has 8 but there are no ions present.

Electron-dot Diagram:

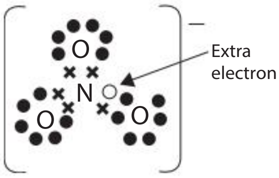


With water, two hydrogen atoms covalently bond with one oxygen atom, so the Electron-dot Diagram is:



We can see that, with the water molecule, two of the bonds are not attached to another atom. These are called "lone pairs" or "non-bonding pairs" and affect the shape of the molecule (see later).

A covalent co-ordinate or Dative bond is formed when one element donates both of the electrons in a covalent bond. An example of this is the nitrate ion, which has 1 electron extra. The left and top bonds shown here are both co-ordinate bonds.



Example

a) Show the electron-dot diagram for ammonia

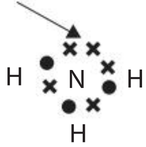
b) State how many valence electrons are present

c) Indicate any lone pairs.

Answer

a) b) 8 valence electrons are present

c) Lone pair



Set 1 Questions

Multiple-choice

1. Which one of the following is a compound?

   (A) Co (B) CO (C) Cl (D) Cf

2. Any element is a substance which consists of:

   (A) Atoms with the same number of neutrons

   (B) Atoms having the same number of protons.

   (C) Atoms, all of which have the mass number

   (D) An aggregate of single atoms only with no molecules.

3. C-12 and C-14 are regarded as isotopes of the same element because

   (A) their atoms have similar physical properties

   (B) their atoms have the same mass number.

   (C) their atoms have six protons in their nuclei

   (D) they are both in Period 1.

(Questions 4 and 5 refer to the table below)

This table shows the number of protons, neutrons and electrons present in each of five atomic nuclei.

Atom	Electrons	Protons	Neutrons
A	6	6	8
B	8	5	7
C	7	7	7
D	9	8	8
E	8	8	10

4. Which two are isotopes of the same element?

   (A) D and E (B) B and C (C) C and D (D) A and D

5. The correct chemical symbol for C would be:

   (A) $^{13}_{7}C$ (B) $^{14}_{7}C$ (C) $^{13}_{6}C$ (D) $^{13}_{8}C$

6. An element has an atomic number of 33. The element is located in

   (A) Group 13, Period 3 (B) Group 14, Period 5

   (C) Group 15, Period 4 (D) neither A, B or C

7. The ion X^{3-} is from an element X. This element can be located in

(A) Group 3 (B) Group 5 (C) Group 15 (D) Group 16

8. The formula of a compound containing As^{3+} ion and S^{2-} ion is

(A) AsS (B) As_2S_3 (C) As_3S_2 (D) As_2S_2

9. An example of the same two elements combining in different ratios to form two different compounds is

(A) Fe_2O_3, $FeCl_2$ (B) AgCl, NaCl (C) P_2O_5, PCl_5 (D) CO_2, CO

10. How many protons and neutrons, respectively, are contained in the nucleus of plutonium-244?

(A) 94, 150 (B) 150, 94 (C) 94, 94 (D) 244, 244

11. The charges on an electron, proton and a neutron are respectively:

(A) -, +, 0 (B) +, -, + (C) -, 0, + (D) 0, -, +

12. A compound containing twice as many potassium atoms as chromium atoms, and four times as many oxygen atoms as chromium atoms is

(A) $K_2Cr_2O_7$ (B) $K_2Cr_3O_4$ (C) KCrO (D) K_2CrO_4

13. The symbols for tungsten, arsenic, mercury and antimony are respectively:

(A) Sb, Hg, As and W. (B) As, Hg, Au and Ag

(C) W, As, Hg and Sb (D) T, Ar, Me and An

14. Which of the following elements would have similar chemical properties?

(i) K (ii) B (iii) Cs (iv) Te (v) I (vi) Li

(A) (i), (iii), (vi) (B) (ii), (iv), (v) (C) (i), (iii), (iv) (D) (iii), (v), (vi)

15. Which of the following statements is true?

(A) All p-block elements have similar chemical properties

(B) All Group 4 elements have similar physical and chemical properties

(C) $^{114}_{49}In$ and $^{114}_{50}In$ are isotopes with similar chemical but different physical properties.

(D) All elements with 3 valence electrons have the similar chemical, but different physical properties.

16. Which of the following statements is false?

(A) Iodine has a larger radius than chlorine.

(B) Iodine has a higher melting point than chlorine.

(C) Iodine has more valence electrons than chlorine.

(D) Iodine has electrons in the d sub-shell but chlorine has none.

17. Naturally occurring bromine contains both ^{79}Br and ^{81}Br isotopes so that the average molar mass of an atom of bromine is 79.9. The ratio of ^{79}Br atoms to ^{81}Br atoms in naturally occurring bromine would be, respectively, about:

(A) 11 : 9 (B) 6 : 5 (C) 12 : 11 (D) 11 : 13

18. The electron configuration of an element X is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $5s^2$ and its nucleus contains 11 more neutrons than protons. The atomic number of X is:

(A) 87 (B) 38. (C) 49 (D) 76

19. The number of protons plus neutrons in a carbonate ion (CO_3^{2-}) is:

(A) 62 (B) 60 (C) 50 (D) 24

20. An element has an atomic number of 37. It have similar chemical and physical properties to another element with an atomic number of:

(A) 11 (B) 13 (C) 38 (D) 54

21. The electron-dot diagram of the carbon disulphide molecule has:

(A) 4 bonding electrons and 4 non-bonding electrons

(B) 4 bonding electrons and 4 lone pairs

(C) 4 pairs of bonding electrons and 4 non-bonding electrons

(D) 4 pairs of bonding electrons and 4 lone pairs

22. Select the correct statement regarding the Caesium ion, Cs^+ and the xenon atom, Xe:

(A) They are isotopes

(B) They have the same number of protons

(C) They have the same number of electrons

(D) Xe has a different number of neutrons to the caesium ion.

23. An ionic bond would most likely be formed between the following species:

(A) Na and Ne

(B) A period 1 element and a group 7 element

(C) Elements with configurations $1s^22s^2$ and $1s^22s^22p^4$

(D) An element in period 1 and an element in group 1

24. A metallic element M forms an oxide with formula M_2O_3. The formula for its chloride would be:

(A) M_3Cl (B) MCl_3 (C) M_3Cl_2 (D) MCl

25. Which statement is true?

(A) The atomic radius in period 3 increases from Na to Cl

(B) The melting points of elements in Group 1 increases from Li to Cs

(C) The boiling points of the Alkali metals increases down the group

(D) The melting points of the chlorides of Group 4 elements increases down the group.

Longer questions

26. Fill in the entire table below with any missing numbers or symbols relating to the 5 atoms shown in the top row.

Symbol	Mg-25	$^{26}_{12}Mg$	$_{17}Cl^-$	Cd	S^{2-}	$_{29}Cu^+$
Protons						
Neutrons			18	64	16	35
Electrons						
Atomic No.						
Mass No.				48		
Net charge	0					
Symbol	W-184	$^{27}_{59}Co^{2+}$	Pb^{4+}	As^{3-}	Xe	$^{238}U^{5+}$
Protons						92
Neutrons				42	78	
Electrons			78			
Atomic No.					54	
Mass No.			207			
Net charge	0					5+

27. In the table above identify:

(a) A halogen ________

(b) 4 Transition metals ________

(c) Two isotopes ________

(d) 3 metals that are not from the Transition series. ________

(e) A member of the Alkaline Earth group ________

(f) 2 elements that are gases ________

28. Write the atomic symbol for each of the isotopes described below as with ${}^{A}_{z}X$

(a) Z = 8, neutron number = 9 ________

(b) An isotope of chlorine in which A = 37 __________

(c) Z = 28; A = 60 _________

(d) Proton number = 26, neutron number = 31 __________

(e) An isotope of iodine with 78 neutrons __________

(f) Z = 3 and the number of neutrons = 4 __________

29. How many protons, neutrons and electrons are contained in each of these atoms? What period and group are they in?

(a) $^{25}_{12}\mathrm{Mg}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

(b) $^{118}_{50}\mathrm{Sn}^{4+}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

(c) $^{81}_{35}\mathrm{Br}^{-}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

(d) $^{133}_{55}\mathrm{Cs}^{+}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

(e) $^{79}_{34}\mathrm{Se}^{2-}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

(f) $^{56}_{25}\mathrm{Mn}^{7+}$ n(p) = ____ n(n) = ____ n(e) = ____ Period = ____ Group = _____

30. How many protons, electrons and neutrons in the following isotopic elements/ ions?

Br-80 e^- number = ____ p^+ number = ____ n number = ____

S^{2-} -32 e^- number = ____ p^+ number = ____ n number = ____

Ba-137 e^- number = ____ p^+ number = ____ n number = ____

K^+-39 e^- number = ____ p^+ number = ____ n number = ____

31. Thallium has two stable isotopes, Tl-203 and Tl-205. If 204.38 is the average atomic weight of thallium, which isotope has higher abundance?

____

32. Rubidium is an element in Group 1 of the Periodic Table with two main isotopes and abundances:

Rb-85 (72.2%) and Rb-87 (27.8%)

a) (i) Predict what the formula would be for a compound produced when rubidium reacts with selenium from the position of these two elements in the Periodic Table.

____

(ii) Calculate the Weighted Average for the Standard Atomic Weight for rubidium/

____

____

(iii) What similarities and differences would you expect for the atomic structure, chemical and physical properties of Rb-85 and Rb-87?

____

____

b) (i) Nickel has 3 main isotopes Ni-58, Ni-60 and Ni-62 with abundances of 69%, 27% and 4% respectively. Calculate a values of the Weighted Average for the atomic mass of nickel.

____

____

____

(ii) Give the numbers of electrons in each period (shell) for nickel

1st ____, 2nd ____, 3rd ____, 4th ____

(iii) Write the numbers of electrons in sub-shells for nickel in s, p, d notation: $1s^2$, $2p^5$, $3d^1$, etc.

____

c) The scientist who discovered the element cerium originally calculated its weighted average for its atomic weight to be 139.8. He had originally discovered an isotope A with an abundance of 88.5% and another B with an abundance of 11.5%. He found that isotope A had a mass number of 140 and realised from these data that he would be able to calculate the mass number of isotope B. Assuming only two isotopes of cerium existed, what was the value he would have found for B?

____

____

____

____

33. What is the total number of electrons are contained in each of the following ions?

(a) Fe^{2+} __________ (b) Ca^{2+} __________

(c) Co^{2+} __________ (d) I^- __________

(e) S^{2-} __________ (f) Cl^- __________

(g) Cr^{3+} __________ (h) K^+ __________

34. Give the electron configurations for each of the ions above (e.g. 2, 8, 4 system)

(a) Fe^{2+} __________ (b) Ca^{2+} __________

(c) Co^{2+} __________ (d) I^- __________

(e) S^{2-} __________ (f) Cl^- __________

(g) Cr^{3+} __________ (h) K^+ __________

35. On the basis of its location (group) in the Periodic Table, what simple ions are each of the following elements likely to form?

(a) Tl __________
(b) Se __________
(c) Ba __________
(d) As ___________
(e) Fr __________
(f) Cs ___________

36. For the following ions or atoms, write the formulae of the simplest compound each can form.

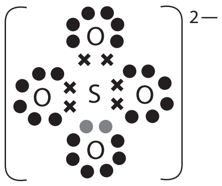
(a) Ca^{2+} and O^{2-} _________
(b) Na and H __________
(c) Al^{3+} and Cl^{-} _________
(d) Mg and S __________
(e) Ca^{2+} and C^{4-} _________
(f) Zn and N __________

37. a) Use an electron-dot diagram to explain why oxygen exists as the molecule O_2.

b) What is meant by the term "non-bonding" or Lone Pair of electrons? Use the diagram from part a) to label a lone pair.

c) Using an electron-dot diagram, show the bonding arrangement for the compound Cl_2O

(d) Illustrate what is meant by a co-ordinate covalent bond, using the sulfate ion electron-dot diagram as an example.



38. What was the basic difference between the Thompson Model of the atom and the Bohr Model of the atom?

____

____

____

39. In a thousand measurements of the charge present on oil drops that were charged by irradiation a scientist in the early 1900s found the following distribution percentages.

Charge found (x 10^{-19} C)	1.6	3.2	4.8	6.4	8.0	9.6	11.2	12.8
Percentage of total drops	2.3%	1.9%	2.2%	2.5%	1.8%	2.0%	2.4%	2.0%

a) Why were no drops found with a charge lower than 1.6 x 10^{-19} coulombs?

____

____

b) What conclusions can be drawn about the fundamental charge on an electron?

____

____

40. Are the energy levels that electrons can occupy in an atom equally spaced from lowest to highest?

What evidence for spacing is there?

____

____

41. Schrodinger proposed that an electron revolving round the nucleus had wave-like properties so its actual position could only be de determined by a probability equation and this led to “Fuzzy” orbitals.

The calculated radius of a hydrogen atom is 52 picometres ± 5%.

Calculate the maximum and minimum radius of a hydrogen atom expressed in scientific notation.

____

____

42. The electrostatic repulsion of two protons very close together in an atom of helium is incredibly high as they are so close together as force is inversely proportional to their distance apart squared.

How is it then, that the helium atom can exist with 2 protons in its nucleus?

____

____

43. 1 atomic mass unit (1 amu) is 1.667 x 10^{-24} grams.

a) Calculate the mass of a lithium-7 atom if mass of a proton is 1.00728 amu and the mass of a neutron is 1.00867 amu (assume the mass of an electron is very small by comparison)

____

____

b) Calculate how many lithium atoms there are in 1 gram of lithium.

____

44. The abundances of magnesium isotopes are: Mg-24 = 79%, Mg-25 = 10%, Mg-26 = 11%, A student uses 10.0 g of magnesium metal for an experiment where it reacts with acid.

How many atoms of magnesium-26 would there be in the sample?

____

____

45. A metal ion is injected into the chamber of a mass spectrometer in order to find its mass and then identify the element. The velocity of all singly-charged ions injected into the magnetic field is set at 2.63×10^4 m s^{-1}, with the field strength (B) set to 0.080 tesla.

a) If the radius of the circular path that this ion moves in is 23.6 cm, calculate the mass of the ion from the formula $r = \frac{mv}{Bq}$

____

____

b) If 1 amu is 1.66×10^{-24} grams, determine what the element was from its atomic mass.

____

____

46. Give the electron sub-shell configuration (s, p, d) of the elements below.

(E.g. Silicon z = 14 is $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$.) Fill in the numbers that go above the letters.

Mg is: $1s^?$ ___ $2s^?$ ___ $2p^?$ ___ $3s^?$ ___ $3p^?$ ___

N is: $1s^?$ ___ $2s^?$ ___ $2p^?$ ___ $3s^?$ ___ $3p^?$ ___

Ar is: $1s^?$ ___ $2s^?$ ___ $2p^?$ ___ $3s^?$ ___ $3p^?$ ___

47. Which of the following are ionic compounds? (Circle answer)

HCl K PCl_3 CaF_2 H_2

48. Name the noble gas whose structure these ions possess.

Cs^+ ____ Cl^- ____ Al^{3+} ____ P^{3-} ____ Ca^{2+} ____ O^{2-} ____

49. Some of the elements in the list above combine to form compounds. Write the formula for each compound formed with the elements shown (e.g. Mg combines with N to form Mg_3N_2).

Ca and Cl combine to form ______, Al and O combine to form ________,

Cs and P combine to form _______.

Set 2 Questions

1. (a) What is the Quantum theory of light?

   (b) Why is it that ultraviolet light is dangerous to the skin but red light is not? Explain.

   (c) How are the colours produced in a flame test?

   (d) Why is it that distinct coloured lines are given out by an excited atom, rather than the production of a continuum of wavelengths, as with a rainbow?

   (e) Why do potassium compounds produce a lilac colour in a flame test and yet lithium, which is in the same group, gives off a red colour? Which wavelength light of the two has larger "packets" of energy? Explain.

2. (a) White light is passed through a solution of strawberry cordial. What colours would be absorbed by this solution (assume white light is made up of red, blue and green).

   (b) Why does copper ore that has been vaporised in a flame absorb blue light?

   (c) It was suspected that a dead person discovered in room had been poisoned with arsenic by his partner, so the Police used a sample of his hair in an atomic absorption Spectrometer and noted the spectrum produced. Explain how the Police would be able to tell from this absorption spectrum that the dead person had arsenic in his body?

3. (a) What is the maximum number of electrons that the 2nd shell of an atom can accommodate?

   ____

   (b) Give the electron configuration of the elements phosphorus, oxygen and magnesium (e.g. 2, 4, etc).

   P __________ O ___________ Mg ____________

   (c) How many valence electrons do the following elements have?

   F __________ Ca _________ Si _________ Cl ___________

   (d) What are the valencies of these elements?

   F _______ Ca _________ Si _________ Cl ___________

4. (a) Which has the larger atomic radius in the following pairs? (Circle the answer)

   C N F Cl Ca Be P Si

   (b) How many sodium atoms could be fitted into a gap 1 mm wide side by side?

   ____

5. (a) Which of the following would react more vigorously with water: Lithium or Sodium?

   Explain.

   ____

   ____

   (b) Explain why fluorine has a higher ionisation energy that nitrogen.

   ____

   ____

   (c) Which has the higher ionisation energy out of the following (circle correct answer)

   N P Se Kr Ga Al Ar Ne

   (d) Why was it so difficult to produce compounds of the Noble gases?

   ____

   ____

   (e) Why was it that xenon was the first noble gas with which compounds could be formed?

   ____

   ____

6. (a) Boron and aluminium are in the same group, and yet boron is classified as a non-metal and aluminium as a metal from their properties. Explain this difference in classification.

   ____

   ____

(b) What is it about the atomic structure of boron that makes it a poor conductor?

____

____

(c) Looking at Group 15, why is it that antimony (Sb) is malleable and yet arsenic (As) is brittle if they are in the same group?

____

____

7. (a) In the following bonds between elements shown below, draw a delta negative sign (δ -) on the most electronegative element in the bond.

H--- Cl N--- Br F---Cl C---O

(b) In the example above the HCl molecule will have one end negative and the other end positive. How would another HCl molecule close to it behave? i.e. what would happen?

____

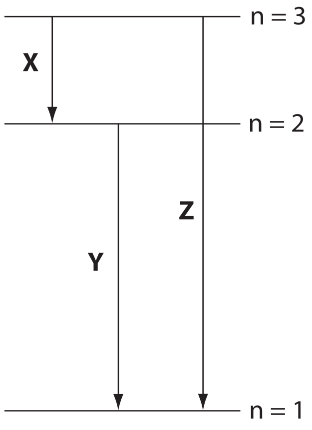
____

(c) What effect would you expect the situation in b) with HCl have on its boiling point compared with a non-polar substance?

____

____

8. (a) The energy level diagram shown indicates possible energy jumps from the n = 3 level of an atom of element S.



Which of the jumps X, Y or Z would produce light with the longest wavelength? __________

(b) One line in the metal's spectrum is blue, another yellow and another green. Show which of the jumps could give each of these lines (write X, Y or Z in the spaces below.

Blue _____ Yellow ______ Green ______

(c) When element S is heated in a flame an absorption spectrum is seen like a rainbow, but with some colours missing. What colours would be missing?

____

9. (a) Explain what a spectrophotometer is used for and how it works.

____

____

____

(b) Suppose you wanted to find the percentage of copper in a farm's water supply. How could you do this using a spectrophotometer?

____

____

____

10. (a) The following results of Absorbance were obtained in a photometer by making up solutions of a red food colouring with different concentrations. Fill in the bottom row by finding the log of the absorption.

Concentration c (mmol L^{-1})	0.8	0.7	0.6	0.5	0.4	0.2	0.0
Absorbance A (%)	100	50	32	23	8	5	0
Log A							

(b) Plot a graph of Log A (up) against concentration c (along), using an Excel spreadsheet and click to let the program draw in the line of best fit and display the equation of the graph.

Write down the gradient of the graph here ___________.

(c) A sample of cordial containing the red food colouring gives a reading of 16.2% absorbance.

Find the concentration of the colouring component from your graph.

Concentration = _____________ mmol L^{-1}.

Notes

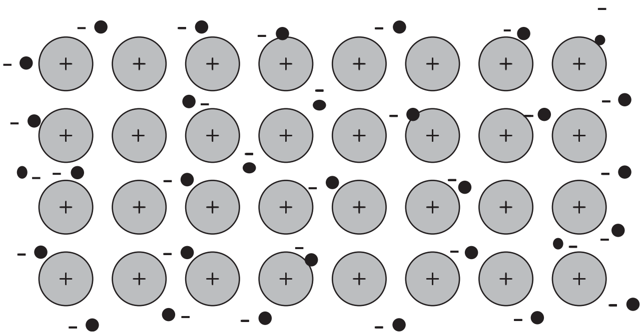
Chapter

3

Types of Bonding

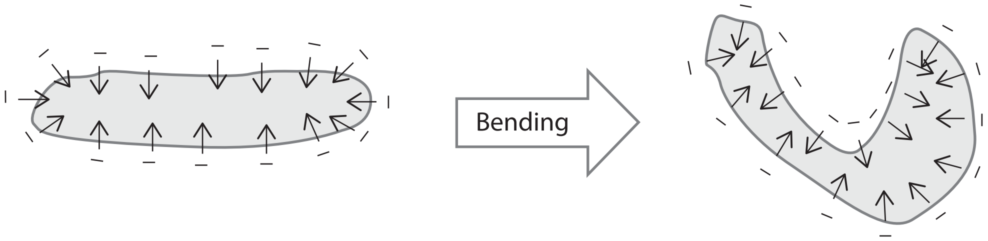
3.1 METALLIC BONDING

Due to the low ionisation energy of metals, at room temperature there is sufficient heat energy available to completely ionise all the valency electrons of metals. Consequently these electrons become "delocalised", which means that they drift around not attached to any particular nucleus. Hence valence electrons can move throughout the lattice of positive metal ions.



This availability of free electrons means that all metals will be good conductors of heat and electricity.

The attractive force between the lattice of positive ions and the electron cloud in metals gives rise to a strong force that hold the metal particles together. Strong metallic bonding accounts for the high melting and boiling points of metals and also their other physical properties, such as hardness, ductility and malleability.



As the attractive force of the electrons towards the positive is non-directional and always inwards, however you stress a metal it will not break apart. Metallic bonding pulls the particles together very strongly and explains why metals are strong and dense (large mass for their size). The movement of the delocalised electrons accounts for metals having lustre (shiny or glossy)

Metals can also be drawn out into wires without breakage. This property is called Ductility – all metals are ductile.

When metals are cooled to a very low temperature their resistance goes down as the particles vibrate less and some metals turn into superconductors. A superconducting metal has no resistance at all - which is the case with mercury when it reaches a temperature of -269°C.

Metal Uses

Metals with different properties are used in different applications depending on these properties. For instance, most metals can be cast in moulds or forged, as with iron cannons, armour and wheels and can be beaten out into flat sheets, as with swords and horseshoes. The low resistance of some metals makes them ideal for electrical cables, especially with copper wires or gold-plated electrical connectors in computers. The high strength and low density makes aluminium ideal for aircraft fuselages and makes titanium perfect for high tension anchors, tooth implants and for engine parts. Tungsten has a melting point of 3410°C and is used in spotlight filaments at high operating temperatures, whereas mercury is a liquid and is a good heat conductor which makes it useful in thermometers. Transition metals are found in the middle of the Periodic table in the d-block and are generally hard with high melting point and tensile strength, due to their small atomic size and large nuclear charge. Their compounds tend to be coloured and hence have been used for thousands of years to make paint pigments, such as ochre and cobalt blue. The colour in many gemstones is due to small quantities of the oxides of transition metal, such as iron or titanium. Some Transition metals are useful for plating steel due to their ability to withstand corrosion e.g. chromium, nickel, gold and silver. This property has made some of these useful in jewellery, rings and necklaces over the ages. The lustre of metal surfaces has made them ideal for use as mirrors from prehistoric times and good heat transfer makes copper, aluminium and iron useful metals for producing cooking pots and pans.

Below is a table of some properties of some common metals for comparison of melting points (MP), electrical conductivity (C_E), heat conductivity (C_H) and density (D) – the later 3 of these are shown as a comparison with the value for copper.

Table 1

Element	MP (°C)	C_E	C_H	D
Copper	1083	100%	100%	100%
Sodium	98	36%	35%	11%
Titanium	1668	4%	5%	50%
Iron	1540	17%	20%	81%
Lead	327	8%	9%	49%
Mercury	-39	2%	2%	150%
Tungsten	3410	33%	46%	215%
Aluminium	1220	59%	53%	30%

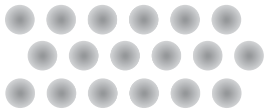
Tensile strength values are show for different common metals and non-metals for comparison:

Table 2

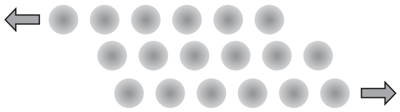
Material	Tensile strength (MPa)
Mild steel	841
Stainless steel 420	1440
Titanium	950
Carbon fibre	6370
Graphene	130,000

Metal Alloys

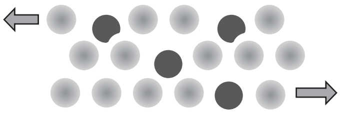
Alloys have been mentioned before for their superior properties over a single base metal but they are more than just a mixture of two or more metals. One metal is actually dissolved in another to produce a metallic "solution". Metal atoms arrange themselves in a solid into a crystal lattice which makes them difficult to pull apart but if stretched one layer of atoms can slide over the one below. With an Interstitial Alloy smaller atoms another metal become lodged into the matrix making it more difficult for the layers to slide and making the alloy stronger than the base metal overall. This is why steel is far stronger than the base metal, iron. Steel has a small amount of carbon in its crystal lattice.



Iron crystal lattice



Shear force slippage



“Jamming” by carbon atoms

Some useful alloys

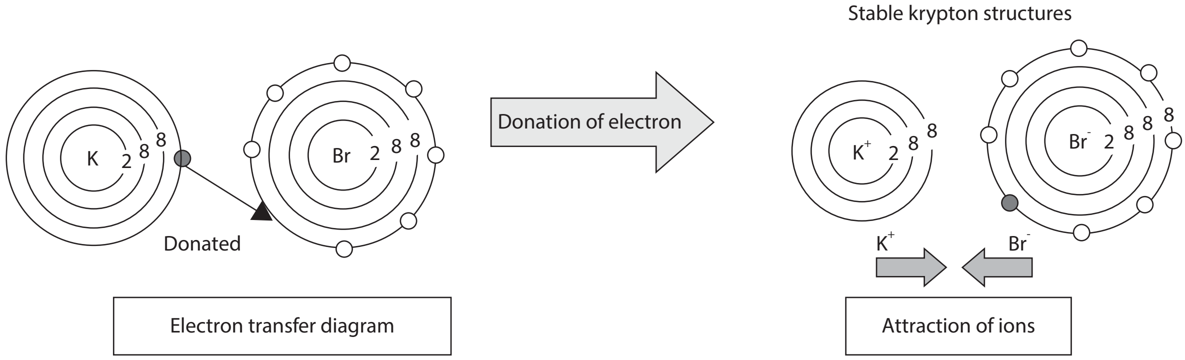
Alloy	Composite metals	Uses
White gold	Au, Pb, Ag, Cu	Jewellery
Pewter	Sn, Cu, Pb	Mugs, ornaments
Alnico	Al, Ni, Co	Speaker magnets
Brass	Cu Zn	Taps, locks, ship fittings
Amalgam	Hg, Ag, Cu, Sn	Dental fillings
Stainless steel	Fe, Cr, Ni, Mn, Mo	Cutlery, tools, jewellery
Nichrome	Ni, Cr	Heating elements
Gunmetal	Cu, Sn, Zn, P	Guns, ornaments

3.2 IONIC BONDING

Ionic bonding takes place between a metal and a non-metal so that a stable electron configuration can be produced for both elements, as mentioned in Chapter 2.

Electrons will always move from an element with a low ionisation energy (IE) to another with higher IE (e.g. Potassium and Bromine)

Here IE for K = 419 kJ mol^{-1}, IE for Br = 1140 kJ mol^{-1} hence about 721 kJ mol^{-1} of energy can be released by the reaction and if energy is released, then a lower energy state will be achieved. If a potassium atom donates a single electron to a bromine atom both atoms then become ions and achieve a stable noble gas structure of lower energy. K^+ is now called a Cation and Br^- is called an Anion.



Electron transfer diagram

Attraction of ions

Deriving a formula

In the example above the potassium needs to lose one electron and the bromine needs to gain one to achieve a stable noble gas structure – so the formula for the compound formed links one K with one Br to form KBr.

Group 2 metals need to lose 2 electrons and Group 16 need to gain 2 so the formula for magnesium oxide, for instance would be MgO, but the formula for magnesium bromide would be $MgBr_2$, as 2 bromine atoms are needed for the 2 magnesium electrons to transfer to.

Aluminium is in Group 13 and has 3 electrons to lose to achieve stability, so its bromide would have the formula $AlBr_3$ and its oxide would be Al_2O_3 where the electrons transferred from 2 aluminium atoms is 2 x 3 = 6 and the electrons accepted by 3 oxygen atoms is 3 x 2 = 6, so there are no electrons in excess.

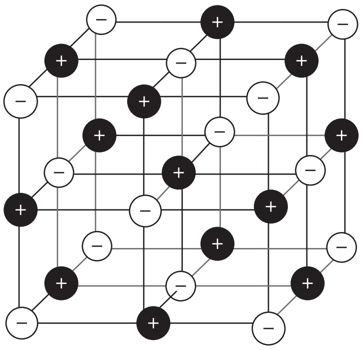
In the table below are shown some common ionic formations found in nature with the charges they normally possess. Note that one of the characteristics of Transition metals is that they can exhibit several different valencies. For instance, iron can be Fe^{2+} or Fe^{3+}.

Valencies of some common Anions and Cations

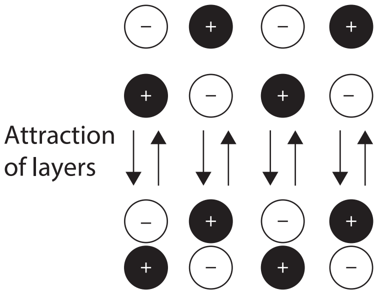
Cations +1		+2		+3		+4	
Lithium	Li^+	Magnesium	Mg^{2+}	Aluminium	Al^{3+}	Tin (IV)	Sn^{4+}
Sodium	Na^+	Calcium	Ca^{2+}	Chromium	Cr^{3+}	Lead (IV)	Pb^{4+}
Potassium	K^+	Barium	Ba^{2+}	Iron (III)	Fe^{3+}		
Caesium	Cs^+	Iron (II)	Fe^{2+}				
Silver	Ag^+	Nickel	Ni^{2+}				
Copper (I)	Cu^+	Copper (II)	Cu^{2+}				
Ammonium	NH_4^+	Zinc	Zn^{2+}				
		Tin (II)	Sn^{2+}				
		Lead (II)	Pb^{2+}				
		Manganese (II)	Mn^{2+}				
		Strontium	Sr^{2+}				
Anions -1		**-2**		**-3**			
Hydride	H^-	Oxide	O^{2-}	Nitride	N^{3-}		
Fluoride	F^-	Sulfide	S^{2-}	Phosphide	P^{3-}		
Chloride	Cl^-	Sulfate	SO_4^{2-}	Phosphate	PO_4^{3-}		
Bromide	Br^-	Carbonate	CO_3^{2-}				
Iodide	I^-	Sulfite	SO_3^{2-}				
Hydroxide	OH^-	Dichromate	$Cr_2O_7^{2-}$				
Nitrate	NO_3^-	Chromate	CrO_4^{2-}				
Hydrogen carbonate	HCO_3^{2-}	Thiosulfate	$S_2O_3^{2-}$				
Hydrogen sulfite	HSO_3^-	Hydrogen phosphate	HPO_4^{2-}				
Nitrite	NO_2^-						
Permanganate	MnO_4^-						
Hypochlorite	OCl^-						
Cyanide	CN^-						

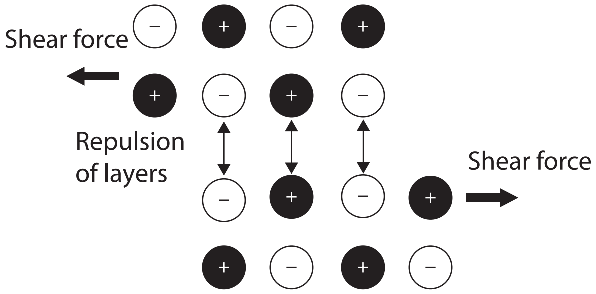
In a crystalline structure formed with ionic compounds positive and negative ions form a 3-D crystal lattice of alternative + and - ions held together by electrostatic attraction, which is very strong.

Due to the strong attractive forces, substances with ionic lattices have a high melting point and boiling point because a large amount of heat energy is required to separate the ions against the strong electrostatic attraction.



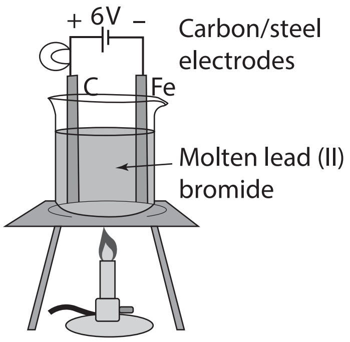
Ionic lattices are brittle (easily shattered) due to repulsion of adjacent layers when they slip under shear forces which cause layers to be pulled out of place so that a positive ion is now above another and a negative above another negative and hence repulsion occurs.





If ionic compounds are melted then the ionic bonds are broken and the ions are now free to move. These mobile ions are now available for conduction in a circuit with a battery. The + cations will move through the liquid to the cathode (negative plate) and the anions will move to the positive plate. Note that liquids do not conduct using electrons – only by ionic movement and transfer of charge.

In the solid form Ionic substances cannot conduct because the ions are locked into position in the lattice.



Electrolysis is a way of obtaining elements from ionic compounds. Here we see the apparatus for electrolysing a molten salt using inert electrodes connected to a battery.

Lead bromide liquid would contain lead ions (Pb^{2+}) and bromide ions (Br^-). The lead cations would be attracted to the negative electrode (carbon) and the bromide anions would be attracted to the positive electrode (iron). Hence, after electrolysis there would be lead metal coating the negative electrode (cathode) and bromine liquid around the positive electrode (anode).

Summary of properties for ionic materials:

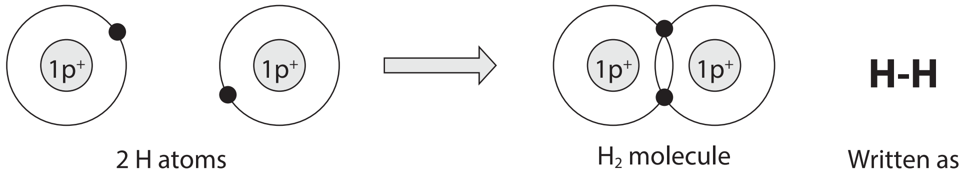
Crystalline, Hard, Brittle, High melting and boiling points, Non-conductive in the solid form but conductive as a molten liquid or solution, Soluble in water to some extent.

Some Ionic compounds and their uses

Compound	Soluble in water	Conductivity	Use
Sodium fluoride	Yes	Molten/aqueous	Toothpaste
Sodium hydroxide	Yes	Molten/aqueous	Oven cleaner
Ammonium nitrate	Yes	Molten/aqueous	Fertilizer
Copper sulfate	Yes	Molten/aqueous	Fungal fruit spray
Sodium chloride	Yes	Molten/aqueous	Common food salt
Magnesium oxide	No	Molten only	Electrical insulator
Zinc oxide	No	Molten only	Sun block
Calcium carbonate	No	Molten only	Limestone/chalk

3.3 COVALENT BONDING

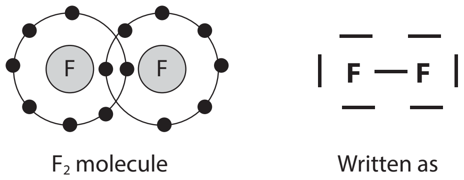
When two non-metals form compounds they both need to gain electrons to reach a stable noble gas structure and so a compromise is reached where they share electrons to make a covalent bond. For instance, a hydrogen atom has a single electron in its valence shell but if it groups together in twos then each atom can contribute one electron to a covalent bond and so both atoms have two shared electrons – a full 1st shell.



A single horizontal or vertical line is a short way of showing bonds

Other gases, such as oxygen, nitrogen and fluorine also exist as 2 atoms sharing electrons in covalent bonds. Some have double bonds or even triple bonds.

Fluorine has 7 electrons it its valence shell so it forms diatomic molecules to achieve stability.



Note that each fluorine atom in the molecule has three lone pairs i.e. bonds that are not attached to another atom. These contribute to the overall shape of the molecule, as will be seen later.

In an oxygen molecule two pairs of electrons are shared so O_2 bonding would be shown as $\underline{\overline{\text{O}}}=\underline{\overline{\text{O}}}$ And N_2 is written as $|\text{N}\equiv\text{N}|$. O_2 has a double bond and N_2 has a triple bond.

How to work out a covalent bonding diagram

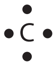
When two or more non-metals combine we need to take into account the number of valence electrons available and how they can be shared in single, double or triple bonds so that each element has an octet of electrons (except where hydrogen is one of the elements, as it only needs 2 electrons for a full shell).

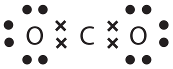
Example 1 Draw the electron-dot diagram for CO_2.

Rule 1: Find the number of valence electrons → O has 6 and C has 4

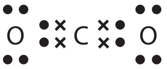
Rule 2: Place the least common element in the middle → O C O

Rule 3: Always place electrons as pairs in vertical and horizontal lines i.e. oxygen as  not 

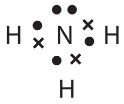
And carbon as  not 

Place the atoms together →  but this does not work because carbon has only 4 electrons.

Rule 4: Move pairs of electrons until all atoms have 8 – or 4 pairs (4 bonds)

Final solution →  or $\underline{\overline{\text{O}}}=\text{C}=\underline{\overline{\text{O}}}$

Example 2 Draw the electron-dot diagram for ammonia NH_3.



N has 5 electrons and needs another 3 for a complete shell but each H only needs 1.

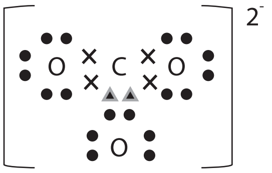
Sometimes it is useful to show the electrons from one of the atoms differently e.g. as a cross instead of a dot – just so it can be seen where it comes from.

We can see that nitrogen has a lone pair of electrons in a bond at the top.

Example 3 Draw the electron-dot diagram for the carbonate ion.

Here, we have an extra 2 electrons to add as carbonate has a charge of -2. Another useful tip with ions is to put the extra electrons onto the central atom.

Solution: Crosses show the 4 electrons from the carbon atom and the triangles represent the extra electrons of the ion.



Co-ordinate bonds

Where one atom supplies **both** electrons in a bond, this bond is called a Co-ordinate bond. In the carbonate diagram above the left and right-hand bonds of carbon with oxygen are both supplied by the carbon only (the crosses), so they are designated Co-ordinate bonds.

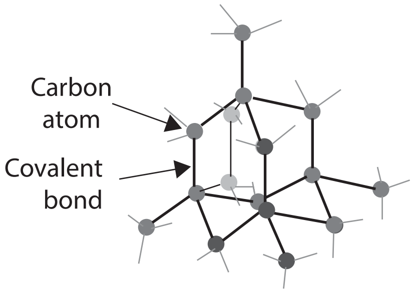
3.4 COVALENT NETWORKS

With group 4 compounds they can have the greatest bonding capacity as they can link in 4 directions. With 4 possible bonds this means each atom can have a tetrahedral configuration as shown below.

Diamond

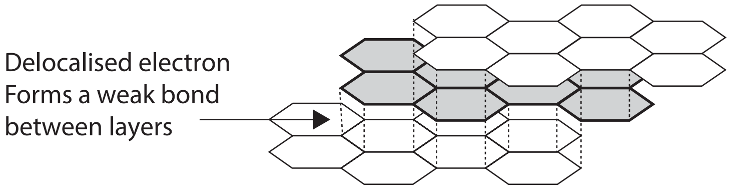
Each diamond is actually a giant molecular structure bonded into a gigantic network which makes diamonds hard, strong and with a very high melting point of around 4000°C.

To melt it (diamond actually sublimes) covalent bonds have to be broken, rather than weaker intermolecular forces.



Graphite

Graphite is another giant covalent network form of carbon (an Allotrope) which is bonded only in 2 dimensions as only 3 of carbon's 4 available electrons are used in bonding, whilst the other electron is delocalised, as with a metal.

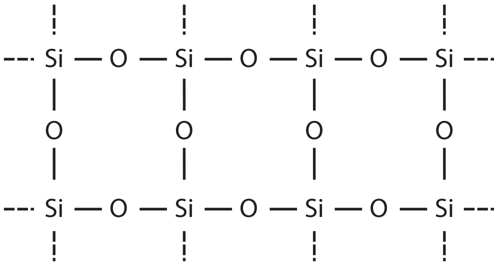


These delocalised electrons form very weak bonds between the flat layers of bonded carbon atoms. This means that each layer can be easily moved sideways by shear forces. The ability of layers to move relative to each other gives graphite its lubricating properties (slippery) and makes it useful in graphite greases. Pencil lead is actually graphite so that when we write the layers come off one at a time onto the paper.

The freely-moving electrons between layers make graphite an unusually good conductor, even though it is a non-metal and the strong forces in each layer give graphite a very high melting point of over 4000°C.

Silicon Dioxide

Silicon, itself has a giant covalent network structure, like diamond and so does its oxide SiO_2. Sand, quartz and glass are forms of SiO_2 with a tetrahedral structure centred around the silicon atom. This makes a very strong structure with a high melting point of 1610°C.



Compare this with CO_2 - a simple covalent molecular substance which is a gas at room temperature and has a melting point of -80°C. Silicon, itself is also a giant molecular structure with a melting point of 1420°C so we can see how the tetrahedral bonding in 3 dimensions affects the properties of a compound.

In general, giant covalent network substances such as diamond, Si, SiO_2 and SiC are hard and dense with very high melting points, due to the large amount of heat energy required to disrupt the covalent structure. They do not conduct electricity in either the solid or liquid phase due to tightly bound electrons, but graphite is an exception because it has delocalised electrons.

Set 1 Bonding

1. Complete these sentences below by adding words or crossing out incorrect ones.

(a) An atom with an electron removed from its valence shell this is called an ______.

The energy needed to ionise a mole of gas atoms of an element is called its __________ energy. For metals this energy is very (*small*/*large*), whereas for the ____________ gases the value is extremely (*small*/*large*).

Going from top to bottom of a Group, the ionisation energy becomes (*larger*/*smaller*), whereas going across a Period it becomes (*larger*/*smaller*).

The bonds between a metal and a non-metal are called _________ bonds. With these, the metal (*receives*/*donates*) valence electrons and the non-metal (*receives*/*donates*) them so that both species can achieve a ______ gas configuration. This is very (*stable*/*unstable*) e.g. if potassium gains an electron its structure becomes isoelectronic with the element called _________.

The ions in an ionic solid are arranged in a 3-D ________ structure which is strong and gives it a very (*high*/*low*) melting point. Ionic solids are (*good*/*bad*) electrical conductors unless they are changed into the _________ state by heating, where the ______ can then move around to transfer charge. When stressed, ionic solids snap with (*ease*/*difficulty*) as they are brittle.

(b) List of words to be used:

Salt, graphite, diamond, wax, silicon carbide, covalent, calcite, free, captured, silicon dioxide, calcium carbide lattice, nitrogen triiodide, sulfur., two, three, good, bad, weak, rigid, low, high.

The 3 molecular solids in the list above are: ___________, ____________ and _______________________. These compounds are held together in ________ dimensions by strong ___________ bonds. This makes them very ______ and __________ conductors, with __________ melting points.

The reason that graphite is slippery and conductive is because of the ___________ electrons from the carbon atoms, not used in covalent bonding. These form __________ bonds between the molecular sheets of graphite molecules.

2. (a) Which would you expect to have the highest value for its first ionization energy, magnesium or calcium? Why?

____

____

(b) Which would you expect to have the highest value for its first ionization energy, sodium or chlorine? Why?

____

____

3. (a) Draw an electron-dot diagram for calcium chloride and describe the type of bonding present.

____

____

(b) In the above compound, what elements are the ions present isoelectronic with?

____

____

(c) What is the electron configuration of the calcium ion in calcium chloride?

____

____

4. (a) If a sample of rock-salt (NaCl) is struck with a hammer it breaks cleanly into cuboid pieces. Explain this in terms of the bonding present in the mineral.

____

____

(b) A miner is convinced that he can obtain sodium metal by the electrolysis of a solution of Rocksalt, but fails in his attempt. Explain why this is so and describe a successful method by which sodium could be obtained from this mineral.

____

____

5. List: CO_2 K_2SO_4 SiO_2 CCl_4 $Ca(OH)_2$ NH_3.

(a) From the above list, classify the chemicals into groups of: (i) Molecular compounds, (ii) Ionic compounds, (iii) Covalent network solids.

____

____

(b) Explain, in terms of the intermolecular forces present, which one of the above would have the highest boiling point and which one would have the lowest boiling point.

____

____

(c) Draw electron-dot diagrams for CO_2, CCl_4 and NH_3.

6. (a) The gas SO_2 contains a "co-ordinate covalent bond". Explain the characteristic of this type of bond and use its electron-dot diagram to illustrate this.

____

____

____

____

(b) Draw the electron-dot diagrams for the nitrate and sulfate polyatomic ions

7. Write the name for each of the following compounds of non-metallic elements.

(a) XeF_6 __________________ (b) $SiCl_4$ __________________

(c) P_2O_5 __________________ (d) H_2O __________________

(e) $AsBr_3$ __________________ (f) HClO__________________

(g) NH_4Cl __________________ (h) P_4O_{10} __________________

(i) OCl_2 __________________ (j) CaH_2 __________________

(k) HCl __________________ (l) NO__________________

8. Write the name of each of the binary compounds using the Periodic Table and determine if the compound is likely to be ionic or molecular (Write I or M)

(a) ClF ___ (b) MgS____ (c) Rb_2O ____ (d) ClBr _____ (e) As_2O_5 ____

9. Name each of the following compounds:

(a) K_2CO_3 __________________ (b) NH_4NO_2 __________________

(c) $Ca(OH)_2$ __________________ (d) $Al(HSO_4)_3$ __________________

(e) $(NH_4)_2SO_4$ __________________ (f) $Ca_3(PO_4)_2$ __________________

(g) AgCN __________________ (h) $KClO_4$ __________________

(i) $Fe_2(SO_4)_3$ __________________ (j) K_2O_2 __________________

10. Write the formula of each of the following binary compounds of non-metallic elements.

(a) nitrogen dioxide ________________ (b) dinitrogen monoxide ___________

(c) barium peroxide ________________ (d) magnesium iodide ____________

(e) ammonium nitrite ________________ (f) aluminium sulfide ____________

(g) caesium sulfite ___________________ (h) sulfur dioxide _________________

(i) phosphorus pentachloride _________ (j) sulfur hexafluoride ____________

(k) xenon tetrafluoride _______________ (l) potassium acetate _____________

(m) beryllium bromide _______________ (n) potassium dichromate _________

Multiple choice Questions

1. The element samarium (Sm) forms the carbonate salt, $Sm_2(CO_3)_3$. The charge on the samarium ion in this compound is:

(a) +3 (b) -6 (c) -3 (d) +6

2. Which one of the following formulae is <u>incorrect?</u>

(a) $NaNO_3$ (b) $Mg_3(PO_4)_2$ (c) $KHSO_4$ (d) Al_2CO_3

3. Element "X" forms an ionic compound with the formula, $X(OH)_2$, "X" would be

(a) silver (b) lithium (c) calcium (d) aluminium

4. A metal "Y" readily forms a nitrate with the formula, YNO_3. Which one of the following compounds is "Y" <u>least</u> likely to form?

(a) YCO_3 (b) Y_2SO_4 (c) YOH (d) YH_2PO_4

5. The valency of the cation (positive ion) in $K_2Cr_2O_7$ is

(a) +2 (b) +1 (c) +6 (d) -2

6. The metallic element europium (Eu) has a valency of +3. The formula of europium sulfide is

(a) Eu_3S_2 (b) Eu_2S_3 (c) EuS_3 (d) Eu_3S

7. An element X is in Group 1 of the Periodic Table and another element, Y is in Group 15. A compound formed by the two elements is likely to have the simplest formula

(a) X_2Y (b) XY_5 (c) X_5Y (d) X_3Y

For the next three questions select from the key below the group in the Periodic Table to which the element would most likely belong.

Key:

Group 1	Group 2	Group 16	Group 18
a	b	c	d

8. An element X which forms ionic compounds with oxygen of the general formula, X_2O is _______.

9. An element which forms compounds by gaining two electrons is _____.

10. An element which forms compounds by losing 2 electrons is _____.

11. The number of atoms in a formula unit of $Al(OH)_3$ is

    (a) 4 (b) 5 (c) 6 (d) 7

12. The correct name of the compound $Fe_2(SO_4)_3$ is

    (a) Iron (III) sulfate (b) Iron sulfate

    (c) Iron sulfate (II) (d) Iron (II) sulfite

13. The formula of potassium acetate (ethanoate) is

    (a) CH_3COOK (b) $KHCH_3COO$ (c) K_2CH_3COO (d) PCH_3COO

14. The formula of ammonium phosphate is

    (a) $(NH_4)_2PO_4$ (b) NH_3PO_4 (c) $(NH_4)_3PO_4$ (d) $(NH_4)_2PO_3$

15. In which one of the following compounds does carbon not have an apparent valency of -4?

    (a) CO (b) CH_4 (c) CO_2 (d) H_2CO_3

16. Liquid mercury solidifies at a temperature of -39°C. Which one of the following statements about liquid mercury is not correct?

    (a) It is malleable (b) It expands when heated

    (c) It is denser than water (d) It very volatile

17. Molten sodium chloride has a higher electrical conductivity than solid sodium chloride because in molten sodium chloride the

    (a) Delocalized electrons are able to move more freely

    (b) Electrostatic forces between the ions are much smaller

    (c) Electrons can pass from one ion to another

    (d) Ions are able to move freely

18. Which of the following substances is most likely to be the best electrical conductor in the molten state?

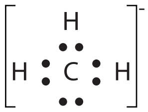
    (a) potassium fluoride (b) magnesium chloride

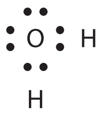
    (c) aluminum bromide (d) sodium iodide

19. A characteristic of metallic elements is that:
    (a) Their atoms have only a small number of electrons in the valence shell and these can be removed relatively easily.
    (b) Their electronegativities are high which means they lose electrons easily.
    (c) Their atoms usually share electrons with atoms of non-metals.
    (d) In the solid state electrostatic forces are not important since strong metallic bonds hold the atoms together

20. Which of the following electron dot formulas is <u>incorrect</u>?

(a) 

(b) 

(c) 

(d) 

21. The number of lone pairs in a molecule of chlorine is
    (a) 3 (b) 6 (c) 4 (d) 7

22. The number of bonding electron pairs in a molecule of nitrogen is
    (a) 1 (b) 2 (c) 3 (d) 4

23. The formation of an ionic compound from a reaction between two elements involves:
    (a) sharing of pairs of electrons between atoms.
    (b) donation of valence electrons to both elements
    (c) transfer of electrons between atoms.
    (d) ionization of the atoms of the more electronegative element.

24. The melting temperature of some common molecular substances are given below:

Substance	Melting temperature / °C
Br_2	-7
Cl_2	-101
N_2O_4	-10
HBr	-85

From the boiling points listed, the species in which forces between the molecules are least is:
    (a) Br_2 (b) Cl_2 (c) N_2O_4 (d) HBr

25. Which one of the following substances does <u>not</u> have strong bonds throughout its overall structure?
    (a) $Ca_{(s)}$ (b) $KNO_{3(s)}$ (c) $SiC_{(s)}$ (d) $NH_{3(s)}$

26. An ionic substance can be distinguished from metallic and molecular substances by measuring the electrical conductivity of the substance in

(a) the solid state only.
(b) the liquid state only.
(c) an aqueous solution only.
(d) the solid and liquid states.

27. Which of the following bond types are NOT electrostatic in nature?

(a) ionic bonds
(b) metallic bonds
(c) covalent bonds
(d) They are all electrostatic in nature

The next three items refer to the following information.

Three solid substances were tested in three ways:

	Test 1	**Test 2**	**Test 3**
	Hit a small lump of the substance with a hammer	**Place substance in a crucible and heat gently**	**Test some of the substance for electrical conductivity**
Result for substance I	flattened	melted easily	non-conductor in both the solid and liquid state
Result for substance II	shattered	no visible change	non-conductor in the solid state: conducted electricity in the liquid state
Result for substance III	shattered	melted at high temperature	non-conductor in both the solid and liquid state

28. The most probable chemical structure for solid substance I is

(a) metallic lattice
(b) covalent molecular
(c) covalent network lattice
(d) ionic lattice

29. The most probable chemical structure for solid substance II is

(a) metallic lattice
(b) covalent molecular
(c) covalent network lattice
(d) ionic lattice

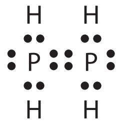
30. The most probable chemical structure for solid substance III is

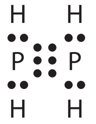
(a) metallic lattice
(b) covalent molecular
(c) covalent network lattice
(d) ionic lattice

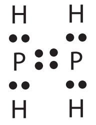
31. The physical properties of solid metals can best be explained by proposing that:

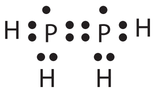
(a) each metal atom is bonded in the crystal lattice by covalent bonds.
(b) positive metal ions are arranged in an orderly way, with valence electrons able to move freely through the crystal lattice.
(c) positive and negative metal ions are arranged in an orderly way, with all the electrons able to migrate easily around the crystal lattice.
(d) each metal atom is surrounded by a variable number of valence electrons, which complete a Noble Gas electronic structure in the crystal lattice.

32. Phosphorus is in the group 15 of the periodic table. The bonding in a P_2H_4 molecule would be best represented by the electron dot formula

(a)


(b)


(c)


(d)


33. Copper wire may be bent easily without breaking. The best explanation of this is that:

(a) Slight changes in relative positions of adjacent copper particles do not break the metallic bonds as these are non-directional.

(b) The forces between copper atoms are weak, allowing the copper particles to be easily moved around.

(c) Copper particles are strongly bonded in layers but only weakly bonded between layers.

(d) Copper particles are arranged in flat molecules which freely slide over each other, allowing the material to be bent.

34. Looking at Table 1 in this chapter, the metals which would be liquid at a temperature of 1200°C would be:

(a) Ti, Fe, W (b) Cu, Al, Ti (c) Fe, W, Cu (d) Pb, Al, Ti

35. Looking at Table 2 in this chapter, the material that is >7 times stronger than mild steel but nearly 8000 time lighter is:

(a) Graphene (b) Titanium (c) Carbon fibre (d) Stainless steel

Chapter 4

Organic Chemistry

4.1 UNIQUE CARBON

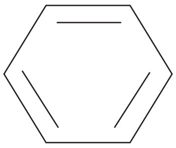
Life on Earth depends on carbon – we are "Carbon-based bipeds". The reason that carbon is so prominent in life-forms is that high order organisms need very complex molecules, such as DNA to perform complex processes, such as respiration, digestion and reproduction. Only Group 14 elements have the ability to join up in so many ways due to the fact that they have 4 valence electrons and can form 4 bonds – the maximum number. This means that bonding can occur in 3 dimensions, giving a virtually unlimited number of different combinations of atoms. It seems possible that another element in Group 14, silicon, might be able to take the place of carbon in life processes but, in fact although silicon can form complex chains, it does not react like carbon in respiration processes, producing SiO_2 when oxidized, which is a solid. Hence no life forms have ever been found using silicon as its basis, rather than carbon.

Originally the term Organic Chemistry was thought to be restricted to the chemicals found only in living things and not reproducible by man, but nowadays molecules can be produced in a laboratory which are the same as ones produced in organisms e.g genes containing amino acids in a combination not found in nature. Maybe in the future scientists will be able to produce a whole human genome.

Carbon's ability to form chains, branches and rings of carbon atoms and the ability to form single and multiple bonds with itself and with many other elements, makes it, then, a unique element in the Periodic Table and so Organic Chemistry is the study of the compounds of carbon.

4.2 HYDROCARBONS

Hydrocarbons, one of the main groups of organic compounds, contain only carbon and hydrogen atoms. Carbohydrates is another group containing carbon, hydrogen and oxygen. Compounds containing a benzene ring in their structure are classified as Aromatic compounds and those not containing this ring are classified as Aliphatic compounds.



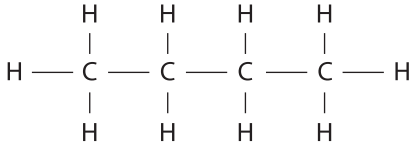
A benzene ring

Aliphatic hydrocarbons are arranged in 3 families, or homologous series: Alkanes, Alkenes and Alkynes. Compounds in each series include the same type of bonds (single, double, triple), but with different numbers of carbon atoms linked together.

In general, the longer the chain, the higher the melting point and boiling point, due to stronger intermolecular forces.

4.3 ALKANES

Alkane chains all contain single bonds joined to each other in lines and to hydrogen. Compounds with single bonds are known as "saturated" hydrocarbons as all the external bonds have hydrogen atoms attached to them.



$$\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H}$$

Alkane chain

All homologous series have the same stem in their names (meth-, eth-, etc) which indicates the number of carbon atoms in the chain. All alkanes end in the suffix –ane.

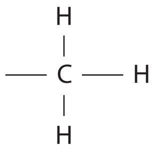
The nomenclature (naming system) is shown in the table below.

No of carbons	Stem	Alkane name	Structure	Formula	Alkyl Group	Alkyl name
1	Meth-	Methane	-C-	CH_4	CH_3-	Methyl
2	Eth-	Ethane	-C-C-	C_2H_6	C_2H_5-	Ethyl
3	Prop-	Propane	-C-C-C-	C_3H_8	C_3H_7-	Propyl
4	But-	Butane	-C-C-C-C-	C_4H_{10}	C_4H_9-	Butyl
5	Pent-	Pentane	-C-C-C-C-C-	C_5H_{12}	C_5H_{11}-	Pentyl
6	Hex-	Hexane	-C-C-C-C-C-C-	C_6H_{14}	C_6H_{13}-	Hexyl
7	Hept-	Heptane	-C-C-C-C-C-C-C-	C_7H_{16}	C_7H_{15}-	Heptyl
8	Oct-	Octane	-C-C-C-C-C-C-C-C-	C_8H_{18}	C_8H_{17}-	Octyl

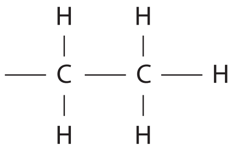
If one of the hydrogen atoms in an alkane is taken off then it is called an alkyl group (R) and its name ends in –yl. With this extra bond available, an alkyl group is able to link to another chain.

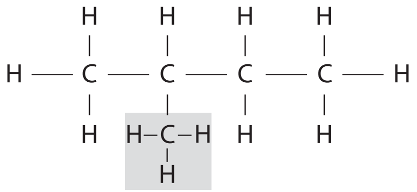
eg

Methyl group CH_3



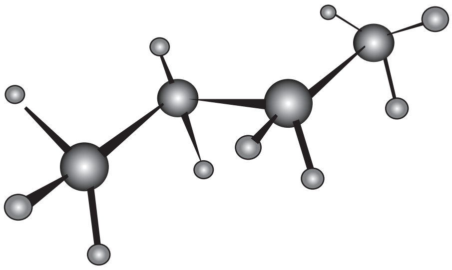
Ethyl group C_2H_5





For instance, a methyl group bonded to a butane molecule would be called methyl butane, as shown here. (The methyl group is shown in the grey box, often denoted as the letter R)

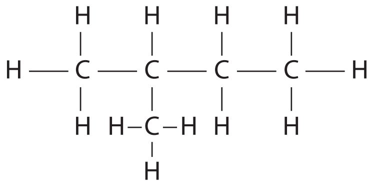
From the 5th column in the table above we can see the generalised formula for alkanes is C_nH_{2n+2} Note that, although we represent these molecules as linear on the page, bonds on each carbon atom actually arrange themselves tetrahedrally due to the VSEPR forces repelling the carbon bonds. This will be discussed in Chapter 7 later.



Spatial (3-D) arrangement for the butane molecule

The alkane chain structure presentation of molecules is called a Structural formula but structures can also be shown by what is called the Condensed Structural formula, show in groups of atoms in a row and by another method called the Skeletal or Line-Angle Formula.

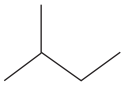
All the structures below are for the same compound – methyl butane.



Structural formula

$CH_3CH(CH_3)CH_2CH_3$

Condensed structural formula



Skeletal formula

Note that, with the condensed structural formula, 2 groups are on the same carbon atom are shown with one of them in a bracket (CH_3 group). Skeletal diagrams are a shorthand version where each intersection of bond lines represents a carbon atom with the required number of hydrogens attached.

4.4 PHYSICAL AND CHEMICAL PROPERTIES OF ALKANES

Physically, the lower the number of carbons in the molecule, the lower the boiling point so methane, ethane, propane and butane all boil below zero degrees but alkanes from pentane onwards are liquids or solids with the case of the long chain members of the group. This trend is due to the intermolecular forces (between the molecules) growing larger with molecular mass. The increase in intermolecular forces also makes them more viscous (less "runny") as the chain gets longer. (Honey is a viscous liquid and water is less viscous). All alkanes are insoluble in water but will dissolve in other non-polar solvents, such as petrol.

As a whole alkanes are chemically quite unreactive but do burn to give carbon dioxide and water in Combustion reactions which makes them useful as fuels e.g. propane burning in excess air:

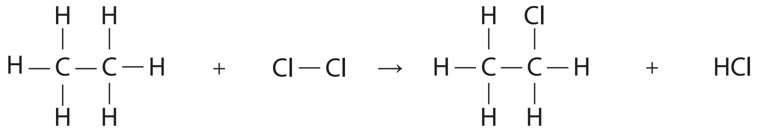
$$C_3H_8(g) + 10O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) + \text{heat}$$

If we limit the amount of oxygen available for burning the gas carbon monoxide (CO) will be formed instead:

$$2C_3H_8(g) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(g) + \text{heat}$$

Petrol is an example of an alkane fuel with from 4 to 12 carbon atoms in its molecules and methane is used in a gas stove.

Alkanes undergo what is called Substitution Reactions, where a hydrogen atom in the chain is replaced by another atom. This will not happen unless photons with a high energy (ultraviolet light) are used to break the bonds first. Example Ethane reacting with chlorine:



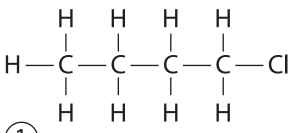
If excess chlorine is used then more than one hydrogen can be substituted with chlorine to obtain dichloroethane, trichloroethane, etc.

4.5 NAMING SUBSTITUTED ALKANES

There is an internationally agreed way of naming organic compounds so that all nations will know and understand the same nomenclature (naming system). The rules are called the IUPAC system.

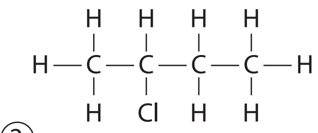
Rule 1 You must state which carbon a functional group is attached to. A Functional Group is a group, such as chlorine, bromine, hydroxide or alkyl radical.

For instance, chlorobutane can have the chlorine atom attached in two different places – either on the 1st or 2nd carbon atom:



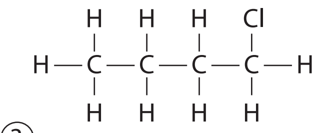
①

1-chlorobutane



②

2-chlorobutane

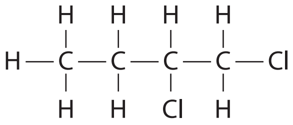


③

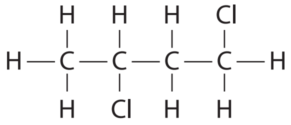
1-chlorobutane

Compound 1 and compound 2 are called Structural Isomers, as they have the same chemical formula, but a different arrangement in space. The 3rd structure is not an isomer as it is exactly the same as structure 1 but rotated in space!

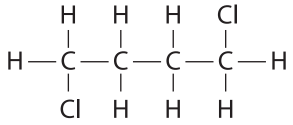
If more than one functional groups are present, then they must be numbered similarly:



1,2-dichlorobutane

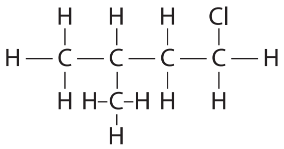


1,3-dichlorobutane



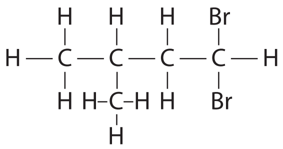
1,4-chlorobutane

Rule 2: If more than one substituted groups are present, the naming must be in alphabetical order.



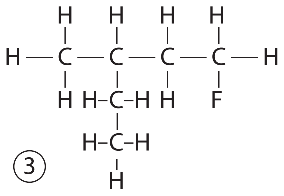
①

1-chloro- 3-methyl butane



②

1,1-dibromo-3-methyl butane



③

1-fluoro-3-methylpentane

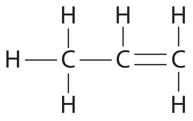
With compound 1 the prefix "chloro" comes before "methyl" and with compound 2 the "bromo" must come alphabetically before "methyl".

Rule 3 comes into play with compound 3. This rule says that naming must prioritize the longest chain. So, instead of it being named 2-ethyl-4-fluoro butane we must take the longest chain as 5 carbons (pentane) and the methyl group is therefore attached to the 3rd carbon along from the fluorine.

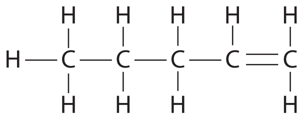
4.6 ALKENES

Alkenes all have a carbon-carbon double bond in their chain and are said to be Unsaturated as, not all the carbon bonds are attached to hydrogen. The general formula for alkenes is C_nH_{2n}.

The prefix names in this series are the same as before with the alkanes, except that they all end in the suffix –ene.



Propene

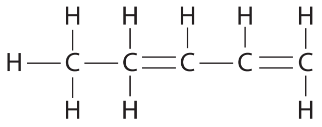


Pent-1-ene

Note that Rule 1 applies with pentene where you have to number the carbon which is attached by a double bond. Wherever the double bond is has to have the lowest number i.e. pent-1-ene, rather than pent-4-ene.

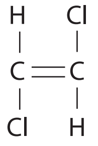
Where there are 2 double bonds are present, these compounds are called dienes.

e.g. The molecule below is called penta-1,3-diene. Note: because of Rule 4 – the "lowest number" rule where it is named 1,3, rather than 2,4 because in a choice, the lowest numbers possible must be selected.

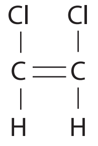


Cis-trans Isomers

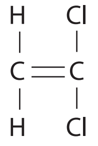
These isomers can only occur with alkenes where 2 different groups are attached on one side of a double bond. E.g There are two isomers of 1,2-dichloroethane, where the chlorine atoms are side-by-side (cis form) or where they oppose each other (trans form).



trans-1,2-dichloroethene



cis-1,2-dichloroethene



1,1-dichloroethene

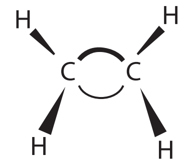
1,1-dichloroethene cannot have any cis/trans forms as both chlorine atoms are on the same side of the double bond.

Physical Properties

These are similar to the alkanes in that they are non-polar, insoluble in water, and have a fairly low boiling point which rises with molecular weight – ethene and propene BP is below zero.

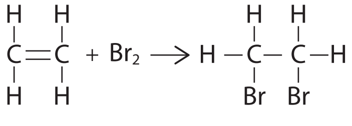
Chemical Properties

Alkenes are much more reactive than alkanes due to the strain on the double bond which is trying to form a tetrahedron and so, in reacting with halogens, such as bromine, the reaction occurs without the need for UV light. This reaction is called an Addition Reaction.

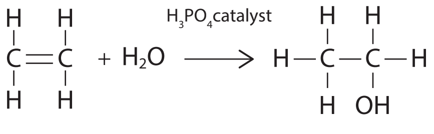


Alkenes can react with various other reactants, apart from halogens,

For example: HCl, HBr, HI, H_2 and H_2O. All of these compounds react by adding across the double bond. Some of these reactions require a catalyst to speed the reaction up. Examples:

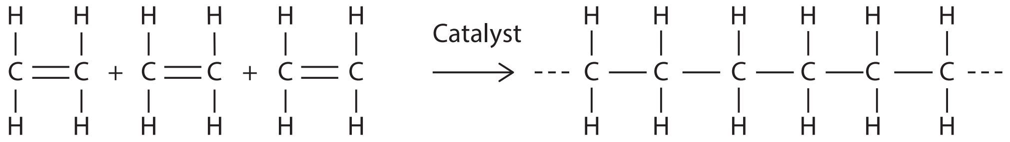


1,2-dibromoethene



Ethanol

Alkenes can also join up into very long chains if the double bonds are broken by catalytic action. This process is known as polymerisation.



Ethene monomers

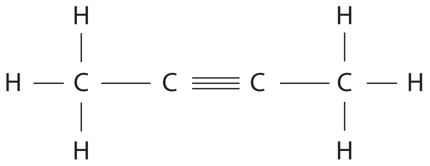
Polyethene polymer

4.7 OTHER HYDROCARBONS

There is another homologous series of hydrocarbons which have triple bonds which are called Alkynes. These use the same prefixes as with alkanes and alkenes.

e.g

But-2-yne



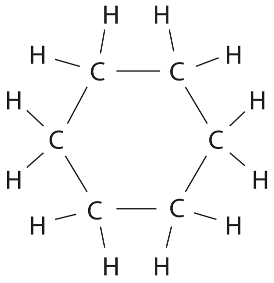
Alkynes are not a focus of our syllabus.

There is also another kind of linkage system used where bonds are formed in a cyclic fashion. The general name for these is Alicyclic hydrocarbons and they all have the prefix “cyclo”.

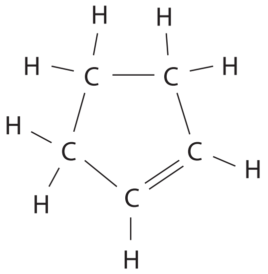
Cycloalkanes are saturated and have ring like molecules and cycloalkenes contain one or more double bonds.

<u>Examples:</u>

Cyclohexane, C_6H_{12}



Cyclopentene, C_5H_8

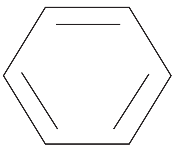


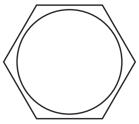
There is a whole section of chemistry dealing solely with compounds containing a benzene ring. Hydrocarbons containing a benzene ring are called Aromatic hydrocarbons.

Benzene has the formula C_6H_6 but the structure of it was unknown until Kekule realised that there had to be three double bonds in the ring structure.

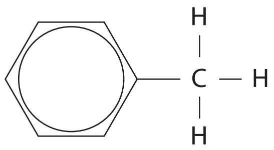
Many other compounds were found to exist or could be created containing benzene rings. Some are shown below with the alternative symbol representing benzene.

Benzene

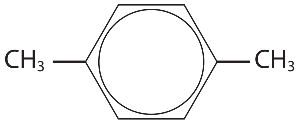




Benzene



Methyl benzene



1, 4 - dimethyl benzene

You might predict that benzene would undergo addition reactions due to its double bonds but an interesting fact is that is does not. This is due to a property found out later that the bonds are not really double bonds but that the electrons in the ring are actually being shared between all six carbon atoms equally. The electrons are said to be delocalized, as they are free to move around the molecule.

Set 1 Organic Chemistry

PART A: Multiple Choice

1. Which of the following compounds is a hydrocarbon?

I $C_6H_{12}O_6$ (glucose)
II C_6H_6 (benzene)
III C_5H_{12} (pentane)
IV CH_3Cl (chloromethane)

(a) I, II and III only
(b) I only
(c) II and III only
(d) They are all hydrocarbons

2. Which one of the following groups of formulae would represent members of a homologous series?

(a) CH_3Cl CH_2Cl_2 $CHCl_3$ CCl_4
(b) CH_2CH_2 $CH_2CH_2CH_2$ $CH_2\ CH_2CH_2CH_2$ $CH_2\ CH_2CH_2CH_2CH_2$
(c) CH_4 CH_3CH_3 $CH_3CH_2CH_3$ $CH_3CH_2CH_2CH_3$
(d) CH_4 CH_3Cl CH_3OH HCHO

3. Two organic compounds are structural isomers of each other if they

(a) Have the same molecular formula but different structural formula.
(b) Have the same structure in the solid state but different melting temperatures.
(c) Differ from each other by a CH_2 unit.
(d) Have the same physical properties but different molecular formulae.

4. Which of the following compounds does <u>not</u> exist in two or more structural forms?

(a) C_4H_{10}
(b) $C_2H_4Cl_2$
(c) $CHCl_3$
(d) C_2HCl_3

5. Which of the following is NOT a physical property of alkanes?

(a) The long chain alkanes can be solids
(b) The short chain alkanes have a high viscosity
(c) All alkanes can react with bromine
(d) All long chain alkanes will burn in a limited supply of oxygen

6. Which one of the following compounds will have the greatest number of structural isomers?

(a) C_3H_8
(b) $C_3H_6Cl_2$
(c) C_4H_{10}
(d) CH_3Cl

7. A hydrocarbon was found to have a molecular formula of C_6H_{12}. To which of the following classes of compounds could this hydrocarbon belong?

(a) Alkane
(b) Alkyne
(c) Cyclic alkene
(d) Cyclic alkane

8. The formula of 2,2-dimethyl-propane may be correctly written as

(a) $(CH_3)_3CCH_3$
(b) $(CH_3)_2CHCH_2CH_3$
(c) $CH_3CH(CH_3)_2$
(d) $(CH_3)_2CHCH_2CH(CH_3)_2$

9. Which one of the following compounds is saturated?

(a) CH_2CH_2
(b) CH_3CHCH_2
(c) C_6H_6
(d) $(CH_3)_3CH$

10. Which one of the following hydrocarbons is least likely to react with hydrogen?

(a) C_6H_6
(b) C_3H_6
(c) C_2H_2
(d) C_4H_{10}

11. The reactions between chlorine and methane in ultra violet light is an example of

(a) an elimination reaction
(b) a substitution reaction
(c) an addition reaction
(d) a condensation reaction

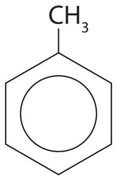
12. The product formed when ethene reacts with bromine at room temperature is likely to be

(a) CH_3CH_2Br
(b) CH_2CHBr
(c) CH_2BrCH_2Br
(d) CH_3CHBr_2

13. Which of the following compounds is least likely to undergo addition reactions with chlorine?

(a) CH_2CH_2
(b) CH_3CHCH_2
(c) CH_2CHCl
(d) $CH_3CH_2CH_3$

14. For a molecule with this chemical structure the correct formula is:



(a) $C_6H_6CH_3$
(b) $C_7H_6CH_3$
(c) C_7H_8
(d) C_7H_3

15. Petrol consists of compounds with mostly which number of carbon atoms in its molecules?

(a) C_1 to C_5
(b) C_6 to C_{10}
(c) C_{11} to C_{12}
(d) C_{13} to C_{25}

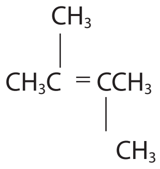
16. The name of the compound represented by the structure shown is:

(a) Dimethyl butene

(b) *Cis* – dimethyl butene

(c) *Trans* – dimethyl butene

(d) Tetramethyl ethene



$CH_3C(CH_3)=C(CH_3)CH_3$

17. Samples of three of the following hydrocarbons are found to be alkenes, and one an alkane. Which one is the alkane?

(a) C_2H_4 (b) C_4H_8 (c) C_5H_{12} (d) C_8H_{16}

18. The type of reaction that occurs between bromine and ethane, C_2H_6 is best called

(a) An addition reaction. (b) A substitution reaction.

(c) A reorganization reaction. (d) A restitution reaction.

19. How many isomers are possible with formula C_3H_6?

(a) 1 (b) 2 (c) 3 (d) 4

20. Which one of the following compounds is a saturated hydrocarbon?

(a) C_2H_6 (b) C_2H_4 (c) C_2H_2 (d) C_3H_6

21. Which of the following formulae could represent a cycloalkane?

(a) C_5H_{12} (b) C_4H_{10} (c) C_4H_8 (d) C_4H_6

22. Substances that have the same molecular formula but a different structural formula are called

(a) Isotopes (b) Isomers (c) Allotropes (d) Aliphatic

23. Which one of the following reactions is not an addition reaction?

(a) $C_2H_2(g) + 2Cl_2(g) \rightarrow C_2H_2Cl_4(g)$

(b) $C_3H_4(g) + HNO_2(l) \rightarrow C_3H_5NO_2(l)$

(c) $CH_3Br(g) + H_2O(g) \rightarrow CH_3OH(g) + HBr(g)$

(d) $C_2H_2Cl_2(g) + 2HBr(g) \rightarrow C_2H_3Cl_2Br(g) + HBr(g)$

24. Which of the following has the lowest boiling point?

(a) Butane (b) Ethane (c) Methane (d) Propane

25. Which of the following exists in two geometric (cis – trans) forms?

(a) 1,1 – dibromo propene (b) 1,3 – dibromo propene

(c) 3,3 – dibromo propene (d) 1,2 – dibromo propene

26. Which of the following names is correct according to the IUPAC system?

(a) tetramethyl methane (b) tetramethyl ethane
(c) tetramethyl propane (d) tetramethyl butane

27. Which of the following will react with chlorine, resulting in just one product (no left-over molecules)?

(a) Butene (b) Benzene (c) Butane (d) Hexane

28. Which of the compounds in the following would burn to give the most carbon dioxide?

(a) Butane (b) Benzene
(c) Methyl propene (d) Pentane

29. Which of the following compounds would react with the greatest amount of chlorine?

(a) Ethane (b) Dichloroethane
(c) Ethene (d) Chloroethene

30. How many of the following compounds can exhibit cis-trans isomerism?

1,1-dibromobutene; 2,3-dibromobutene;

1,2-dibromobutene; 4,4-dibromobutene

(a) 1 (b) 2 (c) 3 (d) 4

Longer Questions

1. Classify the following hydrocarbons as saturated or unsaturated, and name them:

(a) $CH_3CH_2CH_2CH_3$ ______________________________
(b) $CH_2CHCH_2CH_3$ ______________________________
(c) $CH_3CH_2CH(CH_3)CH_2CH_3$ ______________________________
(d) $CH_3CH_2CH_2C(CH_3)C(CH_3)CH_2CH_3$ ______________________________

2. Give the formula and the name of

(a) A straight chain alkane with 6 carbon atoms ______________________
(b) A branching chain alkane with 6 carbon atoms ______________________
(c) An alkene with 5 carbon atoms ______________________________
(d) An isomer of (c) ______________________________
(e) Which one would you expect to have the higher boiling point, propene or octene?

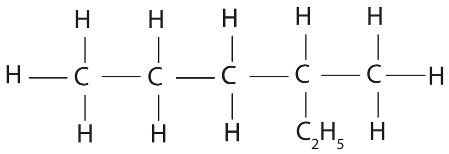
Give your reasoning

____

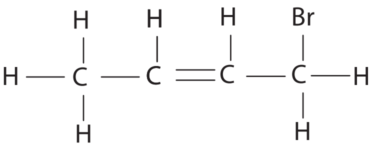
____

3. a) Use the IUPAC rules to name the following compounds:

(i)



(ii)



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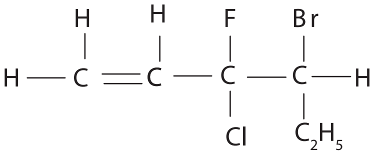

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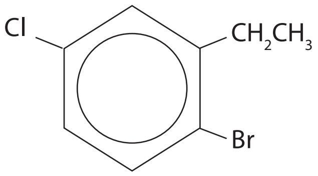

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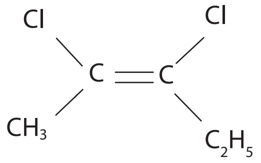

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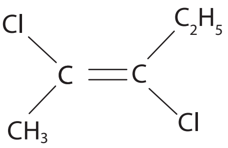


b) Draw the structural formulae for the following compounds:

(i) 1,2-dibromobutane

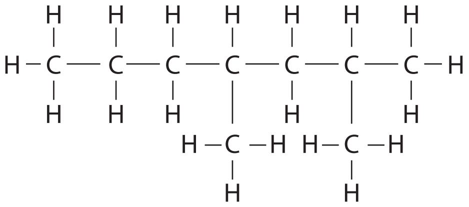
(ii) cis-butene

(iii) 2,3-dimethylpentane

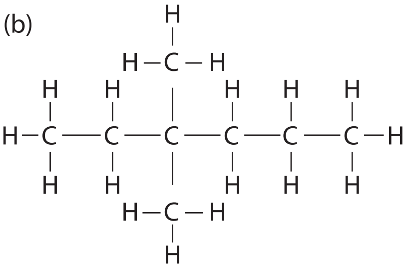
(iv) 1-methyl-3-fluorocyclohexene

4. Write condensed formulae for the following hydrocarbons and name them:

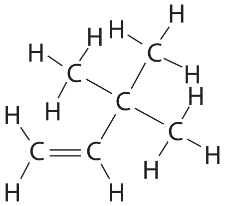
(a)



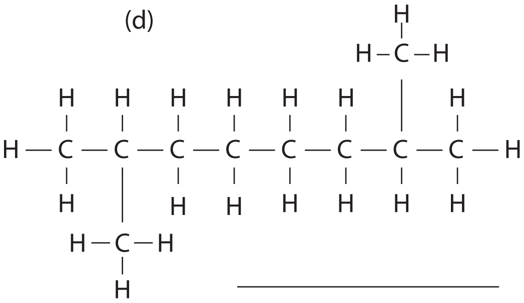
(b)



(c)



(d)



5. Draw structural formulae for the following hydrocarbons showing all bonds and hydrogen atoms, and name them:

(a) $CH_3(CH_2)_2CH(CH_2CH_3)CH_2CH_3$

(b) $CH_3CH(CH_3)(CH_2)_3CH(CH_3)_2$

(c) $CH_3CH(CH_3)CH(CH_3)_2$

(d) $CH_3(CH_2)_4CH(CH_3)_2$

6. Draw structural formulae for the following hydrocarbons and classify them as aliphatic, alicyclic or aromatic:

(a) 2-methylpropene

(b) Cyclopentene

(c) 3-ethyl-2-methylhexane

(d) 1,4-dimethylbenzene

7. Draw structural formulae for the following:
   - (a) Methylcyclopropane
   - (b) 1,3-aimethylbenzene
   - (c) *Trans* hex-3-ene
   - (d) Tetrachloroethene

8. a) Write a balanced equation for the combustion of ethane in a limited supply of air.

   b) Some ethane was mixed with chlorine gas in a flask and exposed to sunlight. Write the equation for the primary reaction. Name and write the condensed structural formula for the main organic product of this reaction.

   c) Starting with but-1-ene, explain how the following compounds could be produced and write the structural equations for the reactions:
   - (i) Butane
   - (ii) 1,2-dibromobutane
   - (iii) 2-chlorobutane

Chapter

5

Moles

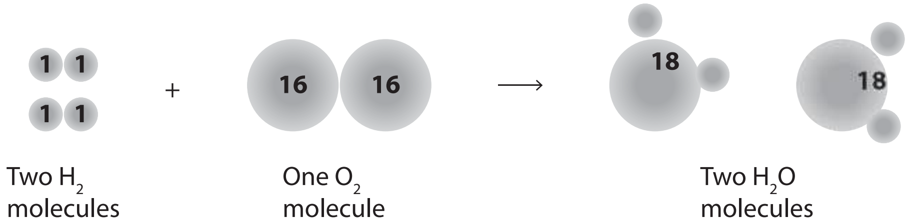
5.1 PARTICLES

We have seen that all matter is composed of very small particles – either single atoms or molecules, where atoms are joined together with bonds. We have also seen that atoms of different elements have different sizes – hydrogen is the smallest atom and uranium is very large. So is we took 1 gram of hydrogen there would be a lot more atoms than what there would be in 1 gram of uranium.

Look at this chemical reaction where hydrogen burns in oxygen to produce water:

$$H_2 + O_2 \rightarrow H_2O$$

According to the Conservation of Mass rule. We must have the same number of atoms on the left as on the right of an equation, hence: $2H_2 + O_2 \rightarrow 2H_2O$ must be the balanced equation. Pictorially, this reaction looks like this:



We can see from this equation that, for every molecule of oxygen two molecules of hydrogen are required to react with it but how do we translate this into finding the masses of O_2 and H_2 needed?

From the Periodic Table and the atomic weights given, we can see that an atom of oxygen is almost exactly 16 times heavier than an atom of hydrogen. Hence, for 4 atoms of hydrogen to combine with 2 atoms of oxygen we would need masses to combine in the ratio of about 4 to 32, or 4 grams of H_2 would react with 32 grams of O_2 to produce 36 grams of H_2O.

The ratio in which the molecules are combining is the ratio of their atomic masses. One atomic mass unit, as mentioned before, is 1.66×10^{-24} grams (1 atomic mass unit), so in 1 gram of hydrogen atoms the number of atoms will be $\frac{1}{1.66 \times 10^{-24}} = 6.022 \times 10^{23}$. In 16 grams of oxygen atoms there are 16 atomic mass units (from the Periodic Table) and hence the number of atoms will be the same:

$$\frac{16}{16 \times 1.66 \times 10^{-24}} = 6.022 \times 10^{23}.$$

Hence, this number is special as it is the number of atoms in the atomic weight of an element, measured in grams. This number is called Avogadro's Number – symbol N_A. The number of grams of any element or compound containing 6.022×10^{23} particles is called one Mole and is important for calculations of reacting quantities.

5.2 CALCULATIONS

Hence, in the above equation: $2 \times 6.022 \times 10^{23}$ molecules of hydrogen must react with $1 \times 6.022 \times 10^{23}$ molecules of oxygen or 2 moles of H_2 will react exactly with 1 mole of oxygen to produce two moles of water – the coefficients in front of the reactant (e.g the 2 in front of H_2) will tell you the number of moles that will react, but this has to be translated into grams.

The formula that converts particle numbers to moles is: $n(X) = \frac{\text{No. of particles}}{N_A}$

e.g. The number of moles in 5 billion atoms of oxygen is $n(O) = \frac{5 \times 10^9}{6.022 \times 10^{23}} = 8.3 \times 10^{-15}$ moles

To convert moles into grams, we need to use this formula: $n(O) = \frac{m}{M_r}$

M_r is the mass given in the Periodic Table for that element, called its Molar Mass (or atomic weight for atoms). Rearranging the last equation gives:

$$m = nM_r$$

The atomic eight of oxygen is 16, so the mass of 8.3×10^{-15} moles will be $m = 8.3 \times 10^{-15} \times 16 = 1.33 \times 10^{-13}$ grams.

These formulae can be very handy in calculations:

$$n = \frac{m}{M_r} \qquad m = nM_r \qquad \text{and } n = \frac{\text{No. of particles}}{N_A}$$

Example 1

a) How many moles of carbon are there in a 3.67 g diamond?

b) How many atoms is this?

c) How many grams of oxygen will it take to react with this diamond?

d) How many grams of carbon would be required to produce 10 g of CO_2?

Solution 1

a) Molar mass of carbon is 12.01 g mol^{-1}.

$n = \frac{m}{M_r} = \frac{3.67}{12.01} = 0.306$ mol.

b) $n = \frac{\text{No of particles}}{N_A}$

So No. of particles = $n \times N_A = 0.306 \times 6.022 \times 10^{23} = 1.84 \times 10^{23}$ carbon atoms.

c) Equation for burning carbon is:

$C + O_2 \rightarrow CO_2$ (1 mole of O_2 will be needed for each mole of carbon)

From the ratios: 0.306 moles of C will need 0.306 moles of O_2.

$m = nM_r = 0.306 \times (2 \times 16) = 9.79$ g of O_2.

d) M_r of $CO_2 = 12.01 + 2 \times 16 = 44.01$ g mol^{-1}

$n(CO_2) = \frac{m}{M_r} = \frac{10}{44.01} = 0.2272$ mol.

Looking at the ratios in the equation $n(CO_2) = n(C)$ so n(C) also = 0.2272 mol.

$m(C) = nM_r = 0.2272 \times 12.01 = 2.73$ grams.

Note how the equation gives us the ratios of reactants and products – in moles.

Example 2

Magnesium metal burns in air to form magnesium oxide. Calculate the mass of magnesium oxide formed from 18.0 g of magnesium metal.

Balanced equation: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

Mass of known: = 18.0 g

Moles of known: $= \frac{18}{24.31} = 0.7404$ mol

Moles of unknown $= \frac{2}{2} \times$ moles of magnesium = 0.7404 mol

Mass of unknown: $= n \times Mr(MgO) = 0.7404 \times (24.31 + 16) = 29.85$ g.

5.3 PERCENTAGE COMPOSITION

If we had a mass of a compound, say CO_2, and we wanted to know what percentage of its mass was made up of one of the elements, then we need to look at its composition in moles first.

In 1 mole of CO_2 there is 1 mole of carbon and 2 moles of oxygen atoms.

So in 44.01 grams of CO_2 there is 12.01 g of carbon and 2 × 16 grams of O_2. Hence % of C is given by this fraction $\frac{\text{mass of carbon}}{\text{total mass}} = \frac{12.01}{44.01} \times 100\% = 27.3\%$ by mass.

Example 3

a) Calculate the percentage of nitrogen in ammonium nitrate (NH_4NO_3)

b) Which would give the most nitrogen atoms to the soil out of these two fertilizers: 10 g of NH_4NO_3 or 10 g of Urea formula $CO(NH_2)_2$.

Solution

a) M_r of $NH_4NO_3 = 2 \times 14.01 + 4 \times 1.008 + 3 \times 16 = 80.052$ g mol^{-1}

M_r of $CO(NH_2)_2 = 12.01 + 16 + 2 \times 14.01 + 4 \times 1.008 = 60.062$ g mol^{-1}

% of N in $NH_4NO_3 = \frac{2 \times 14.01}{80.052} \times 100 = 35.0\%$

% of N in $CO(NH_2)_2 = \frac{2 \times 14.01}{60.062} \times 100 = 46.7\%$

b) Mass of N in NH_4NO_3 = 35% of 10 g = 3.50 g

Mass of N in $CO(NH_2)_2$ = 46.7% of 10 g = 4.67 g

Hence urea is the better fertilizer for adding nitrogen atoms to the soil per gram.

5.4 EMPIRICAL FORMULA

The Empirical Formula of a compound shows the simplest ratio of the elements in it.

e.g. Ammonium nitrite has a molecular formula of NH_4NO_2, so there are 2 Ns, 4 Hs and 2 Os. If we divide by 2 we get a ratio of N: H: O of 1: 2: 1, so the empirical formula is NH_2O.

The empirical formula for the organic compound $C_4H_6O_2$ would be C_2H_3O. The Empirical Formula for glucose $C_6H_6O_{12}$ would be simply CHO_2.

We can determine the empirical formula for a compound by finding the masses of each element present and then converting to moles to find their ratio.

Example

a) A hydrocarbon of mass 10.0 g was found to have a composition of 8.56 g of carbon and 1.44 g of hydrogen. Determine its empirical formula.

b) The molar mass of the hydrocarbon was found to be close to 42 g mol^{-1}. What is its molecular formula?

Solution

a) Finding the number of moles: $n(C) = \frac{8.56}{12.01} = 0.7127$ mol

$n(H) = \frac{1.44}{1.008} = 1.429$ mol

Ratio of moles C: H is 0.7127: 1.429

Divide by smallest number: $\frac{0.7127}{0.7127} = 1$ and $\frac{1.429}{0.7127} = 2$

Empirical formula is CH_2.

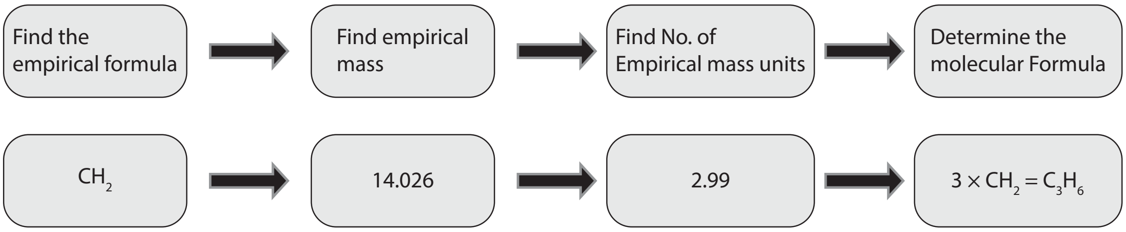
b) Molecular mass (MM) will be a simple multiple of empirical mass (EM).

$EM = 12.01 + 2 \times 1.008 = 14.026$ and $MM = 42$

Ratio is $\frac{42}{14.026} = 2.99$ so the nearest whole number is 3

MM = 3 × EM so there must be 3 units of CH_2 in the molecule and so the molecular formula must be C_3H_6.

The general methodology for finding a molecular formula is therefore



Example

a) A 5.430 g sample of chromium as heated in air until it had all oxidized to chromium oxide which to found to weight 7.93 g. Find the percentage composition of the chromium oxide.

b) Calculate the empirical formula of chromium oxide from these data.

Solution

a) % of Cr in the oxide = $\frac{5.43}{7.93} \times 100 = 68.4\%$ so % of oxygen = 100 – 68.4 = 31.5%

b) Taking % as grams in 100 g, n(Cr) = $\frac{68.4}{52}$ = 1.315 mol. n(O) = $\frac{31.5}{16}$ = 1.97 mol

Ratio of Cr: O is 1.315: 1.97 (divide by smallest number)

Simple ratio is 1: 1.497 – round this to 1 to 1.5.

If we multiply both by 2 we get 2 to 3, so Cr_2O_3 is the empirical formula

5.5 REACTION EQUATIONS

When we see an equation showing a reaction it shows what the reagents are (the compounds reacting) and what the products are (what are produced). The formulae of the reactants and products must also show the correct ratio of elements for that compound and show the states that they are in (solid, liquid, aqueous solution or gas). The conservation rules for element numbers and charges must also apply in every case.

Stating an equation in words, we might have:

Carbon dioxide is mixed with calcium hydroxide solution to produce calcium carbonate and water.

As a chemical equation, this would be:

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Notice that there is one Ca and one C, 4 Os, 2 Hs, on both sides and that their states are given – a solution is shown as (aq), meaning aqueous and (g) is a gas, with (l) representing a liquid.

Example

a) Phosphorus is burnt in air to produce a yellow solid tetraphosphorus decaoxide. Write a balanced equation for this reaction.

b) What is the empirical formula for tetraphosphorus decaoxide and what is its molar mass?

Solution

Tetra means 4 and deca means 10 in Greek

Unbalanced equation: $P + O_2 \rightarrow P_4O_{10}$

Balanced equation: $4P(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$

Set 1 Moles and Equations

Multiple –choice questions

1. The unit for the quantity relative atomic mass is

(a) gram (b) kilogram per molecule

(c) kilogram (d) gram per mole

2. " Mol" is a unit used by chemists to measure the quantity,

(a) relative atomic mass (b) number of atoms

(c) amount of substance (d) concentration of particles

3. The mole is used as a measure of amount of substance in chemistry. In terms of which one of the of the following is it defined?

(a) Volume of particles (b) Size of particles

(c) Number of particles (d) Concentration of particles

4. One mole of argon atoms resembles one mole of magnesium atoms in that both have the same

(a) mass (b) volume

(c) number of protons (d) number of atoms

5. The formula of hydrated sodium carbonate (washing soda) is $Na_2CO_3 . 10H_2O$. What number of moles of oxygen atoms is there in one mole of $Na_2CO_3 . 10H_2O$?

(a) 3 mol (b) 4 mol (c) 13 mol (d) 16 mol

6. Which one of the following has the greatest mass?

(a) 6.022×10^{25} molecules of hydrogen gas

(b) 4 mol of nitrogen molecules

(c) 1.2×10^{24} atoms of iron

(d) 120 g of mercury

7. Which one of the following quantities of nitrogen gas contains the largest number of atoms?

(a) 140 g (b) 14 L measured at STP

(c) 14×10^{23} molecules (d) 14 mol molecules

8. Which one of the following contains the greatest number of atoms?

(a) 12 g of H_2O (b) 17 g of NH_3

(c) 1.5 mol of nitrogen molecules (d) 6.022×10^{23} oxygen molecules

9. Which one of the following does not apply to 1.00 mol of hydrogen molecules?

(a) It has a amass of 1.01 g
(b) It contains 6.022×10^{23} molecules
(c) It occupies 22.71 L at STP
(d) It contains 1.20×10^{24} atoms

10. A gardener wishes to provide a nitrogen fertilizer for his soil. Assuming all prices are equal and equal amounts of nitrogen can be released from each, which one of the following would be the most economical compound for him to purchase?

(a) ammonium chloride (53.5 g mol^{-1})
(b) ammonium nitrate (80 g mol^{-1})
(c) ammonium sulfate (132 g mol^{-1})
(d) potassium nitrate (102 g mol^{-1})

11. The molecular formula of a compound is $\mathbf{ZX_3}$ and provides the information that

(a) In any sample of the compound the mass of **X** is three times the mass of **Z**.
(b) The volume ratio of **Z** to **X** in any sample of the compound is 3 : 1.
(c) Each molecule of this compound contains one atom of **Z** and three atoms of **X**.
(d) The mass of element **Z** is greater than the mass of element **X**.

12. Which of the following equations is NOT balanced?

(a) $2H_2S(g) + 3O_2(g) \Rightarrow 2H_2O(g) + 2SO_2(g)$
(b) $2C_2H_6(g) + 7O_2(g) \Rightarrow 4CO_2(g) + 6H_2O(g)$
(c) $HCl(aq) + NaOH(aq) \Rightarrow H_2O(l) + NaCl(aq)$
(d) $3NO(g) + 2O_2(g) \Rightarrow 3NO_2(g)$

13. In a sealed container, 32.0g of hydrogen gas is burnt with 16.0g of oxygen to produce water vapour. Which one of the following statements is false?

(a) The total mass of gas in the container after the reaction is 48.0g.
(b) 30.0g of hydrogen gas is unreacted.
(c) Twice the mass of hydrogen to oxygen must be reacted because the mole ratio for water is H_2O.
(d) 36g of water vapour is produced.

14. Which of the following chemical equations is balanced correctly?

(a) $NO_2(g) + H_2O(g) \rightarrow HNO_3(g) + NO(g)$
(b) $FeO(s) + O_2(g) \rightarrow Fe_2O_3(s)$
(c) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
(d) $C_3H_8(g) + 8O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

15. When a mixture of silver and sulfur is heated silver sulfide is formed according to the unbalanced equation: $Ag(s) + S(s) \rightarrow Ag_2S(s)$. The number of grams of sulfur that would have reacted with 5.00 g of silver would be about:

(a) 0.55 g
(b) 0.75 g
(c) 0.95 g
(d) 1.05 g

Longer questions

Name each compound and calculate the molar mass of each of the following:

1. (a) NO_2 ______________________________
   (b) XeF_4 ______________________________
   (c) HNO_3 ______________________________

2. (a) $(NH_4)_2S$ ______________________________
   (b) BaH_2 ______________________________
   (c) K_2HPO_4 ______________________________
   (d) $KMnO_4$ ______________________________
   (e) $K_2Cr_2O_7$ ______________________________

Calculate the mass in grams of each of the following:

3. (a) 1.75×10^{-6} mol of gold (III) chloride ____________________
   (b) 2.98 millimoles of potassium phosphate ____________________
   (c) 6.55 mol of ammonia ____________________

4. (a) 1.27 millimoles of carbon dioxide ____________________
   (b) 9.31×10^{-4} mol of gold (III) bromide ____________________
   (c) 62.7 mol of copper (II) sulfate ____________________

5. (a) 0.000305 mol of mercury ____________________
   (b) 10.5 mol of phosphorus ____________________
   (c) 125 mol of lithium ____________________

Calculate the number of moles of the following:

6. (a) 280.9 mg of silver ____________________
   (b) 5.869 g of nickel ____________________
   (c) 3.251 g of lithium ____________________

7. (a) 92.4 g of hydrogen bromide ____________________
   (b) 2.21 kg of sulfuric acid ____________________
   (c) 2.89 g of aluminium chloride ____________________

8. (a) 4.26×10^{-3} g of sodium dihydrogen phosphate ____________________
   (b) 151 kg of iron ____________________
   (c) 1.26×10^{4} g of aluminium ____________________

9. (a) 2.01 g of sodium sulfite ________________________
   (b) 2.01 g of sodium thiosulfate, $Na_2S_2O_3$ ________________________
   (c) 6.31 g of ammonium sulfide, $(NH_4)_2S$ ________________________
   (d) 7.63 g of calcium phosphate, $Ca_3(PO_4)_2$ ________________________

10. Calculate the number of moles of hydrogen atoms in each of the following:
   (a) 451 g of ammonium carbonate ________________________
   (b) 6.25 mg of sulfuric acid ________________________
   (c) 0.824 mol of water ________________________
   (d) 2.71 g of ammonia ________________________

Calculations using Avogadro's Number

11. Calculate the number of molecules present in each of the following:
   (e) 6.37 mol of carbon monoxide ________________________
   (b) 2.62×10^{-6} g of water ________________________
   (c) 5.23 g of benzene ________________________

12. Calculate the number of **carbon atoms** of each element present in each of the following substances.
   (a) 2.26 mol of $C_{12}H_{22}O_{22}$ ________________________
   (b) 0.000221 g of benzene, C_6H_6 ________________________
   (c) 6.81 g of carbon dioxide ________________________
   (d) 4.21 g of ethyne, C_2H_2 ________________________

13. Calculate the number of formula units or moles present in each of the following substances.
   (a) 155 g of $Al(NO_3)_3$
   (b) 1.00 g of B_2H_6
   (c) 250 mg of ICl_5
   (d) 3.45×10^{25} molecules of $C_6H_{12}O_6$
   (e) 3.45 g of Na_2CO_3

Atomic mass Calculation

14. Using average atomic masses for each of the following elements, calculate the mass of each of the following samples.
   (a) 2,780,000 atoms of lithium ________________________
   (b) 5×10^{25} sodium atoms ________________________
   (c) 6.022×10^{23} atoms of cadmium ________________________

15. Using the average atomic masses, calculate the number of atoms present in each of the following samples.

    (a) 749.2 g of arsenic ____

    (b) 2698 g of aluminium __________________________________

Percentage mass Calculations

16. Calculate the percent by mass of the first element in the following compounds.

    (a) H_3PO_3 ____

    (b) NH_4Cl ____

    (c) NH_4NO_3 ____

    (d) Potassium sulfate __________________________________

    (e) Calcium oxalate, CaC_2O_4 __________________________________

Empirical – Molecular Formula Calculations

17. Magnesium is used in flash bulbs, flares and fireworks. A salt of magnesium contains 16.39% of magnesium, 18.89% of nitrogen and 64.72% of oxygen. Determine its empirical formula.

18. A compound is found to contain 3.09% of hydrogen, 31.60% of phosphorus and 65.31% of oxygen. Determine its empirical formula.

19. A sulfate compound of cobalt contained 38.02% cobalt by mass. What is the empirical formula of the compound?

20. Sodium is a soft, silvery white solid metal which is used as a cooling medium in nuclear reactors.

    A very poisonous sodium compound consists of 46.91% of sodium, 24.51% of carbon and 28.59% of nitrogen on a mass basis. If its molecular mass is about 50 g, determine its empirical and molecular formulae.

21. A compound with the empirical formula “CH”, was found to have a molar mass of approximately 78 g. Determine the molecular formula of the compound.

22. A 0.7221 g sample of a compound contains 0.2990 g of carbon, 0.05849 g of hydrogen, 0.2318 g of nitrogen and the rest, oxygen. Determine the empirical formula of the compound.

23. Barium is a soft, silvery white metal used in bearings, alloys and pigments. When barium metal is heated in chlorine gas, a binary compound forms that contains 34.05% of chlorine by mass. Determine the empirical formula of the compound.

24. Mercury is a heavy, silvery liquid metal which is used in mercury vapour lamps. When 4.01 g of mercury is strongly heated in air, the oxide formed weighed 4.3g.

    Calculate the empirical formula of the oxide.

Moles, Mass and Avogadro’s Number

25. Aluminium is a metal with a high resistance to corrosion and a high strength to weight ratio. Calculate the number of moles of atoms in a 10.0 g sample of aluminium.

26. A silicon chip used in an integrated circuit of a microcomputer has a mass of 5.68 mg. How many silicon atoms are in this chip?

27. Cobalt is a metal that is added to steel to improve its resistance to corrosion. Calculate the number of moles and the mass of cobalt containing 5.00×10^{20} atoms of cobalt.

28. Juglone is a dye which is produced from the husks of black walnuts. It is a weed killer with the formula $C_{10}H_6O_3$.
    (a) Calculate its molecular mass.
    (b) A sample of 1.56×10^{-2} g of pure Juglone was extracted from walnut husks. How many moles of Juglone is this?

29. Isopentyl acetate ($C_7H_{14}O_2$) is the compound that gives banana its scent. It is also released in bee-sting. A bee releases 1 μg of isopentyl acetate per sting. How many molecules does one sting release? How many atoms of carbon are present in one sting?

30. Penicillin, an antibiotic, was discovered by Alexander Fleming in 1928. It has the formula $C_{14}H_{20}N_2SO_4$. Calculate the mass percentage composition of each element in this compound.

31. Determine the empirical and molecular formula for a compound that gives the following analysis in percentage composition. The molecular mass is known to be 98.96 g mol^{-1}.

    71.65% Cl 24.27% C 4.07% H

32. Caffeine, a stimulant found in coffee contains 49.48% carbon, 5.12% of hydrogen, 28.87% nitrogen and 16.49 % of oxygen by mass and has a molecular mass of 194.2 g mol^{-1}. Determine the molecular formula of caffeine.

33. Calculate the number of moles of sodium nitrate produced when 0.06 mol of sodium carbonate is reacted with excess nitric acid.

$$Na_2CO_3(s) + 2HNO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

34. Determine the mass of sodium chloride required to react with 10.0 mol of silver nitrate according to the following equation:

$$AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$$

35. Calculate the number of moles of sulphuric acid needed to produce 60.0g of ammonium sulphate when it reacts with ammonia gas as follows:

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

36. Determine the mass of lead (II) iodide precipitated by adding excess potassium iodide to 7.50 g of potassium iodide. The reaction is as follows:

$$Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$

Notes

Chapter 6

Thermochemistry

6.1 ENTHALPY

When we burn a fuel to obtain heat where does that heat come from? Obviously some compounds can give out a lot of heat to the surroundings – like petrol and other hydrocarbons. By the Law of Conservation of Energy, the energy output must come from somewhere else where energy has been lost. If combustion occurs, the bonds in the reactants have a greater energy content than the bonds of the products i.e. reactant bonds are stronger than those of the products and this difference in energy content shows up as heat.

For instance, let us look at the energies of the bonds holding hydrogen and chlorine together in their individual bonds. H-H bonds have a measured energy of 436 kilojoules per mole and Cl-Cl bonds have an energy of 243 kJ/mole. These figures indicate the energy required to break the molecule apart against the attractive forces of the two atoms. If we react hydrogen and chlorine together hydrogen chloride is formed – HCl, which has a bond energy of 432 kJ/mole between its atoms.

$$\underbrace{\mathrm{H}\overset{436}{\text{—}}\mathrm{H} \quad + \quad \mathrm{Cl}\overset{243}{\text{—}}\mathrm{Cl}}_{-679\ \mathrm{kJ}} \quad \rightarrow \quad \underbrace{2\ \mathrm{H}\overset{432}{\text{—}}\mathrm{Cl}}_{-864\ \mathrm{kJ}}$$

Total bond energies:

Bond energies are actually negative (the more negative energy a substance has, the more stable it is).

And the total heat energy content of a compound is called its Enthalpy, given the symbol H. So the total enthalpy difference (ΔH) in this reaction is $E_{Final} - E_{Initial}$

So $\Delta H = -864 - (-679) = -185$ kJ per mole of reactant.

A negative sign indicates that energy is given out to the surroundings – in this case the energy given out is in the form of heat. If heat is given out in a reaction it is said to be an Exothermic reaction.

If heat is taken in by a reaction, then the sum of the bond energies of the products is greater than those of the reactants and the reaction is said to be an Endothermic reaction. i.e. heat is taken in from the surroundings and they become colder.

In the reaction above we can see that enthalpy of the products is less than the enthalpy of the products and that the change in enthalpy ΔH is negative, which means the reaction is exothermic.

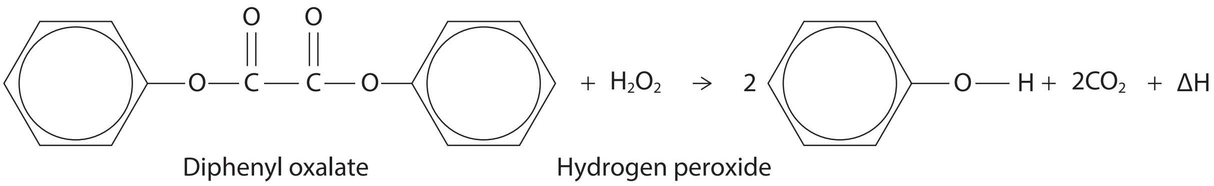
An example of an endothermic reaction is one where ammonium nitrate crystals are added to water.

$$\Delta H + NH_4NO_3(s) + H_2O(l) \rightarrow NH_4^+(aq) + NO_3^-(aq) + H_2O(l)$$

The hydrated ammonium and nitrate ions have more bond energy (attached to the water molecules) than the crystal ions and so, to separate them energy (ΔH) needs to be put in. This is obtained from the heat content of the surrounding water - hence the water cools. If ΔH is on the left of an equation, we say that the reaction is endothermic and ΔH is positive. If ΔH has a negative value then the reaction is exothermic.

The ammonium nitrate reaction is made use of in cooling packs used for sports sprains.

Some reactions give energy out in the form of light, instead of heat. An example of this is found in Glow Sticks used at parties to give out coloured light when they are broken - without the use of batteries. The light is produced in an exothermic chemiluminescent reaction between diphenyl oxalate and hydrogen peroxide.



6.2 FUELS AND ENERGY

Fuels as a ready source of energy have been important for our society from early prehistoric days when humans burned wood and oil for heating and light. Fuels are a valuable source of chemical energy or enthalpy which can be turned into other forms of energy or work (electrical energy, heat, light, potential energy, etc).

With so many countries moving to industrialisation this century, the need for new fuel sources has become critical – but so has the problem of pollution of our environment and the effect on the Earth's climate due to the Enhanced Greenhouse Effect.

The Greenhouse Effect is where the Earth seems to act like a greenhouse, due to an outer layer of greenhouse gases (CO_2, H_2O and methane mainly) that surround it and are trapped in the upper atmosphere.

The Earth heats up due to the sunlight falling on it and therefore emits infrared (heat) rays (IR) towards the sky. The theory is that this IR becomes absorbed by the upper greenhouse gas or reflected downwards again, keeping the heat in – just like a greenhouse does.

If the average temperature of the earth rises by only a few degrees it will cause massive melting of the polar ice caps. Hence many countries are now trying to limit the greenhouse gas emissions by switching more of their energy generation to renewable systems, such as solar panels, hydroelectric generators, wind and wave turbines and geothermal heating plants.

Traditional fossil fuels such as petrol, oil, coal and natural gas all produce these greenhouse gases when they are burned but these will run out some time in the future. Hence, more sources of renewable energy need to be found that emit little or no carbon dioxide. Solar panels, wind turbines and wave power generators have become important in this respect, but only contribute a tiny part to the overall needs of society at present. It is estimated that humans are using about 4×10^{14} megajoules of energy each year at present – a figure which is constantly growing but about 90% of our energy still comes from Coal and oil. Below is a table which compares the energy density of different fuels. This is the amount of energy in megajoules that can be obtained from 1 kilogram of the fuel.

Fuel	Petrol	Diesel	Ethanol	Coal	LNG	Uranium
Energy density (MJ/kg)	46.4	48	26.4	26	53.6	81×10^6

From this table we can see how important Liquid Natural Gas (LNG) is as a fuel, which could actually be manufactured as Carbon-Neutral, although it is much easier at the moment to just pump it from the ground. The US Chevron company has recently invested $55 billion in an LNG production plant on Barrow Island in Western Australia, but some fuels can be manufactured and are classed as Renewable.

Germany plans to build a plant that will manufacture synthetic methane giving a 20 MW power output (20 million joules per second). They will use a carbon-neutral system which consumes as much CO_2 as it produces when burnt. The system by which methane is produced is called the Sebatier process:

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(l) + \Delta H$$

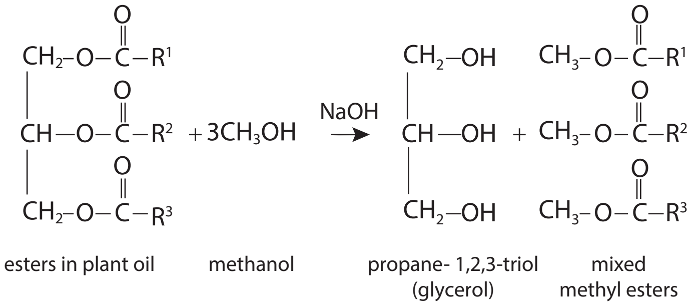
The hydrogen is obtained by electrolysing water and the CO_2 that is emitted when the methane is burned in the power station is recycled and used again to produce more methane.

There are other systems in use which capture carbon but prove to be expensive: One method liquefies the CO_2 and buries it underground and another reacts it with other chemicals to produce calcium carbonate which is more stable and can be buried.

6.3 BIOFUELS

Instead of using non-renewable sources of energy, such as petrol and coal, in the last few decades new fuels have been manufactured from existing renewable products, such as animal fat or vegetable oils.

Biodiesel is non-toxic, biodegradable and a useful renewable fuel source. It is considered a carbon neutral fuel as the carbon dioxide produced in its combustion is equivalent to that which was used by the plant from which it was made. Biodiesel can be manufactured by converting the triglycerides obtained from animal fats or vegetable oils into methyl esters which constitute biodiesel. The fatty acids undergo a process called Transesterification. If the reaction is performed in the presence of methanol it transforms the triglycerides into methyl esters which can be burned and have a high energy density. Biodiesel is better for the environment than normal diesel produced from oil as it emits no sulfur when burned.



Bioethanol

Ethanol (C_2H_5OH) is a useful renewable fuel in use in many countries and stands at about 6% of the total fuel consumption in the World. Brazil was able to completely transform its economy by altering car engines so they could use ethanol instead of imported petrol. Ethanol is mostly produced by a fermentation process using sugar cane, potato or corn as a main reactant and enzymes which converts the starch to alcohol: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \Delta H$ (an exothermic reaction).

Another method of production is to use a natural gas component, ethene, as a starting compound and using an addition reaction with water as the other reactant:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

6.4 CALCULATION OF ENERGY DENSITY

The energy per gram of a fuel can be found by burning it and measuring how much the temperature of a known mass of water rises. It is important to know that 1 gram of water needs 4.2 joules of heat for its temperature to rise by 1 °C.

The experiment shown below was to find the heat content in the oil in a peanut.

A peanut is suspended on a digital balance to find its initial mass and then weighed again after a known time for which it burned. The flame from the peanut was used to heat up a known mass of water whose temperature could be measured with a thermometer.

Here are the results of the experiment:

Mass of water used = 32.2 g

Initial temperature = 17°C

Final temperature = 31°C

Time of heating = 68 s

Initial mass of peanut = 2.89 g

Mass of peanut after burning = 2.33 g

Calculation

Mass of oil lost by the peanut = 2.89 – 2.33 = 0.56 g

Temperature rise by the water = 41 – 17 = 24°C

For 1 g of water to rise by 1°C 4.2 J is needed

For 32.2 g of water to rise by 1°C 4.2 x 32.2 J is needed = 135.2 J

For 32.2 g of water to rise by 24°C 135.2 x 24 J is needed = <u>3246 J</u> (this is the heat absorbed)

Heat obtained for 0.56 g is 3244 J so heat per gram of oil is $\frac{3246}{0.56}$ = 5794 J

Therefore the heat per kilogram of oil = 5796 x 1000 = 5796000 J kg^{-1} = 5.796 MJ kg^{-1}.

Foods

The Calorific Values of foods can be determined by burning them in a Bomb Calorimeter and seeing how much heat they give out – in a similar way to the rough experiment shown above.

The table below shows the energy content of some common foodstuffs.

Foodstuff	Energy content (kJ/kg)
Fat	37
Alcohol	29
Protein	17
Carbohydrate	16
Salmon	6.5
Cheese	10.3
Chocolate chip biscuit	20
Banana	3.4

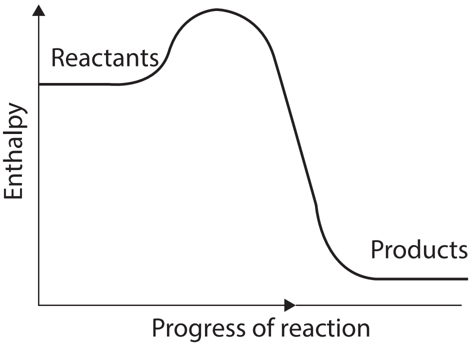
Set 1 Thermochemistry

1. Which of the following is endothermic?
   (a) Burning magnesium metal.
   (b) Condensation of water.
   (c) Melting candle wax.
   (d) Combustion of petrol.

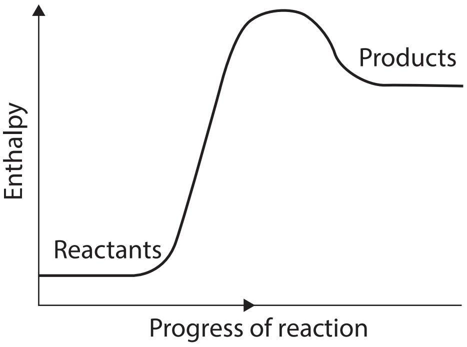
2. Which of the following statements is INCORRECT?
   (a) An exothermic reaction releases heat and has a negative ΔH.
   (b) In an exothermic reaction the temperature of the surroundings would decrease.
   (c) In an exothermic reaction the products have a lower enthalpy (heat content) than the reactants.
   (d) An example of an endothermic reaction is the dissolution of ammonium nitrate

3. Which of the following graphs shows enthalpy changes involved in an endothermic reaction.

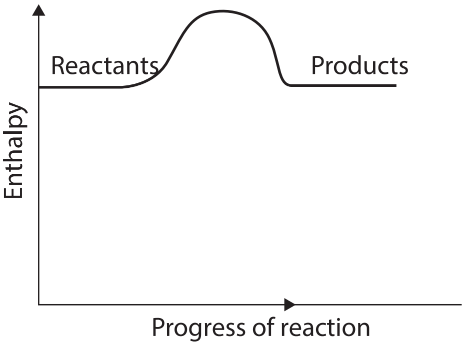
a)



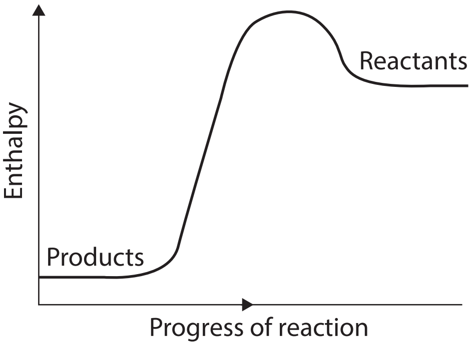
b)



c)



d)



4. Consider the following equations:

(I) $C_4H_{10}(l) + 6O_2(g) \Rightarrow 4CO_2(g) + 5H_2O(l)$ $\Delta H = -2727\ \text{kJ mol}^{-1}$

(II) $6CO_2(g) + 6H_2O(l) \Rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ $\Delta H = +2816\ \text{kJ mol}^{-1}$

(III) $CO(g) + \frac{1}{2}O_2(g) \Rightarrow CO_2(g)$ $\Delta H = -283\ \text{kJ mol}^{-1}$

(IV) $H_2(g) + \frac{1}{2}O_2(g) \Rightarrow H_2O(l)$ $\Delta H = -286\ \text{kJ mol}^{-1}$

(V) $C_3H_8(g) \Rightarrow 3C(s) + 4H_2(g)$ $\Delta H = +104\ \text{kJ mol}^{-1}$

Which equations are exothermic?

(a) I, III and IV (b) I, II and IV

(c) III and V (d) II and V

5. When solid ammonium chloride dissolves in water, there is a decrease in the temperature of the solution. This type of reaction is called

(a) An endothermic reaction. (b) A neutralisation reaction.

(c) An exothermic reaction. (d) A precipitation reaction.

6. The neutralization reaction between hydrochloric acid and sodium hydroxide may be represented as:

$HCl(aq) + NaOH(aq) \Rightarrow NaCl(aq) + H_2O(l) + 57.2kJ$

In this reaction, you would expect the temperature of the resulting solution to

(a) Increase, due to the reaction being endothermic.

(b) Decrease, due to the reaction being exothermic.

(c) Decrease, due to the reaction being endothermic.

(d) Increase, due to the reaction being exothermic.

7. Study the following two equations:

(I) $H_2(g) + ½O_2(g) \Rightarrow H_2O(g)$ $\Delta H = -242$ kJ

(II) $H_2(g) + ½O_2(g) \Rightarrow H_2O(l)$ $\Delta H = -285$ kJ

The best explanation for the difference in the values of ΔH for these two reactions is:

(a) More heat is given off in equation I because the water is in gaseous form.

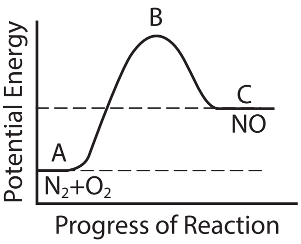
(b) Water in the liquid phase has more stored energy than water vapour so reaction II releases less heat energy to its surroundings.

(c) Water vapour has greater enthalpy than liquid water so reaction II releases more heat energy to its surroundings.

(d) Water in the liquid phase stores less energy than water vapour and so releases less heat energy to its surroundings.

8. The following diagram shows the changes in Potential Energy for the reaction:

$N_2(g) + O_2(g) \Rightarrow 2NO(g)$



Which of the following statements is FALSE?

(a) The reaction is endothermic with ΔH = C – A.

(b) The reactants have less potential energy than the products.

(c) B represents the transitional state where intermediate compounds are formed in the course of the reaction.

(d) The activation energy would be equal to B – C.

9. Consider the reaction between marble chips (calcium carbonate) and dilute hydrochloric acid:

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

Which one of the following would increase the *rate* at which the marble chips react?

(a) Decreasing the concentration of the hydrochloric acid.

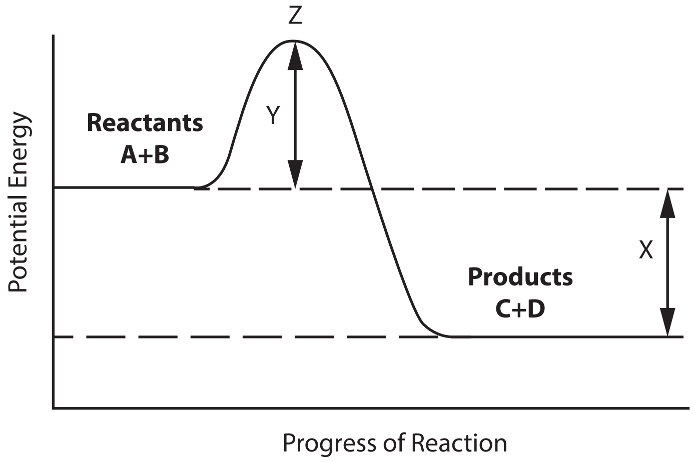
(b) Adding more water to the solution.

(c) Crushing the marble chips into powder form.

(d) Decreasing the temperature of the acid solution added.

The next question refers to the energy profile diagram below for the generalised reaction:

$A + B \leftrightharpoons C + D$



10. Which one of the statements below is incorrect?

(a) At Z, the molecules in the transition state are most likely to form products C and D.

(b) Z is the activated complex.

(c) The activation energy for the forward reaction is equal to Y.

(d) The activation energy for the reverse reaction is equal to X + Y.

11. The bond energies for the following interatomic bonds are:

H-Cl = 432 kJ mol^{-1}; Cl-O = 203 kJ mol^{-1}; H-O = 467 kJ mol^{-1}.

In the molecule H-Cl-O, what is the total enthalpy of all the bonds per mole of substance?

(a) 670 kJ (b) 635 kJ (c) 899 kJ (d) 1102 kJ

12. Which statement is FALSE for a mass of gas in a sealed container?

(a) The molecules are constantly moving.
(b) Particles are moving randomly
(c) The pressure is constant regardless of conditions
(d) The movement of the particles creates pressure

13. Which statement is true for photosynthesis?

(a) It might occur in the dark
(b) Carbon dioxide is released
(c) Oxygen is consumed
(d) Carbon atoms are joined together.

14. Which statement is true regarding the Enhanced Greenhouse Effect?

(a) It is caused by the radiation from the Sun
(b) It is caused by high ozone levels in the atmosphere
(c) It causes a stunted growth of plants
(d) It causes gases to dissolve in the rain which makes the sea less acidic

15. Which of the following are classed as Fossil Fuels?

(I) Wood (II) Carbon dioxide
(III) Methane (IV) Oil

(a) (I) and (III) (b) (II) and (IV)
(c) (III) and (IV) (d) (I) and (II)

16. The energy density of petrol is quoted as 46.4 MJ kg^{-1} and our civilisation uses about 4 x 10^{14} MJ of energy per year. How many tonnes of petrol does this approximately equate to? (1 tonne = 1000 kg)

(a) 4 x 10^{6} T (b) 5 x 10^{9} T (c) 9 x 10^{9} T (d) 6 x 10^{10} T

17. From the table of foodstuffs, chocolate biscuits have an energy value of 20 kJ per gram. If an average man needs 8700 kJ per day to survive, how many chocolate chip biscuits is this equivalent to? (One biscuit has a mass of about 12 grams)

(a) 36 (b) 41 (c) 58 (d) 72

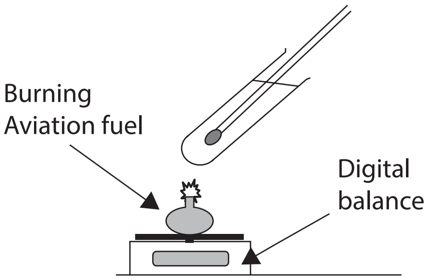
18. Comparing the bond energies of the reactants in a reaction with the bond energies of the products, Which is true?
    (a) Energy is conserved to they will always be the same.
    (b) Heat released will equal the reactant bond energies.
    (c) In an endothermic reaction the reactant bond energies are lower than the product bond energies.
    (d) In a exothermic reaction the heat released equals the sum of the reactant and product bond energies.

19. In a coal-fired power station, the lumps of coal are always pulverised (powdered) before burning because.
    (a) Coal does not give out so much CO_2 in this process
    (b) More of the coal will react with air
    (c) Less oxygen is consumed
    (d) The combustion reaction is faster

20. Some houses in Australia burn LNG for heating and cooking. Ethanol is not used for this purpose because.
    (a) Its energy content is lower
    (b) Its boiling point is too low
    (c) It has more carbon bonds than LNG
    (d) Its reactions are endothermic.

PART 2 : Short answers

Q1. An experiment aimed to calculate the energy density of aviation fuel. To do this two students filled a spirit burner with some fuel and weighed it. Then they lit the burner and heated up some water in a test tube, noting the temperatures at start and finish and then re-weighed the spirit burner.



The results are show below:

Original mass of burner + fuel = 127.65 g

Final mass of burner + fuel = 127.31 g

Mass of water in tube = 98.76 g

Initial temperature of water = 14.6°C

Final temperature of water = 47.9°C

Heat needed to heat 1 gram of water up by 1°C = 4.2 joules

Complete:

(i) Mass of fuel burned = __________ g

(ii) Temperature rise of water (ΔT) = __________ °C

(iii) Heat needed to raise the temperature of the water (m x 4.2 x ΔT) = __________ J

(iv) Heat/mass of fuel burned = __________ J/g

Change this figure into MJ/kg = __________ MJ/kg

Q2. (a) Sketch a reaction profile for the chemical reaction shown below.

The activation energy is 230 kJ mol^{-1}. Sketch the graph to scale.

$H_2\,(g) + F_2\,(g) \rightarrow 2\,HF\,(g)$ $\Delta H = -538$ kJ mol^{-1}

(b) The overall change in heat energy describes this reaction as an __________________ reaction.

Q3. Consider the following two reactions.

(A) $Pb^{2+}(aq) + 2\ I^{-}(aq) \rightarrow PbI_2(s)$ $\Delta H = -59$ kJ

(B) $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$ $\Delta H = -611$ kJ

Reaction (b) produces considerably more heat energy than reaction (a). Provide an explanation for why reaction (a) is faster at room temperature.

____

____

Q4. The fermentation process involves the use of an enzyme as an organic catalyst to cause this reaction to produce alcohol from glucose solution:

$C_6H_{12}O_6(s) \rightarrow 2\ C_2H_5OH(l) + 2CO_2(g)$ where $\Delta H = -82$ kJ mol^{-1}

(a) Would you expect the solution of glucose to get warmer or cooler as the reaction proceeds?

____

(b) If 5 moles of glucose were used in this reaction, how much heat would be produced?

____

(c) If a solution containing 5 moles of glucose with a mass of 3500 g was fermented, what would be the expected temperature rise for this solution? (assume that it takes 4.2 J to heat 1 gram of the solution by 1°C)

____

____

Q5. On the International Space Station the CO_2 expired by the astronauts is recycled by the Sebatier Process to give methane, which can be further used as fuel.

In this reaction carbon dioxide is mixed with hydrogen to produce methane and water.

(a) Write a balanced equation for this reaction.

____

The hydrogen for this reaction is obtained by the electrolysis of water on the Station and the overall reaction has a value of ΔH of -165 kJ mol^{-1}.

(b) On a particular day 1.78 megajoules of heat was given out by this reaction. How many moles of CO_2 had been converted to methane?

____

____

Q6. (a) Explain why a fuel such as petrol burns steadily when poured onto the ground and ignited and yet will explode inside the cylinders of a car engine.

____

____

(b) A petrol and air mix is quite stable until it is ignited with a match. Explain the role of the match in this reaction, relating your explanation to a reaction energy diagram.

____

(c) Draw a roughly-scaled reaction energy profile diagram for the reaction of nitrogen dioxide and oxygen: $NO_2(g) + O_2(g) \rightarrow NO(g) + O_3(g)$, given that E_a for the reaction is 210 kJ mol^{-1} and $\Delta H = +200$ kJ mol^{-1}.

Q7. A bottle containing aftershave lotion is left uncapped all night. Even though the aftershave boils at 78°C, some has been lost from the bottle by the following morning. If the cap is put on the aftershave bottle no more is lost.

(a) Explain this using kinetic/collision theory and equilibrium principles.

____

(b) Why does sugar dissolve quicker in warm tea than in cold tea?

____

(c) Explain how tea can become saturated with sugar if too much is added and what is happening at the molecular level.

____

____

Chapter

7

Shapes and Intermolecular Forces

7.1 CHEMICAL BONDS

In chapter 3 you studied the three types of **chemical bonds**. These are strong electrostatic bonds or attractions between oppositely charged particles.

In metallic substances the strong electrostatic attraction is between the positive metal ion and the delocalised valence electrons in the crystal lattice. With ionic substances it is between oppositely charged ions in the crystal lattice. In covalent substances the attraction is between the shared electrons in the covalent bond and the nuclei of the two adjacent atoms that are sharing them.

These strong electrostatic bonds largely determine the physical and chemical properties of the substance.

Metallic, ionic and covalent network substances are all lattices or networks of particles and so the strong bonding occurs throughout the substance. This generally results in high melting and boiling points and hardness. Properties such as malleability/ductility, solubility and electrical and heat conductivity are determined by the types of charged particles present.

Intermolecular forces are **physical bonds.**

Covalent molecular substances exist as discrete separate molecules. They have strong electrostatic covalent bonds within their molecules holding them together. These are called intramolecular bonds. They also have **weak physical bonds** between molecules which are called **intermolecular forces**. These weak intermolecular forces give rise to low melting and boiling points and covalent molecular substances are generally soft or waxy, and gases or liquids at room temperature. They don’t conduct electricity as they do not have any mobile charge-carrying particles. Their electrons are all held in bonds.

There are three types of intermolecular forces. There are **dispersion forces**, which are the weakest and occur between non-polar covalent molecular substances. **Dipole-dipole interactions** are stronger than dispersion forces and occur between polar covalent molecular substances. The strongest intermolecular forces are called **hydrogen bonds** and these can be thought of as very strong dipole-dipole interactions. They occur between very polar covalent molecular substances.

Dispersion forces < dipole-dipole interactions < hydrogen bonds

The physical properties of a covalent molecular substance depend upon its structure, which determines its polarity and therefore the type of intermolecular forces present.

7.2 POLAR BONDS

Polar bonds are covalent bonds that have a separation of charge, or a partial positive charge at one end of the bond and a partial negative charge at the other end. These partial charges are not as large as those held by ions or electrons.

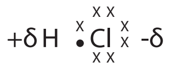
In Chapter 3 the concept of electronegativity was introduced. Electronegativity is a measure of the tendency of an atom to attract the shared electrons in a covalent bond to itself. It is a competition. If one of the atoms in the bond has a greater electronegativity than the other, the shared pair of electrons will spend more time in the vicinity of this atom.

When a covalent bond is formed between two identical atoms with the same electronegativity the electrons are shared equally and the bond is non-polar. There is no separation of charge.

e.g. H_2

When two different atoms with different electronegativities form a covalent bond the shared electrons are attracted to one of the atoms more than the other. This gives rise to a separation of charge and the bond is polar. One atom has a small positive charge, delta plus (+δ) and the other a small negative charge, delta minus (-δ). In the example below the chlorine atom has a greater electronegativity than the hydrogen atom and so the shared electrons spend more time in the vicinity of the chlorine atom.

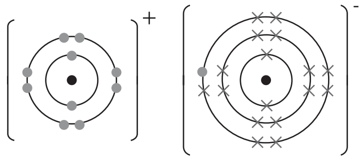
e.g. HCl



The larger the difference in electronegativity the more polar the bond.

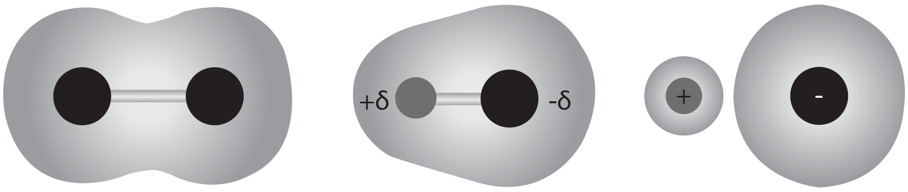
Note that with ionic substances the difference in electronegativity between metals and non-metals is so great that electrons are transferred completely from the metal to the non-metal, forming ions.

e.g. Na^+ and Cl^-



sodium ion, Na^+ $[2,8]^+$

chloride ion, Cl^- $[2,8,8]^-$



Nonpolar Covalent Bond Polar Covalent Bond Ionic Bond

7.3 POLAR MOLECULES

A polar covalent molecular substance is one that has an overall nett dipole, or polarity over the whole molecule. A dipole means that the molecule has a partial positive charge on one side of the molecule separated from a partial negative charge on the other.

For a molecule to be polar;

- it must contain one or more polar bonds
- it must not be symmetrical

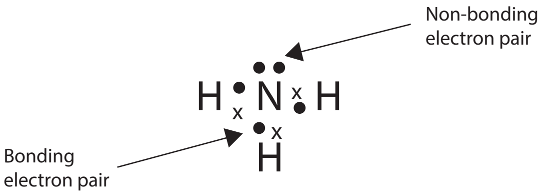
To determine whether a molecule is polar you must draw its Lewis structure, or electron dot diagram, as in Chapter 3. The Lewis structure will provide information about the bonding around the molecule's central atom. Check for polar bonds and if polar bonds are present you can use the valence shell electron pair repulsion theory (VSEPRT) to predict its shape and to decide if it is symmetrical (see below).

Symmetrical molecules are non-polar as their polar bonds cancel each other out and there is no nett dipole, or partially positive and partially negative end to the molecule.

Asymmetrical molecules are polar as their polar bonds cannot cancel each other out and contribute to an overall nett dipole.

Bonding electron pairs are valence shell electrons involved in a covalent bond between two atoms. These could be single, double or triple bonds.

Non-bonding electron pairs, or lone pairs, are valence shell electrons not involved in a covalent bond.



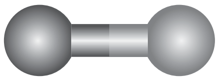
Valence shell electron pairs, both bonding and non-bonding, will repel each other as they are of like charge. The VSEPRT suggests that the shape of a simple molecule, or ion, is one which minimises repulsion between electron pairs. This means that bonding and non-bonding electron pairs will be equally spaced and as far apart as possible around the central atom.

If the central atom is surrounded by bonding pairs only, most simple molecules will have standard shapes with equal bond angles. If there are non-bonding pairs around the central atom these exert greater repulsion and can affect the shape.

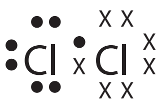
7.4 MOLECULAR SHAPES

Linear

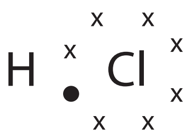
A diatomic molecule will be linear as there is no central atom. e.g. Cl_2, HCl



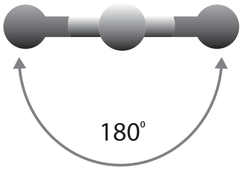
If a linear diatomic molecule is elemental or made up of only one type of atom, then it will be non-polar as there will be no nett dipole.



If it is made up of two different types of atoms then it will have a polar bond and it will have a nett dipole. It will be polar.

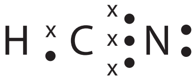


Molecules with three atoms can be linear if there are only two bonding pairs and no non-bonding pairs around the central atom. The furthest that two electron pairs can be apart around a central atom is with a bond angle of 180°. e.g. $BeCl_2$, CO_2, HCN



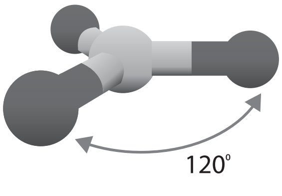
If a linear molecule consists of two of the same atoms on either side of the central atom then it will be non-polar. This is because the two polar bonds will cancel each other out and there will be no nett dipole.

If it has two different atoms surrounding the central atom then it will have polar bonds of different magnitude. These will not cancel each other out but will contribute to a nett dipole, and so it will be polar.

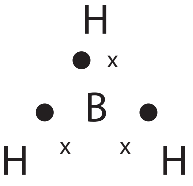


Trigonal planar (triangular planar)

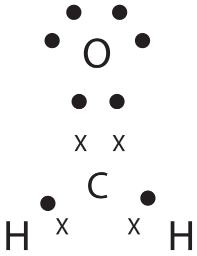
Molecules with only three atoms surrounding the central atom and no non-bonding pairs will adopt the trigonal planar shape. The furthest that three electron pairs can be repelled around the central atom is 120°. e.g. BCl_3, CH_2O



If a trigonal planar molecule has three identical atoms attached to the central atom then there will be polar bonds but they will cancel each other out. Hence there will be no nett dipole and it will be non-polar. e.g. BH_3



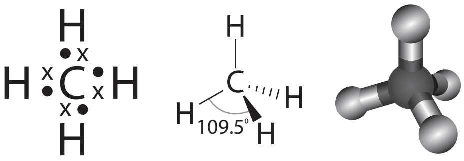
If the molecule has two or three different atoms surrounding the central atom then it will have polar bonds and is asymmetric, so these polar bonds will not cancel each other out. There will be a nett dipole and so the molecule will be polar. e.g. CH_2O



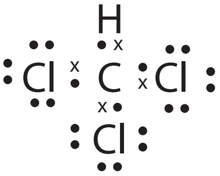
Tetrahedral

Molecules with four atoms surrounding the central atom will adopt the tetrahedral shape. The furthest that four electron pairs can be repelled around the central atom in 3D is when bond angles are 109.5°.

If a tetrahedral molecule has four of the same atoms attached to the central atom then it will have polar bonds but these will cancel each other out and it will have no nett dipole. It will be non-polar. e.g. CH_4.



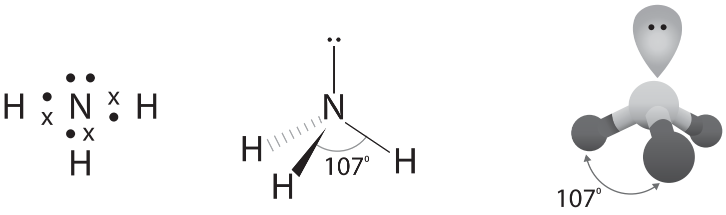
If there are different atoms surrounding the central atom then the module will have polar bonds and it will be asymmetric so the polar bonds will not cancel each other out. There will be a nett dipole and the molecule will be polar. e.g. $CHCl_3$.



Pyramidal

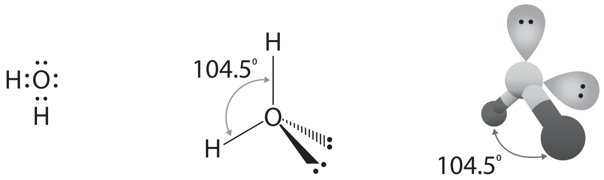
Molecules with three atoms surrounding the central atom and one non-bonding pair of electrons will have a similar geometry to a tetrahedral molecule as there are four electron pairs repelling each other. The shape, however, will be determined by the atoms. The shape is based on a triangular based pyramid and is called pyramidal. The bond angles in this case are 107° as the non-bonding pair exists closer to the central atom and repels the three bonding pairs more than another bonding pair would. e.g. NH_3

All pyramidal molecules are polar as they are always asymmetrical.

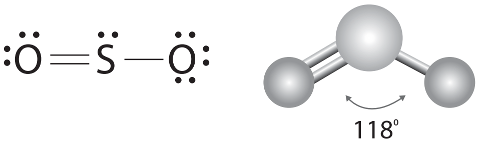


V-shaped or bent

Molecules with two atoms surrounding the central atom and two non-bonding pairs of electrons will also have a similar geometry to a tetrahedral molecule as there are four electron pairs repelling each other. The shape will once again be determined by the atoms. The shape is called V-shaped, or bent. The bond angle in this case is 104.5° as the non-bonding pairs repel the two bonding pairs more than two bonding pairs would. e.g. H_2O

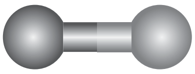
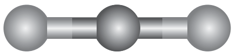
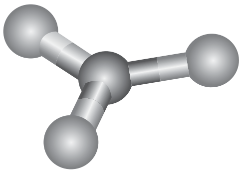
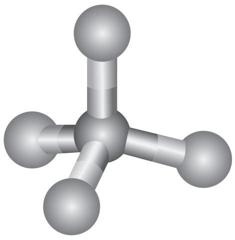
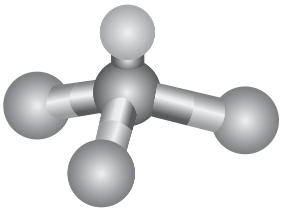
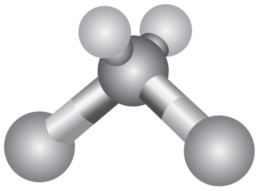
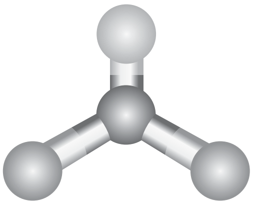


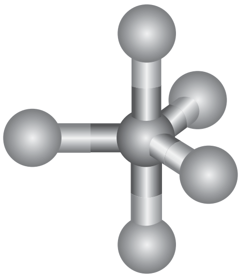
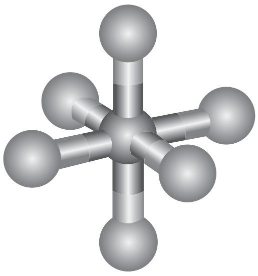
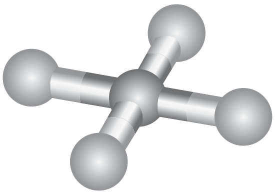
Molecules with two atoms surrounding the central atom and only one non-bonding pair of electrons will also have a similar geometry to a trigonal planar molecule as there are three electron pairs repelling each other. The shape will once again be determined by the atoms. This shape is also called V-shaped, or bent. The bond angle in this case is 118° as the non-bonding pair repels the two bonding pairs more than a bonding pair would. e.g. SO_2



All V-shaped molecules are polar as they are always asymmetrical.

This information is summarised in the table below.

shape	Bonding pairs around central atom	Non-bonding (lone) pairs around central atom	Bond angle	examples
Linear 	1	0,1,2,3	N/A	HCl, Cl_2
Linear 	2	0	180°	CO_2 $BeCl_2$ HCN
Trigonal (triangular) planar 	3	0	120°	BCl_3 CO_3^{2-}
Tetrahedral 	4	0	109.5°	CH_4 CCl_4 CCl_2F_2 SO_4^{2-}
Pyramidal 	3	1	107°	NH_3 PCl_3
V-shaped or bent I 	2	2	104.5°	H_2O H_2S
V-shaped or bent II 	2	1	<120°	SO_2

shape	**Bonding pairs around central atom**	**Non-bonding (lone) pairs around central atom**	**Bond angle**	**examples**
These shapes below are not examinable:				
Trigonal bipyramidal 	5	0	120° & 90°	PCl_5
Octahedral 	6	0	90°	SF_6
Square planar 	4	2	90°	XeF_4

Set 1

1. Identify each of the following as ionic or covalent molecular substances:
   (a) RbCl (b) HBr (c) PI_3 (d) $MgCl_2$
   (e) CBr_4 (f) SI_2 (g) ClBr

2. Which of the following molecules have polar bonds?
   (a) N_2 (b) HCl (c) NO_2 (d) Br_2
   (e) CCl_4 (f) H_2O (g) CO_2

3. Draw electron dot diagrams for the following covalent molecular substances:
   (a) NF_3 (b) $SiCl_4$ (c) Cl_2O (d) HBr
   (e) I_2 (f) HCHO (g) CS_2 (h) SO_2
   (i) CH_2Cl_2 (j) PH_3 (k) BF_3 (l) H_2O_2
   (m) HCN (n) CH_3COOH (o) H_2S

4. Predict the shapes of each of the substances in Q3 above.

5. Which of the substances in Q3 have polar molecules?

6. Draw electron dot diagrams for the following polyatomic ions and state their shape:

   (a) NO_3^- (b) SO_3^{2-} (c) OH^- (d) PO_4^{3-}

   (e) CO_3^{2-} (f) NH_4^+ (g) SO_4^{2-} (h) CN^-

7. List the bond angles for the each of the molecular shapes below:

   (a) tetrahedral (b) V-shaped or bent

   (c) linear (d) pyramidal

   (e) trigonal planar

8. Which of the molecular shapes in Q7 always produce polar molecules?

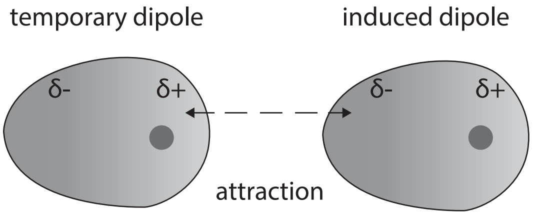
7.5 INTERMOLECULAR FORCES

Although the intramolecular covalent bonding within molecules is strong, the intermolecular forces between molecules are weak. Molecules and monatomic noble gases are subject to weak attractive intermolecular forces, which determine their physical properties.

Dispersion forces (temporary dipole – induced dipole forces)

Dispersion forces are the weakest attractive intermolecular forces. They result from the uneven distribution of electrons in atoms of noble gases and covalent molecules, and are also called temporary dipole- induced dipole forces.

Electrons are constantly moving in their orbitals so their position is constantly changing. This means that at any instant one side of a molecule or noble gas may have more electrons than the other. This will give rise to a temporary polarity, or dipole. When an atom or molecule with a temporary dipole comes near another atom or molecule, it influences and induces a dipole in that atom or molecule. The partially negative end of one repels the electrons in the other, inducing a dipole in it. The two dipoles interact with each other and attraction results. This interaction may only be for an instant but is enough to influence properties such as melting and boiling point, solubility and vapour pressure.



Dispersion forces are the only ones existing between the atoms of noble gases.

Substances with large molecular masses contain many protons and electrons. The greater the number of electrons, the stronger the dispersion forces. Therefore more energy is needed to separate the particles. Hence their melting and boiling points are higher than those of smaller molecules.

Halogens	Boiling point (°C)
F_2	-188
Cl_2	-34
Br_2	59
I_2	184

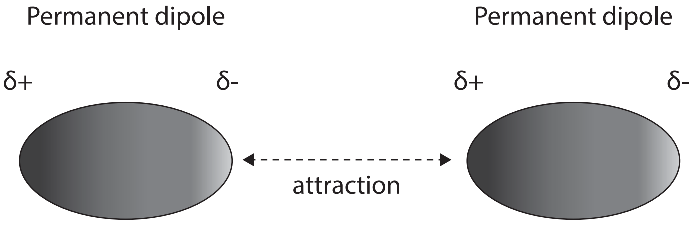
Noble gases	Boiling point (°C)
He	-269
Ne	-246
Ar	-186
Kr	-153

Alkanes	Boiling point (°C)
CH_4	-162
C_2H_6	-89
C_3H_8	-42
C_4H_{10}	-1

Dipole-dipole interactions (Dipole-dipole forces)

Dipole-dipole interactions exist between polar molecules. The dipole of a polar substance is permanent and larger than that of a non-polar molecule. When two polar molecules approach each other, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. These dipole-dipole interactions act in addition to the dispersion forces. The extra attraction between dipoles means that more energy is required to separate molecules and so the melting and boiling points of substances are higher than that of non-polar molecules with similar mass.

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\text{-----}\overset{\delta+}{H}-\overset{\delta-}{Cl}$$



Note that dipole-dipole forces are stronger and more long-lived than dispersion forces. Very large non-polar molecules can have many temporary dipole-induced dipole interactions, so there are large non-polar molecules with higher melting and boiling points than smaller polar molecules.

Hydrogen bonding

Hydrogen bonding is a special and much stronger type of dipole-dipole interaction. It occurs between hydrogen atoms directly bonded to a fluorine, oxygen or nitrogen atom on one molecule and a non-bonding electron pair on a fluorine, oxygen or nitrogen on another molecule. Bonds between hydrogen and the three most electronegative elements are very polar. The small sizes of hydrogen, fluorine, oxygen and nitrogen atoms means that the partial positive and negative charges of the polar bond are concentrated in a small volume and lead to a high charge density and a very strong dipole.

The significantly high increase in the melting and boiling points of some covalent molecular substances is due to the presence of hydrogen bonding.

Consider the boiling points of the first four Group 14, 15, 16 and 17 hydrides.

Group 14 hydrides	M_r	Boiling point (°C)
CH_4	16.042	-161
SiH_4	32.122	-112
GeH_4	76.622	-88
SnH_4	122.732	-52

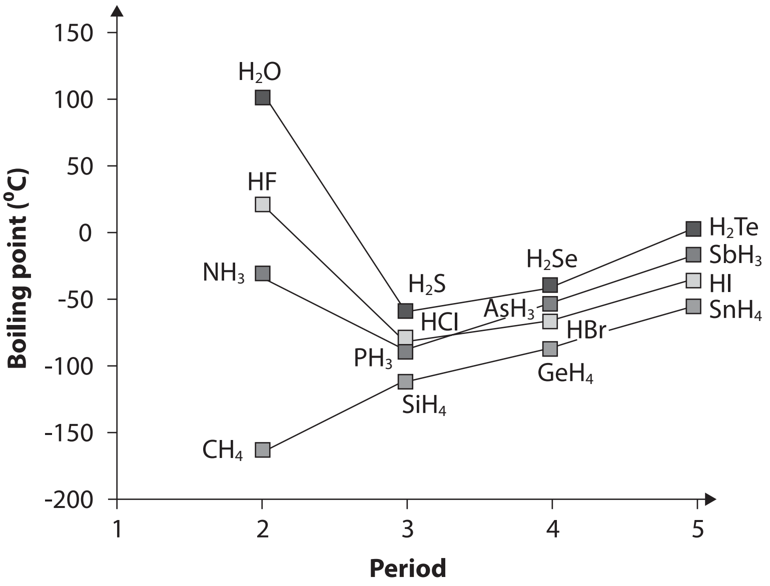
Group 15 hydrides	M_r	Boiling point (°C)
NH_3	**17.034**	**-33**
PH_3	33.994	-88
AsH_3	77.944	-63
SbH_3	124.824	-17

Group 16 hydrides	M_r	Boiling point (°C)
H_2O	**18.016**	**100**
H_2S	34.086	-60
H_2Se	80.976	-41
H_2Te	129.616	-2

Hydrogen bonding

Group 17 hydrides	M_r	Boiling point (°C)
HF	**20.008**	**20**
HCl	36.458	-85
HBr	80.908	-66
HI	127.908	-34

Boiling points of the first four Group 14, 15, 16 and 17 hydrides

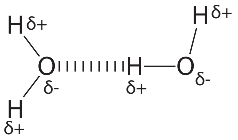


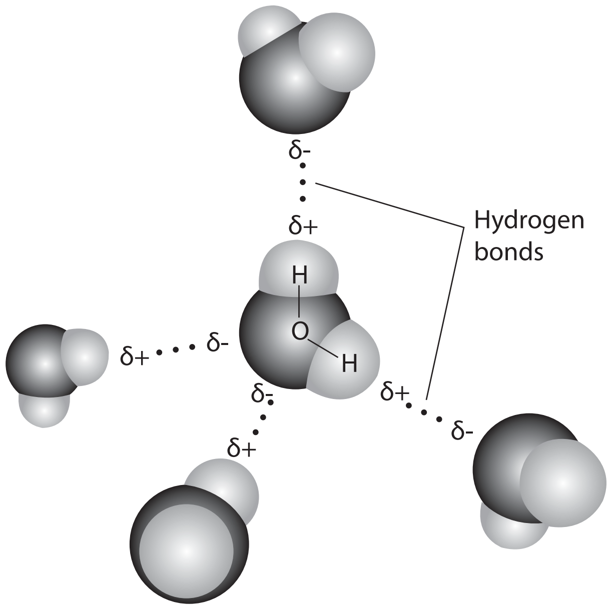
All of the graphs show the general trend that as M_r increases, boiling point increases. The Group 14 hydrides are all non-polar and therefore only have dispersion forces. As the M_r increases from CH_4 to SnH_4 the boiling point increases, due to increased dispersion forces. All molecules experience dispersion forces and this is why we see a similar trend for the other hydrides.

Groups 15, 16 and 17 hydrides are polar molecules and experience dipole-dipole interactions. This is why their boiling points are higher than those of the Group 14 hydrides of similar M_r.

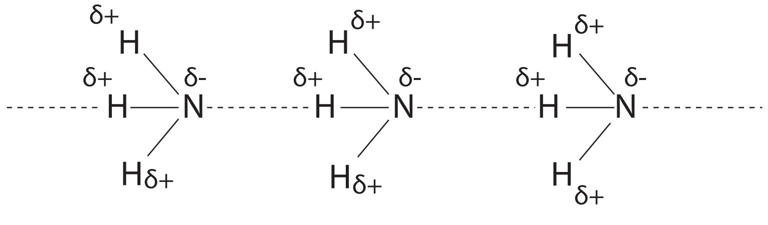
The boiling points of water, ammonia and hydrogen fluoride are significantly higher than those of the other hydrides in their groups, and this is due to their having the significantly stronger hydrogen bonding.

Water has the highest boiling point of these three as it can potentially form four separate hydrogen bonds with other water molecules. Each of its hydrogen atoms can hydrogen-bond with non-bonding electron pairs on neighbouring water molecules and each of its non-bonding electron pairs can hydrogen-bond with hydrogens atoms on neighbouring molecules.

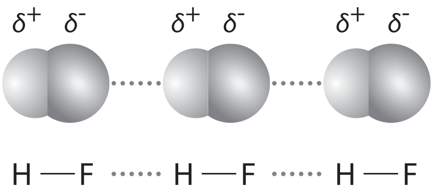




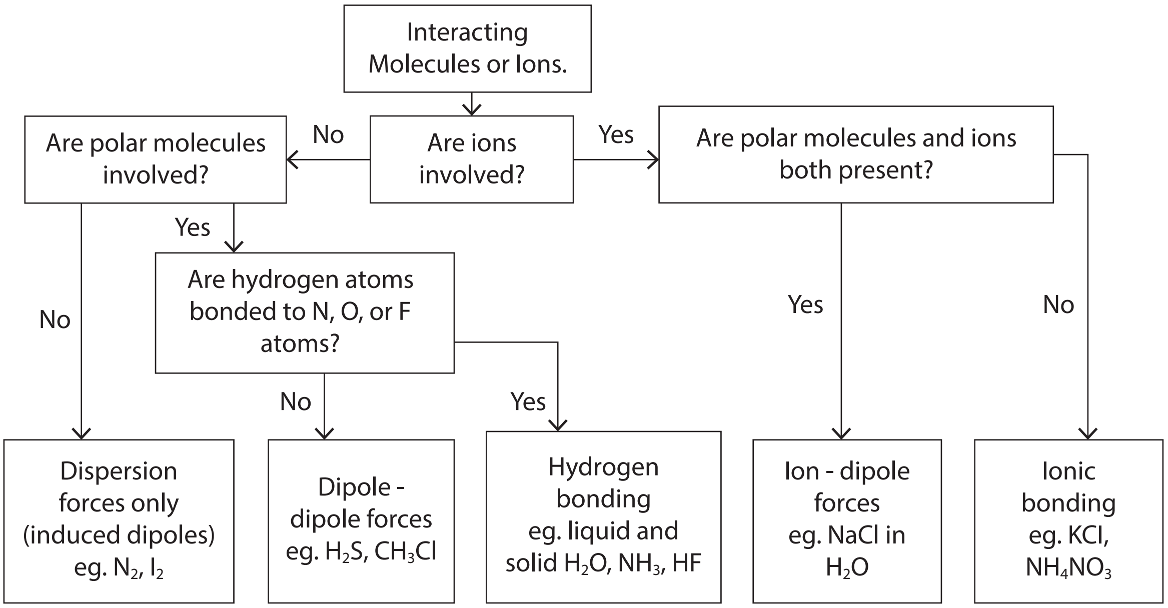
Ammonia has a higher boiling point than hydrogen fluoride but lower than water. This is because it can only potentially form two hydrogen bonds per molecule. Each of its hydrogen atoms could hydrogen-bond with the non-bonding electron pair on a neighbouring ammonia molecule and its non-bonding electron pair can hydrogen-bond with hydrogen atoms on neighbouring molecules, but there aren't enough non-bonding electron pairs to satisfy all of the hydrogens available.



Hydrogen fluoride has the lowest boiling point of the three. It too can only form potentially two hydrogen bonds. One between its hydrogen atom and one of the non-bonding electron pairs on a neighbouring molecule and one between one of its non-bonding electron pairs and the hydrogen atom of a neighbouring molecule. Each molecule has too many non-bonding electron pairs that cannot hydrogen-bond.



A Summary of Intermolecular Forces



Set 2

1. Name the intermolecular forces that exist between molecules (or atoms) of the following:

(a) Ne
(b) H_2S
(c) N_2H_4
(d) CO
(e) HBr
(f) CH_4
(g) F_2O
(h) H_2O
(i) N_2
(j) SO_3
(k) CH_3CH_2OH
(l) BeF_2
(m) He

2. What are dispersion forces and how do they arise?

3. What is the difference between dipole-dipole interactions and hydrogen bonding?

4. Explain why ammonia has a significantly higher boiling point than the other group 15 hydrides.

5. Explain why the boiling points of the group 14 hydrides increase steadily from $CH_4 \rightarrow SiH_4 \rightarrow GeH_4 \rightarrow SnH_4$

6. Examine the boiling points of the covalent molecular substances in the table below and answer the following questions.

H_2O	100˚C
HF	20°C
HBr	-66°C
F_2	-188°C
I_2	184°C

a. List the main intermolecular forces that exist between molecules of each substance.

H_2O: ____________________

HF: ____________________

HBr: ____________________

F_2: ____________________

I_2: ____________________

b. Explain why water has a higher boiling point than hydrogen fluoride.

____

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c. Explain why hydrogen fluoride has a higher boiling point than hydrogen bromide.

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d. Explain why hydrogen bromide has a higher boiling point than fluorine.

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e. Explain how iodine could have a higher boiling point than water.

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9. Explain why iodine is a solid, bromine is a liquid and chlorine is a gas at room temperature.

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10. In the Haber Process, nitrogen and hydrogen are reacted over an iron catalyst to produce ammonia. As they emerge from the reaction vessel the ammonia produced must be separated from any unreacted nitrogen and hydrogen. This is achieved by cooling the gas mixture under pressure. The ammonia condenses and can be removed, whereas the nitrogen and hydrogen remain as gases and can be recycled.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

a. What are the predominant intermolecular forces in each of these molecules?

Nitrogen ____________________

Hydrogen ____________________

Ammonia ____________________

b. With reference to intermolecular forces, explain why ammonia condenses whereas the nitrogen and hydrogen do not.

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Chapter

8

Chromatography

8.1 CHROMATOGRAPHIC METHOD

Chromatographic techniques, including paper chromatography, thin layer chromatography (TLC), column chromatography, high performance liquid chromatography (HPLC) and gas chromatography (GC), can be used to separate and determine the components of a wide range of mixtures. The decision to use a particular chromatographic technique depends on a number of factors, including the properties of the substances being separated, the amount of substance available for analysis and the sensitivity of the equipment.

All methods of chromatography work on the same principle. They all have a **stationary phase** which is typically a solid or a liquid supported on a solid, and a moving or **mobile phase** which can be a liquid or a gas. The mobile phase, sometimes called the eluent, flows through the stationary phase carrying the components of the mixture with it. Components move through the stationary phase and are separated out based on their polarity.

Why do components separate out?

The distance that a component moves through the stationary phase depends upon its ability to form intermolecular bonds with the material of the stationary phase relative to the mobile phase.

As the mixture moves through the stationary phase there are two processes occurring: **Adsorption,** which is where components from a mixture adhere to (bond with) the stationary phase and **desorption** where the components dissolve into (bond with) the mobile phase.

The rate of movement of any component depends upon how well it adsorbs onto the stationary phase, and how well it dissolves into the mobile phase.

So different components travel at different rates through the stationary phase depending upon the polarity of the components in the mixture and the polarities of the stationary and mobile phases.

8.2 PAPER CHROMATOGRAPHY

In paper chromatography, the stationary phase is an absorbent paper. The mobile phase is a liquid solvent or mixture of solvents like water or ethanol.

The stationary phase is attractive to polar substances as it is made of cellulose fibres which are also polar.

Paper chromatography with a non-polar solvent

When the mobile non-polar solvent moves up the stationary phase the non-polar substances in the mixture being analysed stay dissolved in the solvent and aren’t attracted to the paper. They move further through the stationary phase. Substances in the mixture that are more polar are adsorbed onto the paper and don’t move as far.

Paper chromatography with a polar solvent, like water. (A bit different…)

When water is used as the mobile phase, both it and the stationary phase are polar. The more polar substances in the mixture being separated will move further up the paper as they stay dissolved in the water longer.

8.3 THIN LAYER CHROMATOGRAPHY (TLC)

Thin layer chromatography is similar to paper chromatography. It uses a thin layer of silica gel, which is a porous form of silicon dioxide, or aluminium oxide coated onto a piece of glass, metal or plastic.

The stationary phase is usually silica gel or aluminium oxide. The mobile phase is a liquid solvent or mixture of solvents like water or ethanol.

Silica gel and aluminium oxide are polar and so the process is much the same as with paper chromatography. Adsorption and desorption occur and the components of the mixture separate out according to their polarities. They may form hydrogen bonds, dipole-dipole interactions or dispersion forces with either the stationary phase or the mobile phase. If they bond with the stationary phase they will not travel as fast through it. If they bond with the mobile phase they will stay dissolved in it and move with it through the stationary phase.

8.4 USING PAPER AND THIN LAYER CHROMATOGRAPHY

These techniques are often used for qualitative analysis, to detect which substances are present in the sample. They are not able to determine quantities of substance present. A spot of the sample is placed on one end of either the chromatography paper or chromatography plate (stationary phase). This spot is at the **origin**. The paper or plate is then placed into a container with a solvent (mobile phase). The solvent level must be below the origin so that it moves up through the sample through capillary action. The distance that the solvent reaches is called the **solvent front**.

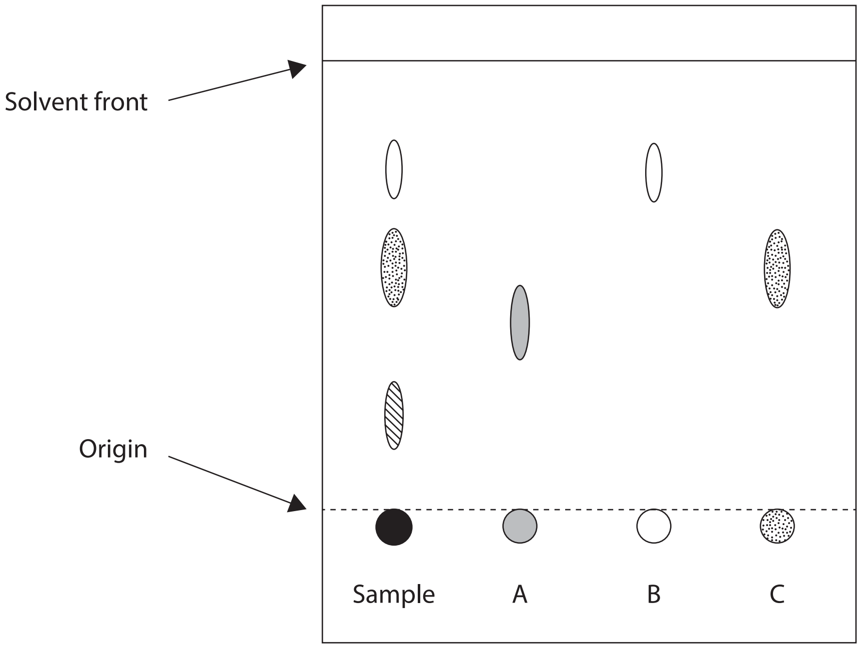
N.B. TLC is often carried out in a closed container. The space inside the container is ideally saturated with solvent vapour. This is to prevent the solvent from evaporating. It is important for good separation that the only process occurring in the chamber is the movement of the sample up the plate via capillary action, and not evaporation.

The components of the sample then spread out and are separated as the mobile phase moves through the stationary phase. When the chromatogram is developed it indicates the number of components in the sample and can also be used to identify specific components.

There are two ways that these techniques can be used to identify components in a sample.

1. Comparison with known substances

One way to identify components present in a sample is to include known substances in the chromatogram. Spots of possible components A, B and C are placed at the origin alongside the sample being tested. The chromatogram is developed and the components that separate out can be compared with the movement of known substances.

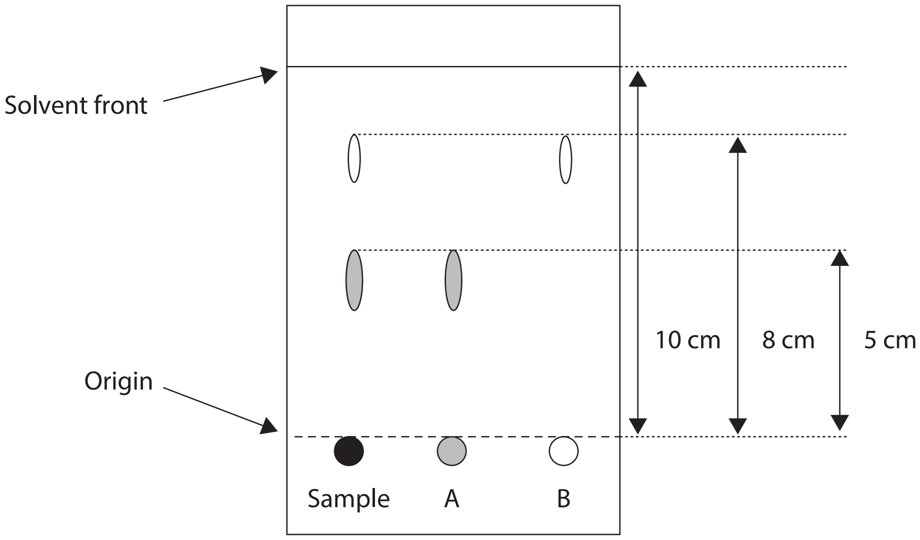


The sample being tested above contains three components. Two can be identified using this chromatogram. As they have travelled the same distance as components of the sample it can be seen that B and C are very likely present in the sample. The sample did not contain A. One component in the sample remains unidentified.

2. Retention factor (R_f)

The retention factor is a value that can be assigned to each component in a sample once a chromatogram is developed. It is a ratio expressing how far the component moved from the origin relative to how far the solvent front moved. Each component will have a characteristic retention factor if developed under the same conditions. R_f values will be less than 1 as the component cannot travel further than the solvent.

$$\boxed{R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}}$$



The sample contains A and B. Their R_f values can be calculated as below.

R_f (A) = 5/10 = 0.50

R_f (B) = 8/10 = 0.80

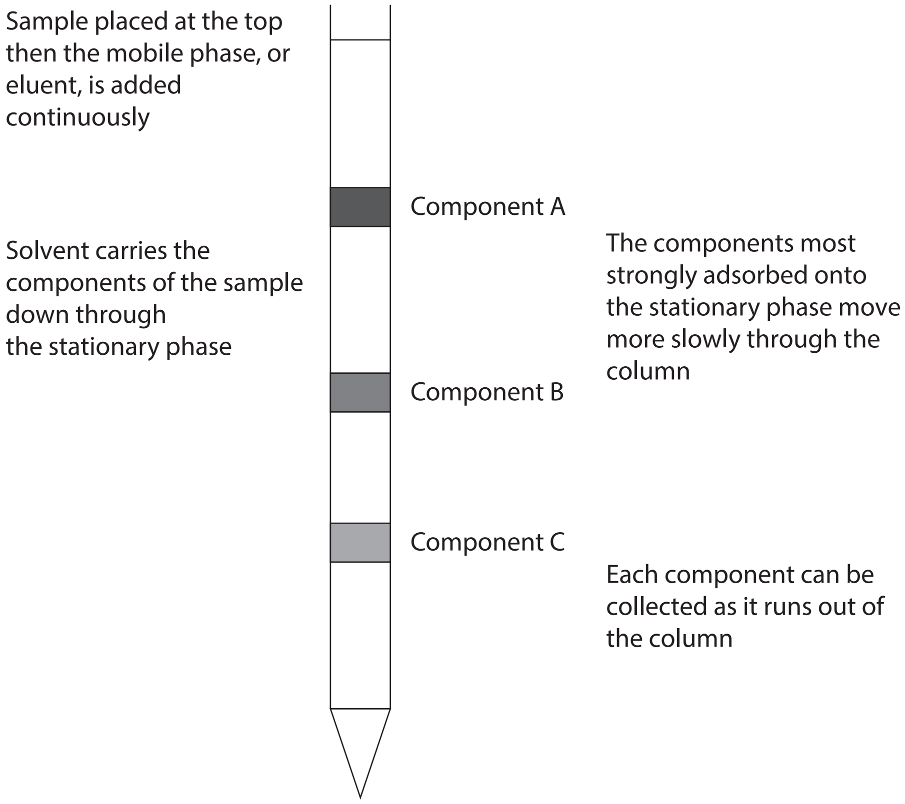
If further chromatograms were developed in the same way and under the same conditions then these R_f values will be identical for a given component and can then be used for identification.

Paper chromatography is a cheap and convenient analysis method. Thin layer chromatography often achieves better separation when the sample contains components of similar polarity, and can be used when smaller quantities are present.

8.5 COLUMN CHROMATOGRAPHY

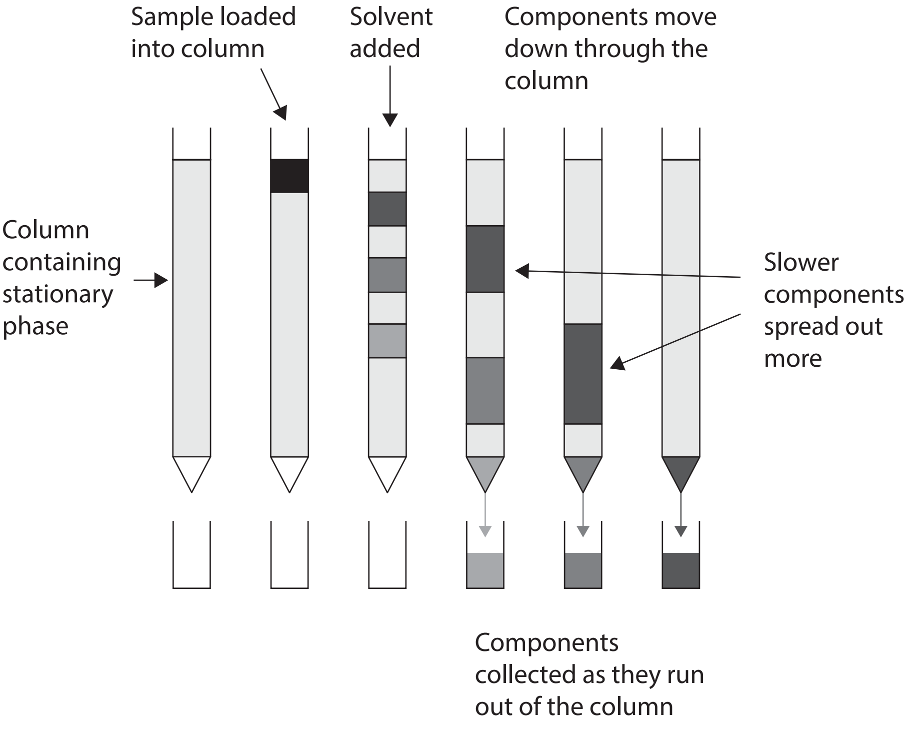
In column chromatography, the stationary phase is solid (usually silica gel or aluminium oxide), packed into a vertical glass column. The mobile phase is a liquid solvent or mixture of solvents like water or ethanol. These are chosen in order to minimise the R_f, the time and quantity of eluent required, and also to achieve maximum separation of components.

Rather than utilising capillary action, the sample is placed on top of the column packed with the stationary phase. The mobile phase, or eluent, is then continuously added at the top and moves down through the column under gravity taking the components in the sample with it. This process is called Elution.



As with previous techniques, adsorption onto the stationary phase and desorption into the mobile phase is dictated by the polarity of each phase and the components. Components that bond better with the stationary phase spend longer in the column and those that bond better with the mobile phase move through faster.

Each separate component can then be collected as it runs out of the column.

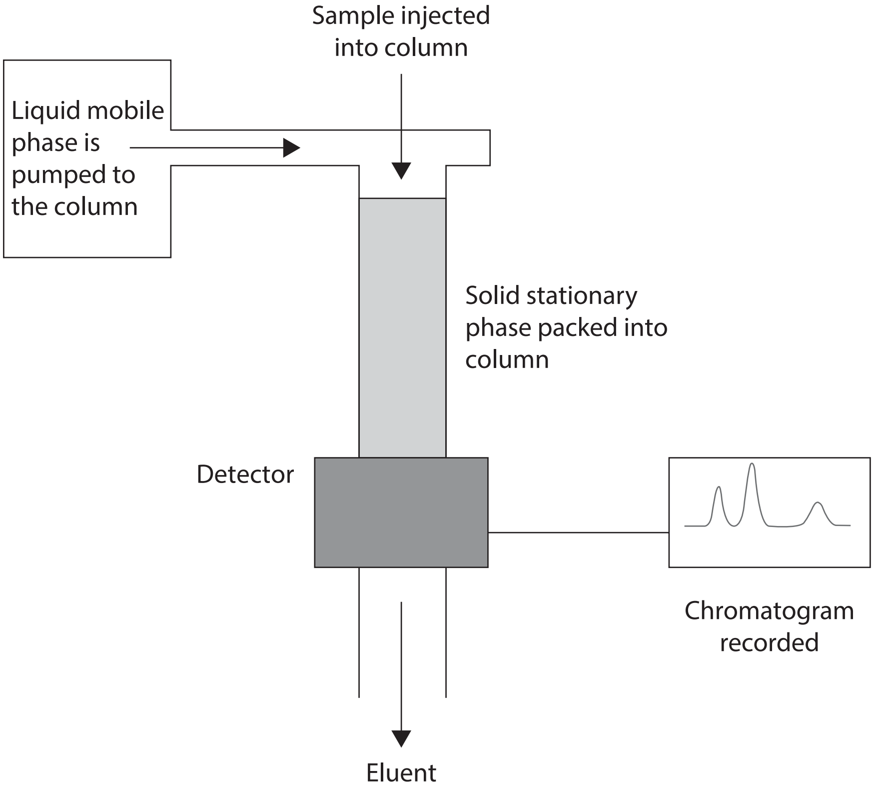


8.6 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

High performance liquid chromatography is very similar to column chromatography but instead of relying on gravity the liquid mobile phase is forced under high pressure through the column, containing the solid stationary phase. The sample is injected into the column and is carried through by the mobile phase. This makes it a lot faster than column chromatography.

The mobile phase is usually a non-polar solvent like chloroform or hexane, or a mixture of polar solvents like water or methanol. The HPLC column or stationary phase is packed with much smaller particles, usually polar silica beads when a non-polar mobile phase is used, or silica beads that have been coated so as to be non-polar when a polar mobile phase is used. Smaller particles means that the stationary phase has a larger surface area and therefore has more opportunity for adsorption and desorption of components to occur as they are forced through. This leads to better separation, especially if the components have similar polarities.

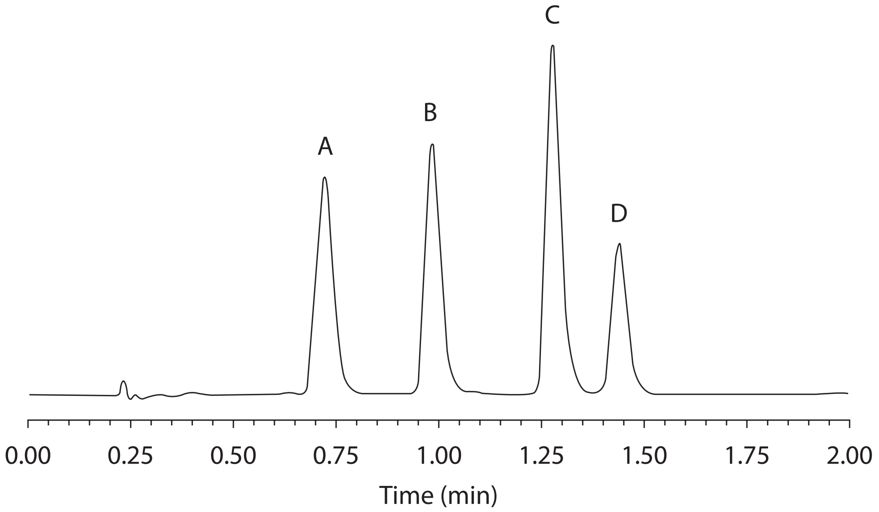
HPLC set-up



As the eluent emerges from the column the various components can be detected. The most common detector uses UV absorbance. The eluent passes through a beam of UV light and the components absorb the UV light to varying degrees. This absorbance is recorded and a chromatogram is produced as a series of peaks, each corresponding to a particular component, plotted against time.

The time that a component takes to elute from the column is called its **retention time** (R_T). It is the time from when the sample is injected until a peak is measured for a particular component. This is similar to the retention factor (R_f) in paper and thin layer chromatography and if conditions are carefully controlled it can be used to identify the components. The area under each peak can provide information about the relative quantities of each component. A mass spectrometer can also be coupled with a UV detector for identification purposes.

An example of a HPLC chromatogram for a mixture of components A, B, C and D is shown below.



Component D has the highest retention time and spent longest in the column. This means that it had the greatest ability to adsorb onto the stationary phase. Component A had greater affinity for the mobile phase as it spent the shortest time in the column and was eluted first.

It can be seen that component C has the highest peak and greatest area under its peak, which suggests that it was the most abundant component in the mixture.

8.7 GAS CHROMATOGRAPHY (GC)

Gas chromatography is a sensitive technique and can detect very small traces of a compound in a sample. The mobile phase, or carrier gas, is an unreactive gas such as helium or nitrogen, which is non-polar. The stationary phase can either be a polar solid such as silica or alumina, or a porous solid coated with a non-polar high boiling point liquid hydrocarbon, in each case packed into a column. The column is made of glass or stainless steel and can be up to 4 m in length. This greater length allows for more efficient separation. Due to its length the column is coiled. The polarity of the stationary phase is carefully chosen to match the polarity of the sample being analysed.

GC can only be used for analysing compounds that can be vaporised without decomposing, as the sample is heated to a vapour as it is injected into the column. Components are then carried through the column by the mobile gas phase. The column is coiled within an oven where its temperature can be accurately controlled.

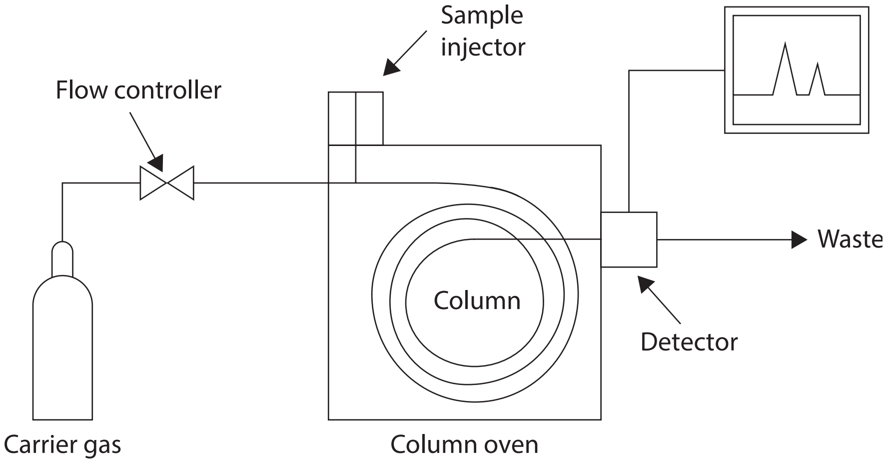
As in other techniques, the components continuously adsorb onto the stationary phase and desorb into the mobile phase. If they adsorb strongly onto the stationary phase they will move more slowly through the column, and vice versa. Depending upon their boiling points, the components may condense onto the stationary phase, dissolve into the liquid on the stationary phase, or remain as a gas as they move through. Higher temperatures will enable components to move more quickly through the column, but better separation of components is achieved with lower temperatures.

As with HPLC the separated components emerge from the column, are detected, and a chromatogram recorded. The chromatogram delivers a series of peaks from which the retention time and relative abundance of components can be determined.

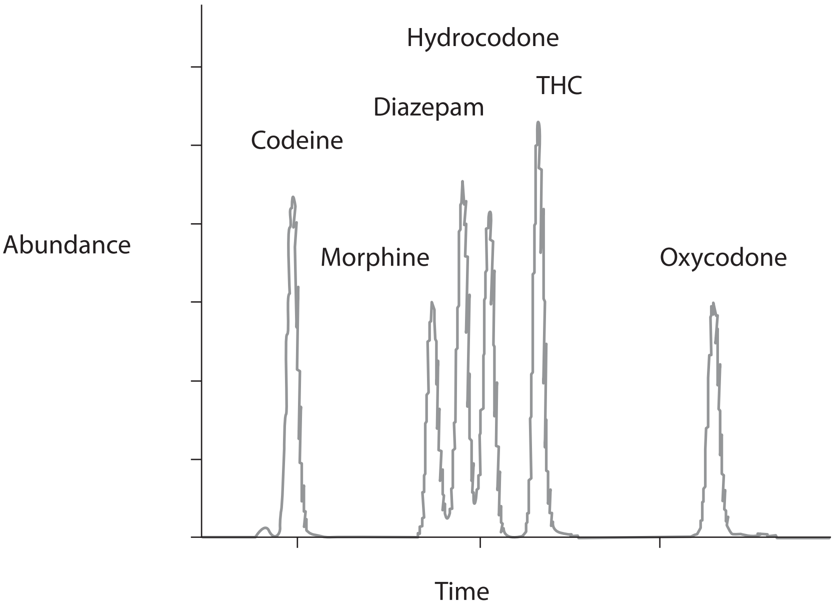
A flame ionisation detector is typically used. Here the components pass through a flame and are ionised, becoming positively or negatively charged. They then pass between a positively charged anode and a negatively charged cathode. The positive ions move to the cathode and accept electrons. The negative ions move to the anode and give up electrons. This electron flow (current) can be measured and produces the chromatogram.

For small samples, a mass spectrometer can be used as a detector for gas chromatography (GC-MS). The chemical species are ionised as they are eluted and the mass spectrometer sorts the ions based on their mass to charge ratio. This is a very sensitive technique. Applications of GC-MS include drug detection, fire investigation, environmental analysis and explosives investigation.

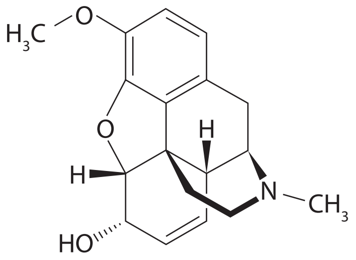
GC set-up

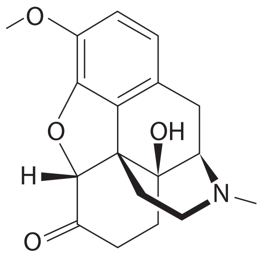


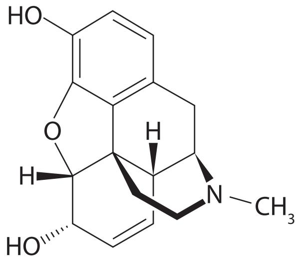
An example of a GC chromatogram for a mixture of pain killing drugs is shown below.

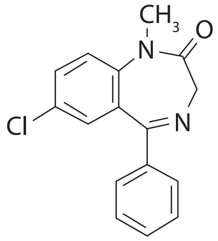


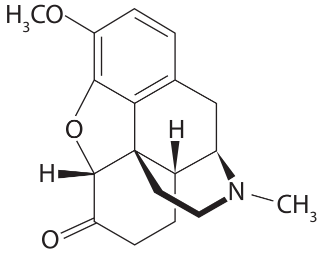
The structure of the various components is shown in the table below. They all have similar numbers of carbon atoms and molar masses. If you look closely at codeine, morphine, hydrocodone and heroin you will notice that the right hand side of each molecule is identical, and oxycodone is very similar in structure. This makes them difficult to separate. GC utilises the differing polarities of the left hand side of each molecule in order to enable separation.

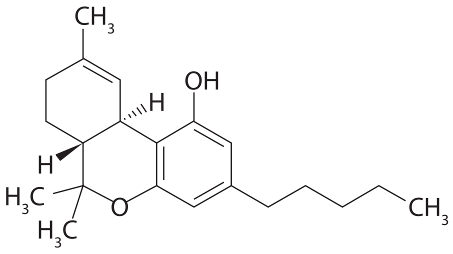

Codeine (C-18)

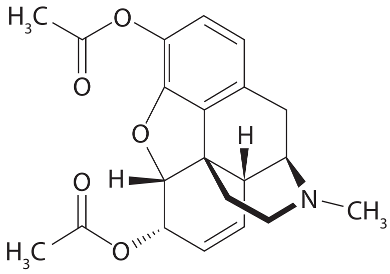

Oxycodone (C-18)


Morphine (C-17)


Diazepam (C-16)


Hydrocodone (C-18)


THC (C-21)


Heroin (C-21)

Set 1

1. Complete the passage below, filling in the missing words.

Chromatography is used to separate mixtures of substances into their _______________ and to detect them within a mixture. All methods of chromatography work on the same principle. They all have a _______________ phase which is typically a solid or a liquid supported on a solid, and a moving or _______________ phase which is a liquid or a __________. The mobile phase flows through the stationary phase, carrying the components of the mixture with it. Components move through the stationary phase and are separated out based on their _______________.

The distance that a component moves through the stationary phase depends upon its ability to form _______________ bonds with the material of the stationary phase and/or the mobile phase.

As the mixture moves through the stationary phase there are two processes occurring. Adsorption which is where components from a mixture _______________ into (bond with) the _______________ phase and _______________ where the components dissolve into (bond with) the _______________ phase.

The rate of movement of any component depends upon how well it adsorbs onto the stationary phase and how well it dissolves into the mobile phase.

So different components travel at different _______________ through the stationary phase, depending upon the _______________ of the components in the mixture and the polarities of the stationary and mobile phases.

2. What is the difference between qualitative and quantitative analysis?

____

____

____

____

3. Which two chromatographic techniques are purely qualitative?

____

____

4. What are the main differences between paper chromatography and column chromatography?

____

____

____

____

5. Complete the flowing table.

	Stationary phase	**Mobile phase**
Paper chromatography	Absorbent paper	Liquid solvent
TLC		
Column chromatography		
HPLC		
GC		

6. Which chromatographic technique would you choose if the quanitites of sample available were very small? Explain.

____

____

7. Which chromatographic technique is unsuitable for a sample that decomposes on heating? Explain.

____

____

8. Why is TLC often carried out in a closed container?

____

____

____

9. What is the retention factor and how is it calculated?

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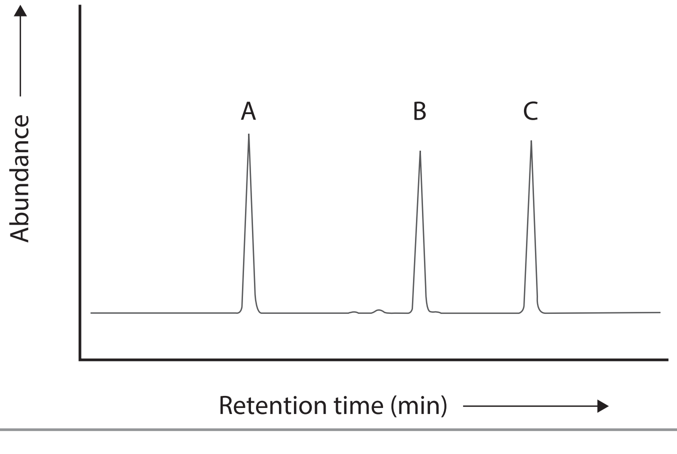
____

10. The HPLC chromatogram for a mixture of organic compounds below was obtained using a non-polar chloroform mobile phase and a stationary phase of polar silica beads.

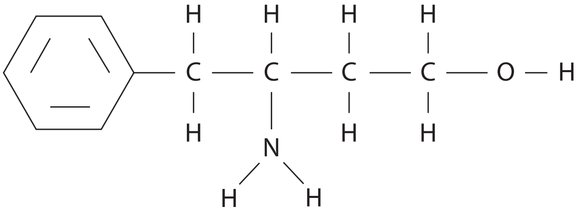


a. Which component was eluted first? Explain your choice.

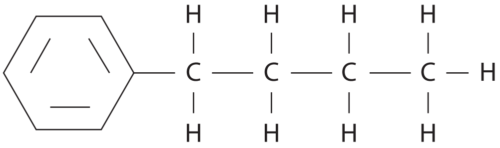
b. Which component is the most polar? Explain your choice.

11. Which of the following substances will have the greatest retention time when passing through an HPLC column with a non-polar stationary phase and a polar mobile phase.

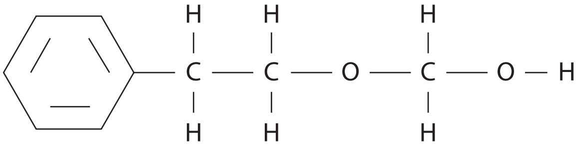
A.



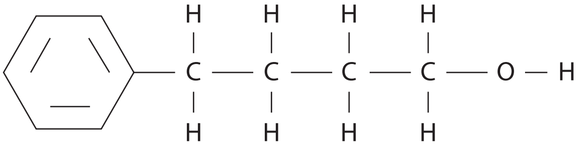
B.



C.

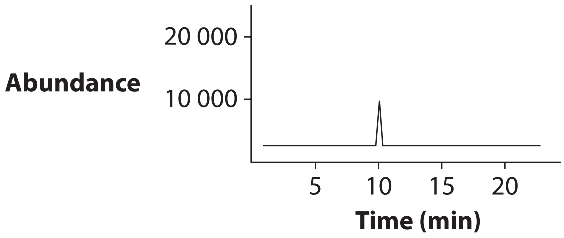


D.



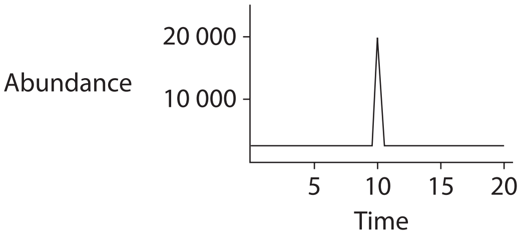
Explain your answer.

12. The following chromoatogram was obtained for 1.0 μg of a hydrocarbon passing through a GC column.

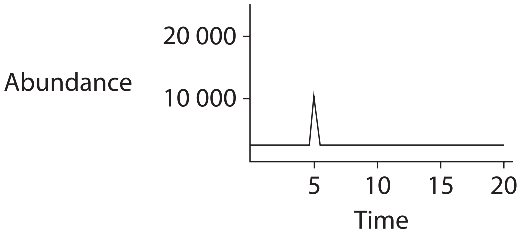


If 2.0 μg of the same hydrocarbon was passed through the column under the same conditions, which of the following chromatograms would result?

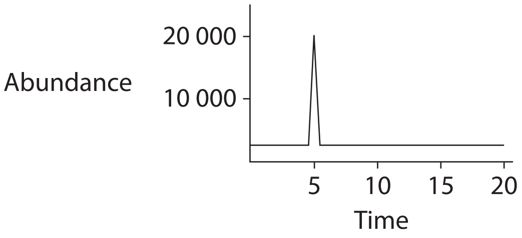
A.



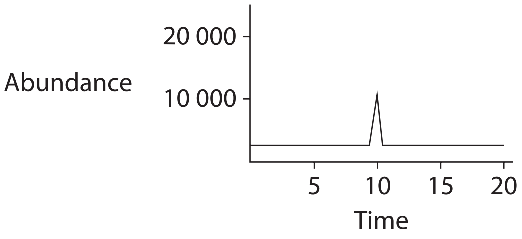
B.



C.

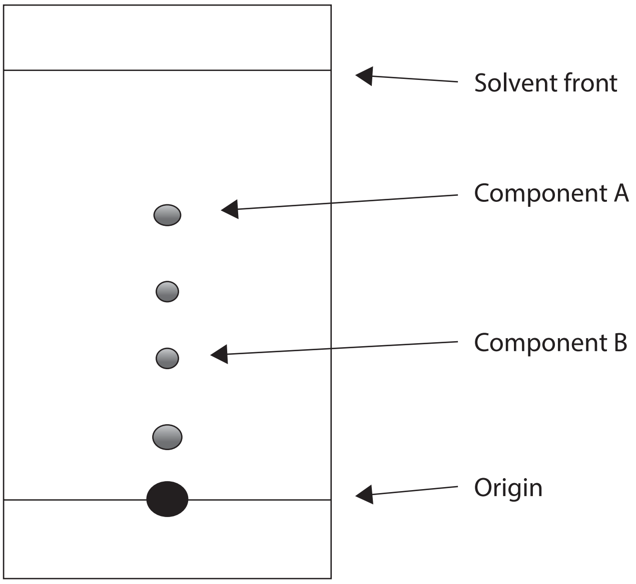


D.



Explain your choice.

13. A sample containing four amino acids was applied to a TLC plate and the plate was placed into a suitable solvent. The following chromatogram was obtained.



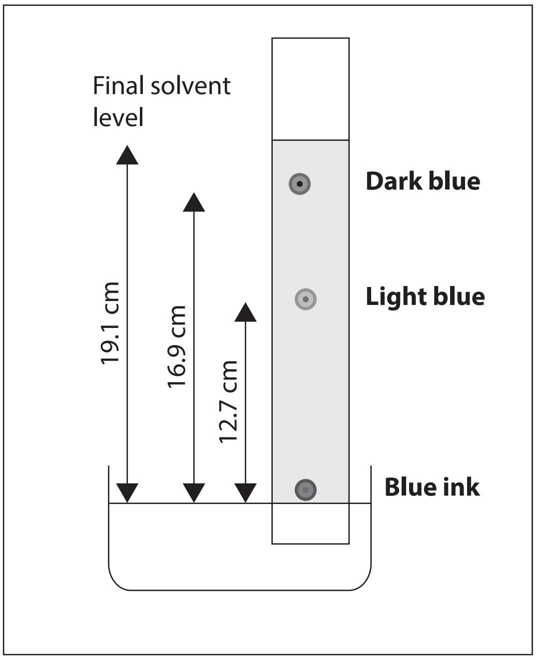
The table below shows the R_f values for the four amino acids.

Amino acid	**R_f**
Glutamic acid	0.15
Phenylalanine	0.70
Aspartic acid	0.35
Serine	0.50

a. Calculate the retention factor and identify component ‘A’?

b. Calculate the retention factor and identify component ‘B’?

14. A sample of blue ink from a rollerball pen was analysed using a paper chromatography apparatus. The filter paper was held in an ethanol solvent with a blue ink dot just above it. After 5 minutes the solvent had risen as shown in the diagram and measurements taken.



a. What do the results tell you about the composition of the blue ink used?

____

____

b. What is meant by the 'mobile phase' in this case?

____

____

c. Which of the two blue components was most attracted to the stationary phase?

d. Calculate values of R_f for the two blue components:

R_f for light blue = _________ R_f for dark blue = _________

e. In another experiment with a different ink that was black but had 3 different components X, Y, Z.

The final solvent level was 20.9 cm and the 3 components' levels were:

X = 14.7 cm, Y = 13.9 cm and Z = 12.7 cm.

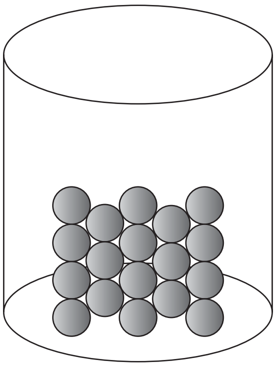
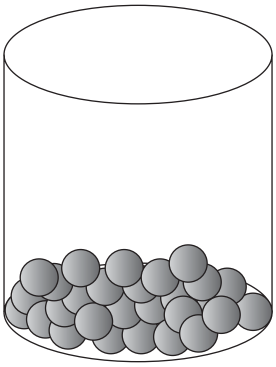
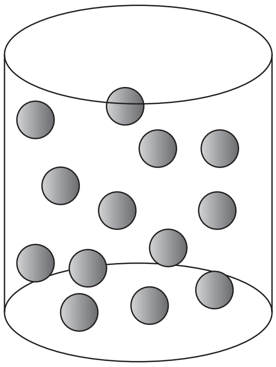
Which of these component colours in the black in was the same as in the blue ink used in the experiment?

Chapter

9

Kinetic Theory of Gases

9.1 THE PHYSICAL PROPERTIES OF GASES, LIQUIDS AND SOLIDS

Solid	Liquid	Gases
		
Particles very close together	Particles close together	Particles are much further apart than solids and liquids
Particles vibrate about a fixed point	Particles can move about freely and randomly within the liquid	Particles move about freely with very little attraction between them
Incompressible	Virtually incompressible	Very compressible
High density	High density	Low density
Fixed shape and volume	Fixed volume and can take the shape of their container	Diffuse to fill the container that they are in

9.2 GASES

There is a great deal of similarity between the physical properties of different gases.

Chemists have established a set of laws and relationships that they apply to all gases in order to predict their behaviour. The laws and relationships are based on the idea of an ‘ideal gas’.

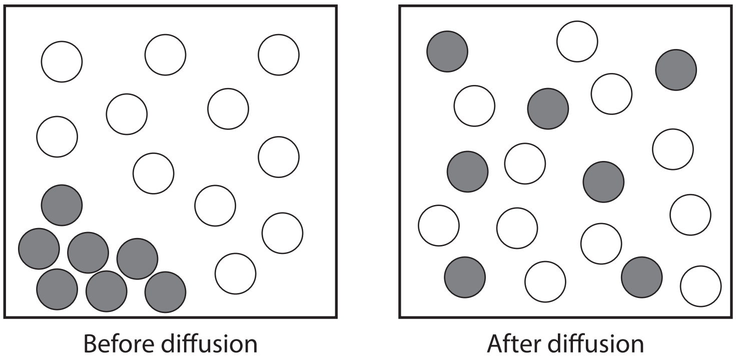
No gas behaves ideally, however, under normal conditions, the behaviour is close enough for these laws and relationships to be applied.

The kinetic theory of gases is based on the following:

- Gases consist of tiny particles called molecules (except for the noble gases) which consist of atoms.
- The average distance between the molecules of a gas is large compared to the size of each molecule.
- The molecules of a gas move in rapid, random straight line-motion. They collide with each other and the sides of their container to produce pressure.
- The molecules of a gas exert negligible attractive or repulsive forces on one another.
- Collisions between gas molecules are perfectly elastic. There is no overall energy loss during collisions.
- The average kinetic energy of the molecules increases as the temperature of the gas increases.

Diffusion in gases

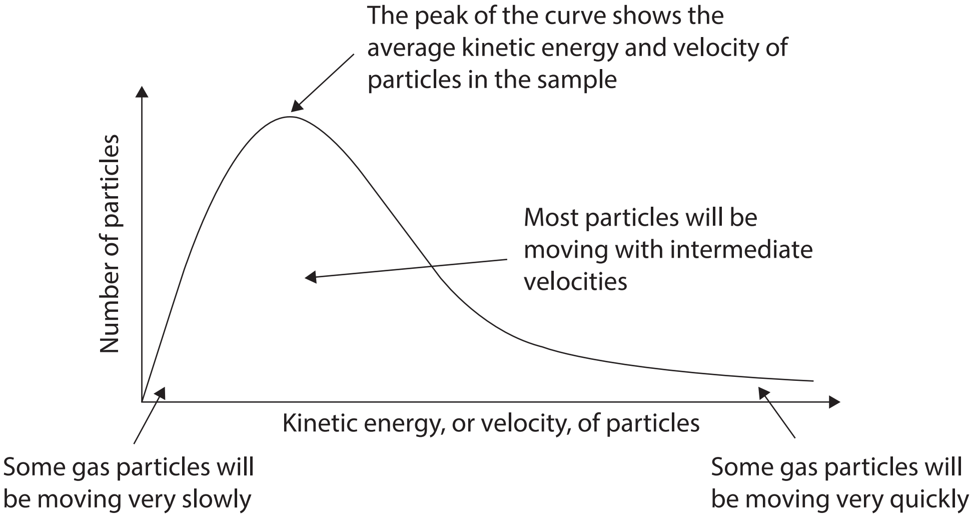
Since gas particles are in constant and random straight line motion they will move from an area of high concentration to fill a space. They collide with each other, any other gas particles present and the walls of their container until they are evenly dispersed.



Kinetic theory and temperature

In any sample of a gas molecules have a wide range of kinetic energies and velocities.

The **Maxwell-Boltzmann distribution** below shows this.



Temperature is the only factor that affects the average kinetic energy of the molecules of a gas. Increasing the temperature increases the average kinetic energy and therefore the velocity of particles since

$E_k = \frac{1}{2} mv^2$

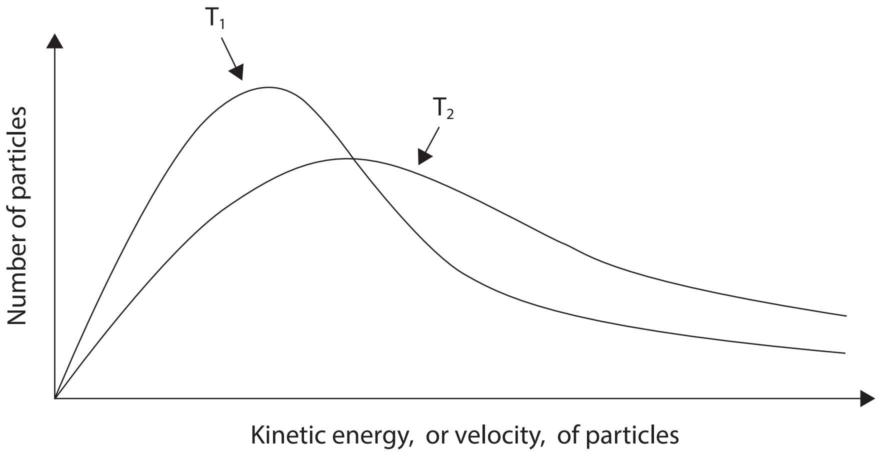
where E_k = kinetic energy

m = mass

v = velocity

The diagram below shows the distribution of energies for a sample of gas at two temperatures, T_1 and T_2, where $T_2 > T_1$. It can be seen that the average kinetic energy and average velocity of the particles at T_2 are greater.

Note that the area under each graph should be the same, as the number of particles has not changed. Therefore the peak of the curve representing T_2 will be lower.

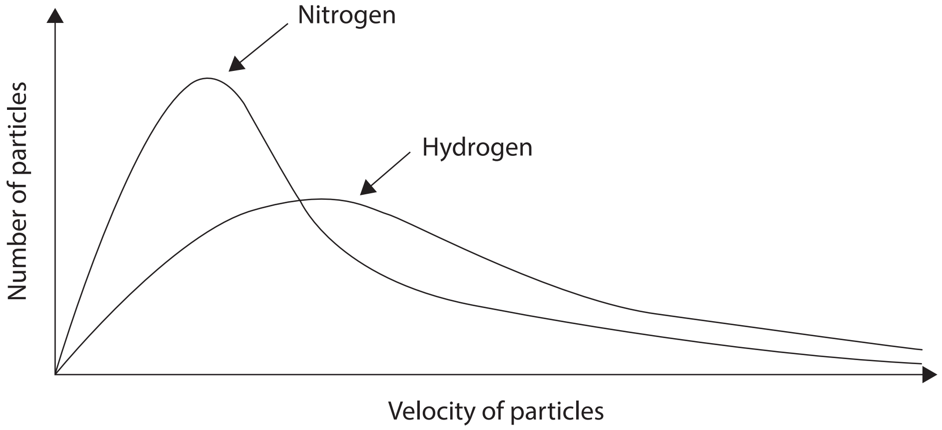


The average kinetic energy of the molecules of all gases is the same at any particular temperature. In a sample of gas there will be many collisions, some of which will result in some molecules losing velocity (and E_k) and some gaining velocity (and E_k). The total E_k of the system remains constant since energy is conserved in molecular collisions.

If samples of two gases, say nitrogen (molar mass 28.02 g mol^{-1}) and hydrogen (molar mass 2.016 g mol^{-1}) are at the same temperature they will have the same average kinetic energy. The lighter of the two gases will have molecules of less mass and therefore must be moving quicker at the same temperature if the average kinetic energies are to be the same.

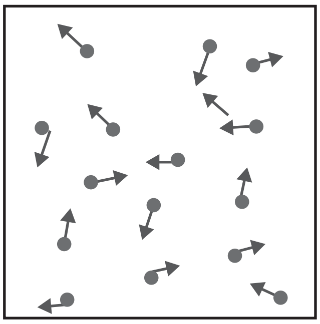
$$\begin{aligned} \text{Average kinetic energy (nitrogen)} &= \text{Average kinetic energy (hydrogen)} \\ \tfrac{1}{2} mv^2 &= \tfrac{1}{2} mv^2 \\ \tfrac{1}{2} \uparrow m \downarrow v^2 &= \tfrac{1}{2} mv^2 \end{aligned}$$

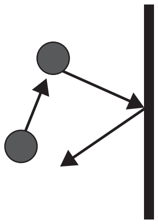
In order for the equality to remain true, increased mass requires decreased velocity.



Kinetic theory and gas pressure

Kinetic theory can also be used to explain the pressure exerted by gases. The molecules of a gas move in rapid, random straight line-motion. They collide with each other and the sides of the container that they are in. Pressure is caused by the collisions between gas molecules and the walls of their container.





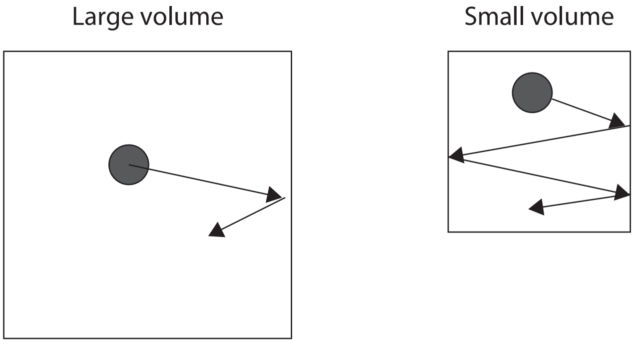
Atom moving at random and colliding with the wall to create a force and hence pressure

9.3 THE GAS LAWS

Boyle's law

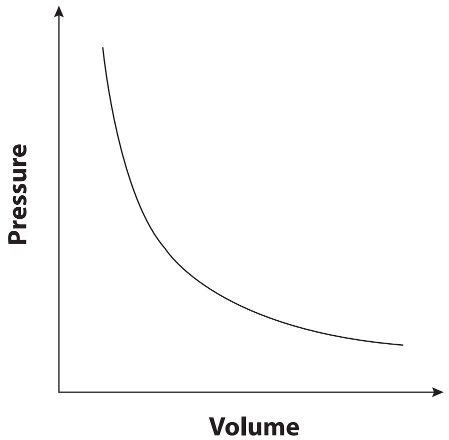
During the 1600's, Robert Boyle studied the behaviour of gases and found numerical relationships relating pressure and volume. Boyle observed that when the temperature of a sample of gas is held constant, and the external pressure on the sample of gas is increased, the volume occupied by the gas decreases. Conversely, when the external pressure on the gas sample is decreased the volume occupied by the gas increases. This is described as an inverse relationship.

From a kinetic theory perspective, if the volume of a sample of gas is decreased there will be more collisions between gas molecules and also between gas molecules and the container, hence an increase in pressure.



Boyle's Law states that the volume of a fixed amount of gas maintained at constant temperature is inversely proportional to the gas pressure.

$$\mathbf{V \ \alpha \ 1/P}$$



If the amount of gas and temperature are held constant, P times V is always equal to the same constant for that sample. For a given sample of gas under two different sets of conditions at constant temperature, we can say that

$$\mathbf{P_1 \times V_1 = k}$$

$$\mathbf{P_2 \times V_2 = k}$$

And therefore

$$\mathbf{P_1 V_1 = P_2 V_2}$$

Where P_1 = initial pressure
V_1 = initial volume
P_2 = final pressure
V_2 = final volume

Example

A sample of helium gas occupying 10.0 L is contained in a balloon at room temperature of 20.0°C and an external pressure of 100.0 kPa. If the external pressure is increased to 110.0 kPa and the temperature kept constant, what is the final volume of the balloon?

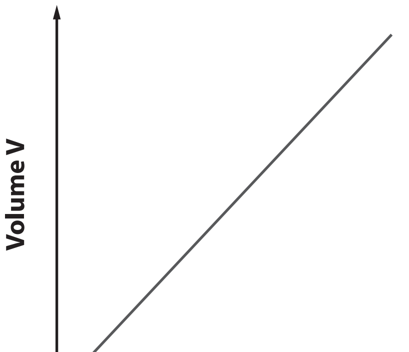
$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ V_2 &= P_1 V_1 / P_2 \\ &= 100.0 \times 10.0 / 110.0 \\ &= 9.09 \text{ L (3 s.f.)} \end{aligned}$$

Charles' law

Jacques Charles and Joseph Gay-Lussac studied the relationship between the temperature of a gas and the volume it occupies. They found that, at constant external pressure, the volume of a sample of gas increases when heated and decreases when cooled. Increasing temperature increases the kinetic energy and velocity of the gas molecules. Increased velocity results in more collisions between gas molecules and the walls of the container, so the pressure exerted by the gas can overcome the external pressure and the volume increases accordingly.

Charles' Law states that the volume of a fixed amount of gas maintained at constant external pressure is directly proportional to the absolute temperature, in Kelvin, of the gas.

$$\mathbf{V \propto T}$$



If the amount of gas and external pressure are both held constant, V divided by T is always equal to the same constant for that sample.

$$\mathbf{V = k \times T}$$

and

$$\mathbf{\frac{V}{T} = k}$$

So for a given sample of gas under two different sets of conditions at constant external pressure, we can say that

$$\mathbf{\frac{V_1}{T_1} = k}$$

$$\mathbf{\frac{V_2}{T_2} = k}$$

And therefore

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

Where V_1 = initial volume

T_1 = initial temperature (in Kelvin)

V_2 = final volume

T_1 = initial temperature (in Kelvin)

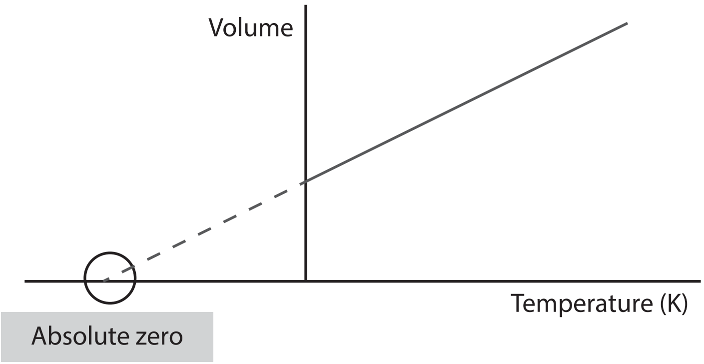
Example

A sample of helium gas occupying 10.0 L is contained in a balloon at room temperature of 20.0°C and an external pressure of 1 atm. If the balloon is cooled to 10.0°C and the external pressure is kept constant, what is the final volume of the balloon?

$$\begin{aligned} V_1/T_1 &= V_2/T_2 \\ V_2 &= V_1 \text{ x } T_2 \ / \ T_1 \\ &= 10.0 \text{ x } (10.0 + 273.15) \ / \ (20.0 + 273.15) \\ &= 9.66 \text{ L (3 s.f.)} \end{aligned}$$

9.4 ABSOLUTE TEMPERATURE

As discussed above, Charles Law states that at any given external pressure, the plot of volume versus temperature gives a straight line. By extending the line to zero volume, we find the intercept with the Kelvin temperature axis to be -273.15°C. At any constant pressure, we obtain a different straight line for the volume-temperature plot, but we get the same zero-volume temperature intercept at -273.15°C.

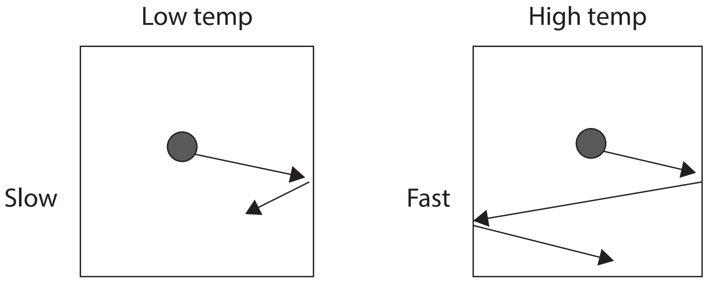


The significance of this was realised by William Thomson (Lord Kelvin) in 1848. He identified -273.15°C as theoretically the lowest attainable temperature, absolute zero. All substances would be solids at absolute zero, because the individual atoms would not be vibrating within the solid lattice structure as they have no kinetic energy. Using his findings, Kelvin set up the absolute temperature scale, now called the Kelvin temperature scale. One degree Celsius (°C) is equal in magnitude to one Kelvin (K).

$$\mathbf{K = {}^\circ C + 273.15}$$

9.5 GAY-LUSSAC'S LAW

If a sample of gas is kept at constant volume, an increase in temperature will result in an increase in pressure. Increasing temperature increases the kinetic energy and velocity of the gas molecules. Increased velocity results in more collisions between gas molecules and the walls of the container, so the pressure increases.



Pressure is therefore directly proportional to the Kelvin temperature.

$$\mathbf{P \alpha T}$$

$$\mathbf{P = k \times T}$$

and

$$\mathbf{\frac{P}{T} = k}$$

So for a given sample of gas under two different sets of conditions at constant volume, we can say that

$$\mathbf{\frac{P_1}{T_1} = k}$$

$$\mathbf{\frac{P_2}{T_2} = k}$$

And therefore

$$\mathbf{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

Where P_1 = initial pressure

T_1 = initial temperature (in Kelvin)

P_2 = final pressure

T_1 = initial temperature (in Kelvin)

Example

A sample of oxygen gas occupying a 50.0 L steel gas cylinder has a temperature of 25.0°C and a pressure of 15.0 atm. If the temperature is increased to 100.0°C, what is the gas pressure in the cylinder?

$$P_1/T_1 = P_2/T_2$$
$$P_2 = P_1 \times T_2 / T_1$$
$$= 15.0 \times (100.0 + 273.15) / (25.0 + 273.15)$$
$$= 18.8 \text{ atm (3 s.f.)}$$

9.6 AVOGADRO'S HYPOTHESIS AND MOLAR VOLUME

In 1811 Italian scientist Amadeo Avogadro published his hypothesis that at the same temperature and pressure, equal volumes of all gases would contain the same number of molecules (or atoms, if the gas is monatomic).

So, the volume of a gas is directly proportional to the number of moles of the gas present.

$$\mathbf{V \alpha n}$$

It follows therefore that a mole of **any gas** occupies the same volume under the same conditions of temperature and pressure.

Gas volumes are usually expressed at S.T.P. or standard temperature (0°C or 273.15 K) and pressure (1 bar or 100.0 kPa). One mole of any gas at S.T.P. will occupy 22.71 L.

$$\mathbf{n = \frac{V}{22.71}}$$

Where n = the number of moles (in mol)

V = the volume of gas (in litres) at S.T.P.

Standard temperature is 0°C or 273.15 K

Standard pressure is 1 bar or 100.0 kPa

At other temperatures and pressures, the volume of one mole of a gas will differ from 22.71 L.

Example

How many moles of oxygen gas are there in a 50.0 L container at S.T.P.?

$$n(O_2) = 50.0 / 22.71$$
$$= 2.20 \text{ mol}$$

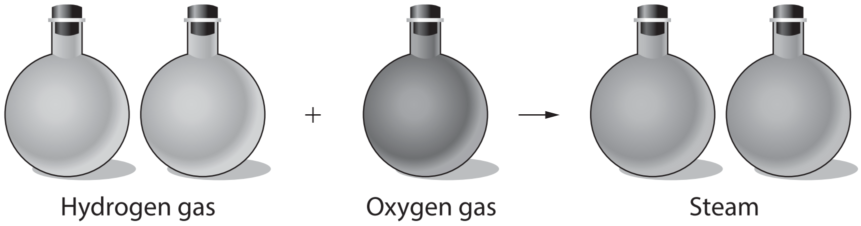
9.7 VOLUMES OF GASES AND STOICHIOMETRY

If a chemical reaction involving gases is carried out at constant temperature and pressure, the volumes of the gases are directly proportional to the number of moles of each gas present. Instead of converting volume to moles, one can just use the reaction stoichiometry to calculate unknown volumes.

For example, the synthesis of water from hydrogen gas and oxygen gas:

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

The stoichiometric ratio of H_2: O_2: H_2O is 2:1:2, so the ratio of volumes is also 2:1:2.



Example

If 5.00 L of hydrogen gas is reacted with excess oxygen gas at constant temperature and pressure, what volume of water is produced?

$$\begin{aligned} V(H_2O) &= 2/2 \times V(H_2) \\ &= 5.00 \text{ L} \end{aligned}$$

The ideal gas equation

Boyle's Law, Charles' Law and Avogadro's Hypothesis can be combined, as they show the relationship between volume and pressure, temperature and moles.

Boyle's Law	$V \alpha 1/P$	(at constant n and T)
Charles' Law	$V \alpha T$	(at constant n and P)
Avogadro's hypothesis	$V \alpha n$	(at constant P and T)

So $V \alpha \frac{\mathbf{nT}}{\mathbf{P}}$

$$\rightarrow V = \frac{\mathbf{RnT}}{\mathbf{P}}$$

$$\rightarrow PV = nRT$$

This is the ideal gas equation

PV = nRT

Where R is the universal gas constant, 8.314, when using pressures in kPa (and 0.08206 if using atmospheres)

The ideal gas equation enables us to calculate the pressure, volume, temperature or moles of a gas at specified conditions other than S.T.P.

Example

a) What is the mass of ammonia gas contained in a 25.0 L vessel at a temperature of 50.0°C and a pressure of 110.0 kPa?

$n(NH_3)$ = PV/RT

= 110.0 x 25.0 / 8.314 x (50.0 + 273.15)

= 1.02 mol

$n(NH_3)$ = m/M

$m(NH_3)$ = n x M $M(NH_3) = 17.034\ g\ mol^{-1}$

= 1.02 x 17.034

= 17.4 g

b) If the temperature of the vessel above is increased to 150.0°C, what will be the resultant pressure?

$P(NH_3)$ = nRT/V

= 1.02 x 8.314 x (150.0 + 273.15) / 25.0

= 144.0 kPa

9.8 REAL GASES

Theoretical ideal gas behaviour is based on the premise that ideal gas molecules have no attraction for one another and that their molecules occupy no volume. Real gases do have some forces of attraction between their molecules and their molecules do occupy significant space. In most cases their behaviour can be predicted by applying ideal gas theory, but when conditions of temperature and pressure approach that which is required to condense the gas (i.e. low temperatures and high pressures) there are some observable differences because particles are very close.

The table below shows the molar volumes of several gases at S.T.P. It can be seen that there are differences in the molar volumes of real gases compared to that of an ideal gas, 22.71 L.

Gas	Molar volume (L) at S.T.P.
Hydrogen, H_2	22.71
Nitrogen, N_2	22.70
Carbon dioxide, CO_2	22.56
Ammonia, NH_3	22.39
Sulphur dioxide, SO_2	22.18

This can be explained by examining the intermolecular forces of attraction between real gas molecules. As strength of bonding increases, the molar volumes are smaller than that of the ideal gas.

H_2 is non-polar and has only dispersion forces between its molecules so its molar volume is very close to that of an ideal gas.

N_2 and CO_2 are also non-polar but have greater molar masses and more electrons, resulting in stronger dispersion forces and lower molar volumes.

NH_3 is polar and hydrogen bonding is its primary intermolecular force, and so the difference is quite significant.

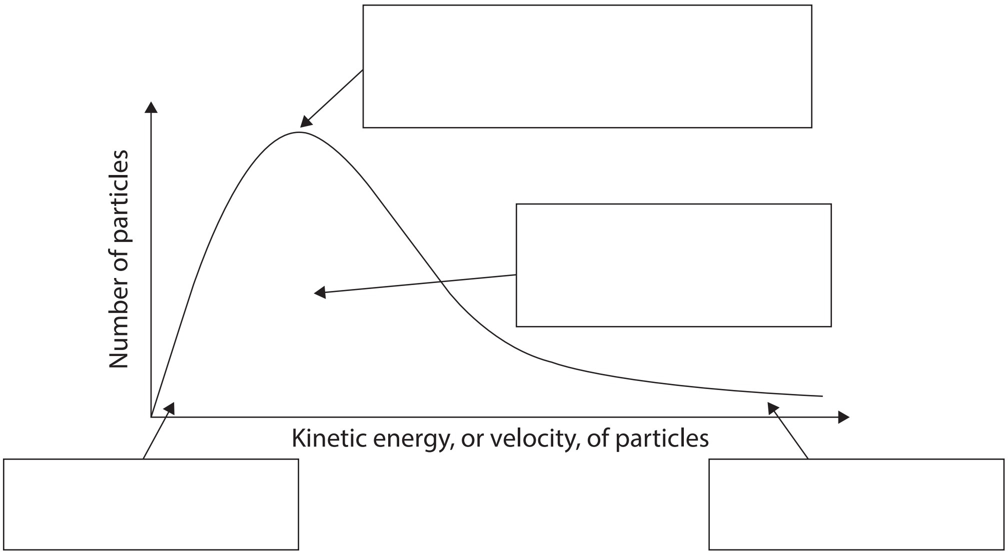
SO_2 is polar and has a high molar mass. Dipole-dipole interactions and strong dispersion forces contribute to a much lower molar volume than that of an ideal gas.

Real gases also differ in their ease of condensation from gas to liquid.

Set 1

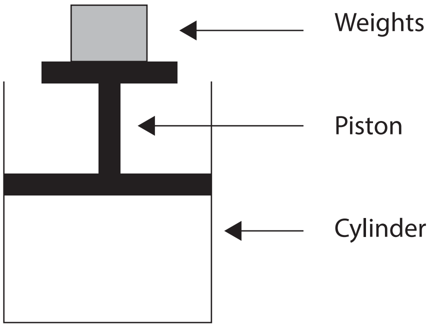
1. The kinetic theory of gases is based on the following assumptions. Complete each by filling in the missing words.
   - Gases consist of particles called ___________, except for the ________ ________ which consist of atoms.
   - The average distance between the molecules of a gas is ____________ compared to the size of each molecule.
   - The molecules of a gas move in ___________, ___________, straight line-motion. They collide with each other and the sides of their container.
   - The molecules of a gas exert ___________ attractive or repulsive forces on one another.
   - Collisions between gas molecules are perfectly ___________. There is no overall energy loss during collisions.
   - The average kinetic energy of the molecules ___________ as the temperature of the gas increases.

2. Label the Maxwell-Boltzmann distribution below using the following terms:
   - Gas particles moving slowly
   - Gas particles moving very quickly
   - Gas particles moving with intermediate velocities
   - Peak shows the average kinetic energy and velocity of gas particles

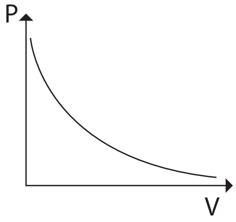


3. The total area under the Maxwell-Boltzmann distribution curve above represents:
   (A) the total energy.
   (B) the activation energy.
   (C) the total number of reacting molecules.
   (D) the total number of molecules present.

4. Some nitrogen gas was trapped inside a cylinder fitted with a movable piston, as shown. The pressure on the gas was increased by placing weights on top of the piston. Which of the graphs below best represents the results for the variation of gas volume with pressure?



A



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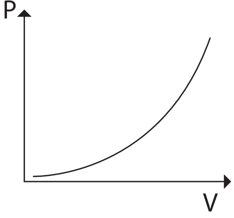

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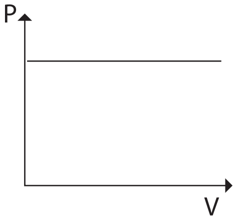

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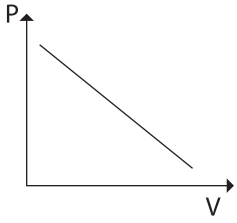

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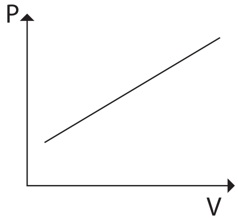


5. Which of the following will cause an increase in the average kinetic energy of a gas?

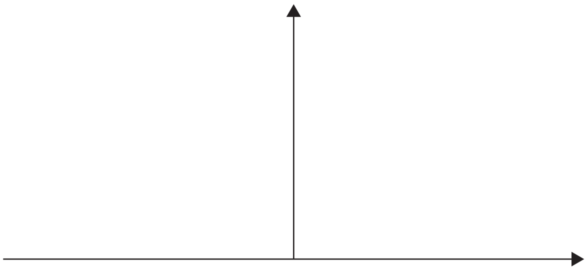
(A) Increasing the pressure of the gas.

(B) Increasing the volume of the container housing the gas.

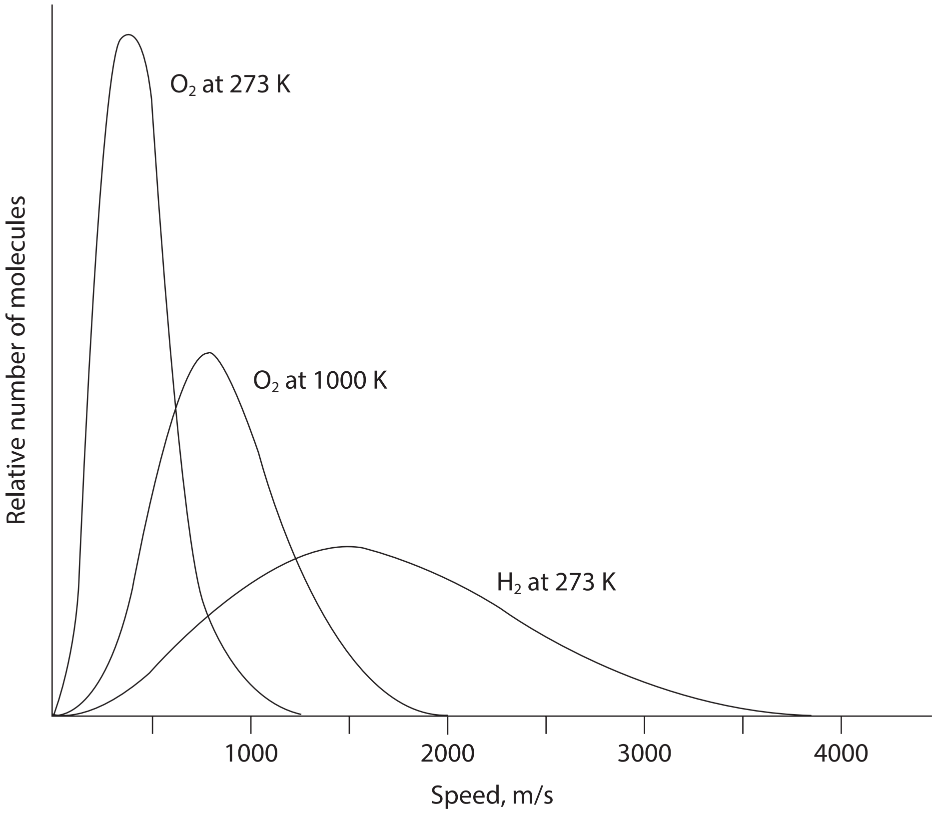
(C) Increasing the temperature of the gas.

(D) Adding more gas particles to the system.

6. On the axes below draw a sketch graph showing the relationship between volume and temperature for a gas at constant external pressure. Label the axes.



7. The graphs below show the distribution of the velocities of equal numbers of moles of oxygen and hydrogen at varying temperatures. Consider the shapes of the graphs, the area under the curves and the average velocity of the particles when answering the questions that follow.



(a) Compare the curves for oxygen gas at 273 K and 1000 K and explain the difference in shape.

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____

(b) Compare the curves for oxygen gas at 273 K and hydrogen gas at 273 K and explain the difference in shape.

____

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____

8. A sample of oxygen gas occupying 50.5 L is contained in a balloon at a temperature of 40.0°C and an external pressure of 110.0 kPa. If the external pressure is increased to 130.0 kPa and the temperature is kept constant, what is the final volume of the balloon?

9. A sample of nitrogen gas occupying 20.0 mL is contained in a gas syringe at a temperature of 30.0°C and an external pressure of 1 atm (101.3 kPa). If the gas syringe is cooled to 15.0°C and the external pressure is kept constant, what is the final volume of the gas syringe?

10. A 25.0 L fire extinguisher containing carbon dioxide gas has a temperature of 20.0°C and a pressure of 25.0 atm. On a hot day the temperature increased to 40.0°C. What is the new pressure in the fire extinguisher?

11. How many moles of carbon dioxide gas are there in the 25.0 L fire extinguisher in Q10?

12. (a) What is the mass of hydrogen chloride gas contained in a 35.0 L vessel at a temperature of 30.0°C and a pressure of 100.0 kPa?

(b) If the temperature of the vessel above is increased to 100.0°C, what will be the resultant pressure?

13. What volume of ammonia would be produced when 7.50 L of nitrogen gas reacts with 3.75 L of hydrogen gas at constant conditions of temperature and pressure?

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

(A) 5.00 L (B) 3.75 L

(C) 2.50 L (D) 15.0 L

14. In the Contact Process for the production of sulfuric acid, gaseous sulfur dioxide is reacted with oxygen over a vanadium pentoxide catalyst to produce gaseous sulfur trioxide.

(a) Write a balanced equation for the reaction.

(b) If 50.0 kL of sulfur dioxide is reacted with excess oxygen and the temperature and pressure are kept constant, what volume of oxygen will be required and what volume of sulfur trioxide will be produced?

15. The volume of one mole of any gas at S.T.P. is taken to be 22.71 L. In actual fact the volume varies based on the intermolecular forces present between gas molecules. Explain, with reference to intermolecular forces, why the molar volumes of carbon dioxide (22.56 L) and ammonia (22.39 L) are less than that of hydrogen (22.71 L).

____

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____

____

16. Hydrogen and oxygen gas react explosively to produce water when the gases are combined and ignited. Determine the volume of hydrogen and volume of oxygen needed to produce a glass-full of water. Assume a full glass of water contains 145 g of water and that all volumes are measured at S.T.P.

17. If 7.60 g of potassium is added to an excess of cold water, calculate the volume of hydrogen gas produced

(a) at S.T.P.

(b) at 25°C and 108.0 kPa

18. The Blast furnace for the production of iron operates at 1500°C. The iron oxide is reduced to iron by carbon monoxide as per the reaction below.

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

(a) Calculate the mass of iron that would be produced if 4.50 kL carbon monoxide at 1500°C and 103.0 kPa is reacted with excess iron (III) oxide.

(b) What volume of carbon dioxide would be produced under these conditions?

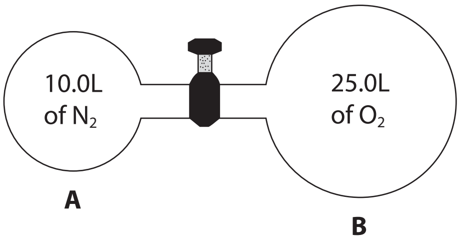
19. A 30.6 g piece of steel, containing only iron and carbon, was treated with an excess amount of hot hydrochloric acid to form 13.2 L of hydrogen gas at 28.0°C and 101.0 kPa pressure according to the reaction below.

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

Calculate the percentage of carbon in the steel.

One for the experts

20. The following diagram represents two bulbs containing gases connected by a valve.



Bulb A has a volume of 10.0 L and contains nitrogen gas at 125.0 kPa. Bulb B has a volume of 25.0 L and contains oxygen gas at 250.0 kPa. If the valve is open to allow mixing of the two gases, what would be the total pressure of the gases in the two connected bulbs? The temperature remains constant and the gases do not react. (Hint: Treat each gas separately. The partial pressures of the two gases can be added to find the total pressure)

9.9 SOLIDS AND LIQUIDS

The kinetic theory can be extended to solids and liquids.

In solids the particles are closely packed and vibrate about fixed positions. They have a definite shape and volume. In liquids the particles are fairly closely packed but can move past each other. They are virtually incompressible, have a definite volume and can take the shape of the container they are in.

As the particles are much closer together in the solid and liquid state, the bonding between particles influences many of its physical properties like melting point, boiling point, vapour pressure, density and solubility.

Changes of state

In solids, liquids and gases energy is stored in two ways.

- As kinetic energy (E_k), or energy due to motion.
- As potential energy (E_p), or energy due to position and attractive forces.

Energy is needed to change a substance from a solid to a liquid to a gas, pulling particles apart against their intermolecular forces.

Increasing the temperature of a substance increases the velocity and kinetic energy of its particles. This energy of motion overcomes the attraction between particles.

Once the attraction has been overcome the particles move further apart. Melting and boiling are endothermic processes so as a substance changes state from solid to liquid to gas its potential energy increases.

Solids < liquids < gases

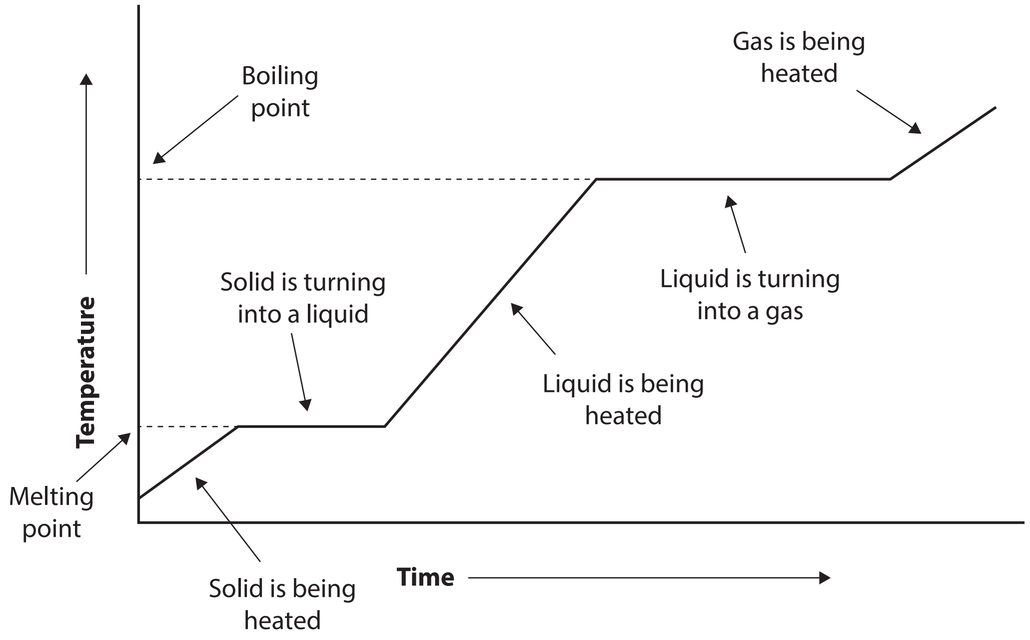
⟶

Increasing potential energy

When gases condense into liquids, and liquids fuse into solids their potential energy decreases. These are exothermic processes where energy is released.

9.10 HEATING CURVES

The energy changes that occur as a substance is heated and changes state from a solid through to a gas can be examined by looking at a heating curve. The heating curve for a substance is a plot of the temperature of the substance against time, or amount of heat added.



Heating the solid

As the solid substance is heated its temperature increases. The kinetic energy of its particles increases as they vibrate more and more rapidly about their fixed positions.

Melting point

The melting point of a substance is the temperature at which it changes from a solid to a liquid at atmospheric pressure.

At melting point, a temperature has been reached where particles vibrate with sufficient kinetic energy to be able to overcome the forces between them and the solid becomes a liquid. The particles are moving apart and their potential energy is increasing. The temperature and kinetic energy of the particles essentially remain constant during this phase change. The energy required to change the solid into a liquid at melting point is called the **latent heat of fusion**.

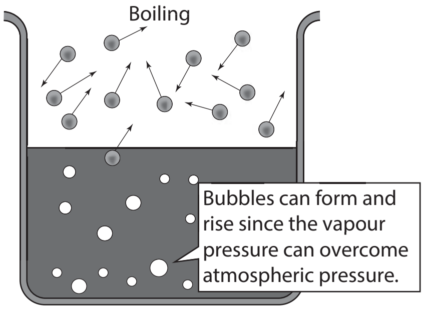
Heating the liquid

Once the substance has completely melted, the temperature of the liquid then begins to rise again. The particles vibrate more and their kinetic energy is increasing.

Boiling point

The boiling point of a substance is the temperature at which it changes from a liquid to a gas at atmospheric pressure.

At boiling point, the particles in the liquid have sufficient energy to overcome the attractive forces between them and turn into a gas and bubbles of the substance form throughout the liquid. The bubbles need to have an internal (vapour) pressure equal to atmospheric pressure in order to form. The potential energy of the particles is increasing again. Continued heating provides the energy for them to all be converted to a gas. Once again, the temperature and kinetic energy of the particles remain constant while the potential energy is increasing. The energy required to change the liquid into gas at boiling point is called the **latent heat of vaporisation.**



The boiling point of a liquid is directly related to the strength of its intermolecular forces. The larger the forces, the more heat energy is required to separate its particles.

Heating the gas

Once the substance has completely boiled, the temperature of the gas rises again and the particles vibrate more. Their kinetic energy is again increasing.

Heats of fusion and vaporisation

At the melting and boiling points of a substance, the heating curve shows that the temperature remains constant despite energy still being added to the system. This heat is used to overcome the attractive forces between the particles. As we have seen, this is accompanied by an increase in the potential energy of the system.

The **molar heat of fusion** is the quantity of heat needed to convert one mole of a substance from solid to liquid at one atmosphere pressure. It is measured in kilojoules per mole (kJ mol^{-1}).

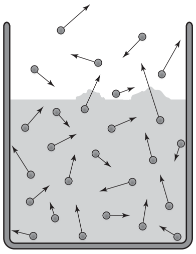
The **molar heat of vaporisation** is the quantity of heat needed to convert one mole of a substance from liquid to gas at one atmosphere pressure. It is also measured in kilojoules per mole (kJ mol^{-1}).

9.11 EVAPORATION AND VAPOUR PRESSURE

Evaporation

Evaporation is the change from liquid to gas at a temperature below the boiling point of that liquid. Unlike boiling, it only occurs at the surface of a liquid.

In any sample of a liquid the particles have a wide range of velocities. Some near the surface will have enough energy and be moving in the right direction to break free from attractive forces of the the liquid and escape into the air.



Vapour pressure

Vapour pressure is the pressure exerted by a vapour in equilibrium with the liquid from which it was derived.

If a liquid is placed in a closed container, evaporation will occur as the more energetic molecules will escape from the body of the liquid into the gaseous state. They will collide with air molecules, other molecules of the liquid and the walls of the container. The pressure produced is the liquid's vapour pressure.

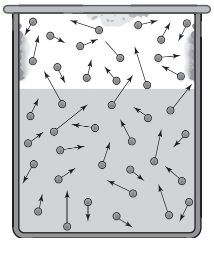
At the same time, some of the gaseous molecules will condense back into liquid. This process continues until the rate of evaporation is the same as the rate of condensation and an equilibrium has been established. If temperature is kept constant the level of liquid in the container will remain constant.

eg. water

$$\text{heat} + H_2O\,(l) \underset{\text{condensation}}{\overset{\text{evaporation}}{\leftrightharpoons}} H_2O\,(g)$$

Vapour pressure of a liquid is determined by temperature as increasing the temperature increases the amount of evaporation. The equilibrium will move to the right and there will be less liquid and more gas/higher vapour pressure at equilibrium.

The vapour pressure of a liquid is also inversely related to the strength of its intermolecular forces.

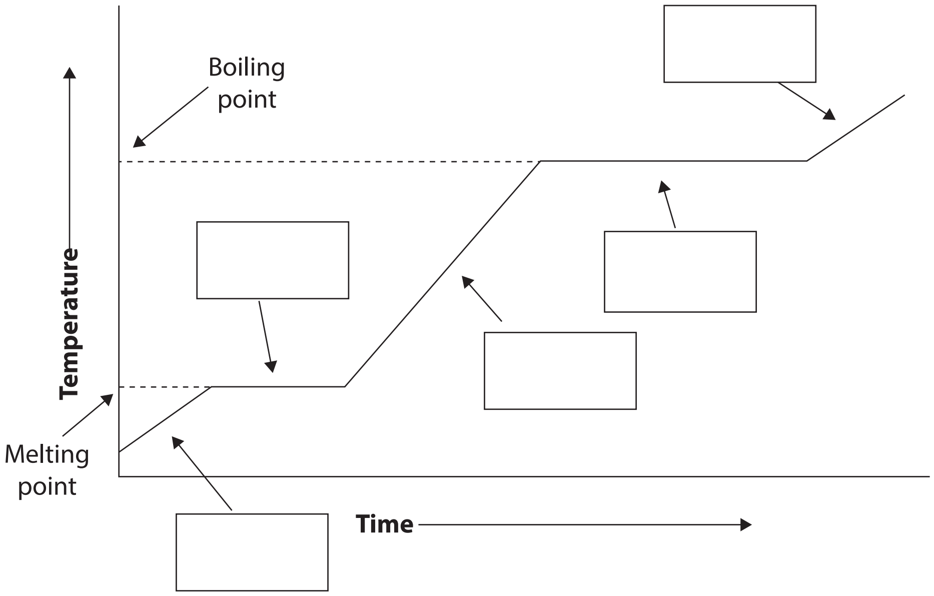


Vapour pressure and solids

Solids that are able to sublime (turn directly from a solid into a gas) can also generate significant vapour pressures. These are mostly non-polar covalent molecular substances with relatively large molar masses. Their dispersion forces are enough to allow them to remain solid at room temperature but some particles with enough energy can still break free and become gas. e.g. carbon dioxide, iodine, naphthalene.

Set 2

1. On the heating curve below, fill in the boxes with either E_k to show that kinetic energy is increasing, or $\mathbf{E_p}$ to show that potential energy is increasing.



2. As liquid is being heated its temperature increases. When it reaches boiling point it begins to turn into a gas. Why does its temperature remain constant during boiling?

3. Explain why steam at 100°C can give a more serious burn than water at 100°C.

4. Explain the difference between evaporation and boiling.

5. Why can a glass of water evaporate to dryness if left out on a hot day, despite not having reached its boiling point of 100°C?

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6. A closed bottle of water at 4°C is taken out of the fridge and allowed to warm up to room temperature at 20°C. Will the level of liquid water in the bottle move up or down at this higher temperature? Explain.

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7. Is melting an endothermic or exothermic process? Explain.

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Notes

Chapter

10

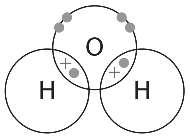
Water and Aqueous Solutions

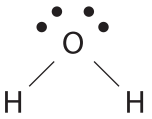
10.1 WATER

Around 71% of the Earth's surface is covered by water, with 96% of this being found in our oceans. Water is also found in rivers and lakes, as ice in glaciers and the polar ice caps, as water vapour in the atmosphere and in the bodies of all living things.

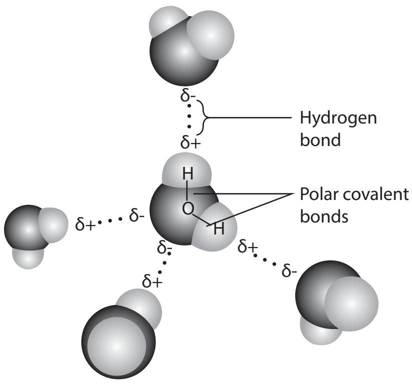
Water is vital for all living organisms. It acts as a solvent for many chemical reactions in biological systems and allows for the transport of dissolved substances into and out of cells.

Water is a covalent molecular compound with many important properties based on its structure and bonding. As discussed in the Bonding section, a water molecule consists of a central oxygen atom covalently bonded to two hydrogen atoms, with two lone pairs of electrons on the central atom. This gives it a V-shaped or bent shape and since it contains polar bonds and is asymmetrical, it is a highly polar molecule.





Water has hydrogen atoms covalently bonded to a highly electronegative oxygen atom and therefore hydrogen bonding is its predominant intermolecular force. Every water molecule can form strong hydrogen bonds with four others and it is this strong bonding that gives rise to many of its special properties.

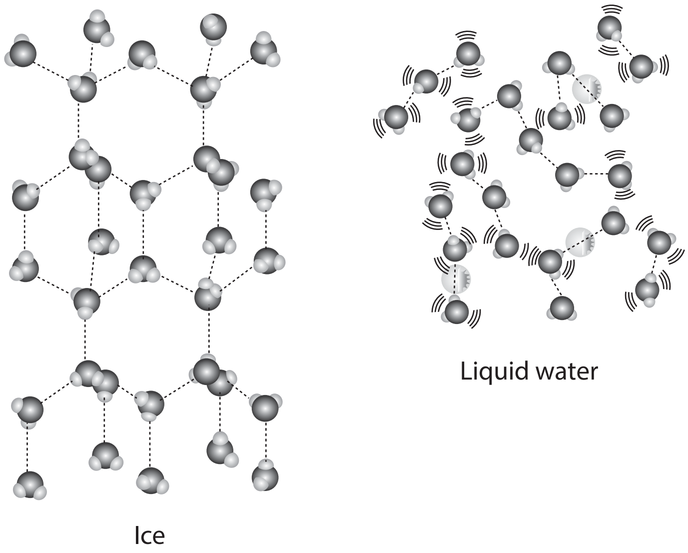


10.2 MELTING AND BOILING POINTS

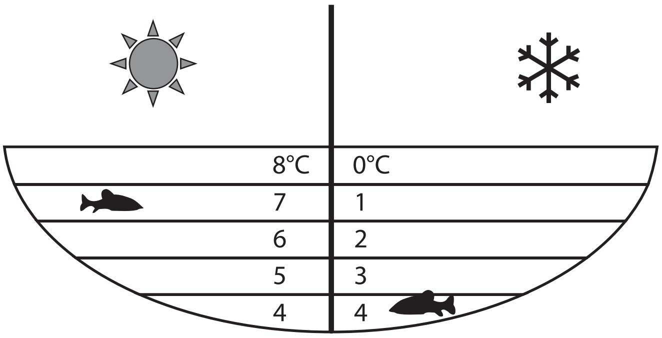
Water has relatively high melting and boiling points when compared to other covalent molecular compounds. This is due to the strong hydrogen bonding that must be overcome in order for it to change state from solid to liquid to gas. Its melting point of 0^{o}C and boiling point of 100^{o}C mean that it is the only naturally occurring compound that can be found in solid, liquid and gaseous states at temperatures that occur on Earth. If this were not the case then the water cycle wouldn't operate in the way that it does and the planet would be a very different place. If its melting and boiling points were more like those of other covalent molecular compounds there would be very little ice on the planet and a whole lot less water in the oceans.

10.3 DENSITY

Water is unusual in that its solid state is less dense than its liquid state. As water is cooled it becomes denser. Its molecules slow down, lose kinetic energy and hydrogen bonding brings them closer together. At 4°C it is at its most dense. As it begins to freeze, it forms an open crystalline structure with each water molecule hydrogen bonded to four others. To enable this shape to form the molecules must move further apart than when they were liquid so water becomes less dense.



So ice floats on water. Why is this important? In times of cold, like winter or an ice age, bodies of water initially freeze on the surface where it is coldest. If ice were denser than water it would sink, taking aquatic life with it! When it forms on the surface it also provides an insulating layer, slowing down heat loss from the water below and preventing it from freezing. Hence animals and plants can live beneath the ice and survive these extremes of cold.



10.4 SURFACE TENSION

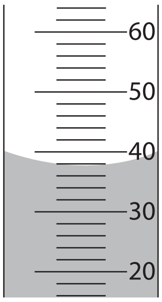
Surface tension is the tendency of a fluid to minimise its surface area and surface potential energy. For example, water forms droplets on a surface rather than spreading out. Water has a high surface tension due to the strong forces of attraction between water molecules at the surface. Surface tension is the property that allows insects to 'walk on water' and is also why a glass filled to the brim does not spill over.

Capillary action

Capillary action is the ability of a liquid to flow in narrow spaces without the assistance of external forces. If you place a narrow tube into water, some of the water will travel up the tube. This occurs because the polar water molecules adhere to the walls of the tube and create an upward force on the water at the edges. Surface tension due to hydrogen bonding holds the surface together. Capillary action occurs when the adhesive force between the water molecules and the walls is greater than the bonding between the water molecules. Water will rise until the force due to gravity pulling the water down matches the upward attractive force. This enables plants to draw water upwards.

Meniscus

Water forms a meniscus, or curved surface, in graduated cylinders, test tubes, burettes and pipettes. The adhesive forces are there but they are not strong enough to lift the water surface upwards and it just rises at the edges.



10.5 LATENT HEAT OF FUSION AND VAPORISATION

Water has relatively high latent heats of fusion and vaporisation. It takes quite a lot of energy to turn ice into water and water into steam. This is due to the strong hydrogen bonding between water molecules that must be overcome. As discussed in Chapter 9, phase changes occur at the melting and boiling points of a substance and are accompanied by an increase or decrease in potential energy. We use the term 'latent' heat as it means 'hidden' heat. Energy is going into or out of the system without a temperature change during the change of phase.

10.6 SPECIFIC HEAT CAPACITY

Specific heat capacity is the amount of energy required to raise the temperature of one gram of a substance by one degree kelvin. Water has a very high specific heat capacity which means that it takes a lot of energy to heat it up.

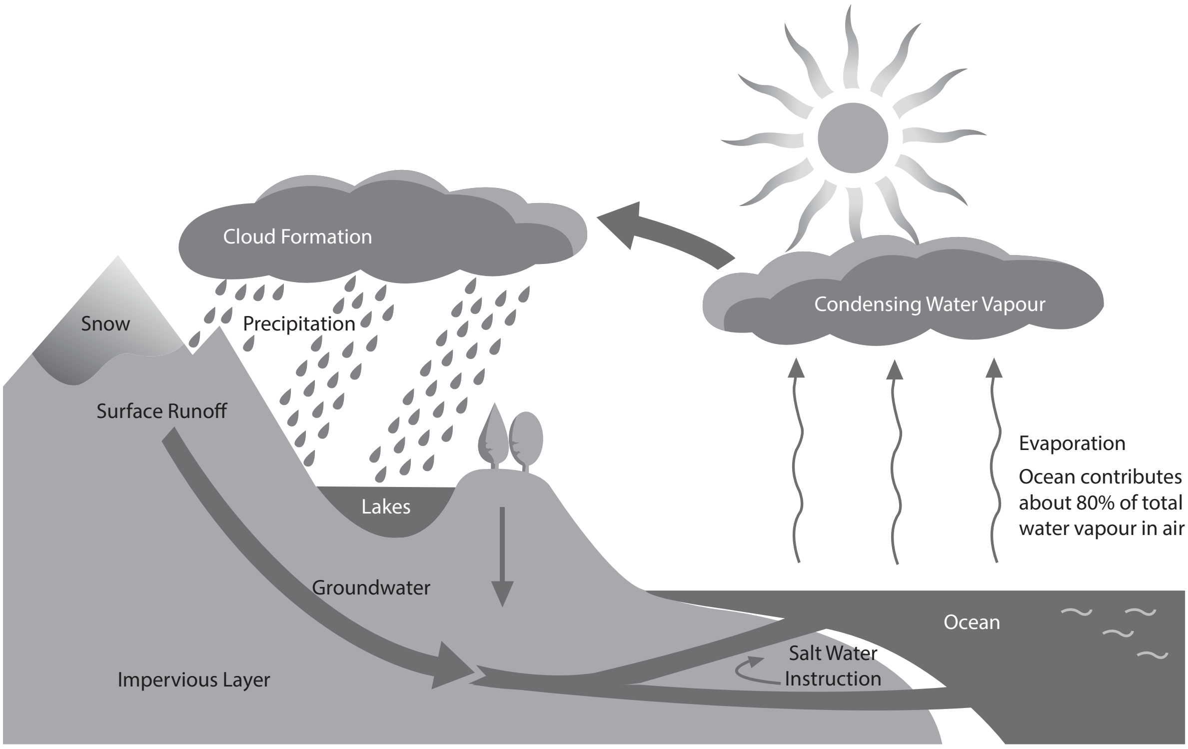
Specific heat capacity is measured in joules per kilogram per kelvin (J kg^{-1} K^{-1}) or joules per mole per kelvin (J mol^{-1} K^{-1}). The specific heat capacity of water is 4.184×10^3 J kg^{-1} K^{-1} at 25^oC (roughly 4.2 J kg^{-1} K^{-1}). This is considerably higher than that of copper at 3.85×10^2 J kg^{-1} K^{-1} and sand (quartz) at 8.30×10^2 J kg^{-1} K^{-1} at 25^oC. This is why beach sand gets so very hot compared to the sea water on a summer's day.

The high specific heat capacity of water is very important for temperature regulation in the environment. Water takes longer to heat up and cool down, so large bodies of water tend to maintain a very even temperature when air temperature varies between seasons.

The difference in specific heat capacities of land and sea also results in land and sea breezes. Sea breezes occur when the land heats up more than the water in the daytime and this heats the air over the land. This warmer air rises and cooler air from the sea moves in to take its place. The opposite happens at night. Water retains its heat more so than the land and rises, being replaced by the cooler air from over the land.

10.7 THE WATER CYCLE

The water cycle is crucial to us as it provides fresh water for living organisms. Pure water evaporates from bodies of salt water, like oceans, then moves over the land, where it condenses and drops as rain or snow. This water then moves through water courses back to the ocean, being used by plants and animals on the way. If water had weaker intermolecular forces there would be a lot less water as liquid on the planet and this water cycle would appear very different indeed.



Set 1

1. Why does water have higher boiling and melting points than other covalent molecular substances with similar molar mass?

2. a. Draw a sketch to show the crystalline structure of ice.

   b. Use your sketch to explain why ice floats on water?

3. What is capillary action and why does it occur?

4. Explain how the high specific heat capacity of water can result in a sea breeze.

10.8 AQUEOUS SOLUTIONS

Water has the ability to dissolve many substances so it is often termed the Universal Solvent and is necessary for the survival of all living organisms. Water acts as the solvent in our blood allowing red blood cells to carry oxygen around. It is the solvent that delivers electrolytes and nutrients to our cells, and carries waste away from them. Water dissolves minerals from rocks and organic material and these then become available for uptake by plants. It is the essential solvent that moves chemicals and nutrients around plants.

Some definitions:

The **solute** is the substance being dissolved e.g. sodium chloride

The **solvent** is the substance doing the dissolving e.g. water

The **solution** is the resulting homogeneous mixture e.g. sodium chloride solution

A **mixture** is when substances are added together but no chemical reaction has taken place. Solutions are mixtures.

Homogeneous mixtures have uniform composition and properties throughout e.g. Homogenised milk.

Heterogeneous mixtures have variable composition and properties throughout e.g. a chocolate chip cookie, concrete.

The **solubility** of a substance is the amount that can be dissolved in a solvent at a given temperature. It is usually given as grams of solute that can dissolve in 100 grams of water. For example, the solubility of sodium chloride in water is 36.0 g/100g at 20^{o}C. Solubility of solids usually **increases** with increasing temperature, whereas solubility of gases **decreases** as temperature increases.

Solutions can be classified as saturated, unsaturated or supersaturated.

A **saturated solution** is a solution where no more solute will dissolve in a solvent at a particular temperature and pressure e.g. 36.0 g dissolved in 100g of water at 20^{o}C. If more than 36.0 g is added the excess will remain as solid in equilibrium with the solution.

An **unsaturated solution** is a solution that contains less than the quantity needed to saturate it at a particular temperature and pressure. e.g. less than 36.0 g dissolved in 100g of water at 20^{o}C.

A **supersaturated solution** is a solution that contains more than the quantity needed to saturate it at a particular temperature and pressure. It can be prepared by increasing the temperature of the solvent, saturating the solution at higher temperature, and then carefully cooling back to a lower temperature. They are often unstable!

Bonding and solubility

The solubility of a solute in a solvent can be explained and predicted by examining the bonding of the solute and the intermolecular forces of the solvent, and is affected by changes in temperature.

For a solution to form, the solute and solvent particles must be rearranged. The solute particles need to become distributed throughout the solvent.

For dissolving to occur:

1. The intermolecular forces or ionic bonds between the solute molecules or ions must be overcome. This requires energy, as bonds are being broken. Bond breaking is an endothermic process.
2. The intermolecular forces between some of the solvent molecules must be overcome. This also requires energy and is endothermic.

3. Intermolecular forces or ion-dipole bonds must be formed between the solute molecules or ions and the solvent molecules. This releases energy, as bonds are being formed, and is an exothermic process.

Whether or not a solute dissolves in a solvent depends upon the relative strengths of the bonds that need to be broken and of the new bonds that would need to be formed. The energy required to break the bonds in the solute and solvent comes from the energy released when the new bonds between the solute and solvent are formed. This happens at the same time when a solution is formed.

The stronger the bond being broken, the more energy is required. The stronger the bond formed, the more energy released. It follows that if the bonds being broken are of similar strength or weaker than the new ones being formed, then the solute should dissolve in the solvent.

A solute tends to dissolve in a solvent if the intermolecular forces/bonding within the solute and those within the solvent are similar to those that will be formed between the solute and the solvent. Polar covalent solutes tend to dissolve in polar covalent solvents and non-polar covalent solutes tend to dissolve in non-polar covalent solvents. Neither the solute nor the solvent can be more attracted to itself than to the other substance if dissolving is to occur.

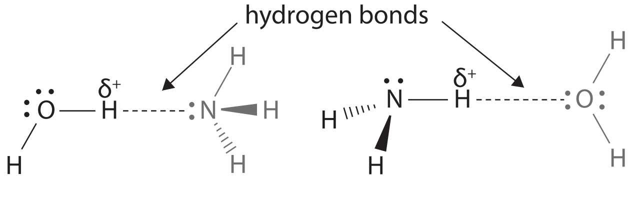
Note "like dissolves like" is not an explanation of solubility!

Polar covalent substances dissolving in water

As we have seen, water is a polar covalent molecule, and so it is predicted that it will dissolve polar covalent substances. For example, ethanol is a polar molecule and does dissolve in water. Ethanol has hydrogen bonding as its major intermolecular force, as does water. The bonds that need to break are ethanol-ethanol hydrogen bonds and water-water hydrogen bonds. The bonds that need to form are ethanol-water hydrogen bonds. Since the energy released when ethanol-water hydrogen bonds are formed is equal to or greater than the energy required for ethanol-ethanol and water-water hydrogen bonds to be broken, ethanol will dissolve in water.

Propanone is a polar covalent molecule with dipole-dipole interactions as its major intermolecular force. For propanone to dissolve in water, propanone-propanone dipole-dipole interactions and water-water hydrogen bonds need to break. The bonds that form are hydrogen bonds between water's hydrogen atoms and the lone pair of electrons on the oxygen of the carbonyl group on propanone. Since the energy released when propanone-water hydrogen bonds are formed is equal to or greater than the energy required for propanone-propanone dipole-dipole interactions and water-water hydrogen bonds to be broken, propanone will dissolve in water.

Interesting: Ammonia bonds very well with water. If 50 mL of ammonia is added to 50 mL of water the final volume is actually less than 100 mL!



Non-polar substances are insoluble in water

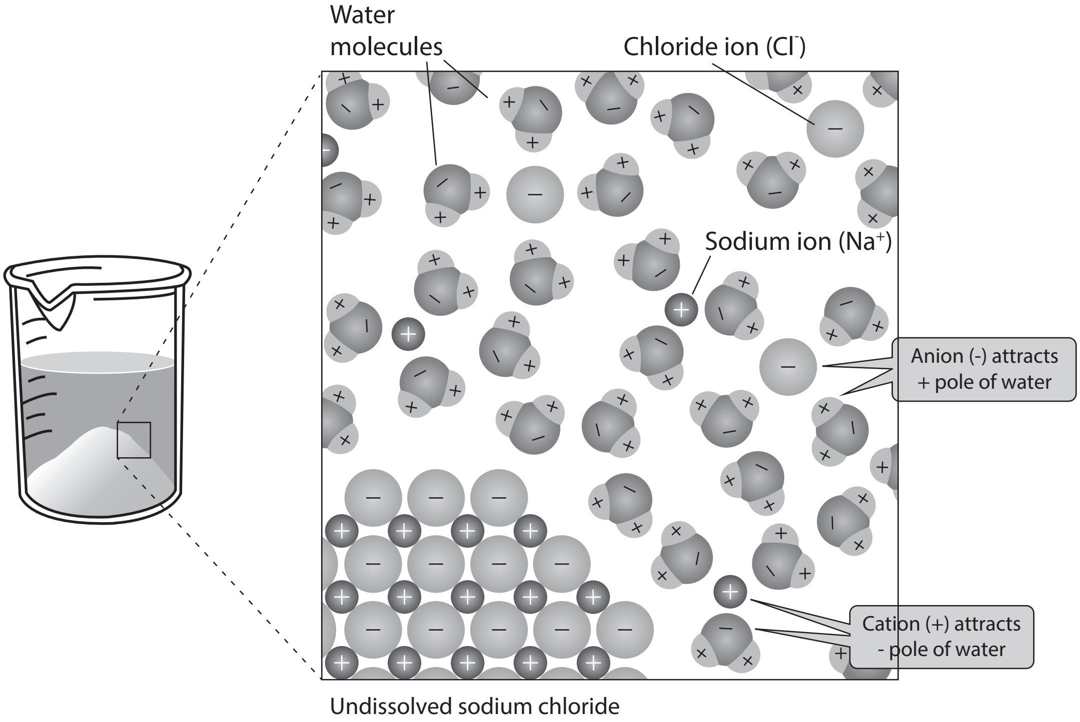
Non-polar substances have dispersion forces between their molecules and the strongest intermolecular forces that they could form with water are dispersion forces. Since these are weaker than the water-water hydrogen bonds that need to break, non-polar substances will not dissolve in water. The dispersion forces would not release sufficient energy to break the hydrogen bonds. e.g. methane will not dissolve in water.

Non-polar substances dissolve in non-polar substances

Non-polar substances have dispersion forces and can form dispersion forces with each other. For example, methane dissolving in hexane. Methane has dispersion forces between its molecules, as does hexane. They can form dispersion forces with each other. Since the energy released when methane-hexane dispersion forces are formed is equal to or greater than the energy required for methane-methane dispersion forces and hexane-hexane dispersion forces to be broken, methane will dissolve in hexane.

Ionic substances dissolving in water

Most ionic substances are soluble in water. For example sodium chloride dissolves to produce an aqueous solution. For sodium chloride to dissolve, ionic bonds between the positive sodium cation, Na^+, and the negative chloride anion, Cl^-, and some hydrogen bonds between water molecules need to break. Ion-dipole forces between the ions and water molecules need to form. Ion-dipole forces are considered equivalent in strength to hydrogen bonds. When solid NaCl is placed into water the slight negative charge of the oxygen atom in the water molecule is attracted to the sodium ion and the slight positive charge of the hydrogen atoms is attracted to the chloride ions. The ion-dipole forces that form provide enough energy to overcome both the ionic bonding in the NaCl crystal and the hydrogen bonding between water molecules and the crystal dissolves.



Ionic compounds tend to be insoluble in non-polar solvents. The only bonds that could form between the ions and the non-polar solvent molecules are dispersion forces, which are not strong enough to disrupt the ionic lattice.

Ionic substances that are insoluble in water

Not all ionic substances are soluble in water. There are exceptions, as shown on the solubility table in your data book. Insoluble ionic compounds are generally those that contain ions that are relatively small and so have a high charge density, strengthening the ionic bonding in the crystal lattice. These will usually not dissolve to an appreciable extent in water, but may react with it.

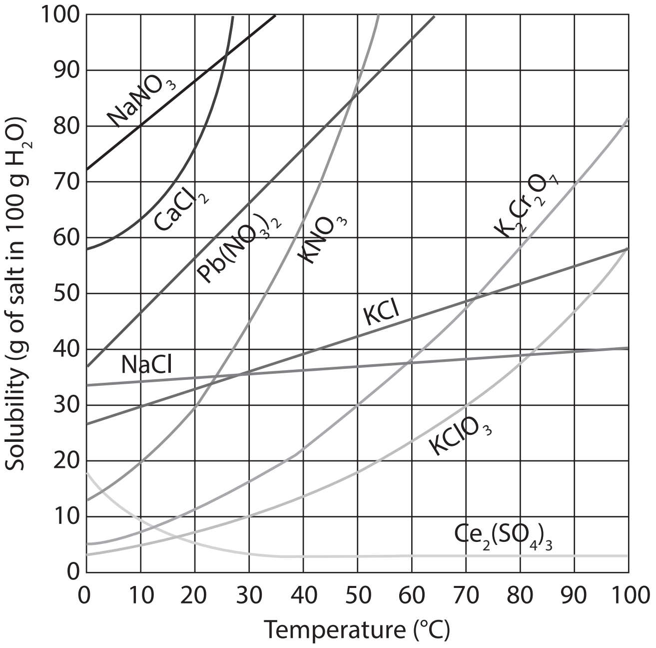
All metal oxides are insoluble except those of calcium, barium and alkali metal cations. These soluble oxides react, or hydrolyse with the water to form hydroxides.

e.g. $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

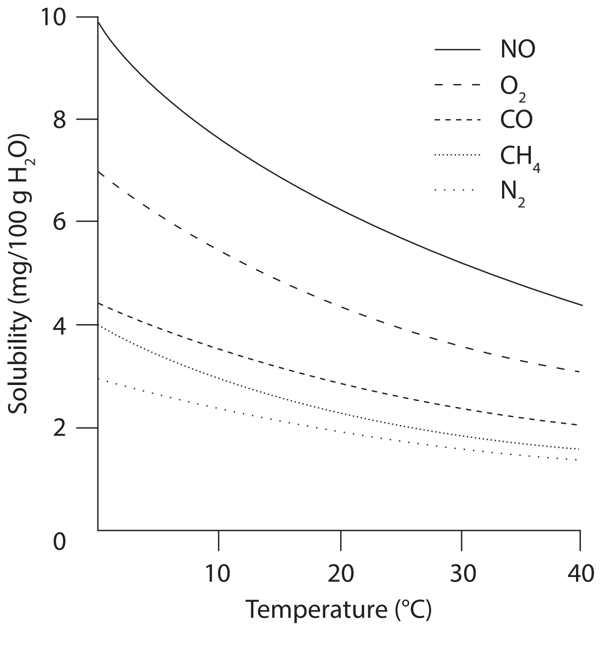
10.9 OTHER FACTORS THAT AFFECT SOLUBILITY OF SUBSTANCES IN WATER

Temperature

An increase in temperature generally increases the solubility of a solid dissolved in a liquid. Increasing the temperature increases the kinetic energy of all particles and this results in more collisions between solute and solvent particles. In addition, the added kinetic energy of the solute particles enables them to more easily break free from the ionic or intermolecular bonding holding them together. These factors allow for greater solubility. See the solubility curves for some salts dissolving in water at varying temperatures below.



An increase in temperature decreases the solubility of a gas dissolved in a liquid. This is because the increased kinetic energy of dissolved gas molecules enables them to break free from the intermolecular forces that they have with the solvent. See the solubility curves for some gases dissolving in water at varying temperatures below.



Gas pressure

The solubility of a gas dissolved in a liquid is directly proportional to the pressure of the gas above the solution. For a gas to come out of solution it must form bubbles and these bubbles need to have a pressure equal to or greater than that of the gas pushing down on the solution, or they will not form. e.g. Opening a bottle of fizzy drink decreases the pressure above the solution and allows carbon dioxide gas to form bubbles and come out of solution.

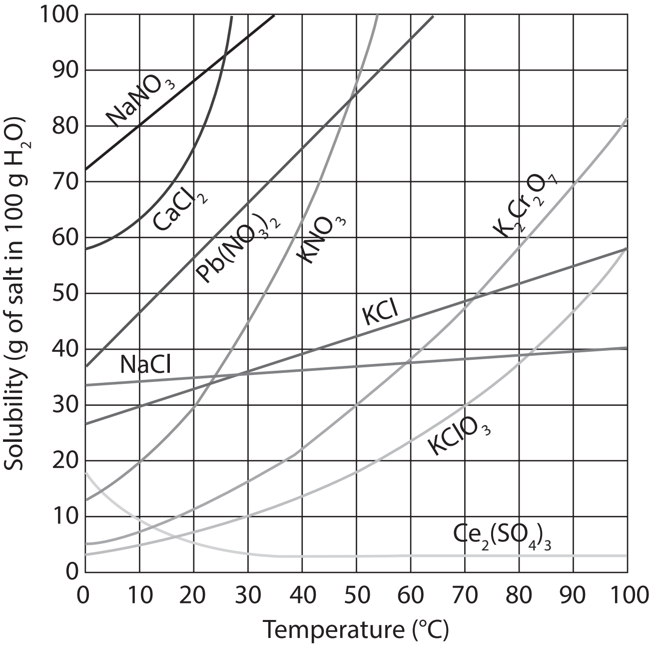
Set 2

1. You are given three solutions of sodium chloride. One is unsaturated, one is saturated and one is super saturated. You also have a sample of solid sodium chloride crystals.

   a. Define unsaturated, saturated and supersaturated.

   b. Describe how you might use the solid sodium chloride crystals to determine which solution is which.

2. The solubilities of various ionic substances are shown on the graph below. Use the information in the graph to answer the questions that follow.



a. What mass of sodium chloride will dissolve in 100g water at 10°C?

b. A solution of potassium chloride has 20 grams of the salt dissolved in 100 grams of water at 60°C. Approximately how many more grams of the salt can be added to the solution before reaching the saturation point?

c. Explain why the solubility of sodium nitrate increases with increasing temperature.

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d. Which salt decreases in solubility as temperature increases?

e. Describe how you would prepare a saturated solution of potassium nitrate at room temperature of 20°C.

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f. A beaker containing 80 grams of lead (II) nitrate in 100 grams of water has a temperature of 30°C. Approximately how many grams of the salt are undissolved, on the bottom of the beaker?

g. What is the solubility of potassium dichromate at 50°C in $molL^{-1}$?

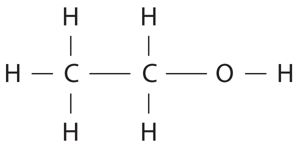
3. Why does the solubility of gases tend to decrease with increasing temperature?

4. Deep-sea divers must be careful when returning to the surface to prevent a condition called the 'bends'. This is when bubbles of nitrogen gas form in the bloodstream and body fluids, interfering with normal functioning of the nervous system. Explain the formation of these nitrogen bubbles.

5. Which of the following substances would be soluble in water?

Methanol	Ethane	Sodium bromide	Benzene	Hydrogen chloride	Carbon tetrachloride	Sulfur dioxide
CH_3OH	CH_2CH_2	NaBr	C_6H_6	HCl	CCl_4	SO_2

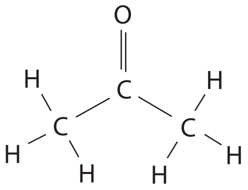
6. Using your understanding of polarity and intermolecular forces, explain why ethanol is soluble in water.



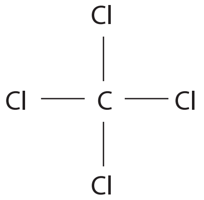
Ethanol

7. Acetone, or 2-propanone, is used as a solvent in nail polish remover and paint thinners. It dissolves readily in water. Explain its solubility in water with reference to the bonds that need to be broken and those that need to form.

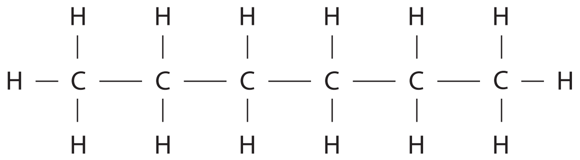
Acetone



8. Explain why carbon tetrachloride readily dissolves in non-polar solvents like hexane, but will not dissolve in water.



Carbon tetrachloride
(tetrachloromethane)



Hexane

9. Why are ionic substances generally soluble in water but not in non-polar solvents?

10. Draw a diagram showing the particles present when sodium hydroxide dissolves in water.

10.10 AQUEOUS SOLUTIONS AS ELECTROLYTES

An electrolyte is a substance which, when dissolved in water, conducts electricity. Electrolytes produce ions in solution when they dissolve, which enable them to conduct.

Ionic substances already have ions, so when they dissolve they are said to undergo **dissociation**.

Covalent substances that dissolve react with water to produce ions and are said to undergo **ionisation** because they didn't have ions to begin with.

Substances can be classified as strong, weak or non-electrolytes.

Strong electrolytes are completely ionised or dissociated in solution.

e.g. potassium chloride completely dissociates into aqueous ions

$KCl\ (s) \rightarrow K^+\ (aq) + Cl^-\ (aq)$

e.g. hydrogen chloride completely ionises to form hydrochloric acid

$HCl\ (g) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

Soluble strong electrolytes exhibit high conductivity, which increases as the concentration increases. Insoluble strong electrolytes exhibit low conductivity, which increases as the solubility increases.

Weak electrolytes are only partially ionised in solution.

e.g. ethanoic acid partially ionises, with most particles remaining as CH_3COOH molecules.

$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

The reversible arrow is used for weak electrolytes to show that as some molecules ionise, some ions reform molecules.

Soluble weak electrolytes exhibit low conductivity, which increases as the concentration increases but remains low.

Non-electrolytes do not produce ions when dissolved and are non-conducting.

eg. Sucrose dissolves but does not produce ions because it remains as molecules.

$C_{12}H_{22}O_{11}\ (s) \rightarrow C_{12}H_{22}O_{11}\ (aq)$

10.11 COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties are those properties that depend upon the concentration of dissolved solute molecules or ions in solution. They include freezing point depression, vapour pressure lowering and boiling point elevation.

When a solute dissolves in a solvent many of the physical properties of the solvent are changed. The more dissolved particles that are present in solution, the more pronounced the effect.

Freezing point depression

The presence of a dissolved solute lowers the freezing point below that of the pure solvent. The solute molecules or ions block the molecules of solvent as they try to form a solid crystal so it is harder for them to freeze. A practical application of this is the use of rocksalt or road grit to prevent ice forming on roads and footpaths in countries with cold climates. The rocksalt lowers the freezing point of the water on the road surface, which stops ice forming. Containers like the one shown below containing crushed rocksalt are found in public places for use when ice is likely to form.

Vapour pressure lowering

The presence of a dissolved solute lowers the vapour pressure to below that of the pure solvent. Solute particles present in a solution prevent solvent particles from escaping into gaseous phase, both at the surface and in order to form bubbles within the body of the solution.

Boiling point elevation

The presence of a dissolved solute raises the boiling point above that of the pure solvent. To boil or form bubbles and turn into a gas the vapour pressure within the bubbles must be equal to or greater than atmospheric pressure. Since the presence of a dissolved solute lowers the vapour pressure of the solvent, the solution requires higher temperatures in order to overcome the atmospheric pressure and boil.

Interestingly, if the solute is non-volatile, then the solvent boils off leaving the solute behind. As the solute concentration increases, so too does the boiling point.

Set 2

1. NaCl and HBr are both strong electrolytes which form ions in solution. NaCl is said to dissociate and HBr is said to undergo ionisation.

   a. What is the difference between dissociation and ionisation?

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   b. Write equations to show the dissociation of NaCl and the ionisation of HBr.

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2. How would you use conductivity to determine whether an acid is a strong or weak electrolyte?

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3. Classify the following as strong, weak or non-electrolytes and predict their electrical conductivities.

	Strong/weak/non electrolyte	High/low/no conductivity
$C_6H_{12}O_6$		
LiBr		
H_2CO_3		
$Ca(OH)_2$		
Br_2		
CH_3CH_2OH		
$Sr(NO_3)_2$		
HNO_3		

4. Colligative properties are dependent upon the number of dissolved particles. Based upon this, which of the following solutions would you expect to have the highest boiling point, and why?

$0.1\ molL^{-1}\ HBr$

$0.2\ molL^{-1}\ CH_3OH$

$0.1\ molL^{-1}\ CrBr_3$

$0.2\ molL^{-1}\ CH_3COOH$

$0.1\ molL^{-1}\ H_3PO_4$

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5. At high altitudes water boils at lower than 100°C. Adding salt to cooking water increases the boiling point. Explain this with reference to vapour pressure and atmospheric pressure.

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6. The following table shows the vapour pressures of some familiar liquids at 20°C.

Substance	**Vapour pressure (kPa)**
Chloroform	19.5
Ethanol	5.9
Ether	59.0
Mercury	0.0002
Water	2.35

Which of the following correctly places the substances in order from lowest boiling point to highest?

(A) Ether, chloroform, ethanol.

(B) Mercury, ethanol, ether.

(C) Water, ethanol, chloroform.

(D) Ethanol, water, ether.

10.12 WATER TREATMENT

The supply of water is an extremely important issue for West Australians. Our drying climate and an increasing population means that we must find new sources of potable drinking water. Surface water from rain in dams provides around 7% of our requirements and groundwater that comes from underground aquifers provides around 46%. We supplement our supply with desalinated water which provides the remaining 47%.

Water sourced from groundwater and seawater must undergo a number of purification and treatment processes before it is delivered into the town water supply. The quality of drinking water is constantly monitored to ensure that it meets the regulations for safe levels of dissolved solutes.

Groundwater

Groundwater comes from rain that has percolated down through rocks and soil and into natural underground aquifers. Aquifers are areas underground where water collects and can be stored. They typically consist of rock material like sandstone and limestone that is porous or that contains connected spaces through which water can move. Water may take many years to make its way down through the ground above to reach the aquifer. Groundwater is pumped to the water treatment plant when required where it is tested, purified and treated before it makes its way to households.

Water testing

Water is analysed at source, at various stages during its treatment, and before it is supplied to the public to ensure that it meets the required water quality standards. Many parameters are tested and, depending upon the source of the water supply, these could include the following.

Total dissolved solids (TDS)

Total dissolved solids are anions and cations dissolved in water. They may include ions such as Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{3+}, HCO_3^-, Cl^- and SO_4^{2-}, NO_3^- and PO_4^{3-} and also soluble organic matter. The TDS provides the total concentration of ions found in the water sample but does not give information about the specific amounts of particular ions. It is determined by testing the electrical conductivity of the sample, or by heating it to remove the water and leaving salts that can be weighed. If accurate information about quantities of specific ions is required water samples can be further analysed using techniques such as atomic absorption spectroscopy.

TDS can find their way into water naturally as water may dissolve ions as it percolates through rock to reach an underground aquifer. Mineral springs or sea water could run into water catchment areas.

Human activity may also contribute to a high TDS result. Wastewater from industrial sources, storm water run-off from urban areas and water containing high levels of fertilisers and pesticides from agricultural areas could end up in water catchments.

If TDS levels are high it may affect the taste or colour of the water. Ions may form precipitates or cause corrosion in pipes and equipment.

Hardness

Hardness in water is caused by the presence of ions such as Ca^{2+}, Mg^{2+} and Fe^{3+}. Chemists can test for these ions to determine whether water is hard or soft. Groundwater in Perth is usually hard as our aquifers are typically sandstone or limestone, which contain $CaCO_3$.

Hard water interferes with the cleaning action of soaps, preventing them from lathering and instead forming an insoluble scum.

$$\underbrace{2\,CH_3(CH_2)_{16}COO^-Na^+}_{\text{soap}} + Ca^{2+} \rightarrow \underbrace{(CH_3(CH_2)_{16}COO^-)_2\,Ca^{2+}}_{\text{scum}} + 2Na^+$$

Hard water can also cause precipitates like lime scale to form in kettles, hot water systems and pipes.

There are several methods that can be employed to reduce hardness in water. Hard water can be boiled or sodium carbonate can be added to precipitate out the Ca^{2+}, Mg^{2+} and Fe^{3+} ions. Ion exchange resins can be used, which remove the Ca^{2+}, Mg^{2+} and Fe^{3+} and replace them with ions like Na^{+} that do not form scale. Commercial water softeners like Calgon can be used, which produces soluble complexes with the ions that contribute to hardness.

Turbidity

Turbidity is a measure of the clarity or transparency of water. Turbid water looks cloudy and this is caused by the presence of suspended particulate material which scatters light. Materials that contributes to turbidity include microscopic organisms, soluble organic compounds, organic matter, clay and silt.

Turbidity is determined by shining light through a water sample and using a light sensor to measure the amount of light scattered at right angles by the sample. The greater the scattering the higher the turbidity.

Acidity

pH is a measure of the acidity of a solution. Australian guidelines state that drinking water should be between pH 6.5 to 8.5. If water falls outside these limits the pH is adjusted accordingly. If it is too acidic, lime (CaO), soda ash (Na_2CO_3) or sodium hydroxide may be added. If it is too alkaline carbon dioxide, sulfuric or phosphoric acid may be added.

Heavy metals

Heavy metals are metals with relatively high densities and atomic numbers that are found naturally in the Earth. Some, like iron, cobalt and zinc are nutrients essential to the human body. Some are harmless in small amounts, like Mn, Cr, Ni, Cu and Ag. There are some heavy metals such as Cd, Hg and Pb that are quite toxic and these can build up in the body and interfere with the functioning of cells.

Heavy metals can find their way into ground water aquifers in a number of ways: mining or industrial wastewater run-off; lead from vehicle emissions and lead-acid batteries; water percolating through the ground can all carry and concentrate heavy metals.

Drinking water is tested for the presence of heavy metals via techniques such as atomic absorption or mass spectroscopy and, if present, these can be removed in a variety of ways. Some can be precipitated out if the pH is adjusted. Some are removed through flocculation (see below). It is also possible to use activated charcoal, filtration and ion-exchange methods to remove heavy metals from water.

Radon

Radon is a radioactive noble gas that is found in nature. It can be found trapped in rock deposits and is sparingly soluble in water, so is often found in water supplies. It is removed by aeration, or spraying the water into the air, where the radon gas dissipates. In Western Australia, workers at water treatment plants wear dosimeters, or radiation detectors, to ensure that they do not exceed recommended exposure to radon gas.

10.13 WATER PURIFICATION AND TREATMENT

Groundwater is treated to remove suspended solids and any of the dissolved contaminants discussed above, and also to remove any gases, odours or colour. Water is also disinfected using chlorine and has fluoride added. Typically the following processes are used:

Aeration

When groundwater arrives at the water treatment plant it is initially aerated by being sprayed into the air. This allows dissolved gases like radon, carbon dioxide and hydrogen sulfide to be released and the water becomes oxygenated through this process. This reduces the solubility of any dissolved organic compounds which may contribute to turbidity, and also any dissolved iron, which gives water a brown colour. This makes them easier to remove in the flocculation and filtration processes.

Flocculation

Flocculation is the process whereby small suspended particles in the water are made to clump together so that they become heavy enough to sink, or settle out of the water. This is achieved by adding alum (aluminium sulfate). The aluminium ions in the alum forms floc, (a gelatinous precipitate of aluminium hydroxide) with the hydroxide ions in the water. If the concentration of hydroxide ions is insufficient, lime or calcium hydroxide is added. The floc then traps any suspended particles and these clump together and sink to the bottom.

Sedimentation

Following flocculation, the water is left to stand in the sedimentation basin for a time to allow the floc to settle. It forms a thick layer on the bottom, which is removed. The remaining water is pumped to the filtration stage.

Filtration

In the filtration stage, the water is passed through a filter bed of anthracite (a type of coal) and then progressively coarser sand and gravel. Any remaining suspended particles are removed at this stage.

Chlorination

Gaseous chlorine is now added to the clear water to kill any bacteria.

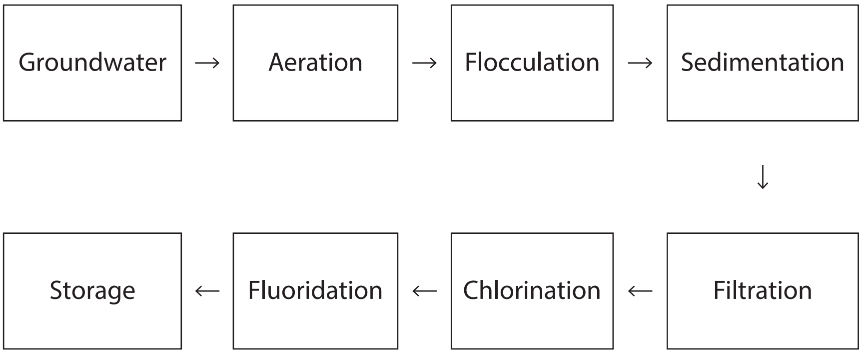
Fluoridation

In Australia most public water supplies have fluoride added. It is thought that adding fluoride will reduce tooth decay in the population. Since toothpastes also contains fluoride there are concerns that we may be ingesting too much fluoride which may have an adverse effect on health. The fluoride is added as sodium fluoride, NaF, fluorosilicic acid, H_2SiF_6, and sodium fluorosilicate, Na_2SiF_6.

Storage

The water is now suitable for drinking and is pumped into reservoirs or elevated water towers, ready to be used by the public.

Flowchart of water treatment



10.14 DESALINATION OF SEA WATER

Sea water contains high concentrations of dissolved salts and is not suitable for drinking. Desalination involves the removal of the dissolved salts in order to produce potable drinking water.

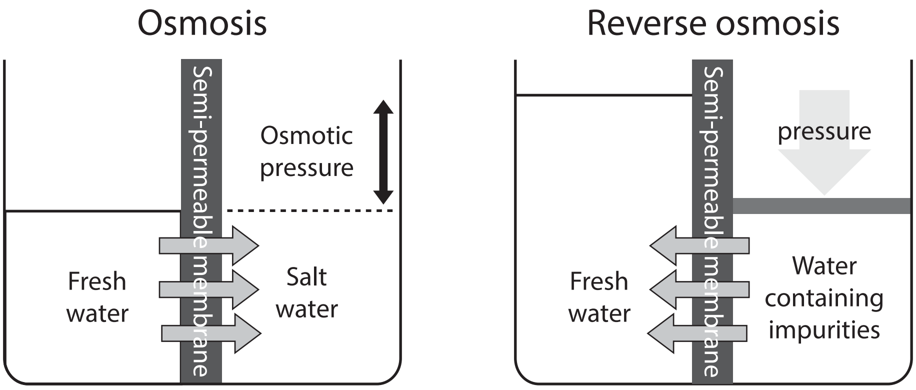
A desalination plant separates salty feed water into two streams: the fresh water stream for drinking and the brine or waste stream, which contains the dissolved salts. Depending upon the method(s) chosen, the efficiency of the process can vary widely but fresh water produced does not usually exceed 70% of the initial input of salty water by volume.

There are two main methods employed to desalinate sea water. **Reverse osmosis (RO)** and **Multi-stage flash distillation (MSF).** The cost and availability of energy often determines the method chosen.

Reverse osmosis (RO)

If separated by a semi-permeable membrane water will naturally move through from an area of low solute concentration to an area of high solute concentration in order to equalise the solute concentrations on both sides of the membrane. This is "osmosis". Pure water will naturally flow towards the most concentrated side. With reverse osmosis, pressure is applied to the salty water side of the membrane and the process is reversed. The fresh water makes it through the membrane and the salt becomes more concentrated and is discharged. This method achieves a high conversion rate of salty water to acceptably fresh water but the water that makes it through still has some dissolved ions present. The main energy required is to pressurise the water.

Mechanism of osmosis and reverse osmosis



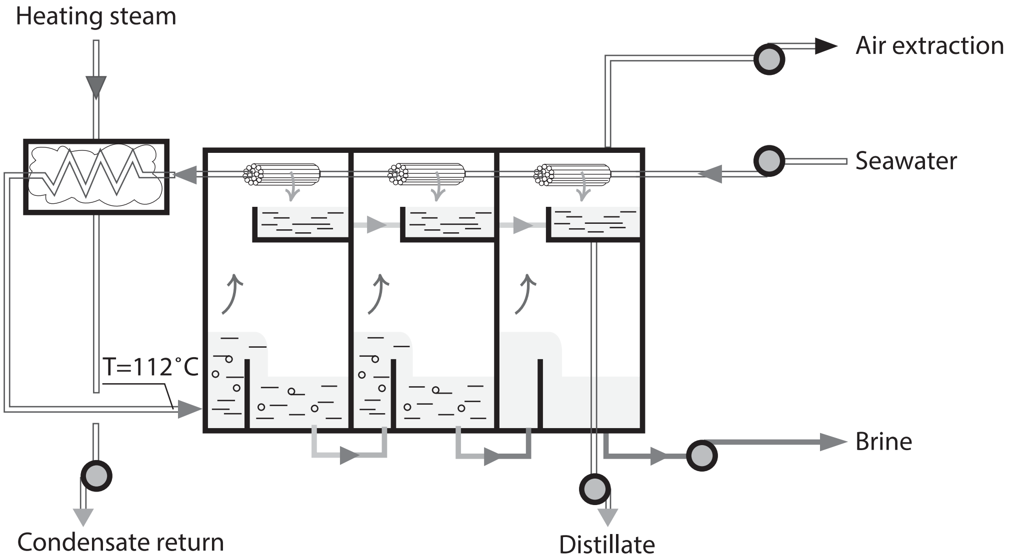
Water moves to the side with higher salt content

Only the water to which external pressure is applied filters through

Multi-stage flash distillation (MSF)

Simple distillation involves boiling the salty water and condensing the pure water (distillate) that boils off. The salt remains behind. (See Chapter 1 for a discussion of distillation.)

To improve the efficiency of the process the salty water in MSF is distilled in several stages. The initial salty feed water is distilled at high pressure and temperature. Pure water is collected and removed as it condenses and the heat given out from condensation is used to heat the salty water in the next stage, which is at a lower pressure and temperature. Once again, the pure water from the second stage is collected and the heat used in the next stage, which is again at a lower pressure and temperature. This is repeated several times, and the resulting water is about four times purer than with RO. About 60% of all desalinated water is collected using this method.



10.15 RECYCLED WATER

Recycled water is wastewater from sewage treatment plants that has been treated to remove solids and impurities. It is not suitable for drinking but can be used for specific purposes like irrigation of parks and crops, for industrial processing as well as in the construction industry. In Perth it is also being used to recharge our groundwater supplies. Hence we are becoming more and more dependent on recycled water in our dry climate.

Set 3

1. Groundwater contains many contaminants that need to be monitored and removed prior to it being used as public drinking water.

   a. What are total dissolved solids, how do chemists test for them and how do they get into the groundwater?

   b. What is turbidity and how is it caused?

   c. List the main heavy metals. How are they removed from groundwater?

   d. What dangers are associated with radon gas and how is it removed from groundwater at the water treatment plant?

2. a. Which ions contribute to water hardness and how do they make their way into groundwater?

b. Hard water does not lather well with soap and instead forms a precipitate called scum. Write an equation to show the formation of scum with soap.

c. What are some of the problems that hard water can cause?

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3. Prepare a simple flowchart showing the stages of water treatment.

a. Why is groundwater aerated?

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b. What is flocculation? Include an equation showing how 'floc' is produced.

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c. Describe the sedimentation process.

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d. What is the purpose of the filtration step?

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e. Why are chloride and fluoride added to our drinking water?

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4. What are the two methods used to desalinate seawater?

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10.16 WATER TESTING IN THE LABORATORY

The presence of specific ions in aqueous solutions can be identified in several ways in the laboratory.

The colour of aqueous solutions

Many ions have characteristic colours when in aqueous solution. If a sample exhibits a particular colour this may indicate the presence of certain ions. Your data booklet lists some of these in the "Coloured ions in aqueous solution" table.

Coloured ions in aqueous solution

Cation	Colour
Cr^{3+}	deep green
Co^{2+}	pink
Cu^{2+}	bule
Fe^{2+}	pale green
Fe^{3+}	pale brown
Mn^{2+}	pale pink
Ni^{2+}	green

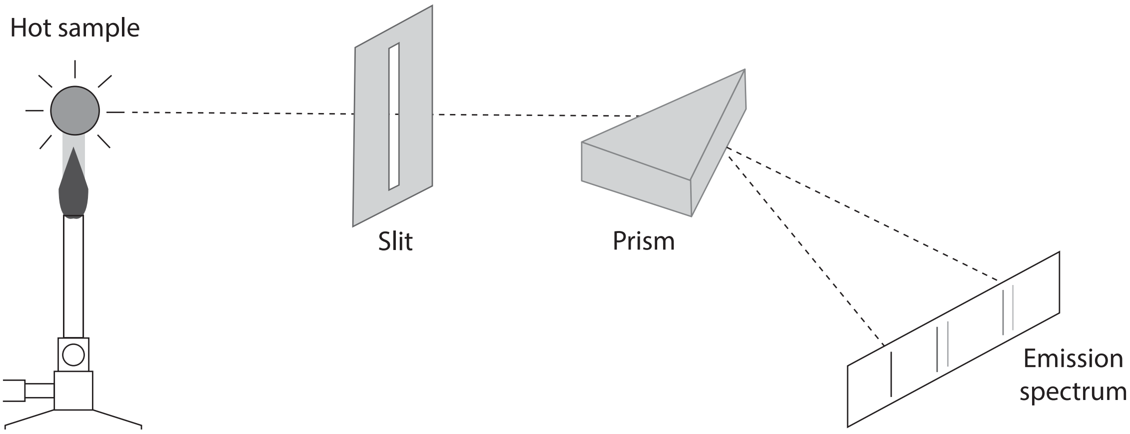
Anion	Colour
CrO_4^{2-}	yellow
$Cr_2O_7^{2-}$	orange
MnO_4^-	purple

Flame Tests

In Chapter 2 flame tests for solids was discussed. It is also possible to use flame tests to analyse solutions for the presence of metal ions. The solution can be sprayed in a fine mist through a Bunsen flame and the colour noted. The table below shows some characteristic flame colours.

Metal ion	Flame colour
Copper	Green
Sodium	Yellow
Lithium	Crimson red
Strontium	Scarlet red
Calcium	Brick red (orange/red)
Barium	Lime green (yellow/green)
Potassium	Lilac

It is also possible to view the light produced by flame tests through a spectrometer, which splits the light into its various wavelengths in an emission spectrum. This method can be used to further confirm the identity of any ions present in a sample.



In the laboratory, atomic absorption spectroscopy uses absorption spectra to quantitatively determine the concentration of ions present in a sample. e.g. lead ions in sample of water near industrial sites.

Chemical reactions

It is possible to identify the presence of ions through chemical reactions.

Addition of sodium hydroxide

If a small amount of sodium hydroxide is added to a solution containing metal ions many produce coloured precipitates. In some cases the addition of an excess amount of sodium hydroxide causes a complex to form and the precipitate redissolves.

Ion	Addition of a small volume of NaOH(aq)	Addition of excess volume of NaOH(aq)
Fe^{3+}	Rust brown ppt	Rust brown ppt
Fe^{2+}	Mud green ppt	Mud green ppt
Cu^{2+}	Blue ppt	Blue ppt
Pb^{2+}	White ppt	Redissolves
Zn^{2+}	White ppt	Redissolves
Al^{3+}	White ppt	Redissolves

Testing for carbonates and hydrogen carbonates

Metal carbonates and hydrogencarbonates produce carbon dioxide when an acid is added. The solution is placed into a boiling tube and an acid like hydrochloric acid is added. Any gas produced can then be bubbled through limewater and if the limewater turns cloudy, carbon dioxide was produced. The sample contained the carbonate or hydrogencarbonate ion.

Testing for chlorides, bromides and iodides (halides)

Chloride, bromide and iodide ions produce precipitates with silver ions. A small amount of silver nitrate can be added to the sample and the colour of any precipitate can indicate the presence of these halide ions. Silver also produces precipitates with other negative ions and so subsequent tests can be carried out to confirm their presence. Silver chloride is white, silver bromide is off-white or cream and silver iodide is pale yellow.

Testing for iodides using lead (II) nitrate

Lead iodide is a bright yellow insoluble solid. If some lead nitrate is added to a sample the formation of this very characteristic precipitate confirms that the iodide ion is present.

Testing for sulfates

The test for the presence of sulfate ions is to add barium chloride. If a white precipitate is formed it is likely that the sample contained the sulfate ion. There are other anions, like carbonate, that also form a white precipitate with barium so a further test is often carried out. If a small amount of acid is added it will dissolve barium carbonate, but not barium sulfate.

Aside from the test for carbonates, each of these tests uses precipitation to identify ions in aqueous solutions.

Precipitation reactions

A precipitation reaction occurs when two solutions of soluble salts are mixed and an insoluble salt is formed. The insoluble salt is called the **precipitate**.

Your data book contains a table of solubility rules with information to enable you to predict the formation of insoluble salts. Precipitation will occur if the combination of any pair of oppositely charged ions, present in a solution, form an insoluble or slightly soluble compound.

Solubility rules for ionic solids in water

Soluble in water

Soluble	**Exceptions**	
	Insoluble	**Slightly soluble**
Most chlorides	AgCl	$PbCl_2$
Most bromides	AgBr	$PbBr_2$
Most iodides	AgI, PbI_2	
All nitrates	No exceptions	
All ethanoates		
Most sulfates	$SrSO_4$, $BaSO_4$, $PbSO_4$	$CaSO_4$, Ag_2SO_4

Insoluble in water

Insoluble	**Exceptions**	
	Soluble	**Slightly soluble**
Most hydroxides	NaOH, KOH, $Ba(OH)_2$ NH_4OH**, AgOH**	$Ca(OH)_2$, $Sr(OH)_2$
Most carbonates	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$	
Most phosphates	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$	
Most sulfides	Na_2S, K_2S, $(NH_4)_2S$	

* NH_3 dissolves in water to form both NH_3 (aq) and NH_4^+(aq)/OH^-(aq)

** Ag^+(aq) reacts with OH^-(aq) to form insoluble Ag_2O

Soluble = more than 0.1 mole dissolves per litre
Slightly soluble = between 0.01 and 0.1 mole dissolves per litre
Insoluble = less than 0.01 mole dissolves per litre

Observations for precipitation and other reactions can be deduced using tables in your data booklet. There are two sections to consult for precipitation reactions.

First check out if any of the reactants or products appears on the "Colours of selected substances" table. If so, then this will give the colour of any precipitate, and can identify the presence of ions in an unknown solution.

Colours of selected substances

In general, ionic solids have the same colour as that of any coloured ion they contain. Two colourless ions in general produce a white solid. Selected exceptions to these two basic rules are noted below.

Ionic Solid	Colour
copper(II) carbonate	green
copper(II) chloride	green
copper(II) oxide	black
copper(II) sulfide	black
lead(II) iodide	yellow
lead(II) sulfide	grey
manganese(IV) oxide	black
silver carbonate	yellow
silver iodide	pale yellow
silver oxide	brown
silver sulfide	black

Then check the "Coloured ions in aqueous solutions" table in 10:16 above. This will tell you whether any aqueous ions have a colour. You can also use to determine the colour of precipitates. If a precipitate forms that contains one of these cations then this gives its colour for examination purposes. If your precipitate does not appear on either of these tables you can assume it is a white solid / precipitate.

Example

Solutions of $AgNO_3$ (aq) and NaI (aq) are combined and mixed.

a) Will a precipitate form?

The ions present are Ag^+, NO_3^-, Na^+ and I^-

Possible precipitates are AgI and $NaNO_3$

Checking the solubility rules, all nitrates are soluble, so $NaNO_3$ will remain in solution, as separate ions.

Most iodides are soluble but AgI is an exception, so a precipitate of AgI will form.

b) Write a balanced equation for the precipitation reaction.

$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$

Aqueous (aq) symbols are used for the soluble salts and the solid (s) symbol is used for the precipitate.

c) Provide observations for the reaction.

Neither of the reactants appears on the tables, so they are both clear, colourless solutions.

$NaNO_3$ is also a clear, colourless solution. AgI appears on the first table and is pale yellow.

Your answer should include all of this information.

A clear, colourless solution is added to a clear, colourless solution. A pale yellow precipitate forms which settles beneath a clear, colourless solution.

10.17 IONIC EQUATIONS

Ionic equations represent only the species that change, or take part, in a chemical reaction. Solids, liquids and gases appear in an ionic equation. Aqueous species that take part in the reaction are included. Aqueous species that do not change are called Spectator Ions and are removed from the equation.

Example 1 Precipitation reaction

Write an ionic equation for the reaction below:

$$\mathrm{AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)}$$

The first step is to write the aqueous species as separate ions.

$$\mathrm{Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + I^-(aq) \rightarrow AgI(s) + Na^+(aq) + NO_3^-(aq)}$$

Next is to identify the spectator ions, or the ions that are the same before and after the reaction. These are removed from the equation.

$$\mathrm{Ag^+(aq) + \cancel{NO_3^-}(aq) + \cancel{Na^+}(aq) + I^-(aq) \rightarrow AgI(s) + \cancel{Na^+}(aq) + \cancel{NO_3^-}(aq)}$$

The final ionic equation is:

$$\mathrm{Ag^+(aq) + I^-(aq) \rightarrow AgI(s)}$$

Example 2 Neutralisation reaction

Write an ionic equation for the reaction below:

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

Write the aqueous species as separate ions.

$$\mathrm{CaCO_3(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-\ (aq) + H_2O(l) + CO_2(g)}$$

Identify spectator ions and remove them from the equation.

$$\mathrm{CaCO_3(s) + 2H^+(aq) + \cancel{2Cl^-}(aq) \rightarrow Ca^{2+}(aq) + \cancel{2Cl^-}\ (aq) + H_2O(l) + CO_2(g)}$$

The final ionic equation is:

$$\mathrm{CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)}$$

Example 3 Halogen displacement reaction

Write an ionic equation for the reaction below:

$$\mathrm{Cl_2(g) + 2NaBr(aq) \rightarrow Br_2(l) + 2NaCl(aq)}$$

Write the aqueous species as separate ions.

$$\mathrm{Cl_2(g) + 2Na^+(aq) + 2Br^-(aq) \rightarrow Br_2(l) + 2Na^+(aq) + 2Cl^-(aq)}$$

Identify spectator ions and remove them from the equation.

$$\mathrm{Cl_2(g) + \cancel{2Na^+}(aq) + 2Br^-(aq) \rightarrow Br_2(l) + \cancel{2Na^+}(aq) + 2Cl^-(aq)}$$

The final ionic equation is:

$$\mathrm{Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)}$$

Set 4

1. A chemist tested three water samples for the presence of dissolved ions and the results are tabulated below. Identify the anion and cation present in each sample.

Sample	**Flame test**	**Addition of $NaOH$ then excess $NaOH$**	**Addition of HCl**	**Addition of silver nitrate**	**Addition of lead nitrate**	**Addition of barium chloride, then HCl**
A	Lilac flame	No precipitate	No bubbles	Off-white precipitate	White precipitate	No precipitate
B	Inconclusive	Brown precipitate does not redissolve	No bubbles	White precipitate	White precipitate	White precipitate that does not react with HCl
C	Yellow flame	No precipitate	Bubbles	White precipitate	White precipitate	White precipitate that produces bubbles on addition of HCl

	Anion	Cation
Sample A		
Sample B		
Sample C		

2. Write balanced equations, ionic equations and observations for each of the following reactions. In each case describe what you would observe. Include colours, precipitates and any gases evolved. If no change is observed, you should state this.

   a. Solid sodium carbonate is added to dilute hydrochloric acid.

   Balanced equation:

   Ionic equation:

   Observations:

   b. Chlorine gas is bubbled through a solution of potassium bromide.

   Balanced equation:

   Ionic equation:

   Observations:

c. Barium nitrate solution is added to aqueous copper(II) sulfate solution.

Balanced equation:

Ionic equation:

Observations:

d. Dilute ethanoic acid is added to sodium hydroxide solution.

Balanced equation:

Ionic equation:

Observations:

e. Lead (II) nitrate solution is added to potassium sulfide solution.

Balanced equation:

Ionic equation:

Observations:

f. Chromium (III) nitrate solution is added to barium hydroxide solution.

Balanced equation:

Ionic equation:

Observations:

g. Magnesium metal is added to dilute sulfuric acid solution.

Balanced equation:

Ionic equation:

Observations:

h. Solid silver oxide is added to dilute nitric acid solution.

Balanced equation:

Ionic equation:

Observations:

i. Bromine water is added to sodium chloride solution.

Balanced equation:

Ionic equation:

Observations:

j. Carbon dioxide gas is bubbled through calcium hydroxide solution (limewater)

Balanced equation:

Ionic equation:

Observations:

10.18 CALCULATIONS IN SOLUTION

Concentration of solutions

The concentration of a solution is defined as the quantity of solute dissolved in a quantity of solution. This can be represented in a variety of ways, including by the number of moles of the solute per litre of solution (mol L^{-1}), the mass of the solute per litre of solution (g L^{-1}) or parts per million (ppm).

Typically we use moles per litre.

Formula: $c = \frac{n}{V}$

Where c = concentration in mol L^{-1} or mol/L

n = number of moles of solute in mol

V = volume of solution in L

Example

If 10.0 g of sodium carbonate is dissolved into 250.0 mL of water what is the concentration in g L^{-1}, mol L^{-1} and ppm?

Grams per litre calculation

$c(Na_2CO_3)$ = 10.0 / 0.250

= 40.0 g L^{-1}

Moles per litre calculation

$M(Na_2CO_3)$ = (2 x Na) + (1 x C) + (3 x O)

= 105.99 g mol^{-1}

$n(Na_2CO_3)$ = m/M

= 10.0 / 105.99

= 0.0943 mol

$c(Na_2CO_3)$ = c/V

= 0.0943 / 0.250

= 0.377 mol L^{-1}

Parts per million calculation

convert mol L^{-1} into g/L	0.377 x 105.99 = 40 g/L
convert g/L into mg/L	40 x 1000 = 40000 mg/L
convert L into kg	Since water has a density of 1g/mL, 1L = 1kg
	So 40000 mg/kg
	and therefore 40000 ppm

Diluting solutions

When a solution of known concentration has water added its concentration is reduced to a lower value.

As only water is being added, the total numbers of moles of solute present does not change, only the volume of solution it is in.

So therefore; moles of solute before water is added = moles of solute after water is added

$n_{before} = n_{after}$

And since $n = cV$

It follows that $c_1V_1 = c_2V_2$

Where c_1 = concentration before dilution

V_1 = volume before dilution

c_2 = concentration after dilution

V_2 = volume after dilution

Example

Calculate the new concentration if 100.0 mL water is added to 50.0 mL of a 1.50 mol L^{-1} HCl solution.

c_1 = 1.50 mol L^{-1}

V_1 = 50.0 mL = 0.050 L

c_2 = ?

V_2 = 150.0 mL = 0.150 L

$c_1V_1 = c_2V_2$

$c_2 = c_1V_1 / V_2$

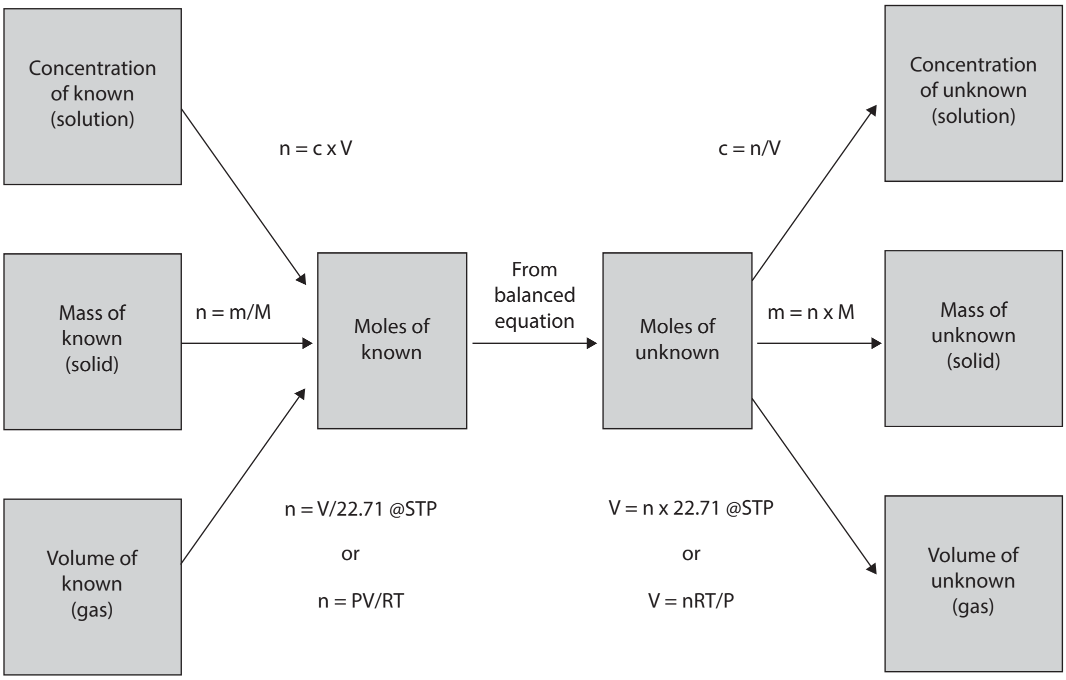
= 1.50 x 0.050 / 0.150

= 0.500 mol L^{-1}

10.19 CALCULATIONS INVOLVING SOLIDS, GASES AND CONCENTRATIONS OF AQUEOUS SOLUTIONS

Once you have information about the concentration and volume of a reactant in a chemical reaction you can use this and the balanced equation to determine the quantities of unknowns in the reaction.

If we know information about the quantity of a reactant, or a product, we can calculate its number of moles and then use the balanced equation to determine the number of moles of any unknown species in the reaction.



<u>Example 1</u>

Calculate the mass of precipitate formed when 250.0 mL of 0.100 molL^{-1} sodium iodide is added to an excess amount of silver nitrate solution.

$NaI(aq) + AgNO_3(aq) \rightarrow AgI(s) + NaNO_3(aq)$

Precipitate will be AgI

n(NaI) = c x V
= 0.100 x 0.250
= 0.0250 mol

n(AgI) = 1/1 x n(NaI)
= 0.0250 mol

m(AgI) = n(AgI) x M(AgI)   M(AgI) = 107.9 + 126.9
= 0.0250 x 234.8   = 234.8 g mol^{-1}
= 5.87 g

<u>Example 2</u>

Calculate the mass of calcium carbonate formed when 2.50 L of carbon dioxide gas at STP is passed through a saturated solution of limewater (calcium hydroxide). (you may assume that the limewater is in excess)

$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$

$n(CO_2)$ = V/22.71
= 2.50 / 22.71
= 0.110 mol

$n(CaCO_3)$ = 1/1 x $n(CO_2)$
= 0.110 mol

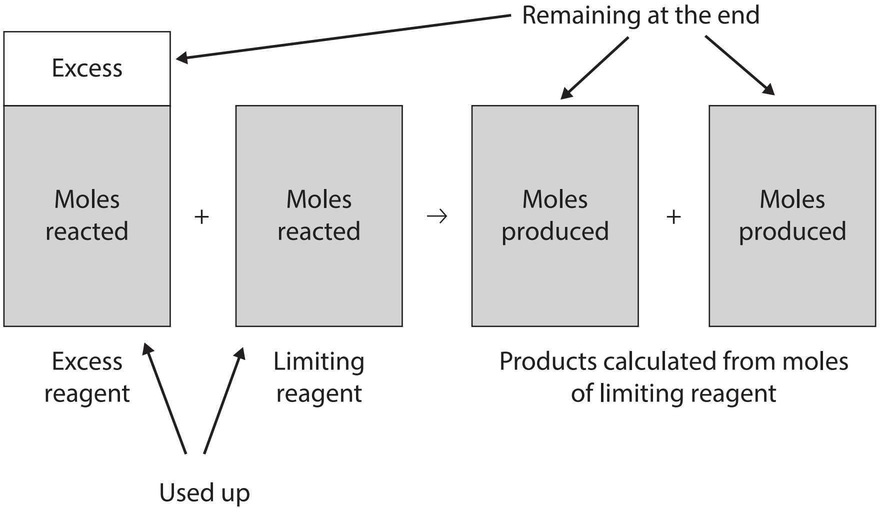
$m(CaCO_3)$ = $n(CaCO_3)$ x $M(CaCO_3)$ $M(CaCO_3)$ = 40.08 + 12.01 + 48.00
= 0.110 x 100.09   = 100.09 g mol^{-1}
= 11.0 g

Limiting reagent calculations

Quantities of products in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent.

In a limiting reagent problem, information is provided about two of the reactants. The chemist must determine which is reactant is the limiting reagent (the one that runs out) and which is the excess reagent.

Once the limiting reagent is determined it can be used to calculate the mass, moles, concentration or gaseous volume of any of the other species in the chemical equation, including the amount of the excess reactant that actually reacted.



Example

Hydrogen gas is produced by the reaction between zinc and hydrochloric acid, according to the equation below.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_{2(g)}$$

If 300 mL of 1.00 mol L^{-1} hydrochloric acid is added to 13.08 g of zinc, calculate the limiting reagent, the volume of hydrogen gas produced at STP and also the mass of excess reactant.

Step 1. Determine the limiting reagent.

Calculate the number of moles of each reactant.

n(Zn) = m/M
= 13.08/65.38
= 0.200 mol of Zn

n(HCl) = c x V
= 1.00 x 0.300
= 0.300 mol of HCl

Step 2. Compare the stoichiometric and actual amounts

Stoichiometric n(Zn) : n(HCl)
1 : 2

Actual n(Zn) : n(HCl)

0.200 : 0.300
or 1 : $\boxed{1.50}$ ← not enough

Therefore HCl is the limiting reagent!

Now you can use the limiting reagent to work out everything else.

Step 3. Calculate moles of H_2 produced

$n(H_2)$ = ½ x n(HCl)
= ½ x 0.300
= 0.150 mol

Step 4. Calculate volume of H_2 produced at STP

$V(H_2)$ = n x 22.71
= 0.150 x 22.71
= 3.41 L

Step 5. Calculate the moles of excess reactant that reacted.

n(Zn) = ½ x n(HCl)
= ½ x 0.300
= 0.150 mol

Step 6. Calculate the mass of excess reactant that reacted.

m(Zn) = n x M $\quad$ M(Zn) = 65.38 g mol^{-1}
= 0.150 x 65.38
= 9.809 g

Step 7. Calculate the mass of excess reactant remaining.

$m(Zn)_{remaining}$ = $m(Zn)_{initial} - m(Zn)_{reacted}$
= 13.08 – 9.809
= 3.371 g

Set 5

1. A 750mL bottle of mineral water was evaporated to dryness to analyse its sodium content. It was found to contain 0.113g NaCl.

   a. What is its sodium ion concentration in g L^{-1} and mol L^{-1}?

   b. If the mineral water has a density of 1g/mL, what is the sodium ion concentration in parts per million?

2. Epsom salts, or magnesium sulfate, is known for its numerous health benefits. What mass of Epsom salts are required to prepare a 60.0 L bath with 1.00 mol L^{-1} concentration?

3. What volume of hydrogen chloride gas at S.T.P. needs to be dissolved in water to prepare 150.0 mL of 1 mol L^{-1} hydrochloric acid?

4. Calculate the new concentration if 125.0 mL water is added to 250.0 mL of a 2.50 mol L^{-1} copper chloride solution.

5. How much water must be added to 175.0 mL of 2.00 mol L^{-1} nitric acid solution to produce a 1.30 mol L^{-1} solution?

6. Calculate the mass of precipitate formed when 250.0 mL of 0.100 mol L^{-1} sodium sulfide is added to an excess amount of copper nitrate solution.

7. When chlorine gas is bubbled through silver nitrate, silver chloride, dinitrogen pentoxide and oxygen gas are formed as per the following reaction.

$$4AgNO_3 + 2Cl_2 \rightarrow 2N_2O_5 + 4AgCl + O_2$$

   a. Calculate the mass of silver chloride formed when 3.00 L of chlorine gas at S.T.P. is bubbled into excess amounts of silver nitrate solution. (You may assume that all of the chlorine reacts)

   b. Calculate the volume of oxygen gas that is produced if the temperature reaches 35.0^{o}C and a pressure of 1.00 atmospheres (101.3 kPa).

8. When nitric acid is added to solid sodium sulfite, sodium nitrate, water and sulfur dioxide are formed.

   a. Write a balanced equation for the reaction.

b. Calculate the volume of sulfur dioxide formed at S.T.P. when 125.0 mL of 0.500 mol L^{-1} nitric acid is added to 5.00 g of sodium sulfite.

c. Calculate the quantity of excess reactant.

9. Sulfur trioxide gas dissolves readily in water to produce sulfuric acid. The reaction is very exothermic. Calculate the final concentration of the sulfuric acid solution formed when 37.0 L of sulfur trioxide gas at 15.0°C and 110.0 kPa is bubbled through a 5.00 L flask of water. Assume that all the sulfur trioxide dissolves.

10. a. Calculate the mass of precipitate formed when 350.0 mL of 0.250 mol L^{-1} sodium iodide is added to 250.0 mL of 0.450 mol L^{-1} lead (II) ethanoate solution.

b. Calculate the concentration of all of the ions remaining in solution after the reaction is complete.

Chapter

11

Acid and Bases

11.1 ARRHENIUS THEORY

The Arrhenius theory can be used to explain the behaviour of strong and weak acids and bases in aqueous solutions.

An acid is a substance that produces hydrogen ions H^+ in solution.

Acids are generally covalent molecular substances, and so when they are dissolved in water they **ionise**, or produce ions in solution.

e.g. hydrochloric acid

$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

An alkali is a soluble base and produces hydroxide ions OH^- in solution.

Alkalis are generally ionic substances, and so when they are dissolved in water they **dissociate** (or come apart) to produce ions in solution.

e.g. sodium hydroxide

$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

Acids and bases can be strong or weak depending upon the extent to which they ionise or dissociate in solution.

Strong acids are completely ionised in aqueous solution

e.g. $HNO_3(l) \rightarrow H^+(aq) + NO_3^-(aq)$

There will be no nitric acid molecules, only hydrogen and nitrate ions.

Weak acids are only partially ionised in aqueous solution.

e.g. $CH_3COOH(l) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

A large proportion of this solution will be ethanoic acid molecules and there will be relatively few ethanoate and hydrogen ions. In an ethanoic acid solution only around 1% of ethanoic acid molecules are ionised.

N.B. The double arrows indicate that an equilibrium exists between unionised molecules of ethanoic acid and the ions in solution. As ethanoic acid molecules ionise, ethanoate and hydrogen ions reassociate, at the same rate at a given temperature.

Strong alkalis are completely dissociated into ions in aqueous solution.

e.g. $KOH(s) \rightarrow K^+(aq) + OH^-(aq)$

Weak alkalis are bases in which only a small proportion of the base species react with water to form hydroxide ions.

e.g. $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The equilibrium between the NH_3 molecules and ammonium and hydroxide ions strongly favours the reactants. A solution of ammonia consists mainly of dissolved NH_3 molecules, and only a small amount of ammonium and hydroxide ions.

11.2 COMMON ACIDS AND THEIR USES

Strong acids

Sulfuric acid, H_2SO_4

Sulfuric acid is produced via the Contact Process.

In chemical industry it is used in mineral processing, detergent and fertiliser manufacture and oil refining.

It is also the electrolyte used in lead-acid batteries.

Hydrochloric acid, HCl

Hydrochloric acid is found naturally in gastric acid in the stomach.

It is a by-product of industrial processes like the manufacture of sodium carbonate.

In the chemical industry it is used in the production of PVC plastic and polyurethane.

Due to its reaction with oxides, hydroxides and carbonates it is used to clean bricks and for descaling.

Nitric acid, HNO_3

Nitric acid is produced via the Ostwald Process.

It is used for nitration, where a nitro group (NO_2) is added to an organic molecule.

It is also used to produce explosives, fertilisers and as pigments in inks and dyes.

Weak acids

Carbonic acid, H_2CO_3

Carbonic acid can be produced by dissolving carbon dioxide in water.

It can be used to produce carbonated drinks, and to prepare metal carbonates and hydrogencarbonates.

It contributes to ocean acidification as carbon dioxide dissolves in the ocean, lowering its pH.

Phosphoric acid, H_3PO_4

Phosphoric acid is produced by reacting sulfuric acid with phosphate containing rock minerals.

It is used as a rust inhibitor, a food additive, an electrolyte and to produce fertilisers and cleaning products.

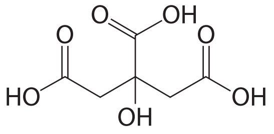
It gives some carbonated soft drinks their tangy, sharp taste.

Citric acid, $C_6H_8O_7$

Citric acid is naturally occurring in citrus fruits.

It is produced industrially reacting biological cultures with glucose and sucrose.

It is used in the food industry as an acidifier and as a flavouring.



Ethanoic acid, CH_3COOH

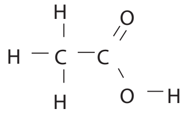
Commonly called acetic acid, ethanoic acid can be produced in small quantities by oxidising ethanol.

On a larger scale it is made by oxidising compounds like ethene from the petrochemical industry.

It is used to produce photographic film, PVA glue and synthetic fibres.

Vinegar is a solution of roughly 5% ethanoic acid by volume in water.

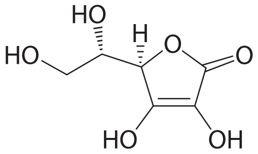
In the food industry it is used as a food additive, a preservative and as a condiment.



Ascorbic acid, $C_6H_8O_6$

Ascorbic acid is one form of Vitamin C.

It is an important nutrient for human health and can be sourced through many foods such as citrus fruits.



Hydrocyanic acid, HCN

Hydrocyanic acid can be produced by reacting methane, ammonia and oxygen, at high temperatures and with a platinum catalyst.

$$2\ CH_4 + 2\ NH_3 + 3\ O_2 \rightarrow 2\ HCN + 6\ H_2O$$

It is very poisonous and can be found naturally in fruits that have a pit, such as cherries, apricots, apples and almonds.

Its main use is in metallurgy to prepare the electrolyte for the electroplating of gold and silver.

Hydrofluoric acid, HF

Hydrofluoric acid is produced by reacting the mineral fluorite (CaF_2) with sulfuric acid.

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

It is used as the fluorine source for the production of Teflon, fluoropolymers and refrigerants.

It can be used to etch glass and in the process of silicon chip manufacture.

11.3 PROPERTIES OF ACIDS

These properties result from the production of H^+ ions (or H_3O^+) in solution.

1. Acids turn blue litmus red (they have a pH less than 7)
2. Acids are molecular in structure and dissolve in water to produce an electrolyte
3. Acids taste sour
4. Acids are neutralised by alkalis

Neutralisation

Since H^+ ions are responsible for the properties of acids and OH^- are responsible for the properties of bases, neutralisation occurs when acids and bases react and these ions combine to produce water.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Except for the first one, the reactions below are all neutralisation reactions:

5. Acids undergo the following general chemical reactions

   Acid + reactive metal → salt + hydrogen

   Acid + metal carbonate → salt + water + carbon dioxide

   Acid + metal hydrogen carbonate → salt + water + carbon dioxide

   Acid + metal oxide → salt + water

   Acid + metal hydroxide → salt + water

   Acid + metal sulfite → salt + water + sulfur dioxide

   Acid + metal sulfide → salt + hydrogen sulfide

11.4 COMMON BASES AND THEIR USES

Sodium hydroxide, NaOH

Sodium hydroxide, sometimes called caustic soda, is produced via the Chloralkali Process where sodium chloride solution is electrolysed to produce sodium hydroxide, hydrogen and chlorine.

It is used in the paper making industry, in soap and detergent manufacture and also in the Bayer process for aluminium production.

Ammonia, NH_3

Ammonia is produced by the Haber Process, where nitrogen and hydrogen are reacted together over an iron catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

It is used in the manufacture of fertilisers, explosives and detergents.

Sodium carbonate, Na_2CO_3

Sodium carbonate, also known as washing soda, is produced via the Solvay Process, where salt water or brine is reacted with calcium carbonate.

$$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

It is used to soften hard water, to prepare washing powder and also in the manufacture of glass.

Calcium oxide, CaO

Calcium oxide, also known as quicklime, is produced by the thermal decomposition of calcium carbonate in a lime kiln.

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

It is used to make cement or mortar, and in the steel making industry.

Calcium hydroxide, $Ca(OH)_2$

Calcium hydroxide, traditionally called slaked lime or hydrated lime, is produced by adding water to calcium oxide. Limewater is a saturated solution of calcium hydroxide.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

It is used as a flocculant in water treatment, to prepare plaster and to decrease acidity of soil in the garden as garden lime.

Sodium hydrogen carbonate, $NaHCO_3$

Sodium hydrogencarbonate, also known as sodium bicarbonate, is produced via the Solvay Process, where sodium carbonate is reacted with carbon dioxide and water.

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2\ NaHCO_3$$

It is used as baking powder (baking soda) in the baking process to enable baked goods like bread and cakes to rise when CO_2 is released. It is also used to treat indigestion, in toothpaste and as a cleaning agent.

Magnesium hydroxide, $Mg(OH)_2$

Magnesium hydroxide, also known as milk of magnesia, is produced by adding magnesium ions to hydroxide ions and is insoluble.

It is used to treat indigestion and in industry to neutralise acids.

11.5 PROPERTIES OF BASES/ALKALIS

These properties result from the production of OH^- ions in solution.

1. Bases turn red litmus blue
2. Bases are neutralised by acids
3. Bases are generally ionic and can dissolve in water to produce electrolytes
4. Bases taste bitter
5. Bases feel slippery to touch
6. Bases may be corrosive
7. Bases are generally metal oxides or hydroxides
8. Bases react with acids to produce salt and water

   Acid + base → salt + water

9. *Bases react with amphoteric metals (metals that can form amphoteric compounds) and water to produce complex ions and hydrogen*

   e.g. $Zn(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Zn(OH)_4^{2-}(aq) + H_2(g)$

   $Zn(OH)_4^{2-}$ *is the zincate ion*

10. *Bases dissolve amphoteric metal hydroxides to produce complex ions*

    e.g. $Zn(OH)_2(s) + 2OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$

11.6 SOME DEFINITIONS

An amphoteric substance is a molecule or ion that can react both as an acid and a base.

Many metals such as zinc, aluminium, and chromium form amphoteric oxides or hydroxides.

Some amphoteric metal oxides and hydroxides can dissolve in bases as well as in acids.

Monoprotic acids

Acids like hydrochloric acid, HCl, have only one hydrogen atom per molecule that can be ionised in aqueous solution. Since it is a strong acid and completely ionised in solution 1 mole of HCl will supply 1 mole of protons. As such they are called monoprotic acids.

Polyprotic acids

Acids such as sulfuric, H_2SO_4 and carbonic H_2CO_3 contain two ionisable hydrogen atoms per molecule of acid and are called diprotic acids.

Phosphoric acid is a triprotic acid. It contains three ionisable hydrogen atoms per molecule and ionises in three steps.

Sulfuric acid in solution

Since it is also a strong acid 1 mole of H_2SO_4 is completely ionised in solution to produce 1 mole of hydrogen ions and 1 mole of hydrogensulfate ions:

$$H_2SO_4(l) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$$

However, the hydrogensulfate ion is a weak acid so only a small proportion ionises further into hydrogen ions and sulfate ions.

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

So a 1 mol L^{-1} sulfuric acid solution would have > 1 mol L^{-1} hydrogen ions present, but not 2 mol L^{-1}.

Sulfuric acid when it reacts

When it reacts with a strong base, one mole of sulfuric acid will react with two moles of hydroxide ions.

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

The second ionisation of the hydrogensulfate ion goes to completion and since it is an equilibrium situation the forward reaction proceeds until all hydrogen has been reacted (Yr12).

Carbonic acid in solution

Since it is a weak acid H_2CO_3 is only partially ionised in solution. Only a small proportion ionises into hydrogen ions and hydrogencarbonate ions:

$$H_2CO_3(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The hydrogencarbonate ion is also a weak acid so only a small proportion of this ionises further into hydrogen ions and carbonate ions.

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

So a 1 mol L^{-1} carbonic acid solution would have considerably less than 1 mol L^{-1} hydrogen ions present.

Carbonic acid when it reacts

When it reacts with a strong base, one mole of carbonic acid will react with two moles of hydroxide ions.

$$H_2CO_3(aq) + 2NaOH(aq) \rightleftharpoons Na_2CO_3(aq) + 2H_2O(l)$$

Both the first and second ionisations are equilibrium situations so both will proceed in the forward direction until all hydrogen has reacted.

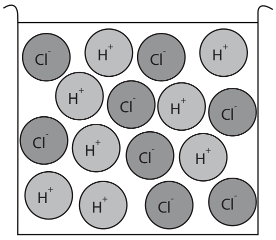
Comparing the two, the sulfuric acid will react faster with the base, since more of its hydrogen ions are available immediately to react.

11.7 STRENGTH VERSUS CONCENTRATION

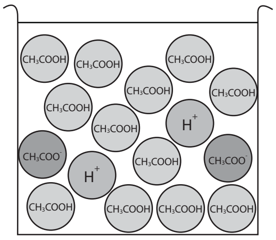
The strength of an acidic or basic solution is determined by the number of ions present and therefore the degree to which it is ionised (or dissociated) in water.

The concentration of a solution is determined by the amount dissolved in a given volume of water, in moles per litre.

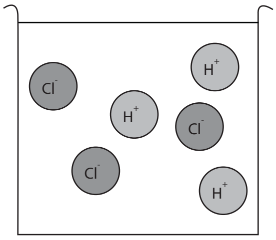
It is possible to have a concentrated weak acid and a dilute strong acid!



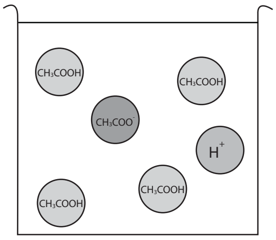
concentrated strong acid



concentrated weak acid



dilute solution of strong acid



dilute solution of weak acid

Set 1

1. Which of the following are strong acids?

   HCl, H_2CO_3, CH_3COOH, HNO_3, H_3PO_4, H_2SO_4, HCN, $C_6H_8O_7$

   Strong acids ____

2. Complete the following passage by filling in the missing words.

   An acid is a substance that produces ________________ in solution. Acids are generally _______________ substances, and so when they are dissolved in water they _______________, or produce ions in solution.

   An alkali is a soluble base and produces ________________ in solution. Alkalis are generally ____________ substances, and so when they are dissolved in water they _______________ (or come apart) to produce ions in solution.

   Acids and bases can be strong or weak depending upon the extent to which they ionise or dissociate in solution. Strong acids are ______________ ionised in aqueous solution. Weak acids are _______________ ionised in aqueous solution. Strong alkalis are completely _____________ into ions in aqueous solution. Weak alkalis are bases in which a _______________ proportion of the base species react with water to form hydroxide ions.

3. Write balanced equations, ionic equations and observations for each of the following acid reactions. In each case describe what you would observe. Include colours, precipitates and any gases evolved. If no change is observed, you should state this.

   (a) Solid zinc is added to dilute hydrochloric acid.

   Balanced equation:

   Ionic equation:

   Observations:

   (b) Solid magnesium carbonate is added to dilute nitric acid.

   Balanced equation:

   Ionic equation:

   Observations:

   (c) Solid copper oxide is added to dilute hydrobromic acid (HBr).

   Balanced equation:

   Ionic equation:

   Observations:

(d) Potassium hydroxide solution is added to dilute carbonic acid.

Balanced equation:

Ionic equation:

Observations:

(e) A sodium hydrogencarbonate solution is added to dilute phosphoric acid.

Balanced equation:

Ionic equation:

Observations:

(f) Solid silver sulfide is added to dilute hydrochloric acid.

Balanced equation:

Ionic equation:

Observations:

(g) Solid calcium sulfite is added to dilute hydrochloric acid.

Balanced equation:

Ionic equation:

Observations:

4. Phosphoric acid is a weak polyprotic acid.

(a) Write a balanced equation for the complete reaction between phosphoric acid and sodium hydroxide and use the stoichiometry of this equation to explain the meaning of the term "polyprotic".

____

____

____

____

____

____

____

(b) Write equations for the dissociation of phosphoric acid.

____

____

____

(c) If a piece of magnesium is added to 1 mol L^{-1} H_3PO_4 it reacts slowly, whereas if it is added to 1 mol L^{-1} HCl it reacts vigorously. Explain this with reference to the equations from part b.

____

____

____

____

5. Give examples of each of the following:

(a) a concentrated, weak base

(b) a dilute, strong acid

(c) a dilute, strong base

(d) a concentrated, weak acid

11.8 IONISATION OF WATER

Water is a weak electrolyte and to a very small extent undergoes ionisation, as shown below:

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

Water is neutral, since the hydrogen and hydroxide ion concentrations are the same.

K_w is the ionisation or dissociation constant for water and it shows the extent to which it ionises.

It is the product of the concentrations of H^+ and OH^- in neutral water at 25°C.

$K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$ @ 25°C

So neutral water will be mostly water molecules.

Since $K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$ @ 25°C

and $[H^+] = [OH^-]$

$\therefore$ $[H^+] = 1.0 \times 10^{-7}$ mol L^{-1} and $[OH^-] = 1.0 \times 10^{-7}$ mol L^{-1}

If hydrogen ions are added to water, the hydroxide ions decrease as they react to form water.

$[H^+] > [OH^-]$

If hydroxide ions are added to water, the hydrogen ions decrease as they react to form water.

$[H^+] < [OH^-]$

So when $[H^+]$ is increased, $[OH^-]$ decreases, and vice versa!

For pure water:	$[H^+] \times [OH^-] = 1.0 \times 10^{-14}$
	so $[H^+] = 1.0 \times 10^{-7}$ mol L^{-1} and $[OH^-] = 1.0 \times 10^{-7}$ mol L^{-1}
For a 0.1 mol L^{-1} HCl solution:	$[H^+] \times [OH^-] = 1.0 \times 10^{-14}$
	$[H^+] = 1.0 \times 10^{-1}$ mol L^{-1} and so $[OH^-] = 1.0 \times 10^{-13}$ mol L^{-1}
For a 0.01 mol L^{-1} NaOH solution:	$[H^+] \times [OH^-] = 1.0 \times 10^{-14}$
	$[OH^-] = 1.0 \times 10^{-2}$ mol L^{-1} and so $[H^+] = 1.0 \times 10^{-12}$ mol L^{-1}
In acidic solutions:	$[H^+] > 1.0 \times 10^{-7}$ mol L^{-1} and $[OH^-] < 1.0 \times 10^{-7}$ mol L^{-1}
In basic solution:	$[OH^-] > 1.0 \times 10^{-7}$ mol L^{-1} and $[H^+] < 1.0 \times 10^{-7}$ mol L^{-1}

11.9 THE pH ACIDITY SCALE

pH is used as a measure of the acidity of solutions and is dependent upon the concentration of hydrogen ions in the solution. It ranges from 1 mol L^{-1} hydrogen ion concentration with pH 0 to 1 mol L^{-1} hydroxide ion concentration with pH 14.

pH is useful when examining the acidity of fairly dilute solutions like plants, soil, medicines, soaps and detergents, pool water and foods.

pH can be calculated using the formula:

$pH = -\log[H^+]$

Example 1

What is the pH of a 0.1 mol L^{-1} HCl solution?

0.1 mol L^{-1} HCl will have a hydrogen ion concentration of 0.1 mol L^{-1}

$$\begin{aligned} \therefore \text{pH} &= -\log(0.1) \\ &= 1 \end{aligned}$$

Example 2

What is the pH of a 0.01 mol L^{-1} NaOH solution?

0.01 mol L^{-1} NaOH solution will have a hydroxide ion concentration of 0.01 mol L^{-1}

Its hydrogen ion concentration will be

$$[H^+] = 1.0 \times 10^{-14} / 0.01$$
$$= 1.0 \times 10^{-12}$$
$$\therefore \text{pH} = -\log(1.0 \times 10^{-12})$$
$$= 12$$

The pH formula can be rearranged to give $[H^+]$ from pH:

$$\mathbf{[H^+] = 10^{-pH}}$$

so pH 1 = 10^{-1} = 0.1 mol L^{-1}

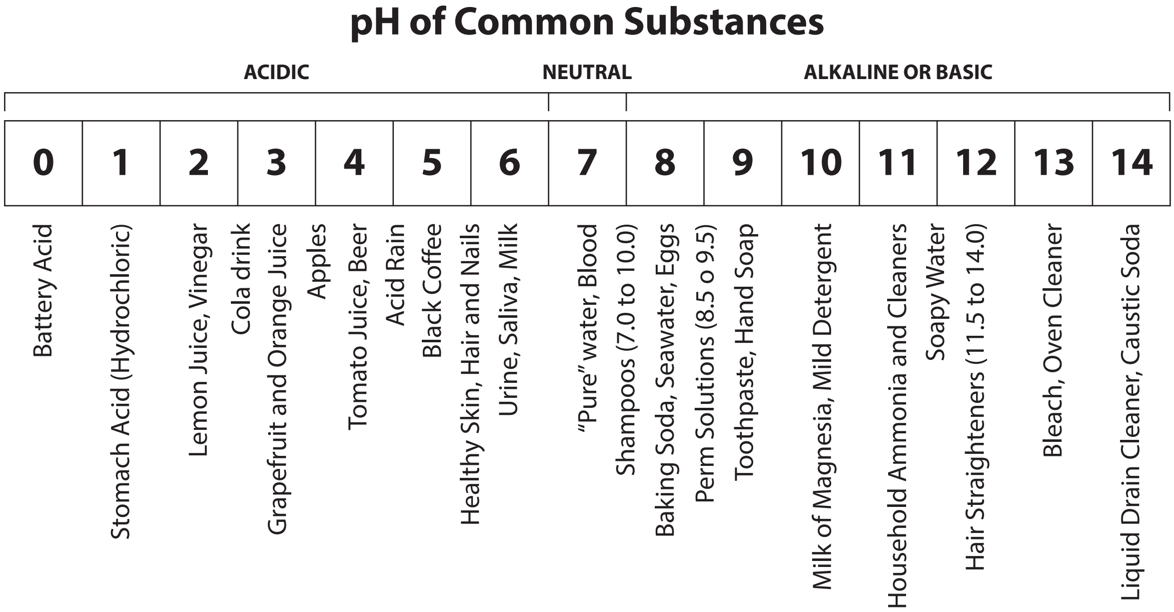
The pH scale and concentration

pH	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
$[H^+]$	10^{0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$[OH^-]$	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}
	← **more acidic**							**neutral**	**more alkaline** →						

1 mol L^{-1} H^+ **1 mol L^{-1} OH^-**

Note that a change of one pH unit represents a tenfold change in the hydrogen ion concentration. So a substance with pH 2 is ten times more concentrated than one of pH 3!

The pH of common substances



11.10 MEASURING pH

The pH of a solution can be measured using indicators or pH meters.

pH Indicators

pH Indicators are chemicals or dyes that change colour at certain pH levels.

There are many types of indicators with specific purposes, but some general ones encountered in the Chemistry course are:

Litmus which is red in acidic solutions with a pH less than 7 and blue in alkaline solutions with a pH of greater than 7.

Universal indicator which is a mixture of dyes and is specific to particular pH levels.

Phenolphthalein which is pink at pH greater than ~8.2 and colourless below this.

Methyl orange is red at pH below 3.1, then orange, then yellow at pH above 4.4.

pH	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Litmus	**red**							**purple**	**blue**						
U.I.	**red**				**orange**	**yellow**		**green**	**blue**			**purple**			
Phenolphthalein	**colourless**									**pink**					
Methyl orange	**red**				**orange**	**yellow**									

These indicators can be used in two ways.

1. As a solution added dropwise to the substance being tested. This is used when the substance is not coloured.
2. As pH paper, where a small sample of the substance being tested is applied to paper that has been treated with the indicator. This is used where the substance is coloured and might mask the indicator colour.

Natural indicators

Many plants change colour during their life cycle, or with the seasons. As they ripen, fruits often change colour. These colour changes are often due to the presence of substances that vary their colour at different pH levels. Red cabbage contains a substance called flavin which can act as an indicator. Cherries, apple skins, grapes and plums also contain this substance. The colours of red cabbage indicator are shown in the table below.

pH	1	2	4	6	8	10	12	14
colour	red	pink	violet	purple	indigo	blue	green	yellow

pH meters

A pH meter is a scientific instrument that can be used to measure pH of a solution quantitatively. It determines the hydrogen ion concentration by measuring the difference in electrical potential between a pH probe and a reference probe. The probe also measures temperature, since pH is temperature-dependent. It provides a digital reading of the pH of a sample.

pH meters are used extensively in the chemical laboratory. They are also used in the food industry for soil and water testing and many other applications.

11.11 ACID/BASE PROPERTIES OF OXIDES

Both metal and non-metal elements can form oxides.

Oxides can be classified into four groups:

- Acidic oxides have acidic properties.
- Basic oxides have basic properties.
- Amphoteric oxides can have both acidic and basic properties, depending upon what they are reacting with.
- Neutral oxides which are have neither acidic nor basic properties.

If an oxide is soluble in water, then the pH can be tested to determine whether it is acidic or basic.

If an oxide is insoluble in water, then it must be reacted with an acid or a base to determine whether it is acidic or basic.

Basic oxides

All basic oxides are metal oxides e.g. Na_2O, MgO, CuO

But not all metal oxides are basic. Some are amphoteric. e.g. Al_2O_3, ZnO

If the basic metal oxide is soluble in water it will react to form hydroxide ions and the solution will have a pH greater than 7.

e.g. $K_2O(s) + H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq)$

Basic oxides will also react with acids to produce salt and water

e.g. $CaO(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l)$

Acidic oxides

Most acidic oxides are non-metal oxides. e.g. CO_2, SO_2, SO_3, NO_2

Acidic oxides dissolve in water to produce acid solutions.

An exception is that some transition metals form acidic oxides. e.g. CrO_3 is an acidic oxide.

If an acidic oxide is soluble in water it reacts with the water to produce hydrogen ions in solution so the pH is less than 7.

e.g. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

$H_2SO_4(aq) \rightarrow HSO_4^-(aq) + H^+(aq)$

When mixed with a base, acidic oxides produce salt and water.

e.g. $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$

Amphoteric oxides

Amphoteric oxides react with both acids and bases

e.g. $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

$Al(OH)_4^-$ is the complex aluminate ion.

Neutral oxides

Neutral oxides are all non-metal oxides and are neither acidic nor basic. They form neutral solutions when dissolved in water and do not react with acids or bases.

e.g. CO, N_2O

Set 2

1. What is the hydroxide ion concentration of the following solutions at 25°C?

   (a) 2.00 mol L^{-1} HCl solution

   (b) 1.50 mol L^{-1} $Ba(OH)_2$ solution

2. What is the hydrogen ion concentration of the following solutions at 25°C?

   (a) 1.00 mol L^{-1} HNO_3 solution

   (b) 1.00 x 10^{-3} mol L^{-1} $Ba(OH)_2$ solution

3. Calculate the pH for each of the solutions below.

   (a) 0.02 mol L^{-1} HCl solution:

   (b) 0.50 mol L^{-1} NaOH solution:

   (c) 0.1 mol L^{-1} HNO_3 solution:

   (d) 1.00 x 10^{-5} mol L^{-1} $Ba(OH)_2$ solution:

4. Classify the following as acidic, basic or neutral oxides

(a) P_4O_{10} (b) Li_2O (c) CO

(d) Cl_2O (e) SrO

5. ZnO is an amphoteric oxide. Write equations for the reaction between ZnO and HCl, and ZnO and NaOH to demonstrate its amphoteric nature.

6. Fill in the table below giving the approximate pH and subsequent indicator colours for the following household substances.

		Colour in indicator				
Substance	Approx. pH	litmus	U.I.	phenolphthalein	Methyl orange	Red cabbage
Milk						
Toothpaste						
Lemon juice						
Household ammonia						

11.12 CALCULATIONS INVOLVING ACIDS AND BASES

1. Calculating $[H^+]$, $[OH^-]$ and pH

It is possible to use pH formula to calculate $[H^+]$, $[OH^-]$ or pH for a solution, given just one of these.

If you are given pH;

Calculate $[H^+]$ using $[H^+] = 10^{-pH}$, and then calculate $[OH^-]$ using $K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$

If you are given $[H^+]$;

Calculate $[OH^-]$ using $K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$, and then pH using $pH = -\log[H^+]$

If you are given $[OH^-]$;

Calculate $[H^+]$ using $K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$, and then pH using $pH = -\log[H^+]$

Example 1

Determine the $[H^+]$, $[OH^-]$ and $[Cl^-]$ of a hydrochloric acid solution with a pH of 4.

$[H^+] = 10^{-pH}$
$= 10^{-4}$
$= 0.0001 \text{ mol L}^{-1}$
$[Cl^-] = [H^+]$
$= 0.0001 \text{ mol L}^{-1}$
$[OH^-] = 1.0 \times 10^{-14} / 0.0001$
$= 1.0 \times 10^{-10} \text{ mol L}^{-1}$

Example 2

Determine the $[H^+]$, $[OH^-]$, $[NO_3^-]$ and pH of 50.0 mL of a 0.750 mol L^{-1} nitric acid solution.

$c(HNO_3) = 0.750 \text{ mol L}^{-1}$
$[H^+] = 0.750 \text{ mol L}^{-1}$
$[NO_3^-] = 0.750 \text{ mol L}^{-1}$
$[OH^-] = 1.0 \times 10^{-14} / 0.750$
$= 1.333 \times 10^{-14} \text{ mol L}^{-1}$
$pH = -\log[H^+]$
$= -\log(0.75)$
$= 0.125$

Example 3

Determine the $[H^+]$, $[OH^-]$, $[Ba^{2+}]$ and pH of 150.0 mL of a 0. 500 mol L^{-1} $Ba(OH)_2$ solution.

$c(Ba(OH)_2) = 0.500 \text{ mol L}^{-1}$
$\therefore [OH^-] = 2 \times 0.500$
$= 1.00 \text{ mol L}^{-1}$
$\therefore [Ba^{2+}] = 0.500 \text{ mol L}^{-1}$
$[H^+] = 1.0 \times 10^{-14} / 1.00$
$= 1.0 \times 10^{-14} \text{ mol L}^{-1}$

pH = $-\log[H^+]$

= $-\log(1.0 \times 10^{-14})$

= 14

2. Dilutions and pH

You may be asked to take a solution of known pH, dilute or concentrate it, and then find its new pH. Or you may be given a solution of known pH and be asked to work out how much water you need to add or remove to arrive at a new pH.

In these cases it is useful to convert the pH of the initial solution into moles of H^+ or OH^- and then use the formula;

$$c_1V_1 = c_2V_2$$

Example 1

If 100.0 mL water is added to 50.0 mL of a HCl solution of pH 3 calculate its new pH.

$c(H^+)_{initial}$ = 10^{-3}

= 0.001 mol L^{-1}

V_1 = 50.0 mL = 0.050 L

$c(H^+)_{final}$ = ?

V_2 = 100 mL + 50 mL = 0.150 L

c_1V_1 = c_2V_2

c_2 = c_1V_1 / V_2

$c(H^+)_{final}$ = $0.001 \times 0.050 / 0.150$

= 3.33×10^{-4} mol L^{-1}

pH = $-\log[H^+]$

= 3.48

Example 2

What volume of water must be added to 100.0 mL of nitric acid of pH 2 to dilute it to pH 2.5?

First determine the concentration before and after addition of water.

$c(H^+)_{initial}$ = 10^{-2}

= 0.01 mol L^{-1}

$c(H^+)_{final}$ = $10^{-2.5}$

= 0.003162 mol L^{-1}

V_1 = 100.0 mL = 0.100 L

V_2 = ?

Then determine the new volume.

c_1V_1 = c_2V_2

V_2 = c_1V_1 / c_2

= $0.01 \times 0.100 / 0.003162$

= 0.3162 L

Then calculate the volume added.

$V_{added} = V_2 - V_1$
$= 0.3162 - 0.100$
$= 0.2162$ L
$= 216.2$ mL

Set 3

1. Determine the $[H^+]$, $[OH^-]$ and $[NO_3^-]$ of a nitric acid solution with a pH of 3.20.

2. Determine the $[H^+]$, $[OH^-]$, $[Cl^-]$ and pH of 150.0 mL of a 0.650 mol L^{-1} hydrochloric acid solution.

3. Determine the $[H^+]$, $[OH^-]$, $[Ba^{2+}]$ and pH of 250.0 mL of a 0. 125 mol L^{-1} $Ba(OH)_2$ solution.

4. 150.0 mL of distilled water is added to 250.0 mL of an H_2SO_4 solution with a pH of 2.00. Calculate its new pH.

5. What volume of water must be added to 500.0 mL of sodium hydroxide of pH 12.00 to dilute it to pH 10.00?

6. 150.0 mL of a solution of pH 3.50 has 200.0 mL of 1.00 mol L^{-1} HCl added. What is the final $[H^+]$ and pH?

7. 100.0 mL of a solution with a pH of 5.00 is added to 100.0 mL of a solution of pH 7.00. Find the pH of the resulting solution.

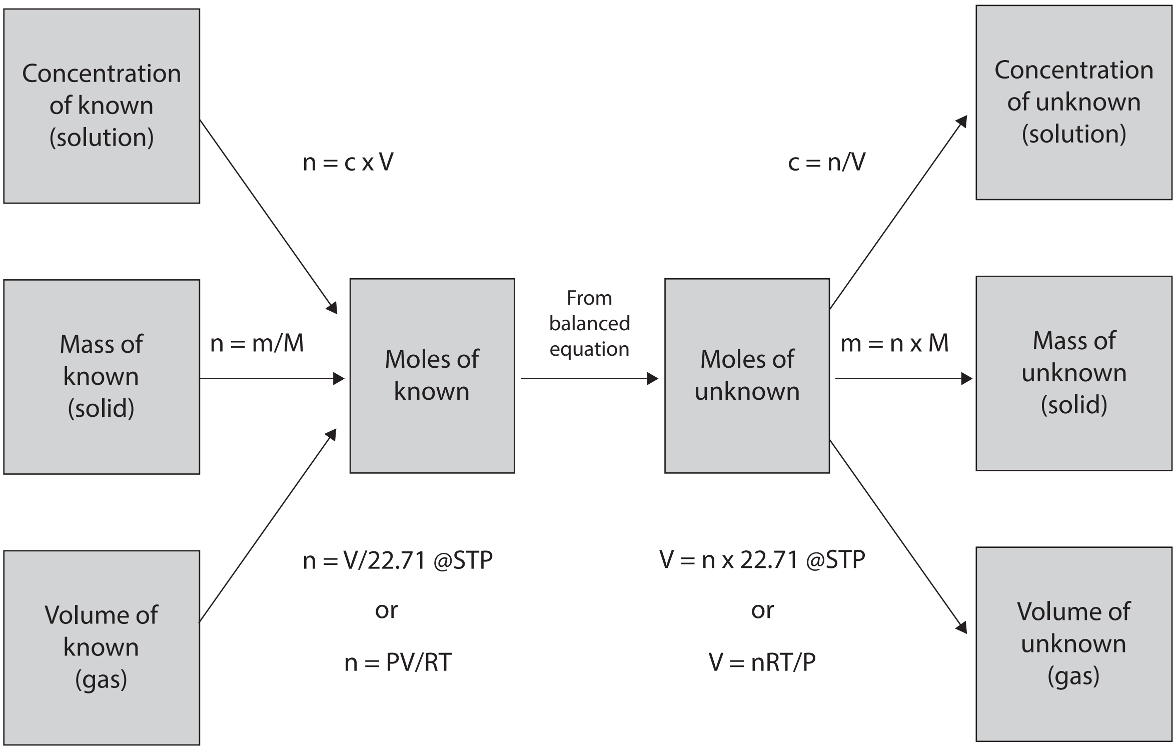
8. What mass of potassium hydroxide must be added to 250.0 mL of a potassium hydroxide solution with pH 9.50 to increase it to pH 11.00?

11.13 REACTING QUANTITIES

With calculations involving acids and bases, the acid or base quantity can be provided as:

- A **solution of known concentration and volume**, in which case we use n = cV to get moles of known.
- A **mass**, in which case we use n = m/M to get moles of known.
- A **pH and volume**, in which case we use $[H^+] = 10^{-pH}$ and then n = cV to get moles of known.

Then the calculation is carried out as per the flowchart below.



Example 1

10.0 g sodium carbonate is added to 150.0 mL 0.750 mol L^{-1} sulfuric acid solution. Determine the final pH, and the volume of carbon dioxide gas produced at 25.0 °C and 101.3 kPa.

Write a balanced equation

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$$

Determine the limiting reagent

$n(Na_2CO_3)$ = 10.0 / 105.99 $M(Na_2CO_3)$ = (2 x Na) + (1 x C) + (3 x O)
= 0.0943 mol = 105.99 g/mol

$n(H_2SO_4)$ = 0.750 x 0.150
= 0.1125 mol

Stoichiometric $n(Na_2CO_3)$: $n(H_2SO_4)$
1 : 1
Actual 0.0943 : 0.1125
0.0943/0.0943 : 0.1125/0.0943
1 : 1.192

Therefore Na_2CO_3 is the limiting reagent!

Now use the limiting reagent to determine unknown quantities.

$n(CO_2) = 1/1 \text{ x } n(Na_2CO_3)$

$= 0.0943 \text{ mol}$

$V(CO_2) = nRT/P$

$= 0.0943 \text{ x } 8.314 \text{ x } (25.0 + 273.15) \ / \ 101.3$

$= 2.31 \text{ L}$

$n(H_2SO_4)_{reacted} = 1/1 \text{ x } n(Na_2CO_3)$

$= 0.0943 \text{ mol}$

$n(H_2SO_4)_{excess} = n(H_2SO_4)_{initial} - n(H_2SO_4)_{reacted}$

$= 0.1125 - 0.0943$

$= 0.01815 \text{ mol}$

$n(H^+) = 2 \text{ x } n(H_2SO_4)_{excess}$

$= 0.03630 \text{ mol}$

$c(H^+) = n/V$

$= 0.03630/0.150$

$= 0.2420 \text{ mol L}^{-1}$

$pH = -\log[H^+]$

$= 0.616$

Example 2

100.0 mL of a 0.150 mol L^{-1} NaOH solution is added to 250.0 mL of an HCl solution of pH 1.50. What is the final pH?

First write a balanced equation.

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

Then work out the limiting reagent.

$n(NaOH) = cV$

$= 0.150 \text{ x } 0.1$

$= 0.015 \text{ mol}$

$c(HCl) = 10^{-1.5}$

$= 0.03162 \text{ mol L}^{-1}$

$n(HCl) = cV$

$= 0.03162 \text{ x } 0.250$

$= 0.0079 \text{ mol}$

Stoichiometric n(NaOH) : n(HCl)
1 : 1
Actual 0.015 : 0.0079
0.015/0.0079 : 0.0079/0.0079
1.897 : 1

Therefore HCl is the limiting reagent!

Find the concentration of hydroxide ions.

$$\begin{aligned}
n(NaOH)_{reacted} &= n(HCl) \\
&= 0.0079 \text{ mol} \\
n(NaOH)_{excess} &= n(NaOH)_{initial} - n(NaOH)_{reacted} \\
&= 0.015 - 0.0079 \\
&= 0.007094 \text{ mol} \\
c(NaOH) &= n/V \\
&= 0.007094 \ / \ 0.350 \\
&= 0.02027 \text{ mol L}^{-1} \\
[OH^-] &= c(NaOH) \\
&= 0.02027 \text{ mol L}^{-1}
\end{aligned}$$

Then find the concentration of hydrogen ions.

$$\begin{aligned}
[H^+] &= 1.0 \times 10^{-14} \ / \ 0.02027 \\
&= 4.934 \times 10^{-13} \text{ mol L}^{-1}
\end{aligned}$$

Now you can find the pH:

$$\begin{aligned}
pH &= -\log[H^+] \\
&= -\log(4.934 \times 10^{-13}) \\
&= 12.31
\end{aligned}$$

Set 4

1. 150.0 mL of a 0.100 mol L^{-1} NaOH solution is added to 150.0 mL of an HCl solution of pH 2.50. What is the final pH?

2. 25.0 g of barium hydroxide is added to 250.0 mL of 2.00 mol L^{-1} hydrochloric acid solution. What is the pH of the resulting solution?

3. 570.0 mL of HCl with a pH of 2.50 is added to 0.100 g of sodium sulfite solid. Calculate the volume of sulfur dioxide formed at 20.0°C and 110.0 kPa.

4. What volume of 0.500 mol L^{-1} sulfuric acid must be added to excess copper sulfide to form 11.34 L of hydrogen sulfide gas at S.T.P.?

5. A gardener took a 200.0 g sample of soil, added it to 500.0 mL of water, and measured the pH as 1.50 using universal indicator paper. What mass of garden lime, CaO, must they add to this sample to increase the pH to 7.00?

6. A sample of vinegar contains 3.97% ethanoic acid by mass. A 25.0 g sample of vinegar was diluted to 250.0 mL and 150.00 mL of 0.260 mol L^{-1} sodium hydroxide solution was added.

   (a) Calculate the ethanoate ion concentration in the final solution.

   (b) Calculate the pH of the final solution.

7. Malachite $Cu_2CO_3(OH)_2$ is a common mineral containing copper. An impure 100.00 g sample of malachite is reacted with excess hydrochloric acid and produces 9.00 L of carbon dioxide at S.T.P. via the reaction below. Calculate the percentage by mass of the malachite in the sample.

$$Cu_2CO_3(OH)_2 + 4HCl \rightarrow 2CuCl_2 + 3H_2O + CO_2$$

8. 250.0 mL of a potassium hydroxide solution with a pH of 10.00 is added to 150.0 mL of a nitric acid solution with a pH of 3.00. Calculate the pH of the final solution.

9. The active ingredient of a drain cleaning powder is sodium hydroxide. A sample of this powder weighing 15.0 g was dissolved in water and made up to 250.0 mL in a volumetric flask. 20.00 mL of the resulting solution was reacted with 0.325 mol L^{-1} sulfuric acid and 22.75 mL was required for a complete reaction. You may assume that none of the other ingredients of the drain cleaning powder react with the sulfuric acid.

   (a) Calculate the concentration of sodium hydroxide in the 250.0 mL solution.

   (b) What is the pH of this solution?

   (c) How many grams of sodium hydroxide are contained in a 500.0 g package of the drain cleaning powder?

10. Sparge water used in the brewing of beer needs to have a pH of 4.8 to maximise sugar extraction from the grain. Brewers could use hydrochloric acid to adjust the pH of their water. How much 2.00 mol L^{-1} hydrochloric acid is required to be added to 3 tonnes of sparge water if it has an initial pH of 6.8?

11. To determine the concentration of sulfuric acid in a sample of battery electrolyte, 2.50 mL was diluted to 250.0 mL in a volumetric flask. A 20.00 mL sample of this diluted solution was titrated against a 0.095 mol L^{-1} sodium hydroxide solution and 18.75 mL was required for a complete reaction.

    What is the concentration of sulfuric acid in the undiluted electrolyte?

12. A laboratory technician prepared three solutions in the following ways.

Solution 1: 20.00 g of potassium hydroxide was dissolved in 250.0 mL of distilled water.

Solution 2: 100.0 mL of 0.750 mol L^{-1} nitric acid was diluted to 250.0 mL with distilled water.

Solution 3: 0.300 L of hydrogen chloride gas at 20.0°C and 100.0 kPa was completely dissolved in distilled water and the volume made up to 250.0 mL

(a) Calculate the concentration of each solution.

(b) If 50.0 mL of Solution 2 is added to 50.0 mL of Solution 3 determine the pH of the final mixture.

(c) What volume of Solution 1 would be required to neutralise the mixture in part b.?

Notes

Chapter

12

Rates of Chemical Reactions

12.1 RELATIVE RATES

Some reactions occur very quickly e.g. gases exploding. Some occur very slowly e.g. the rusting of metal. Most occur at intermediate rates, like metals reacting with acids in the laboratory. There are several factors that determine how quickly a reaction will proceed and having an understanding of these is important both in the laboratory and in everyday life.

Simple things like cooking require us to monitor the time that a reaction takes in order to correctly prepare our food. For example, baking a potato in the oven takes over an hour, but if we cut it into smaller pieces it bakes faster. Food goes off or spoils with time but this can be slowed down in many ways e.g. refrigeration, preservatives, drying.

When building it takes time for concrete to set or for paint to dry. This is determined by several external factors and can dictate the progress of a build.

Steel will rust in time but this can be slowed down or prevented using the correct conditions.

In industry, the reactions used for manufacturing must be safe and easily controlled but also fast enough to be economically viable.

Monitoring the rate of a reaction

In general, the rate of a reaction can be determined by observing:

- The rate of disappearance of reactants during a reaction
- The rate of appearance of products during a reaction

If comparing reactions the relative reaction rate can be determined by measuring the time taken for the reaction (start to finish).

Consider the following reaction;

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

During this reaction several changes occur:

- The mass of Na_2CO_3 decreases
- The concentration of H^+ decreases, or the pH increases
- The concentration of Na^+ and Cl^- increase
- The volume of CO_2 produced increases
- The total mass of the system decreases (since CO_2 is being lost)

The rate of this reaction can be followed by observing the rate of any of these changes. It is quite difficult to measure the mass of sodium carbonate lost over time, and the increase of sodium and chloride ions is difficult to follow as they are in solution.

It is possible to graph the change of pH with time, using a pH meter.

In the school laboratory we could utilise two methods:

1. Measure the increase in volume of CO_2 produced with time.

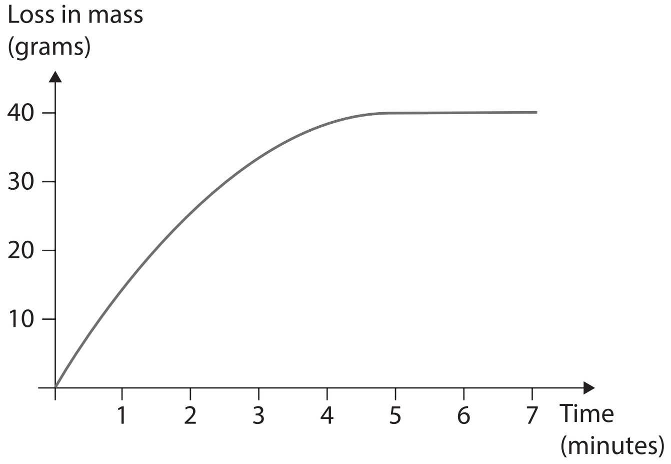
   Reaction rate = volume of CO_2 produced / time

2. Measure the total mass lost from the system due to the loss of CO_2 with time.

   Reaction rate = mass lost from system / time

This data could then be graphed

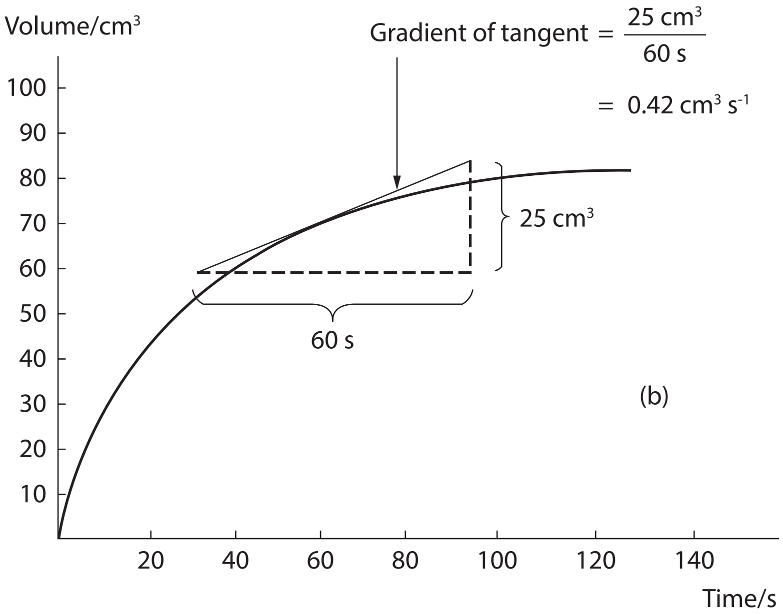
eg loss in mass



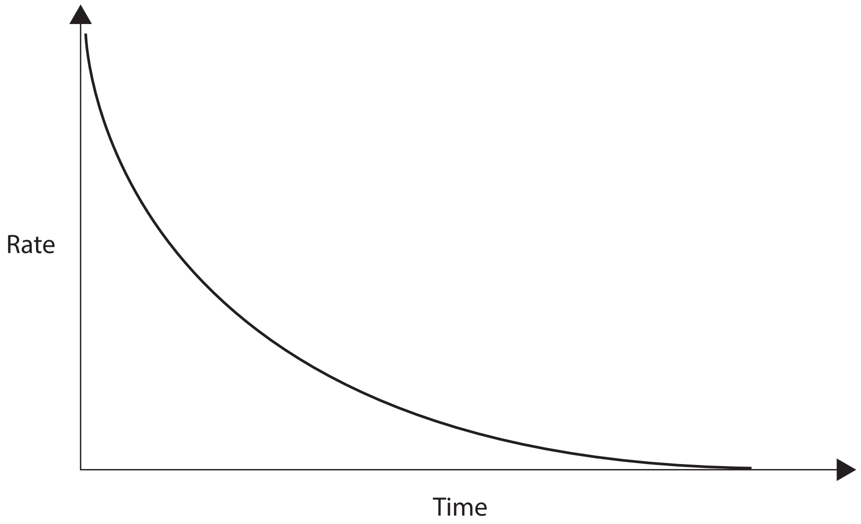
The rate is fastest at the beginning of the reaction when there are the greatest quantities of reactants. The graph shows a steep gradient of mass lost/time at this point. As the reactants are used up the rate decreases and the gradient of the graph decreases accordingly. When the reaction is complete, no more mass is being lost and the graph shows this, as the gradient is zero.

A rate graph can be used to determine the rate at any time in the reaction. The gradient of the tangent to the curve at that time gives its rate.

eg volume gas produced



It is also possible to plot Rate versus Time for a reaction. Once again, one can see that as reactants are used up, the rate of the reaction decreases.



12.2 COLLISION THEORY

For a reaction to occur, the reactant particles must come into contact, or collide.

This collision must have:

- sufficient energy to disrupt bonds of reactants
- suitable orientation for bond breaking and bond forming

Activation energy and the activated complex

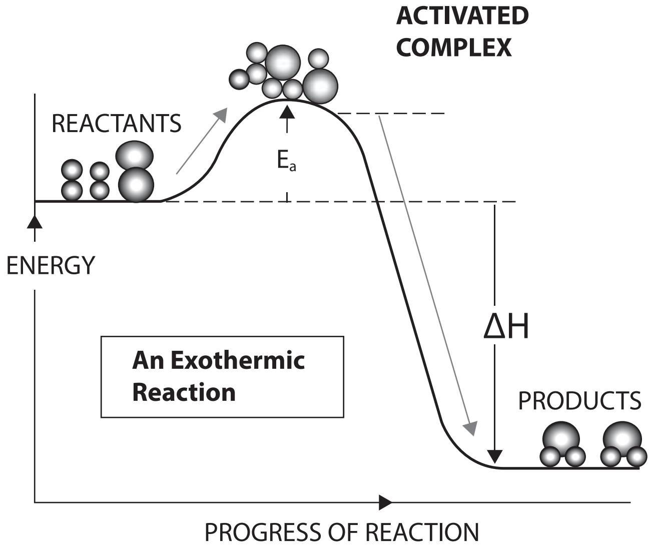
Chemical reactions involve a re-arrangement of atoms on collision. Existing bonds in the reactants need to be broken, so before a reaction proceeds to completion, the collision must provide sufficient kinetic energy for this to occur.

When two reactants approach one another with insufficient energy their atoms' electron clouds interact and they repel each other. No reaction occurs. If they approach with greater kinetic energy they can then overcome this repulsion and react. If this collision has sufficient energy an **activated complex** (or the transition state) will form. The activated complex is an intermediate between reactants and products. Here bonds are broken and new bonds are made, a reaction takes place and products are formed.

The minimum energy required by the activated complex for a reaction to occur is called the Activation Energy, $\mathbf{E_a}$.

12.3 HEAT OF REACTION

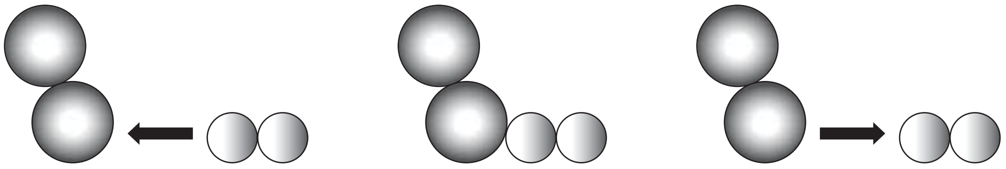
As you have seen in Chapter 6, a reaction may be endothermic or exothermic. If the energy required to break bonds in the reactants is greater than the energy given out when new bonds are formed, then it will be an endothermic reaction and the system absorbs energy. If the energy given out when new bonds are formed is greater than that required to break the bonds of the reactants, then it will be an exothermic reaction and the system releases energy. This difference in energy between reactants and products is called the **heat of reaction, ΔH**.



Suitable orientation

For a reaction to occur the reactants must collide with an orientation that enables the high energy activated complex to form. Atoms forming products need to be in close proximity for bonds to form.

Unsuccessful collision

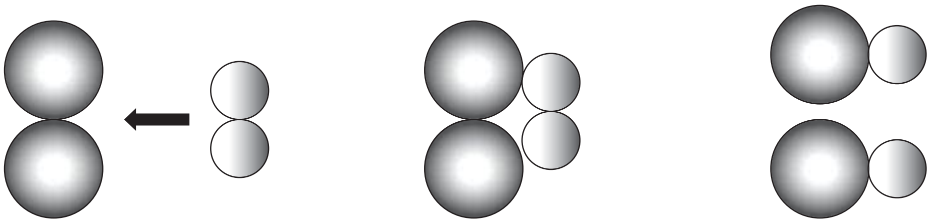


reactant molecules approach each other

incorrect orientation no reaction

reactant molecules separate

Successful collision



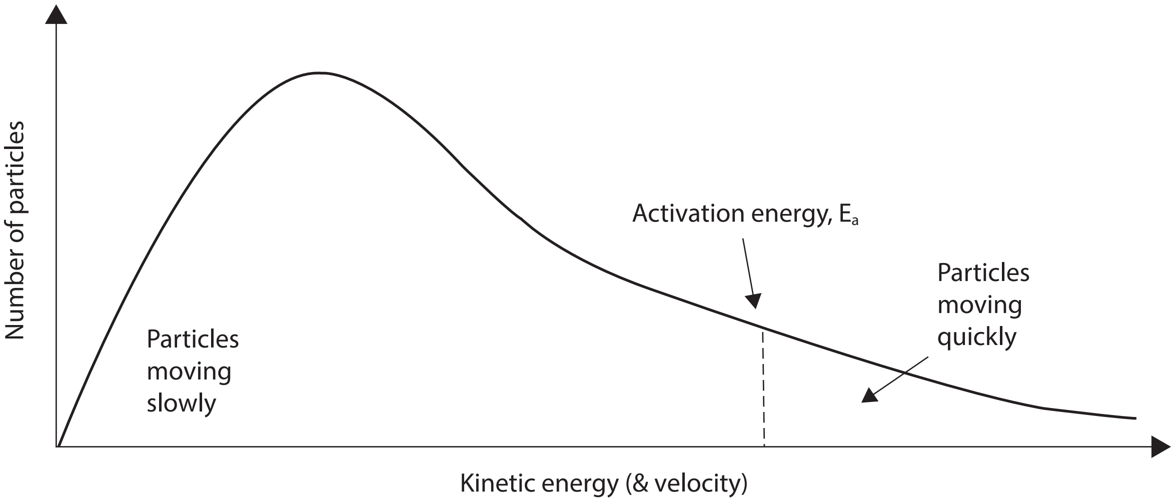
reactant molecules approach each other

correct orientation chemical reaction

products formed

12.4 MAXWELL-BOLTZMANN DISTRIBUTION

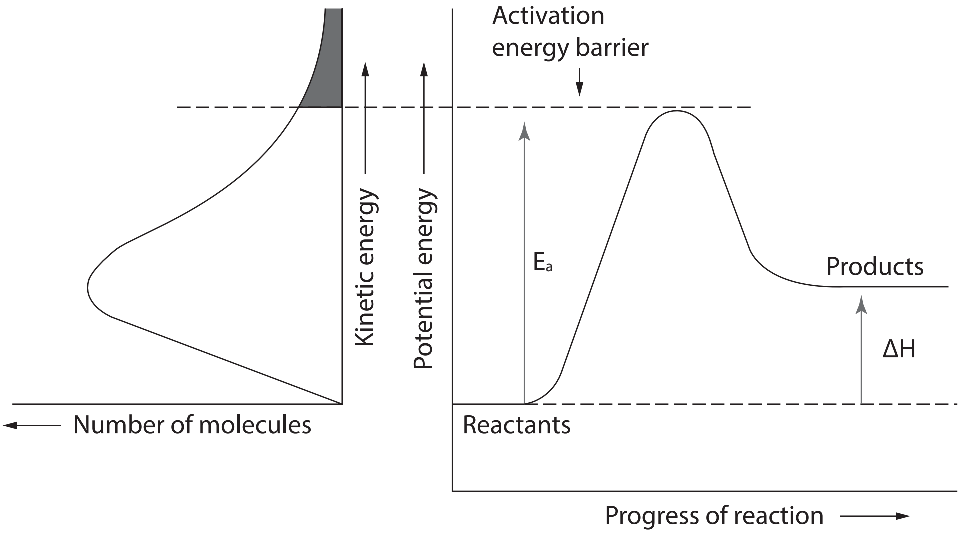
Collisions have to occur with sufficient energy to cause bonds to break – but how many reactant particles have the required energy to break the bonds? The **Maxwell-Boltzmann distribution** discussed in chapter 9 enables us to examine this.



In any sample there are particles with low kinetic energies moving slowly. There are also some particles with high kinetic energies moving very fast. The peak of the graph shows that a majority of particles have intermediate kinetic energies and average velocities. The proportion of molecules with enough energy in collisions to break the bonds at that temperature is shown by the region to the right of the dotted line. These have sufficient energy to overcome the activation energy barrier. So at a certain temperature, a fixed fraction of the total number (to the right of the dotted line) will react. The rate at which the reaction occurs depends on that fraction – the smaller the fraction, the slower the reaction.

The energy profile diagram can be related to the Maxwell-Boltzmann distribution diagram for a reaction.

The rate of the reaction depends on the proportion of collisions with sufficient energy to overcome the activation energy barrier.



Any factor which increases the number of collisions and the energy of collisions between reactants, or allows the reactants to collide with a suitable orientation, will increase the reaction rate.

12.5 FACTORS AFFECTING REACTION RATES

The following factors influence the rate of a reaction.

- Nature of the reactants
- Surface area

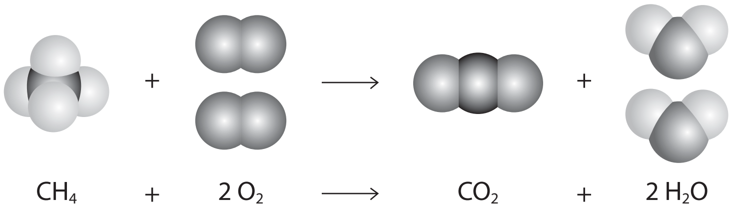
- Concentration of solutions
- Partial pressure of gases
- Temperature
- Catalysts (enzymes and inhibitors)

Nature of the reactants

A reaction in which there are lots of bonds to be broken and formed will generally be slower than one in which there are fewer.

Example

Methane burning in oxygen to produce carbon dioxide and water.



For this reaction to occur, four single bonds between C and H atoms and two double bonds between O atoms must break. Two double bonds between C and O atoms and four single bonds between H and O atoms must form.

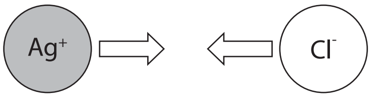
At room temperature, this is a very slow process as it involves quite complex bond rearrangement.

N.B. If the system receives an energy input, like ignition by flame, it will occur much more quickly as the particles will have sufficient energy during collisions for the bonds to break.

Example

Precipitation of silver chloride

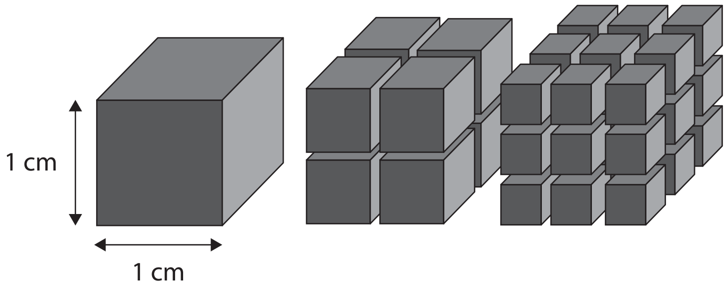
When aqueous solutions containing silver ions and chloride ions are mixed, as silver chloride precipitate is formed. Here there are no chemical bonds to break. All the ions have to do is collide with each other. Since there is no complex bond rearrangement required this reaction proceeds instantly.



$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

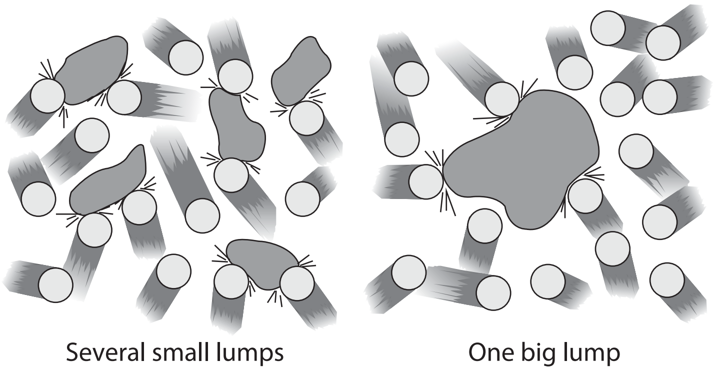
Surface area

To react, substances must collide. In reactions between solids and solutions the larger the total surface area of the solid the more of it will be in contact with the solution. To increase the surface area a solid can be cut into smaller pieces or made into a powder. This increases its state of subdivision.

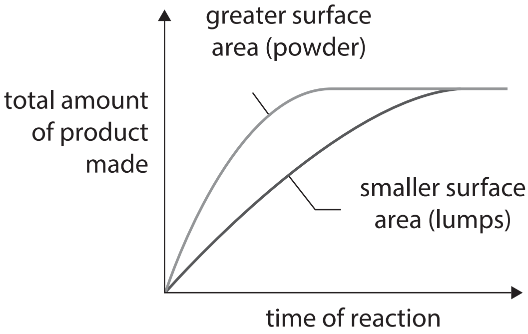


The first block has a surface area of 6 cm^2. The second block has the same volume, but has a surface area of 12 cm^2. Subdividing even further, the third block has a surface area of 18 cm^2.

Increasing the surface area increases the number of collisions between reacting particles, which increases the number of successful collisions and therefore the rate of reaction increases.



When graphed, the initial reaction rate is higher for powder than for lumps (shown by the initial gradient) but the total amount of product produced will still be the same when the reaction is complete.

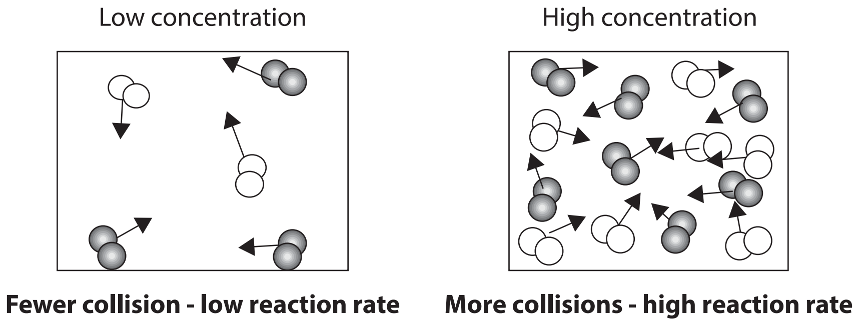


Petrol in a beaker will slowly burn but when vaporised into small particles it will react much faster and explode. Fine powders can also cause explosions. In flour silos, large quantities finely ground flour have been known to explode. In these factories sources of ignition and naked flames are avoided. The increased surface area of the petrol and flour allows more collisions with oxygen molecules in the air and the reactions can proceed at a very rapid rate.

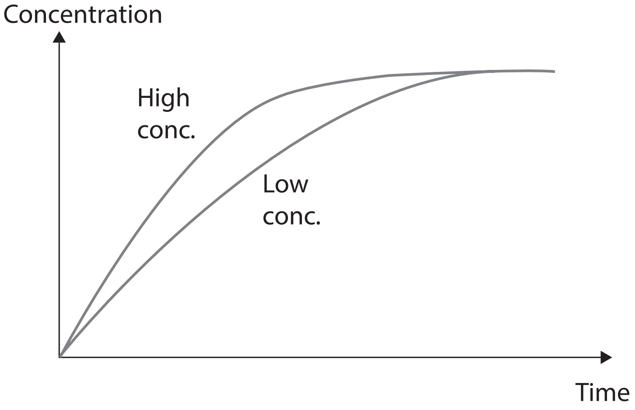
12.6 CONCENTRATION OF SOLUTION

Increasing the concentration of a reactant in solution will increase the rate of the reaction.

If the concentration of a reactant in solution is increased, the number of reacting particles increases, and they are closer together. There will be more collisions between reacting particles, so more successful collisions will occur, and therefore the reaction rate will increase.



When graphed, the initial reaction rate is higher for high concentrations than for low concentrations. The total amount of product made will be the same when the reaction is complete, unless the reactant at lower concentration is a limiting reagent.



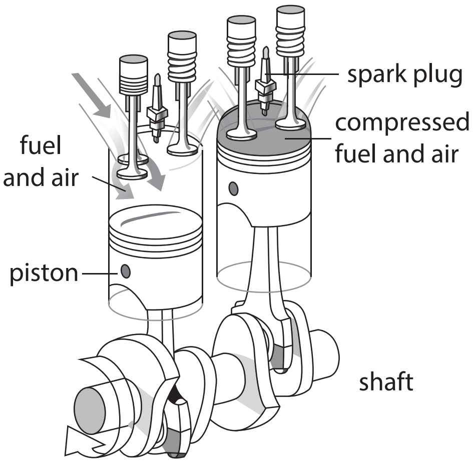
Partial pressure of gases

Increasing the partial pressure of gaseous reactants has the same effect as increasing the concentration of a reactant in solution. It will increase the rate of the reaction.

If the partial pressure of a gaseous reactant is increased the number of reacting particles increases. There will be more collisions between reacting particles, so more successful collisions, and therefore the reaction rate increases.

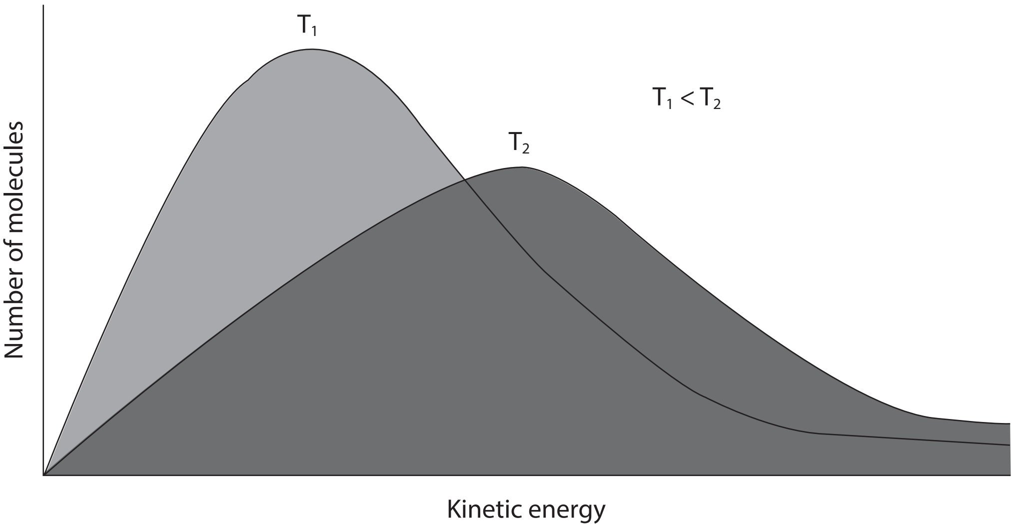
The pressure in a vessel can be increased by adding more of the gaseous reactant, or by decreasing the volume of the reaction vessel.

An example of this principle is in the combustion engine. As an engine operates, a spark explodes fuel in some cylinders forcing pistons down. This turns the crank shaft, causing pistons to move up in other cylinders. The pistons compress the fuel-air mixture in these cylinders and the spark plug fires to continue the process. This is timed very carefully in a well-tuned engine in order to maximise performance. The concentration of fuel and air sprayed into the cylinders is also very carefully controlled.



12.7 TEMPERATURE

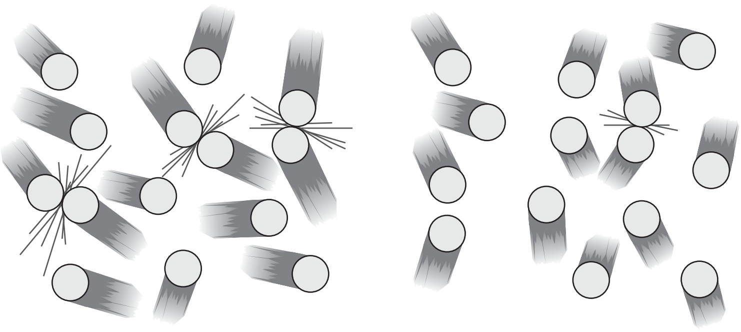
Generally, raising the temperature increases the rate of a chemical reaction. Temperature is a relative measure of the average kinetic energy (E_k) of the particles of a substance, so increasing the temperature increases the average kinetic energy of the particles and so more will be moving at greater velocity.



Increasing the kinetic energy and velocity of the reactant particles has two effects:

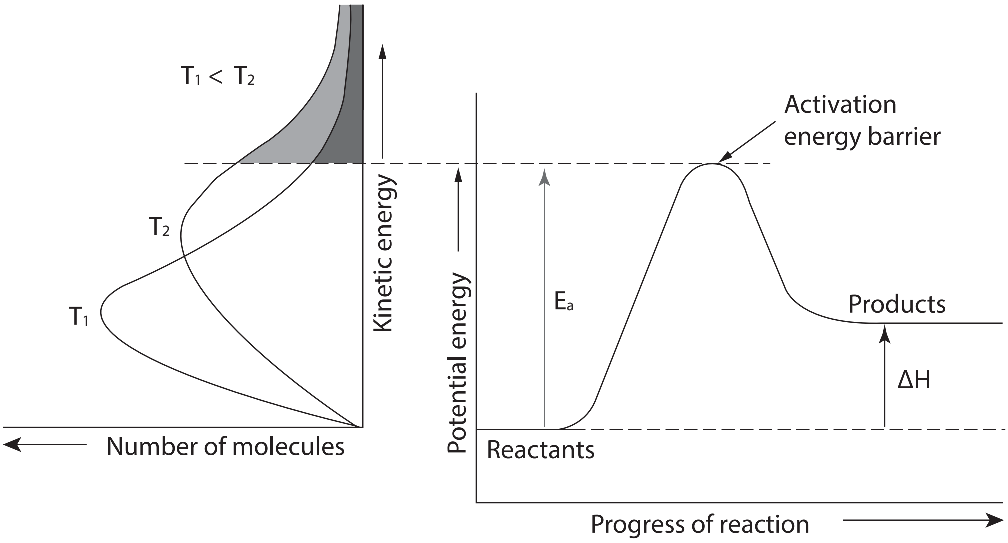
1. The frequency of collisions increases

   This increases the number of successful collisions and this, in turn, increases the rate of reaction.



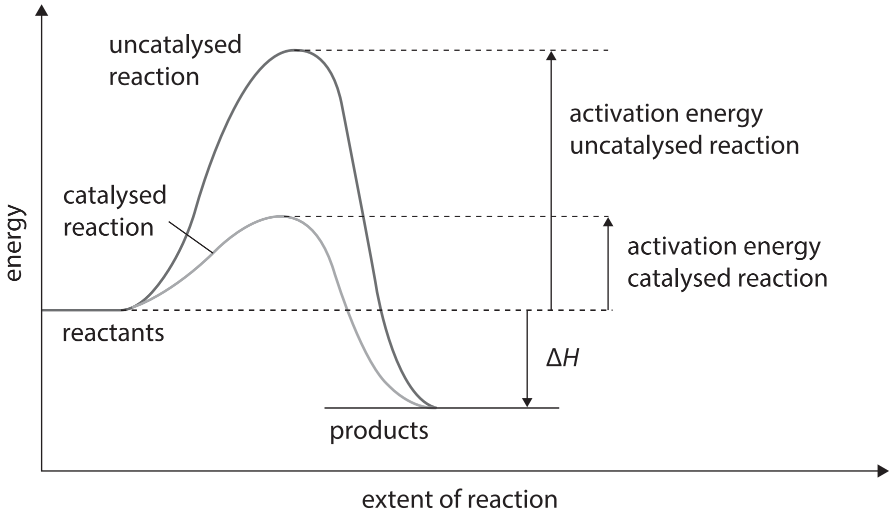
2. The force/energy of the collisions increases

   This increases the number of particles having high energy collisions so more collisions have sufficient energy to overcome the E_a barrier. This increases the rate of reaction.

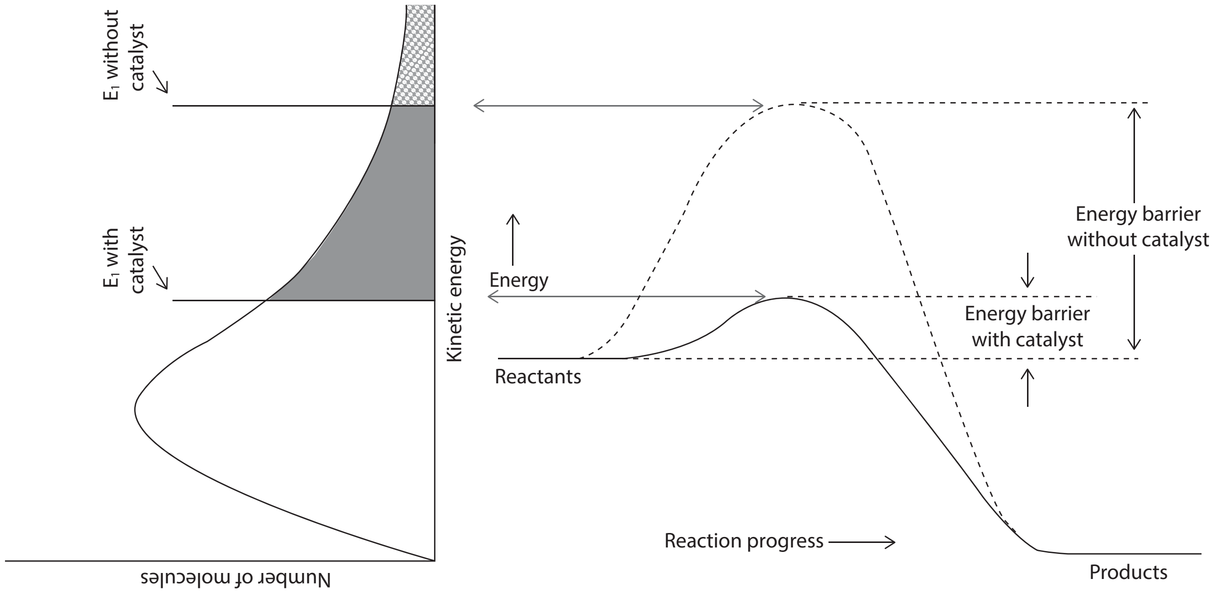


12.8 CATALYSTS

Catalysts increase the rate of a reaction without being (permanently) consumed in reaction. They do this by providing an alternative reaction pathway with lower activation energy requirements.



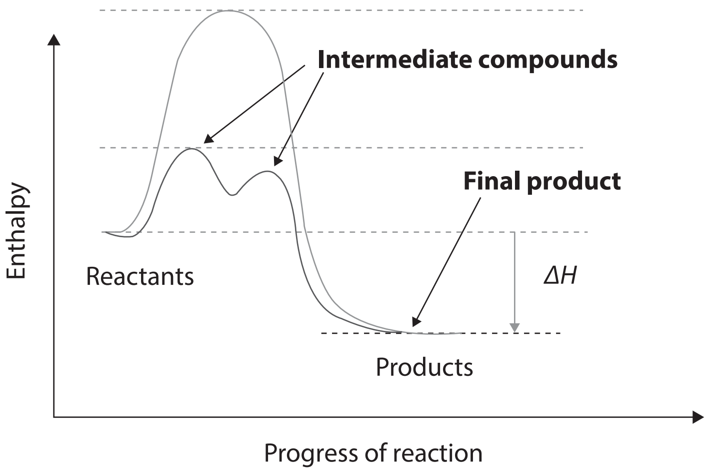
A lower activation energy means that a greater fraction of reacting particles will have sufficient energy to overcome this and the reaction will proceed at an increased rate.



There are two types of catalysts. Homogeneous and heterogeneous catalysts.

Homogeneous catalysts are catalysts which are in the same phase as the reactants. Usually this means that they are soluble and catalyse a reaction taking place in solution.

Homogeneous catalysts usually react with one of the reactants, producing an intermediate product. This intermediate product can then react with the other reactant. Both of these reactions can proceed with a lower activation energy than the un-catalysed reaction and so proceeds at an increased rate.



The reaction between the tartrate ion and hydrogen peroxide to produce carbon dioxide, water and the methanoate ion is an example of a reaction that proceeds very slowly but will react very quickly with the addition of a homogeneous catalyst. The catalyst is the pink cobalt (II) ion, Co^{2+}.

$$^{-}OOCCH(OH)CH(OH)COO^{-} + 3H_2O_2 \rightarrow 2CO_2 + 2HCOO^{-} + 4H_2O$$

Tartrate ion Methanoate ion

The first step is the reaction between hydrogen peroxide and Co^{2+}. The hydrogen peroxide is reduced to water and the Co^{2+} is oxidised to Co^{3+} which is green. The Co^{3+} then reacts with the tartrate ion to produce the methanoate ion, carbon dioxide and Co^{2+}.

The Co^{2+} provides an alternative reaction pathway with lower activation energy and the reaction proceeds very quickly. The Co^{2+} is regenerated following the reaction.

Heterogeneous catalysts are catalysts which are in a different phase to the reactants. They are often solids, which catalyse reactions in solution or between gases.

Heterogeneous catalysts provide a surface upon which the reactants can adsorb (adhere to).

With some catalysts the reactants may react with the catalyst's surface, providing an intermediate product, as with homogeneous catalysis.

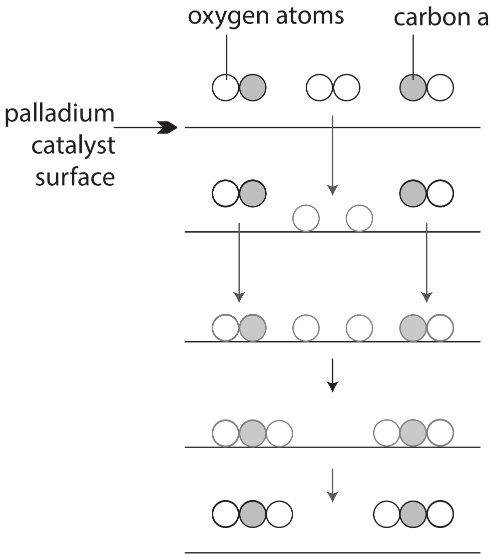
In other cases, the intramolecular bonds within the reactants may be weakened by adsorption onto the catalyst's surface. This means that collisions do not require as much energy to overcome the activation energy barrier.

Both result in an alternative reaction pathway with a lower activation energy.

On some occasions the surface catalyst may promote a more suitable orientation, improving the likelihood of a successful collision.

Example

The reaction between carbon monoxide and oxygen to produce carbon dioxide over a palladium catalyst.



The CO and O_2 in are in gaseous phase.

The O_2 is adsorbed onto the palladium catalyst surface and its double bond is weakened as the bonding electrons are attracted to the palladium.

The CO adsorbs onto the palladium catalyst and its triple bond is weakened as the bonding electrons are attracted to the palladium.

The C and O atoms are now is close proximity and can react to form CO_2.

The CO_2 can be desorbed and leave the surface as gaseous molecules.

Transition metals as catalysts

Transition metals and compounds containing them often make good catalysts. This is because they are able to change oxidation states, as in the cobalt example above, or because they provide a suitable surface for adsorption.

Examples of transition metal catalysts include:

Iron in the Haber process for the production of ammonia.

Vanadium pentoxide in the Contact Process for the production of sulfuric acid.

Nickel for the hydrogenation of unsaturated hydrocarbons such as ethene.

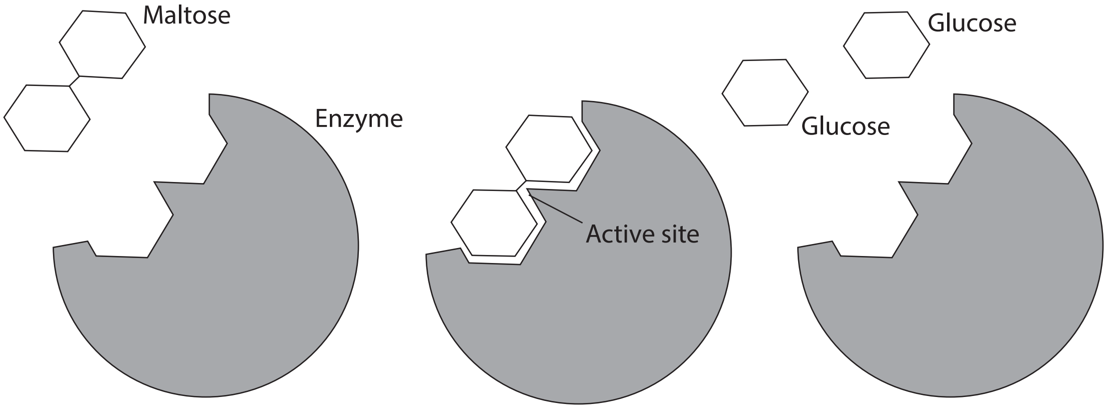
Platinum and rhodium in vehicle catalytic converters to convert poisonous exhaust gases like CO and oxides of nitrogen into less harmful ones.

Enzymes

Enzymes are biological catalysts as they can catalyse biochemical reactions in living things. They are known to catalyse more than 5,000 reactions.

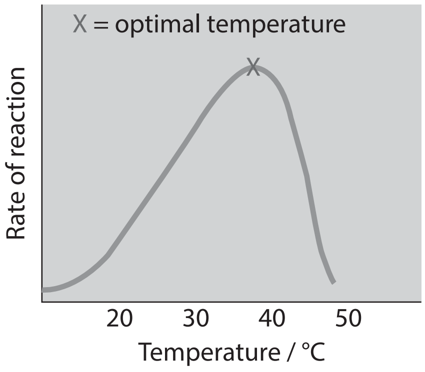
Enzymes are proteins whose shape provides an active site that the reacting molecule, or substrate, can bind to. This weakens bonds in the substrate so it can break more easily into products.

e.g. The enzyme glucosidase converts sugar maltose (the substrate) into two glucose molecules, the products.



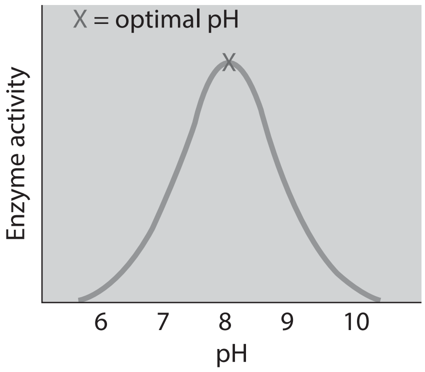
Temperature and enzyme activity

The shape of the enzyme is specific to the substrate that they bind with. Changing temperature changes the shape of the enzyme so they will only operate efficiently at specific temperatures. The optimal temperature for the enzymes in human cells is around human body temperature, at around 37.5°C. Above this temperature the enzyme becomes denatured.



pH and enzyme activity

Enzymes also operate more efficiently within certain pH ranges. Changes in pH can change the bonding that gives the enzyme its shape and so outside its ideal range it cannot bind with the substrate.



Examples of some useful enzymes

Amylase: Digests carbohydrates into glucose.

Lipase: Digests fats and oils to fatty oils for easy absorption.

Pepsin and protease: Digest proteins into amino acids.

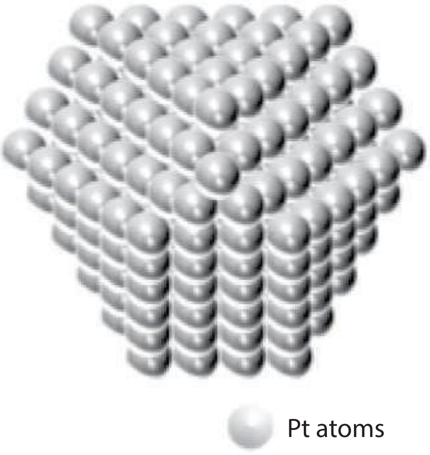
Catalase: Decomposes hydrogen peroxide

Lactase: Breaks down lactose into simpler sugars.

Metal nanoparticles as catalysts

Metal nanoparticles can be used as catalysts. They are usually heterogeneous catalysts broken up into nano-sized particles in order to speed up the catalytic process. Metal nanoparticles have a very high surface area so more catalytic interactions can occur more efficiently.

e.g. platinum nanoparticle catalyst



Inhibitors

Inhibitors are chemical compounds that decrease the rate of chemical reactions.

Enzyme inhibitors bind to enzymes and reduce their activity. This can help control enzymes that can be damaging to a cell, like proteases or nucleases.

Corrosion inhibitors like zinc phosphate, $Zn_3(PO_4)_2$, are often added to paints to prevent corrosion.

Reaction inhibitors can be used to slow down reactions. Acetanilide, C_8H_9NO, slows the decomposition of hydrogen peroxide solution.

12.9 CASE STUDY: RATES AND THE CONTACT PROCESS FOR THE PRODUCTION OF SULFURIC ACID

The Contact Process proceeds via four main steps, as shown below. Chemists carefully control the rates of each of these reactions in order to maintain economical production levels, minimise energy use and also ensure safety. You will study this process in greater detail in the Yr12 course.

Sulfur, air and water are the main raw materials of sulfuric acid production by the Contact Process.

Step 1: Combustion of sulfur

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

Sulfur is burnt in oxygen from the air to produce sulfur dioxide. In order to improve the rate of this reaction the sulfur is first heated until molten and then sprayed into a furnace to combust. The increased temperature increases collisions between particles, thereby increasing rate. Spraying the molten sulfur increases its surface area, also increasing collisions and rate.

Step 2: Production of sulfur trioxide

$$2SO_2(g) + O_2 \leftrightarrows 2SO_3(g) + \text{heat}$$

The sulfur dioxide is transferred to a converter where it is oxidised over a porous V_2O_5 catalyst. This reaction is a reversible one and, whilst high temperatures increase collisions, they actually favour the reverse reaction, so a moderate temperature is chosen. High pressures favour the forward reaction and also increase collisions but are very expensive to achieve so a moderate pressure is chosen. The V_2O_5 catalyst is therefore used to provide an alternative reaction pathway with a lower E_a to maintain a decent rate of reaction at reasonable cost.

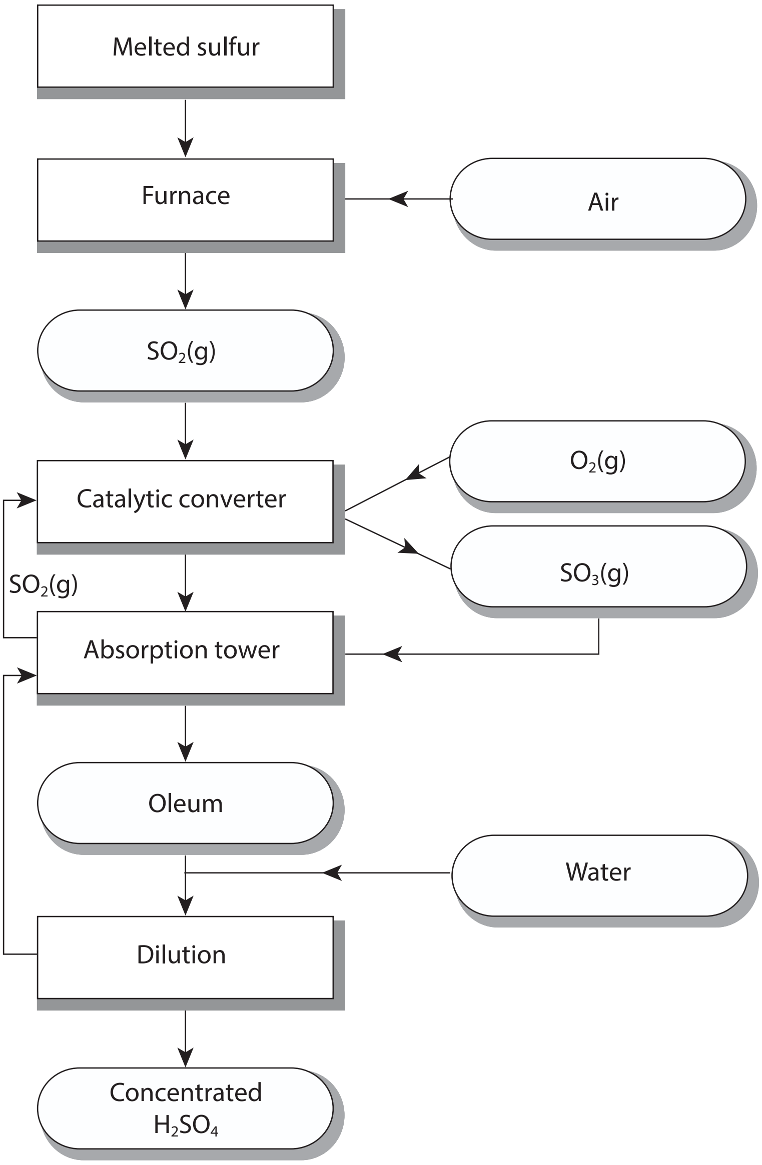
Step 3: Formation of sulfuric acid

Sulfur trioxide can be dissolved in water to form sulfuric acid directly, but this is highly exothermic and produces an acid mist. In this case the reaction needs to be slowed down. To achieve this the sulfur trioxide is dissolved in sulfuric acid to produce oleum ($H_2S_2O_7$), and this can then be dissolved in water to produce the final sulfuric acid product.

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

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

Unreacted SO_2 is recycled back into the converter and over the catalyst again. This reduces SO_2 emissions, which can contribute to acid rain.



Set 1

1. Outline two methods that could be used to determine the rate of the reaction between aluminium and hydrochloric acid.

2. Which of the reactions below would you expect to proceed at the fastest rate at room temperature? Explain your choice.

(A) $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ (B) $2H_2 + O_2 \rightarrow 2H_2O$

(C) $Pb^{2+} + 2I^- \rightarrow PbI_2$ (D) $Mg + 2HCl \rightarrow MgCl_2 + H_2$

3. In the internal combustion engine the carburettor vaporises fuel before it is injected into the engine. Why is this?

4. Using the data below plot a graph of mass lost versus time for the reaction between small pieces of sodium carbonate and 1.00 $molL^{-1}$ nitric acid.

Time (s)	0	15	30	45	60	90	120	150	180	210	240	270	300	330	360
Mass lost (g)	0.00	1.79	4.07	5.41	5.74	6.13	6.23	6.30	6.36	6.40	6.42	6.43	6.44	6.44	6.44

a. During which time interval is the reaction proceeding at the highest rate?

b. What is the rate of the reaction at,

  i) 15 seconds?

  ii) 150 seconds?

c. Why does the rate of this reaction decrease with time?

d. What happens to the rate of the reaction after 300 seconds and why?

e. On your graph add a sketch of the curve that would be obtained if large pieces of sodium carbonate had been used instead of smaller ones.

f. Using collision theory, explain the shape of the curve that you drew in part e.

g. On your graph add a sketch of the curve that would be obtained if 2 mol L^{-1} nitric acid had been used instead of 1 mol L^{-1}.

h. Using collision theory, explain the shape of the curve that you drew in part g.

5. The decomposition of hydrogen peroxide can be catalysed by the addition of powdered manganese dioxide, MnO_2.

   a. Is this homogeneous or heterogeneous catalysis?

   b. Explain how manganese dioxide catalyses this reaction, include the following terms in your answer:

      collisions, adsorb, activation energy, reaction pathway, bonds

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6. Increasing temperature increases the kinetic energy and velocity of reacting particles.

   a. Using collision theory, explain the effect that increasing the temperature has on the rate of a reaction.

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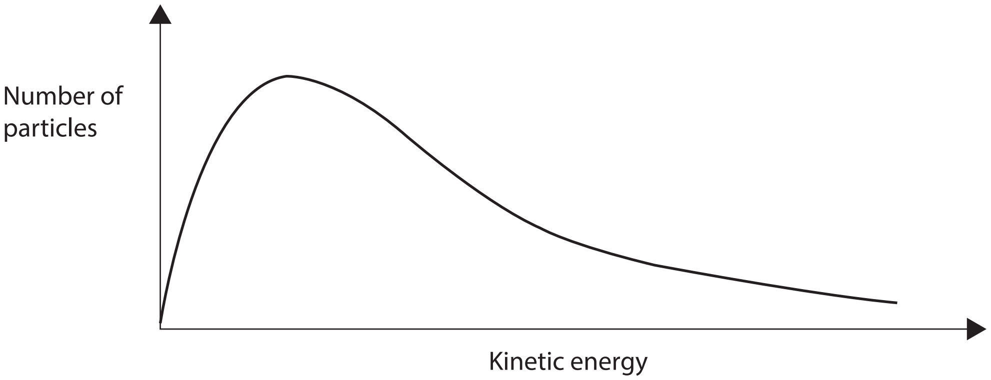
b. The graph below shows the Maxwell-Boltzmann distribution for the kinetic energies of particles in a sample of gas at 20°C. On this graph draw a curve showing the distribution of particles if the temperature is increased to 40°C.



7. The optimal temperature for enzyme activity is around 37.5°C. Beyond this temperature enzymes become denatured. What does this mean and why does it occur?

8. Hydrogen gas and carbon monoxide gas react in the presence of a catalyst to produce methanol.

   a. Write the balanced equation for this reaction.

   b. In addition to the required catalyst, how might the rate of this reaction be increased?

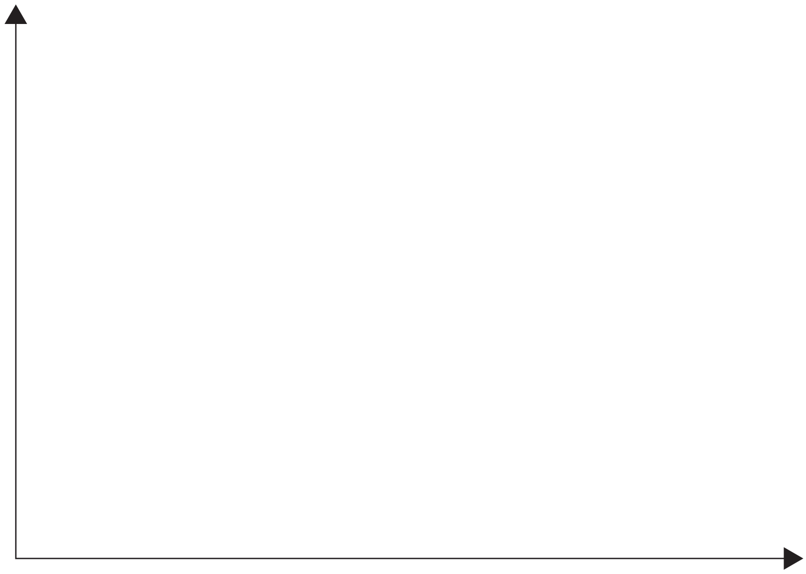
9. Magnesium metal oxidises very slowly in air but when held over a Bunsen flame it ignites and oxidises to magnesium oxide in seconds, releasing large quantities of heat and light.

   a. What does this suggest about the activation energy, E_a for this reaction?

   b. Is this an endothermic or exothermic reaction?

   c. Would this reaction have a large or small heat of reaction, ΔH? Explain.

d. Draw an energy level diagram for the reaction between magnesium and oxygen showing the reactants, products, ΔH and E_a. Label both axes.



10. In the Contact Process for the production of sulfuric acid the reaction conditions of steps 1 & 2 below are carefully controlled to maximise reaction rate.

For each step describe the conditions chosen and explain this choice in terms of the collision theory.

a. Step 1: Combustion of sulfur

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

____

____

____

____

____

____

b. Step 2: Production of sulfur trioxide

$2SO_2(g) + O_2 \leftrightarrows 2SO_3(g) + \text{heat}$

____

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Notes

Chapter

13

Data Analysis

Experimental Data Analysis Task: The Thiosulfate Clock Reaction

Students at Forest Lodge School were asked by their chemistry teacher to set up an experiment that demonstrates how the time for a reaction to occur depends on factors such as Temperature and reactant Concentrations.

Here are the teacher's instructions:

You will be given two solutions: sodium thiosulfate ($Na_2S_2O_3$) and hydrochloric acid, both with a concentration of 1 mole per litre. When they are mixed a reaction occurs which produces a suspension of sulfur by the following reaction:

$$S_2O_3^{2-}\,(aq) + 2H^+(aq) \rightarrow S\,(s) + SO_2\,(g) + H_2O\,(l)$$

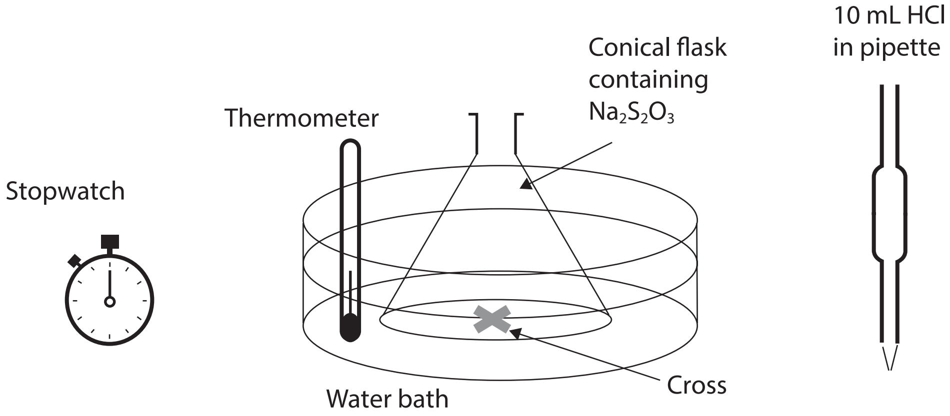
The suspension of sulfur makes the solution cloudy and this cloudiness can be used as an indication that the reaction has gone to completion – a black cross on the flask bottom under the solution will become obscured. This cross can be seen clearly at the start of the reaction but becomes obscured by a layer of colloidal sulfur when the reaction is complete.

Procedure to be followed.

1. Make up a standard 1 mole L^{-1} solution of sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$).
2. Pipette 10 mL of this solution into a clean conical flask specially prepared with black cross painted on the base.
3. Place the flask and its contents in a water bath at room temperature (14^{o}C)
4. Have your stop-watch ready to start. Have a 10 mL pipette-ful of a 1 mole L^{-1} hydrochloric acid solution ready to add to the flask. Add the HCl and swirl the flask, at the same time as starting the stop-watch.
5. Carefully observe the black cross under the mixture and stop the stop-watch when the black cross can no longer be seen by the eye.
6. Record the time taken for the cross to disappear, when the reaction is complete.
7. Add warm water to the water bath until it reaches a suitably higher temperature to perform the experiment again in a warmer environment.

   Using a clean set of equipment, repeat the same experiment several times at different temperatures, noting the reaction times for each temperature.

Diagram

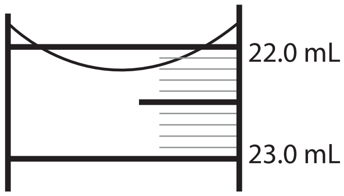


Student Results

Experiment Number	Temperature ± 1°	Time for cross to disappear t ± 0.5 s			Average time T_{Av}	Variance in times
1	14	23.4	23.4	23.3	23.4	± 0.06
2	22	18.2	18.1	18.3	18.2	± 0.10
3	30	14.2	14.2	14.8	14.4	± 0.06
4	36	11.8	11.9	11.8	11.8	± 0.05
5	48	7.7	8.0	8.3	8.0	± 0.30

Error analysis

A Random error is one that leads to an uncertainty in the exact value to be used as a datum point on a graph. Suppose 3 different students measured the volume of solution in a burette they might all record different values, not because any student has made a mistake, but because of their differences in estimating the closest line on the tube showing the volume.



For the same volume in the burette readings judged by 3 students could be:

22.30 mL, 22.35 mL, 22.40 mL.

The way scientists overcome random errors is to take a number of readings and use the average value. In this case, this would be 22.35 mL.

Single Reading Errors

To estimate the error in a single reading it is usual to take the uncertainty as half of the least division on the scale. In this case this "absolute uncertainty" would be ± 0.05 mL. If we take the 22.3 mL reading only we would quote the uncertainty of this reading as 22.3± 0.05 mL, or, converted to a "Relative uncertainty" this is given by: $U_R = \frac{0.05}{22.5} \times 100 = 0.22\%$.

Many Reading Errors

The more readings taken, the more statistically certain we are of the value to be used. Normally 3 readings are sufficient but if the readings vary wildly then this is an indication of an error in the method or the apparatus. When taking 3 readings, we do not use the "± ½ Least division" method but use the "deviation from the mean" method. Mean value = 22.35 and highest value = 22.40, so the deviation from the mean is 22.40 - 22.35 which gives a ±0.05 mL uncertainty again. In this case, both methods yield the same value as estimation of the % error, but this is not always so.

When taking several readings of the same result, the "Many Readings" method is more appropriate.

A relative uncertainty for a classroom experiment which is less than 5% indicates good experimental techniques. For another group of students recording values of this volume as 22.4 mL, 22.5 mL and 22.2 mL must have been displaying less accurate experimental techniques.

Systematic Errors

These kinds of errors are due to some problem with the apparatus e.g. burette is incorrectly calibrated, timer has a zero error (not reading zero before it is read). We cannot really allow for this kind of error and it will eventually lead to a result which is not valid. A valid result is one which tallies with the accepted result. Obviously if there is a fault with the apparatus of some kind then the final answer for, say the concentration of an acid, would not be correct, or valid even if the readings were accurate. An accurate reading is one which is done correctly and is a precise one which can be reproduced consistently.

Validity is a measure of how true or correct the reading is. Firing 4 arrows aiming at the bullseye of a target can produce an accurate score if they are all grouped closely together (reproducible) but if they didn't hit the bullseye then they are not valid as it is not the point where they are aimed at.

Another kind of error that can be made is simply called a Mistake. This would occur if the student used the wrong concentration of acid in the experiment and so an erroneous reading would occur.

Questions

1. Looking at Table 1, there appears to have been a mistake in one of the readings.

   (i) Which reading is this?

   ____

   With an outlier value like this it is customary to exclude it in averaging the results.

   (ii) What value would you use for the average time in the case where the faulty reading has occurred?

   ____

   (iii) The student in charge of adding the acid found that the pipette was dirty and so she rinsed it every time with distilled water before filling it with the acid. What kind of error would this have produced?

   (Circle) *Systematic* *Random* *Mistake*

   (iv) How would rinsing the pipette with water affect the results in this case?

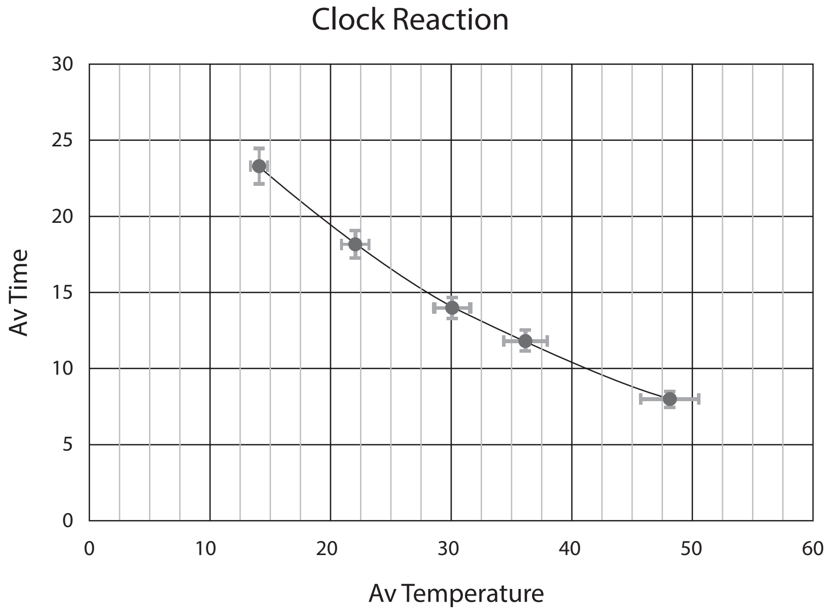
   ____

2. Which of the readings for time has the highest relative (%) uncertainty? Show your calculations.

   ____

   ____

3. Graph



What conclusions can be drawn from the shape of the graph about the accuracy of the students' results?

(i) Predict the time this reaction would have taken at a temperature of 5°C

____

(ii) Explain why the reaction takes longer at a lower temperature.

____

____

(iii) The Rate R of a reaction is given by: $R = \frac{1}{\text{Time}}$.

Estimate the factor by which the reaction rate increases when the temperature is raised from 20°C to 30°C

____

____

4. Calculate the relative uncertainty (%) in the following measurements:

(i) The mass of a piece of zinc measured on a top-pan scale where the smallest division is 0.1 g and whose reading is 1.2 g

____

____

(ii) The volume of carbon dioxide liberated from and acid/carbonate reaction where a syringe reads to the nearest 0.2 mL and the reading is 121.4 mL

____

____

(iii) The area of a strip of magnesium used in an acid/metal reaction, measured with a ruler, reading to the nearest millimetre. The length measures 27 mm and width 4 mm.

____

____

5. The times taken for a reaction to produce 100 mL of hydrogen in 5 repeated experiments are as follows: 1 min 54 s, 1 min 43 s, 2 min 10 s, 1 min 59 s, 2 min 23 s.

(i) Find the average value for time to be used

____

(ii) Find the average rate of production of hydrogen in mL per second, R.

____

(iii) Find the relative uncertainty in the value for R

____

(iv) Quote the rate R with its absolute uncertainty (e.g. 5.0 ml s^{-1} ± 0.05)

____

Notes

Solutions

Chapter 1.
Materials and Their Makeup

Set 1

1.

(a) *Analytical or inorganic chemist.*

(b) *Evaporate the seawater in a dish until dry.*

(c) *Percentage of salt* $= \frac{8}{25} \times 100 = 32\%$

2. *Addition of tin produced a bronze alloy which increased the strength of the metal. This made better weapons and chiselling tools for building more complex structures.*

3. *Copper and tin are fairly unreactive metals so their ores are easy to reduce to the metal by simply heating. Iron is more reactive and requires the higher temperature for reduction of ores achieved by blasting air though a furnace. However aluminium is a highly reactive metal which means its oxide ores are very stable and cannot be reduced using heat alone – much more energy is needed, as with electrolysis of the molten ore. This technology was ony available within the last century or so, hence the production of aluminium metal only occurred from the 1900s onwards.*

4. *Homogeneous materials are: Tap water and sulfur.*

5.

(a) *107 nm* $= 1.07 \times 10^{-5}$ *cm*

(b) *Wood chips are more finely divided than a single plank and would have a larger area of contact with a flame which would make burning occur at a faster rate.*

(c) *Accurate method: 100 pages measures 0.5 cm, so each page thickness is 0.5/100 = 0.005 cm. Thickness of one page* $= 5 \times 10^{-3}$ *cm or* 5×10^{-5} *m. Change to nanometres by multiplying by* 10^{9} *which gives 50,000 nm.*

(d) *Nanoparticles have a very large area-to-volume ratio so 1 gram of carbon as nanoparticles would have a very large area to absorb gases by adsorption compared with solid carbon.*

6.

(a) *Nanotube fertilizers have nutrients stored inside the nanotubes which can release these nutrients slowly like a reservoir and produce steady growth.*

(b) *Carbon can firm 4 bonds but sulfur can only form 2. Carbon bonds would be in a tetrahedral 3-D shape but sulfur can only bond in lines.*

(c) *Graphene has 3 bonds at 120° in 2 dimensions which makes the atoms hard to pull apart.*

7. *There is an argument for regulation, as follows: There should be some limit on the amount of products containing nanoparticles if they can get into the environment and particularly into the food chain. It is possible that these small particles could even end up inside the bodies of humans – and the result of this is unknown.*

8.

(a) *(i) Dissolve the mixture in water (salt will dissolve but pepper will not)*
(ii) Filter the solution (pepper with stay on the filter paper)
(filtrate is salt solution which can be evaporated to dryness to recover the salt and pepper can be dried to recover it.

(b) *(i) Dissolve the mixture in water (sugar will dissolve but sand will not)*
(ii) Decant off the solution, leaving the sand behind as a solid.
(iii) Solution of sugar can be evaporated to dryness to recover the sugar and sand can be dried out.

(c) *Distillation at a temperature below* 100^{o}*C will allow the fuel to boil over and condense, leaving the water behind.*

(d) *Distillation at a temperature of about* 100^{o}*C will allow the vinegar to boil over and condense, leaving the vegetable oil behind.*

(e) *Passing a magnet over the mixture will attract the iron filings and leave the grit behind.*

9.

(a) *Filtration or sieving*

(b) *Decantation if impurities are insoluble or filtration*

(c) *Distillation*

10.

(a) *Volume of cube* $= 1\ cm^3 = \frac{4\pi r^3}{3}$

So $r = \sqrt[3]{\frac{3 \times 1}{4\pi}} = 0.620$ *cm.*

(b) *Cube area* $= 6 \times 1 = 6\ cm^2$*. Sphere area* $= 4\pi r^2 = 4.19\ cm^2$*.*

(c) $8 \times 6 \times 0.5^2 = 12\ cm^2$

(d) *Grains have a larger overall area of exposure to the 'attack' by water*

11. *Circumference of track* $= 2\pi r = 2 \times \pi \times 0.055 = 0.3456\ m$

1 hole + 1 space distance $= 800 + 800\ nm = 1600 \times 10^{-9}\ m$

No of holes plus spaces in one circumference $= \dfrac{0.3456}{1600 \times 10^{-9}} = 2.16 \times 10^5$.

12. *Samples of the tomato colouring in the skins of both kinds of tomatoes could be liquefied or made into a solution and placed in a beaker with chromatography paper dipping into it.*

Different growing method should mean that the tomatoes have different chemical components in the skins.

After some time the paper would be removed and dried and the colour components examined and measured.

Different coloured components at different heights from the base of the paper would indicate that the two types of tomato were different in composition.

13.

(a) *Simple carbon has a large surface area – to-volume ration and can adsorb a large volume of gas.*

(b) *Nano particles of carbon are much smaller than normal car bon particles and will have a much larger adsorption capacity for gas*

Chapter 2.
Atomic Structure

Set 1
Multiple-choice

1. B 2. B 3. C 4. A 5. B 6. C 7. C
8. B 9. D 10. B 11. A 12. D 13. C
14. A 15. D 16. D 17. A 18. B 19. B
20. A 21. D 22. C 23. C 24. B 25. D

Longer Questions

26.

Symbol	Mg-25	$^{26}_{12}Mg$	$_{17}Cl^-$	Cd	S^{2-}	$_{29}Cu^+$
Protons	12	12	17	48	16	29
Neutrons	13	13	18	64	16	35
Electrons	12	12	18	48	18	28
Atomic No.	12	12	17	48	16	29
Mass No.	25	26	35	112	32	64
Net charge	0	0	1-	0	2-	1+
Symbol	**W-184**	**$^{59}_{27}Co^{2+}$**	**Pb^{4+}**	**As^{3-}**	**Xe**	**$^{238}U^{5+}$**
Protons	74	27	82	33	54	92
Neutrons	110	32	125	42	78	166
Electrons	74	25	78	35	54	97
Atomic No.	74	27	82	33	54	92
Mass No.	184	59	207	75	13w2	238
Net charge	0	2 +	4+	3-	0	5+

27.

(a) *Cl*

(b) *Cd, Cu, W, Co*

(c) *Mg-25, Mg-26*

(d) *Mg, Pb, U*

(e) *Mg*

(f) *Cl, Xe*

28.

(a) $^{17}_{8}O$

(b) $^{37}_{17}Cl$

(c) $^{60}_{28}Ni$

(d) $^{57}_{26}Fe$

(e) $^{131}_{53}I$

(f) $^{7}_{3}Li$

29.

(a) $^{25}_{12}Mg$ $n(p) = 12$, $n(n) = 13$, $n(e) = 13$
Period = 3, Group = 2

(b) $^{118}_{50}Sn^{4+}$ $n(p) = 50$, $n(n) = 68$, $n(e) = 46$
Period = 5, Group = 14

(c) $^{81}_{35}Br^-$ $n(p) = 35$, $n(n) = 46$, $n(e) = 36$
Period = 4, Group = 17

(d) $^{133}_{55}Cs^+$ $n(p) = 55$, $n(n) = 78$, $n(e) = 54$
Period = 6, Group = 1

(e) $^{79}_{34}Se^{2-}$ $n(p) = 34$, $n(n) = 45$, $n(e) = 36$
Period = 4, Group = 16

(f) $^{56}_{25}Mn^{7+}$ $n(p) = 25$, $n(n) = 31$, $n(e) = 18$
Period = 4, Group = 7

30. *Br-80* e^- *number = 35* p^+ *number = 35*
n number = 45
S^{2-} *-32* e^- *number = 18* p^+ *number = 16*
n number = 16
Ba-137 e^- *number = 56* p^+ *number = 56*
n number = 81
K^+*-39* e^- *number = 18* p^+ *number = 19*
n number = 20

31. *Thallium 205 has the greater abundance. If % were equal then the weighted average would be 204 but a value of 204.38 means there must be more of the 205 isotope.*

32.

(a) (i) Rb_2Se
(ii) $0.722 \times 85 + 0.278 \times 87 = 85.56$.
(iii) *The atomic structure and chemical properties would be the same but physical properties, such as density, melting and boiling points would be higher for the heavier isotope.*

(b) (i) $0.69 \times 58 + 0.27 \times 60 + 0.04 \times 62 = 58.7$
(ii) *2, 8, 8, 10*
(iii) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

(c) $0.885 \times 140 + 0.115B = 139.8$
$123.9 + 0.115B = 139.8$
$B = \dfrac{15.9}{0.115} = 138.3$

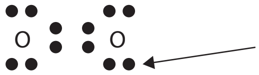
33.
(a) Fe^{2+} 24
(b) Ca^{2+} 18
(c) Co^{2+} 25
(d) I^- 54
(e) S^{2-} 18
(f) Cl^- 18
(g) Cr^{3+} 21
(h) K^+ 18

34.
(a) Fe^{2+} 2, 8, 8, 6
(b) Ca^{2+} 2, 8, 8
(c) Co^{2+} 2, 8, 8, 7
(d) I^- 2, 8, 8, 18, 18
(e) S^{2-} 2, 8, 8,
(f) Cl^- 2, 8, 8
(g) Cr^{3+} 2, 8, 11
(h) K^+ 2, 8, 8

35.
(a) Tl 3^+
(b) Se 2^-
(c) Ba 2^+
(d) As 3^- (5+)
(e) Fr 1^+
(f) Cs 1^+

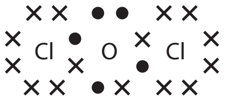
36.
(a) CO
(b) NaH
(c) $AlCl_3$
(d) MgS
(e) Ca_2C
(f) Zn_3N_2

37.
(a) *Oxygen atoms have 6 electrons but need 8 for a full shell, so if 2 atoms join together as a molecule where they share 2 electrons, both atoms can achieve a stable 8 configuration. Electron-dot diagram:*
(b) *A bond consists of 2 electrons. If the bond is on its own and not linking any 2 elements, it is called a "Lone Pair" or a "Non-bonding pair".*

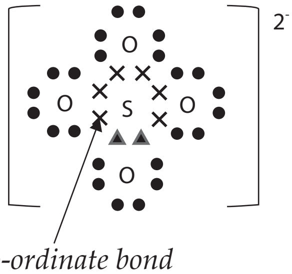


(b) *Non-bonding pair*

(c)



(d)



Co-ordinate bond (both electrons come from the same atom)

38. *In the Thompson model the negative charge and the positive charge were both located in a single ball ('Pudding'), whereas in the Bohr Model the electrons were in an orbit around a positive nucleus at the centre.*

39.
(a) *All values ere multiples of* 1.6×10^{-19} *coulomb, showing that this must be the component charge of all the other charges recorded.*
(b) *This meant that the charge on the electron must be the smallest value of* 1.6×10^{-19} *coulomb.*

40. *Energy levels in an atom cannot be equally spaced as the lines in the emission spectrum are in a quadratic sequence (to a limit). Therefore, when the electrons fall from one level to another the energy of the lines emitted will also be quadratically linked and not linear.*

41. *Max = 54.6 pm, Min = 49.4 pm*

42. *At very short distances* ($< 10^{-15}$ *m) the Strong nuclear force starts to act, which overcomes the electric repulsive force but the repulsion is too strong without the mediation of neutrons.*

43.
(a) *Li – 3protons + 4 neutrons so* $\Sigma m = 3 \times 1.00728 + 4 \times 1.00867 = 7.05652$ *amu*
$1 \text{ amu} = 1.667 \times 10^{-24}$ *so* $\Sigma \text{mass} = 7.05652 \times 1.667 \times 10^{-24} = 1.176 \times 10^{-23}$ *g.*
(b) $1/1.176 \times 10^{-23} = 8.50 \times 10^{22}$ *atoms per gram.*

44. M_r *of Mg is 24.31, which I the weighted average, so in 10.0 g there will be 10/24.31 moles = 0.4114 mol.*
$N°(Mg) = 0.4114 \times 6.022 \times 10^{23} = 2.477 \times 10^{23}$ *atoms. But only 11% of these are Mg-26 atoms*
$N°(Mg\text{-}26) = 2.72 \times 10^{22}$ *atoms.*

45.
(a) $r = \frac{mv}{Bq}$ *so* $m = \frac{rBq}{v}$
$= \frac{23.6 \times 10^{-2} \times 0.8 \times 1.6 \times 10^{-19}}{2.63 \times 10^{4}} = 1.1486 \times 10^{-23}$ *g*
(b) $M_r = \frac{1.1486 \times 10^{-23}}{1.667 \times 10^{-24}} = 6.89 \text{ g mol}^{-1}$ *(The closest ion is lithium where* $M_r = 6.968$*)*

46. *Mg is:* $1s^2, 2s^2, 2p^6, 3s^2, 3p^0$.
N is: $1s^2, 2s^2, 2p^3, 3s^0, 3p^0$.
Ar is: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$.

47. *Ionic: K* CaF_2

48. $Cs^+ = Xe$ $Cl^- = Ar$ $Al^{3+} = Ne$
$P^{3-} = Ar$ $Ca^{2+} = Ar$ $O^{2-} = Ne$

49. *Ca and Cl form* $CaCl_2$*, Al and O form* Al_2O_3*, Cs and P combine to form* Cs_3P*.*

Set 2

1.
(a) *The Quantum Theory sates that energy is not continuous but made up of discrete packets of energy, called quanta.*
(b) *The energy in a quantum of light is proportional to its frequency. Red light has a low frequency and ultraviolet has a high frequency – hence UV light contains more energy than red and hence it can cause more damage to the skin.*

(c) When heated, an element has its electrons promoted to higher energy levels. When they fall down they emit radiation whose frequency depends on the difference between these two energy levels. Each frequency corresponds to a different colour.

(d) If light energy was not quantised then an atom could give out any amount of energy (and any colours). Because electrons can only fall from discrete levels due to quantisation, only certain transitions are allowed – so only specific colours can be emitted from any element.

2.

(a) Strawberry is a red colour. If red passes through the solution then the other colours must have been absorbed (blue and green absorbed)

(b) The copper ions in the flame must be absorbing the red and green wavelengths.

(c) The hair would still contain the arsenic absorbed when the person was alive. If the hair absorbs the specific wavelengths of the arsenic atoms then there must be arsenic in the hair and hence the person's body would contain arsenic.

3.

(a) the 2nd shell has s and p sub-shells which can contain up to 2 and 6 electrons respectively = 8.

(b) **P** $1s^22s^22p^63s^23p^3$ **O** $1s^22s^22p^4$
Mg $1s^22s^22p^63s^2$

(c) F = 7 Ca = 2 Si = 4 Cl = 7

(d) F = -1 Ca = +2 Si = +4, -4 Cl = -1

4.

(a) [✓ C] N F [✓ Cl] [✓ Ca] Be P [✓ Si]

(b) Na size = 186 pm = 1.86×10^{-10} m
$1 \text{ mm} = 1 \times 10^{-3}$ m so number in 1 mm
$$= \frac{1 \times 10^{-3}}{1.86 \times 10^{-10}} = 5.4 \text{ million}$$

5.

(a) Sodium is more reactive that lithium because its ionisation energy is lower, therefore needs less energy to lose an electron to react.

(b) Fluorine has a much smaller ionic radius, so the electron shell is much closer to the nuclear charge and so will hold the electrons more tightly.

(c) [✓ N] P Se [✓ Kr] [✓ Ga] Al Ar [✓ Ne]

(d) Noble gases have such a high ionisation energy which has to be overcome to make it react. It has a full shell which is particularly stable.

(e) Of all the Noble gases Xenon has the lowest ionisation energy, which means it can react with the least input of energy.

6.

(a) Aluminium is a metal by virtue of its malleability and conductivity. Because it ionisation energy is low its outer electrons are free at room temperature so it can have metallic bonding.

(b) Boron is a poor conductor as it has few delocalised electrons. Due to its higher ionisation energy electrons are pulled close to the nucleus.

(c) Antimony has a lower ionisation energy and so its electrons are mainly delocalised which means it will exhibit metallic bonding. Arsenic holds its electrons more tightly and is a nonp-metal – hence it will not be malleable.

7.

(a) H--- Cl$^{\delta-}$ $^{\delta-}$N--- Br $^{\delta-}$F---Cl C---O$^{\delta-}$

(b) An adjacent HCl molecule would attract it so that the δ- end of one molecule would attract the δ+ end of the other.

(c) The large attractive dipole-dipole forces would make the boiling point high.

8.

(a) E = hf so low energy transitions would give the smallest frequency and longest wavelength. X transition is the smallest energy and longest wavelength.

(b) Blue = Z Yellow = X Green = Y

(c) The colours emitted is an emission spectrum would be the same ones absorbed when white light passes through the material. Hence blue, green and yellow colours would be missing (black) in the spectrum.

9.

(a) The spectrophotometer is used to find the concentration of a compound in a solution. It works by finding the amount of a particular wavelength of light that is absorbed by the solution and matching it to concentration on a calibration graph.

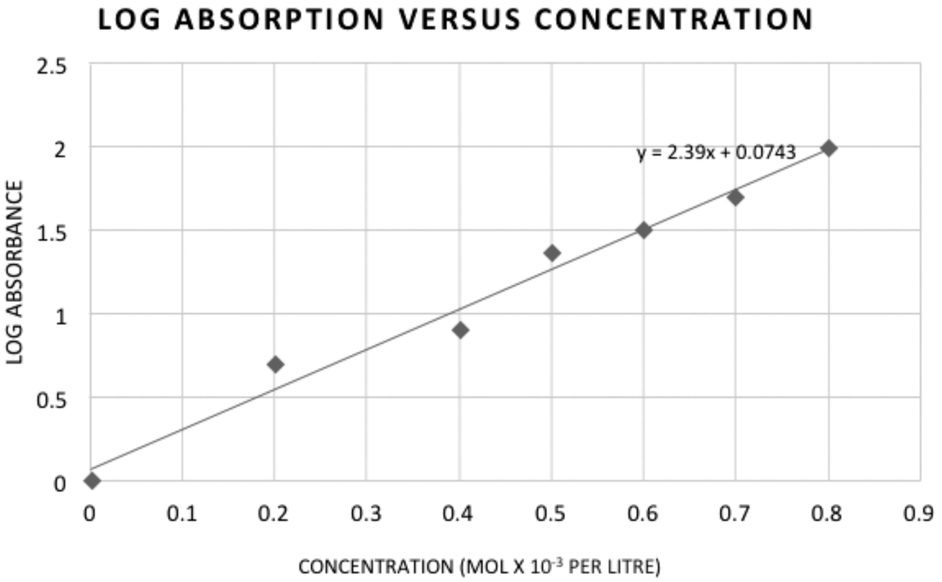
(b) (i) The wavelength of light that is most absorbed by the compound (λ_m) is found by shining all wavelengths through the solution and noting absorption rates.
(ii) Known concentrations of the compound in solution are used to map the amount of absorption for a standard volume for each concentration.
(iii) The test solution is illuminated with light of wavelength λ_m and the amount of absorption is noted.
(iv) This value is placed onto the calibration line to obtain the corresponding concentration value.

10.

(a)

Concentration c (mMol L^{-1})	*0.8*	*0.7*	*0.6*	*0.5*	*0.4*	*0.2*	*0.0*
Absorbance A (%)	*100*	*50*	*32*	*23*	*8*	*5*	*0*
Log A	*2*	*1.7*	*1.5*	*1.36*	*0.9*	*0.7*	*0*

(b)



Gradient = 2.4

(c) Log 15.2 = 1.18 which gives a value of 0.46 m Mol L^{-1}.

Chapter 3.
Types of Bonding

1.

(a) An atom with an electron removed from its valence shell this is called an ion.
The energy needed to ionise a mole of gas atoms of an element is called its ionisation *energy. For metals this energy is very* small, *whereas for the* noble *gases the value is extremely* large.
Going from top to bottom of a Group, the ionisation energy becomes smaller, *whereas going across a Period it becomes* larger.
The bonds between a metal and a non-metal are called covalent *bonds. With these, the metal* donates *valence electrons and the non-metal* receives *them so that both species can achieve a* noble *gas configuration. This is very* stable *e.g. if potassium gains an electron its structure becomes isoelectronic with the element called* neon.
The ions in an ionic solid are arranged in a 3-D lattice *structure which is strong and gives it a very* high *melting point. Ionic solids are* bad *electrical conductors unless they are changed into the* liquid *state by heating, where the* ions *can then move around to transfer charge. When stressed, ionic solids snap with* ease *as they are brittle.*

(b) **Salt, graphite, diamond, wax, silicon carbide, covalent, calcite, free, captured, silicon dioxide, calcium carbide lattice, nitrogen triiodide, sulfur., two, three, good, bad, weak, rigid, low, high.**
The 3 network solids in the list above are: graphite, diamond, *and* silicon carbide
These compounds are held together in two *dimensions by strong* covalent *bonds. This makes them very* rigid *and* bad *conductors, with* high *melting points.*
The reason that graphite is slippery and conductive is because of the free *electrons from the carbon atoms, not used in covalent bonding. These form* weak *bonds between the molecular sheets of graphite molecules.*

2.

(a) Magnesium has the highest ionisation energy as it has a smaller shell and the valence electrons will be closer to the nucleus, giving a greater attraction.

(b) Chlorine would have the highest ionisation energy as it has a smaller shell and there are more protons in the nucleus giving a greater attraction.

3.

(a) 

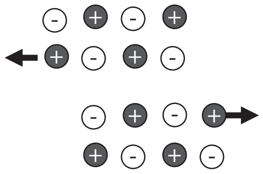
The bonding is ionic, where the two species are attracted by electrostatic forces.

(b) Ca^{2+} is isoelectronic with Argon. Cl^- is isoelectronic with Argon also.

(c) Ca^{2+} configuration is: 2, 8, 8 or $1s^2 2s^2 2p^6 3s^2 3p^6$.

4.

(a) When stressed the adjacent ions become repelled where + and + are side by side. This causes splitting of layers.



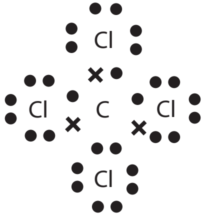
(b) Sodium is far too reactive to be recovered by electrolysis of an aqueous solution. Hydrogen only would be produced. With a molten solid, water is not present to react with the sodium and so it will be deposited on the cathode.

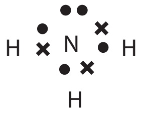
5.

(a) (i) Molecular: CO_2, SiO_2, CCl_4, NH_3.
(ii) Ionic: K_2SO_4, $Ca(OH)_2$
(iii) Covalent network: SiO_2.

(b) CO_2 would have the highest boiling point as it has a network structure. This means that the heat applied has to break strong covalent bonds, rather than just intermolecular forces. The lowest boiling point would be for the substance with the least intermolecular forces i.e. CO_2.

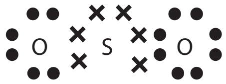
(c) SiO_2 

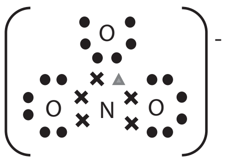
CCl_4 

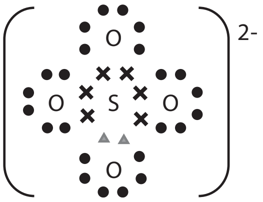
NH_3 

6.

(a) The bond (crosses) to the left of the sulfur atom is co-ordinate as the oxygen atom has supplied no electrons for the bond.



(b) 



7.

(a) XeF_6 xenon hexafluoride
(b) $SiCl_4$ silicon tetrachloride
(c) P_2O_5 diphosphorus pentoxide
(d) H_2O oxygen dihydride (water)
(e) $AsBr_3$ arsenic tribromide
(f) HClO Hypochlorous acid
(g) NH_4Cl ammonium chloride
(h) P_4O_{10} tetraphosphorus decaoxide
(i) OCl_2 oxygen dichloride
(j) CaH_2 calcium dihydride
(k) HCl hydrogen chloride
(l) NO nitrogen monoxide

8.

(a) ClF chlorine fluoride (M)
(b) MgS magnesium sulfide (I)
(c) Rb_2O rubidium oxide (I)
(d) ClBr chlorine fluoride
(e) As_2O_5 diarsenic pentoxide (M)

9.

(a) K_2CO_3 Potassium carbonate
(b) NH_4NO_2 Ammonium nitrite
(c) $Ca(OH)_2$ Calcium hydroxide
(d) $Al(HSO_4)_3$ Aluminium hydrogencarbonate
(e) $(NH_4)_2SO_4$ Ammonium sulfate
(f) $Ca_3(PO_4)_2$ calcium phosphate
(g) AgCN Silver cyanide
(h) $KClO_4$ potassium chloride
(i) $Fe_2(SO_4)_3$ Iron(III) sulfate
(j) K_2O_2 potassium peroxide

10.

(a) nitrogen dioxide NO_2
(b) dinitrogen monoxide N_2O_4
(c) barium peroxide BaO_2
(d) magnesium iodide MgI_2
(e) ammonium nitrite NH_4NO_3
(f) aluminium sulfide Al_2S_3
(g) caesium sulfite $CsSO_3$
(h) sulfur dioxide SO_2
(i) phosphorus pentachloride PCl_5
(j) sulfur hexafluoride SF_6
(k) xenon tetrafluoride XeF_4
(l) potassium acetate CH_3COOK
(m) beryllium bromide $BeBr_2$
(n) potassium dichromate $K_2Cr_2O_7$

Multiple-choice

1. a 2. d 3. c 4. a 5. b 6. b 7. d 8. a
9. c 10. b 11. d 12. a 13. a 14. c 15. a
16. d 17. d 18. c 19. a 20. d 21. b 22. c
23. c 24. b 25. d 26. d 27. d 28. b 29. d
30. c 31. b 32. c 33. a 34. a 35. c

Chapter 4. Organic Chemistry

Multiple-choice

1. c 2. c 3. a 4. c 5. b 6. b 7. d 8. a
9. d 10. d 11. b 12. c 13. d 14. c 15. b
16. a 17. c 18. b 19. b 20. a 21. c 22. b
23. c 24. c 25. d 26. d 27. a 28. b
29. c 30. b

Longer questions

1.

(a) $CH_3CH_2CH_2CH_3$
Saturated *Butane*

(b) $CH_2CHCH_2CH_3$
Unsaturated *But-1-ene*

(c) $CH_3CH_2CH(CH_3)CH_2CH_3$
Unsaturated *3-methyl pentane*

(d) $CH_3CH_2CH_2C(CH_3)C(CH_3)CH_2CH_3$
Saturated *3,4-dimethyl hex-3-ene*

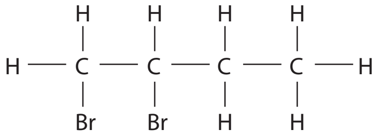
2.

(a) Hexane
(b) e.g. methyl pentane, 2,3-dimetyl butane
(c) Pentane
(d) e.g.2,2-dimethyl propane
(e) Octane would have the higher BP as it has higher dispersion forces due to its larger molar mass (more electrons in the molecule)

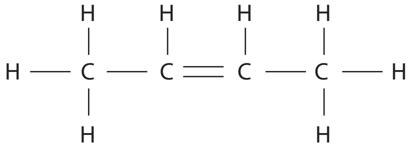
3.

(a) *(i) 3-methylhexane*
(ii) 1-bromobut-2-ene
(iii) 4-bromo-3-chloro-3-fluorohex-1-ene
(iv) 1-bromo-4-chloro-2-ethylbenzene
(v) cis 2,3-dichloropent-2-ene
(vi) trans 2,3-dichloropent-2-ene

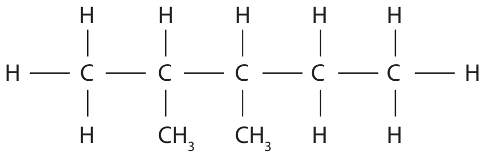
(b) (i)



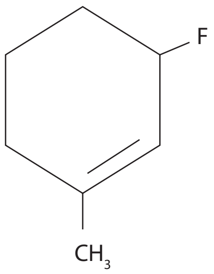
(ii)



(iii)



(iv)



4.

(a) $CH_3(CH_2)_2CH(CH_3)CH_2CH(CH_3)_2$
1,3-dimethylheptane

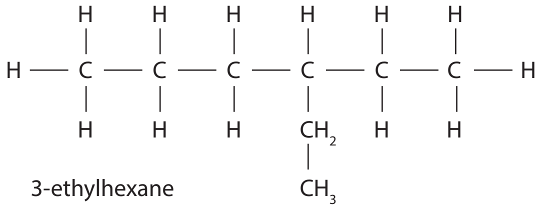
(b) $CH_3CH_2C(CH_3)_2(CH_2)_2CH_3$
3,3-dimethylhexane

(c) $CH_2CHC(CH_3)_2CH_3$
3,3-dimethybut-1-ene

(d) $CH_3CH(CH_3)(CH_3)_4CH(CH_3)_2$
2,7-dimethyloctane

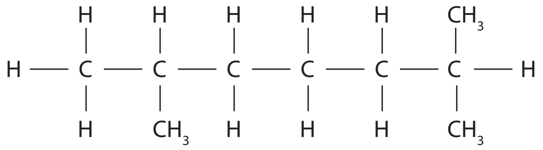
5.

(a)



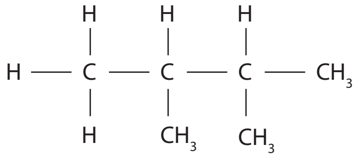
3-ethylhexane

(b)



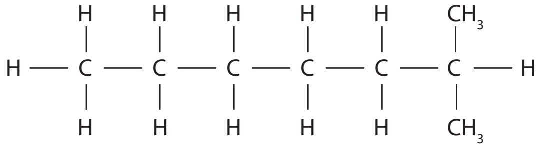
1,6-dimethylheptane

(c)



1,2-dimethylbutane

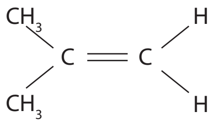
(d)



2-dimethylheptane

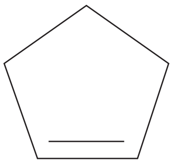
6.

(a)



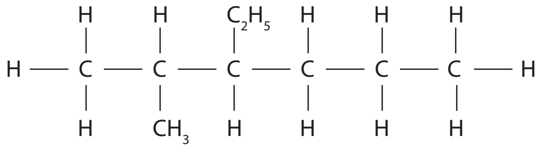
Aliphatic

(b)



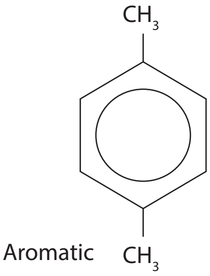
Alicyclic

(c)



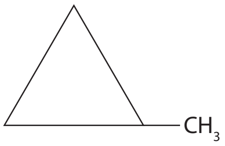
Aliphatic

(d)

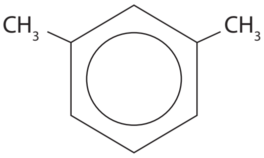


7.

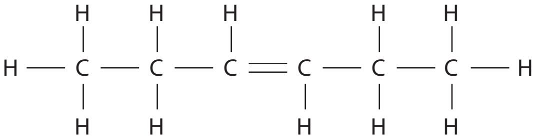
(a)



(b)

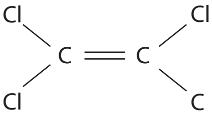


(c)



$H-C-C-C=C-C-C-H$

(d)

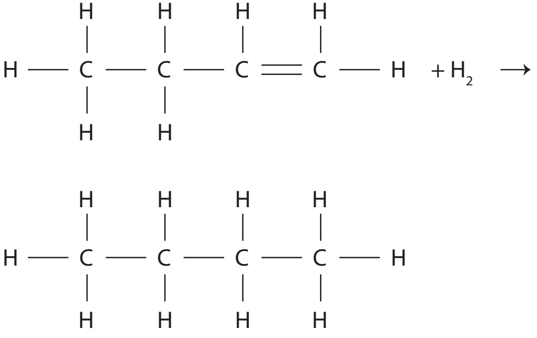


8.

(a) $C_2H_4(g) + 2O_2(g) \rightarrow 2CO(g) + 2H_2O(g)$

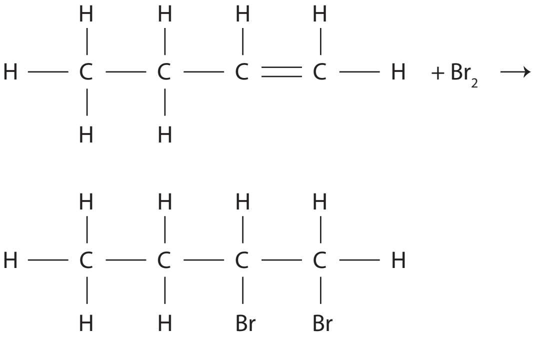
(b) $C_2H_6\,(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$
Chloroethane is the product: CH_3CH_2Cl.

(c) *(i) React the but-1-ene with hydrogen*



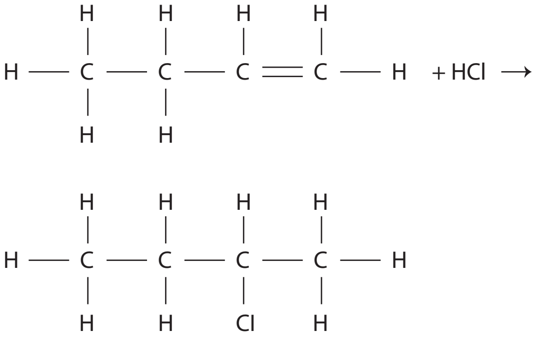
$H-C-C-C=C-H + H_2 \rightarrow H-C-C-C-C-H$

(ii) React the but-1-ene with bromine



$H-C-C-C=C-H + Br_2 \rightarrow H-C-C-C-C-H$

(iii) React the but-1-ene with hydrogen chloride



$H-C-C-C=C-H + HCl \rightarrow H-C-C-C-C-H$

(Note: The H of the HCl always attaches to the carbon with the most H's on it)

Chapter 5.
Moles

Multiple choice

1. d 2. a 3. c 4. d 5. c 6. a 7. d 8. c
9. a. 10. b 11. c 12. d 13. d 14. c 15. b.

Longer questions

1.
(a) Nitrogen dioxide 46.01 g mol^{-1}
(b) Xenon tetrafluoride 207.3 g mol^{-1}
(c) Nitric acid 63.018 g mol^{-1}

2.
(a) Diammonium sulfide 68.154 g mol^{-1}
(b) Barium dihydride 139.316 g mol^{-1}
(c) Potassium monohydrogen phosphate 174.178 g mol^{-1}
(d) Potassium permanganate 158.04 g mol^{-1}
(e) Potassium dichromate 294.2 g mol^{-1}

3.
(a) $AuCl_3\ M_r = 197 + 3 \times 35.45 = 303.35\ g\ mol^{-1}$
$m = nM_r = 1.75 \times 10^{-6} \times 303.35 = 5.31 \times 10^{-4}\ g$
(b) $K_3PO_4\ M_r = 212.27\ g\ mol^{-1}$
$m = nM_r = 2.98 \times 10^{-3} \times 212.27 = 0.633\ g$
(c) $NH_3\ M_r = 17.034\ g\ mol^{-1}$
$m = nM_r = 6.55 \times 17.034 = 112\ g$

4.
(a) $CO_2\ M_r = 44.01\ g\ mol^{-1}$
$m = nM_r = 1.27 \times 10^{-3} \times 44.01 = 0.0559\ g$
(b) $AuBr_3\ M_r = 197 + 3 \times 79.9 = 436.7\ g\ mol^{-1}$
$m = nM_r = 9.31 \times 10^{-4} \times 436.7 = 0.407\ g$
(c) $CuSO_4\ M_r = 63.55 + 32.07 + 64 = 159.62\ g\ mol^{-1}$
$m = nM_r = 62.7 \times 159.62 = 10.0\ g$

5.
(a) $Hg\ M_r = 200.6\ g\ mol^{-1}$
$m = nM_r = 0.000305 \times 200.6 = 0.0612\ g$
(b) $P\ M_r = 30.97\ g\ mol^{-1}$
$m = nM_r = 10.5 \times 30.97 = 325\ g$
(c) $Li\ M_r = 6.968\ g\ mol^{-1}$
$m = nM_r = 125 \times 6.968 = 871\ g$

6.

(a) Ag $n = \frac{280.9 \times 10^{-3}}{107.9} = 2.60$ mol

(b) Ni $n = \frac{5.869}{58.69} = 0.1.0$ mol

(c) Li $n = \frac{3.251}{6.968} = 0.467$ mol

7.

(a) $n(HBr) = \frac{92.4}{(1.008 + 79.90)} = 1.14$ mol

(b) $n(H_2SO_4) = \frac{2210}{(2 \times 1.008 + 32.07 + 64)}$
$= 22.5$ mol

(c) $n(Alcl_3) = \frac{2.89}{(26.98 + 3 \times 35.45)} = 0.0217$ mol

8.

(a) $M_r(NaH_2PO_4) = 119.976$
$n = \frac{4.26 \times 10^{-3}}{119.976} = 3.55 \times 10^{-5}$ mol

(b) $n(Fe) = \frac{151000}{55.85}$ 2703 mol

(c) $n(Al) = \frac{1.26 \times 10^{4}}{26.98}$ 467 mol

9.

(a) $M_r(Na_2SO_3) = (2 \times 22.99 + 32.07 + 48)$
$= 126.05$ g mol^{-1}
$n = \frac{2.01}{126.05} = 0.0159$ mol

(b) $M_r(Na_2S_2O_3) = (2 \times 22.99 + 2 \times 32.07 + 48)$
$= 158.12$ g mol^{-1}
$n = \frac{2.01}{158.12} = 0.0127$ mol

(c) $M_r[(NH_4)_2\ S] = (2 \times 14.01 + 8 \times 1.008$
$+ 32.07) = 68.154$ g mol^{-1}
$n = \frac{6.31}{68.154} = 0.0926$ mol

(d) $M_r[(Ca_3\,(PO_4)] = (3 \times 40.08 + 2 \times 30.97$
$+ 8 \times 16) = 310.18$ g mol^{-1}
$n = \frac{7.63}{310.18} = 0.0246$ mol

10.

(a) $M_r[(NH_4)_2CO_3] = (2 \times 14.01 + 8 \times 1.008$
$+ 12.01 + 48) = 96.094$ g mol^{-1}
$n[(NH_4)_2CO_3] = \frac{451}{96.094} = 4.69$ mol
8 H atoms per molecule so $n(H) = 8 \times 4.69$
$= 37.5$ mol

(b) $n(H_2SO_4) = \frac{6.25 \times 10^{-3}}{(2 \times 1.008 + 32.07 + 64)}$
$= 6.37 \times 10^{-5}$ mol
2 H atoms per molecule so $n(H) = 2 \times 6.37$
$\times 10^{-5} = 1.27 \times 10^{-4}$ mol.

(c) $n(H_2O) = \frac{0.824}{18.016} = 0.0457$ mol
2 H atoms per molecule so $n(H)$
$= 2 \times 0.0457 = 0.0915$ mol

(d) $n(NH_3) = \frac{2.71}{(14.01 + 3 \times 1.008)} = 0.159$ mol
3 H atoms per molecule so $n(H) = 3 \times 0.159$
$= 0.477$ mol.

11. N° of particles in 1 mole $= 6.022 \times 10^{23}$.

(a) $N°(CO) = 6.37 \times 6.022 \times 10^{23} = 3.84 \times 10^{24}$
molecules.

(b) $n(H_2O) = \frac{2.62 \times 10^{-6}}{18.016} = 1.454 \times 10^{-7}$ mol
$N°(H_2O) = 1.454 \times 10^{-7} \times 6.022 \times 10^{23}$
$= 8.76 \times 10^{16}$ molecules.

(c) $n(C_6H_6) = \frac{5.23}{(6 \times 12.01 + 6 \times 1.008)}$
$= 0.0670$ mol
$N°(C_6H_6) = 0.067 \times 6.022 \times 10^{23} = 4.03$
$\times 10^{22}$ molecules.

12.

(a) $N°(C_{12}H_{22}O_{22}) = 2.26 \times 6.022 \times 10^{23} = 1.36$
$\times 10^{24}$ molecules $\times 12 = 1.63 \times 10^{25}$ C atoms.

(b) $n(C_6H_6) = \frac{0.000221}{(6 \times 12.01 + 6 \times 1.008)} = 2.83$
$\times 10^{-6}$ mol
$N°(C_6H_6) = 2.83 \times 10^{-6} \times 6.022 \times 10^{23}$
$= 1.70 \times 10^{18}$ molecules $\times 6 = 1.02 \times 10^{19}$ C
atoms

(c) $n(CO_2) = \frac{4.21}{(2 \times 12.01 + 2 \times 1.008)}$
$= 0.162$ mol
$N°(CO_2) = 0.162 \times 6.022 \times 10^{23} = 9.74$
$\times 10^{22}$ molecules $\times 1 = 9.74 \times 10^{22}$ C atoms.

(d) $M_r(C_2H_2) = 26.036$. $n(C_2H_2)$ $4.21/26.036 =$
0.1617 molecules $\times 2 = 0.323$ C atoms

13.

(a) $n[Al(NO_3)_3]$
$= \frac{155}{(26.98 + \times 3 \times 14.01 + 9 \times 16)}$
$= 0.0728$ mol

(b) $n(B_2H_6) = \frac{1}{(2 \times 10.82 + 6 \times 1.008)}$
$= 0.0361$ mol

(c) $n(ICl_5) = \frac{250 \times 10^{-3}}{(126.9 + 5 \times 35.45)} = 8.22$
$\times 10^{-4}$ mol

(d) $n(C_6H_{12}O_6) = \frac{3.45 \times 10^{25}}{6.022 \times 10^{23}} = 57.3$ mol

(e) $n(Na_2CO_3) = \frac{9.76 \times 10^{13}}{6.022 \times 10^{23}} = 1.62$
$\times 10^{-10}$ mol.

14.

(a) $m(Li) = 2780000 \times 6.968 \times 1.667 \times 10^{-24}$
$= 3.23 \times 10^{-17}$ g

(b) $m(Na) = 5 \times 10^{25} \times 22.99 \times 1.667 \times 10^{-24}$
$= 1920$ g

(c) $m(Cd) = 6.022 \times 10^{23} \times 112.4 \times 1.667$
$\times 10^{-24} = 113$ g.

15.

(a) $n(As) = \frac{749.2}{74.92} = 10.0$ mol $\times 6.022 \times 10^{23}$
$= 6.022 \times 10^{24}$ atoms

(b) $n(Al) = \frac{2698}{26.98} = 10.0$ mol $\times 6.022 \times 10^{23}$
$= 6.022 \times 10^{25}$ atoms.

16.

(a) $\%H = \frac{3 \times 1.008}{(3 \times 1.008 + 30.97 + 64)} \times 100$
$= 3.09\%$

(b) $\%N = \dfrac{14.01}{(14.01 + 2 \times 12.01 + 2 \times 14.01)} \times 100$
$= 26.2\%$

(c) $\%Ca = \dfrac{40.08}{(40.08 + 4 \times 1.008 + 35.45)} \times 100$
$= 43.5\%$

(d) $\%K = \dfrac{2 \times 39.1}{(2 \times 39.1n + 32.07 + 64)} \times 100$
$= 44.9\%$

17.

	Mg	N	O
% of element	16.39	18.89	64.72
Mass (g) in 100g	16.39	18.89	64.72
Molar mass (g/mol)	24.31	14.01	16
No. of moles	0.6842	1.348	4.045
Divide by smallest	1	1.97	5.91
Simplest ratio	1	2	6

E.F. is $MgN_2O_6 \rightarrow Mg(NO_3)_2$

18.

	P	H	O
% of element	31.60	3.09	65.31
Mass (g) in 100g	31.60	3.09	65.31
Molar mass (g/mol)	30.97	1.008	16
No. of moles	1.020	3.065	4.082
Divide by smallest	1	3.03	4.00
Simplest ratio	1	3	4

E.F. is $PH_3O_4 \rightarrow H_3PO_4$

19.

	Co	SO_4
% of element	38.02	61.98
Mass (g) in 100g	38.02	61.98
Molar mass g mol^{-1}	58.93	32.07 + 64 = 96.07
No. of moles	0.6451	0.6451
Divide by smallest	1	1
Simplest ratio	1	1

E.F is $CoSO_4$

20.

	Na	C	N
% of element	46.91	24.51	28.59
Mass (g) in 100g	46.91	24.51	28.59
Molar mass (g/mol)	22.99	12.01	14.01
No. of moles	2.041	2.041	2.041
Divide by smallest	1	1	1
Simplest ratio	1	1	1

E.F. is NaCN.
E.F. mass = 22.99 + 12.01 + 14.01 = 49.01
$M_r \approx 50$ so E.F. = M.F.

21. E.F. mass of CH is 12.01 + 1.008 = 13.018.
$\dfrac{78}{13.018} = 5.99$ so M.F. = CH × 6 = C_6H_6.

22. $m(O) = 0.7221 - (0.299 + 0.05849 + 0.2318)$
$= 0.13281$

	C	H	N	O
Mass (g)	0.2990	0.05849	0.2318	0.13281
Molar mass g mol^{-1}	12.01	1.008	14.01	16
No. of moles	0.02489	0.0580	0.01654	0.00830
Divide by smallest	2.99	6.99	1.99	1
Simplest ratio	3	7	2	1

E.F. is $C_3H_7N_2O$

23.

	Ba	Cl
% of element	65.95	34.05
Mass (g) in 100g	65.95	34.05
Molar mass g mol^{-1}	137.3	35.45
No. of moles	0.4803	0.9605
Divide by smallest	1	1.99
Simplest ratio	1	2

E.F. is $BaCl_2$

24. Mass of oxygen = 4.30 – 3.99 = 0.31 g

	Hg	O
Mass (g)	4.01	0.31
Molar mass g mol^{-1}	200.6	16
No. of moles	0.0200	0.0194
Divide by smallest	1	1
Simplest ratio	1	1

E.F. is HgO

25. $n(Al) = \dfrac{10}{26.98} = 0.371 \text{ mol}$

26. $n(Si) = \dfrac{5.68 \times 10^{-3}}{28.09} = 2.022 \times 10^{-4} \text{ mol}$
$\times 6.022 \times 10^{2} = 1.22 \times 10^{20}$ atoms.

27. $n(Co) = \dfrac{5.00 \times 10^{20}}{6.022 \times 10^{23}} = 8.30 \times 10^{-4} \text{ mol}$
$\times 58.93 = 4.89 \times 10^{-2}$ g.

28.

(a) $M_r = 10 \times 12.01 + 6 \times 1.008 + 6 \times 16.0$
$= 174.16 \text{ g mol}^{-1}$

(b) Number of moles $= \dfrac{1.56 \times 10^{-2}}{174.16} = 8.96$
$\times 10^{-5}$ mol.

29. M_r of isopentyl acetate is = (84.08 + 14.11 + 32.0) = 130.2 g mol^{-1}
The number of moles in 1 μg = $(1.00 \times 10^{-6}$
$= \dfrac{1 \times 10^{-6}}{130.2} = 7.68 \times 10^{-9}$ mol
No of molecules = $7.68 \times 10^{-9} \times 6.022 \times 10^{23}$
$= 4.63 \times 10^{15}$.
Each mole contains 7 atoms of carbon so
N°(C) = $7 \times 4.63 \times 10^{15} = 3.24 \times 10^{16}$.

30. M_r of penicillin $= 14 \times 12.01 + 20 \times 1.008 + 2 \times 14.01 + 32.07 + 64 = 313.238\ g\ mol^{-1}$

$$\%\ C = \frac{14 \times 12.01}{313.238} \times 100 = 53.7\%$$

$$\%\ H = \frac{20 \times 1.008}{313.238} \times 100 = 6.44\%$$

$$\%\ N = \frac{2 \times 14.01}{313.238} \times 100 = 8.95\%$$

$$\%\ S = \frac{32.07}{313.238} \times 100 = 10.2\%$$

$$\%\ O = \frac{64}{313.238} \times 100 = 20.4\%$$

31.

	C	H	Cl
% of element	24.27	4.07	71.65
Mass (g) in 100g	24.27	4.07	71.65
Molar mass g mol^{-1}	12.01	1.008	35.45
No. of moles	2.021	4.038	2.021
Divide by smallest	1	1.99	1
Simplest ratio	1	2	1

E.F. is CH_2Cl E.F. mass = 49.476

$\frac{98.96}{49.476} = 2.00$ so M.F. $= CH_2Cl \times 2 = C_2H_4Cl_2$

32.

	C	H	N	O
% of element	49.48	5.12	28.87	16.49
Mass (g) in 100g	49.48	5.12	28.87	16.49
Molar mass g mol^{-1}	12.01	1.008	14.01	16
No. of moles	4.120	5.079	2.061	1.03
Divide by smallest	4.00	4.93	1.99	1
Simplest ratio	4	5	2	1

E.F. $= C_4H_5N_2O$

E.F. mass $= 4 \times 12.01 + 5 \times 1.008 + 2 \times 14.01 + 16 = 97.10\ g\ mol^{-1}$

$\frac{194.2}{97.10} = 2.00$ so M.F. $= C_4H_5N_2O \times 2 = C_8H_{10}N_4O_2$

33. Ratio of HNO_3: Na_2CO_3 is 2: 1 so $n(HNO_3) = 2 \times n(Na_2CO_3) = 2 \times 0.6 = 0.12$ mol.

34. Ratio of NaCl: $AgNO_3$ is 1: 1 so $n(NaCl) = n(AgNO_3) = 10$ mol.
$m(NaCl) = 10 \times (22.99 + 35.45)$ 584 g.

35. $n[(NH_4)_2SO_4]$

$$= \frac{60.0}{(2 \times 14.01 + 8 \times 1.008 + 32.07 + 4 \times 16)}$$

$= 0.4540$ mol

$n(H_2SO_4) = n(NH_4)_2SO_4 = 0.4540$

$m(H_2SO_4) = nM_r = 0.4540 \times (2 \times 1.008 + 32.07 + 4 \times 16) = 44.5$ g.

36. $n(KI) = \frac{7.50}{(39.1 + 126.9)} = 0.04518$ mol

$n(PbI_2) = ½\ n(KI) = 0.02260$ mol

$m(PbI_2) = 0.02260 \times (207.2 + 2 \times 126.9) = 1190$ g.

Chapter 6. Thermochemistry

Multiple-choice

1. c 2. b 3. b 4. a 5. a 6. d 7. c 8. d
9. c 10. a 11. b 12. c 13. d 14. a 15. c
16. c 17. a 18. c 19. d 20. a

Longer Questions

1.

(i) Mass of fuel burned
= 127.65 - 127.31 0.34 g

(ii) Temperature rise of water (ΔT)
= 47.9 - 14.6 33.3°C

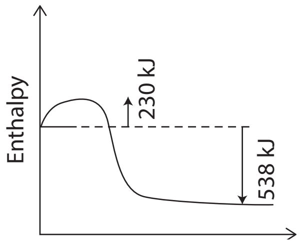
(iii) Heat needed ($m \times 4.2 \times \Delta T$)
= 98.76 × 4.2 × 33.3 13,813 J

(iv) Heat/mass of fuel burned
= 13,813/0.34 40,625 J /g

Change this figure into MJ/kg
= 40,625/1000 40.6 MJ/kg

2.

(a)



(b) Exothermic

3.

(a) Molar mass of $CO_2 = 44.01$ $\Delta H = 889$ kJ mol^{-1} so for 1 gram $H = \frac{889}{44.01} = 20.2\ kJ\ g^{-1}$

(b) 80 grams would give out 80 × 20.2 kJ of heat = 1.62 MJ.

4.

(a) the solution would get warmer as the reaction is exothermic.

(b) 5 × 82 kJ = 410 kJ released.

(c) $H = m \times c\ \Delta T$ so $410{,}000 = 3500 \times 4.2 \times \Delta T$
Temperature rise = 27.9°C

5.

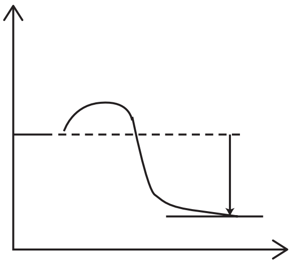
(a) $CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(l) + 165\ kJ\ mol^{-1}$

(b) No of moles $= \frac{1.78 \times 10^6}{165 \times 10^3} = 1079$ mol.

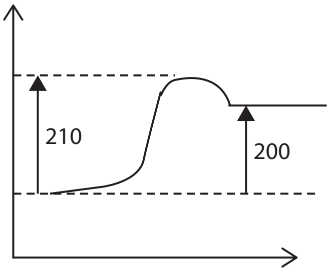
6.

(a) Petrol is vaporised in the carburettor of an engine. As the reactant is now subdivided there is a greater area of contact for the oxygen to react with the petrol molecules which gives a much faster reaction (explosion)

(b) The match provides the activation energy to start the reaction and the heat output then provides enough energy for subsequent reactions (chain reaction).



(c)



7.

(a) *Although the liquid is below its Boiling Point there will be some of the molecules with enough energy to escape due to the Maxwell-Boltzmann distribution. With the cap on, the gaseous molecules can no longer escape and can bombard the surface of the liquid and return to the liquid state. There will be an equilibrium state where the number of molecules leaving the surface = the number returning and so the amount of vapour will become constant.*

(b) *For sugar to dissolve the water molecules must strike its surface. In warm tea the water molecules are bombarding the sugar surface quicker and so the rate of dissolving will be greater.*

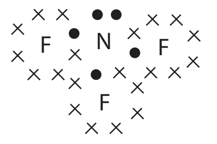
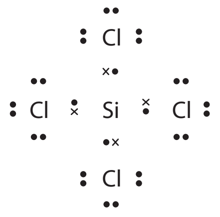
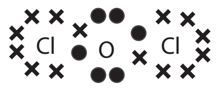
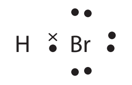
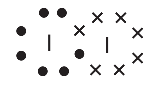
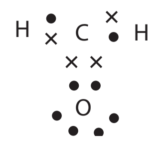
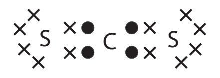
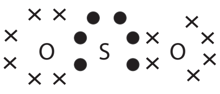
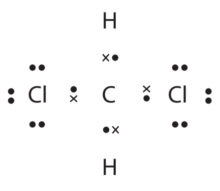
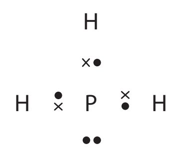
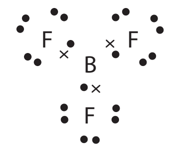
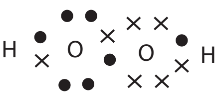
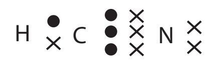
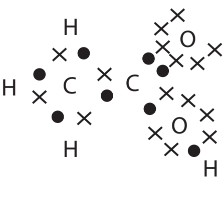
(c) *To start with the number of sugar molecules dissolving will be greater than the number returning to the solid. After a certain time there will be an equilibrium state where the number of molecules leaving the surface = the number returning and so the amount of sugar in the solution will become constant. At this point the solution is said to be saturated.*

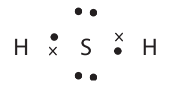
Chapter 7.
Shapes and Intermolecular Forces

Set 1

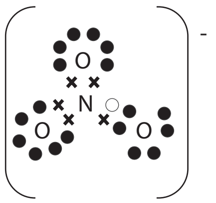
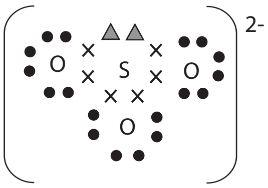
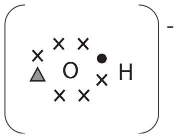
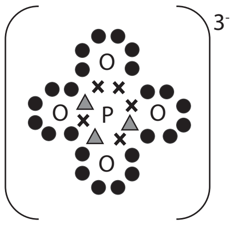
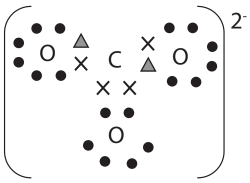
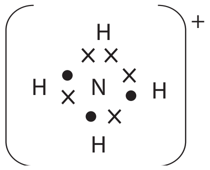
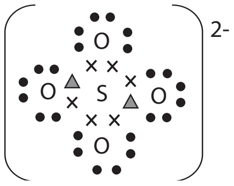
1.
- *(a)* *ionic*
- *(b)* *covalent molecular*
- *(c)* *covalent molecular*
- *(d)* *ionic*
- *(e)* *covalent molecular*
- *(f)* *covalent molecular*
- *(g)* *covalent molecular*

2. $HCl, NO_2, CCl_4, H_2O, CO_2$

	3.	*4.*	*5.*
(a)		Pyramidal	Polar
(b)		Tetrahedral	Non-polar
(c)		V-shaped or bent	Polar
(d)		Linear	Polar
(e)		Linear	Non-polar
(f)		Triangular or trigonal planar	Polar
(g)		Linear	Non-polar
(h)		V-shaped or bent	Polar
(i)		Tetrahedral	Polar
(j)		Pyramidal	Polar
(k)		Triangular or trigonal planar	Non-polar
(l)		V-shaped or bent around both O	Polar
(m)		Linear	Polar
(n)		Tetrahedral around first C, V-shaped or bent around bottom O, Triangular or trigonal planar around top O	Polar

(o)		V-shaped or bent	Polar

6.

(a)		Trigonal planar
(b)		Pyramidal
(c)		Linear
(d)		Tetrahedral
(e)		Trigonal planar
(f)		Tetrahedral
(g)		Tetrahedral
(h)		Linear

7.

(a) *tetrahedral – 109.5°*
(b) *V-shaped or bent – 104.5°*
(c) *linear – 180°*
(d) *pyramidal – 107°*
(e) *trigonal planar – 120°*

8. *pyramidal & V-shaped or bent*

Set 2

1.

(a) *dispersion forces*
(b) *dipole-dipole interactions*
(c) *hydrogen bonding*
(d) *dipole-dipole interactions*
(e) *dipole-dipole interactions*
(f) *dispersion forces*
(g) *dipole-dipole interactions*
(h) *hydrogen bonding*
(i) *dispersion forces*
(j) *dispersion forces*
(k) *hydrogen bonding*
(l) *dispersion forces*
(m) *dispersion forces*

2. *Dispersion forces are the weakest attractive intermolecular forces. They result from the uneven distribution of electrons in atoms of noble gases and covalent molecules. At any instant one side of a molecule or noble gas may have more electrons than the other. This will give rise to a temporary polarity, or dipole. When an atom or molecule with a temporary dipole comes near another atom or molecule, it influences and induces a dipole in that atom or molecule. The partially negative end of one repels the electrons in the other, inducing a dipole in it. The two dipoles interact with each other and attraction results.*

3. *Hydrogen bonding is a much stronger type of dipole-dipole interaction. It occurs between hydrogen atoms directly bonded to a fluorine, oxygen or nitrogen atom on one molecule and a non-bonding electron pair on a fluorine, oxygen or nitrogen on another molecule. Bonds between hydrogen and the three most electronegative elements are very polar and so this influences properties such as melting and boiling point.*

4. *Ammonia exhibits hydrogen bonding whereas the other group 15 hydrides have the weaker dipole-dipole interactions.*

5. *All of the group 14 hydrides are non-polar and so only have dispersion forces. Dispersion forces increase with increasing molar mass and increasing numbers of electrons. As you move from $CH_4 \rightarrow SiH_4 \rightarrow GeH_4 \rightarrow SnH_4$ their molar masses and numbers of electrons increases and so dispersion forces become greater which means more heat is needed to overcome these forces.*

6.

(a) H_2O: *Hydrogen bonding*
HF: *Dipole-dipole interactions*
HBr: *Dipole-dipole interactions*
F_2: *Dispersion forces*
I_2: *Dispersion forces*

(b) *Water has hydrogen bonding between molecules whereas hydrogen fluoride has the weaker dipole-dipole interactions, so water has the highest boiling point of the two.*

(c) *Hydrogen fluoride has hydrogen bonding between molecules, whereas hydrogen bromide has the weaker dipole-dipole interactions, so hydrogen fluoride has the highest boiling point of the two.*

(d) *Hydrogen bromide has dipole-dipole interactions whereas fluorine only has weak dispersion forces, so hydrogen bromide has the highest boiling point of the two.*

(e) *Iodine has quite large dispersion forces due its very high molar mass which exceeds the hydrogen - bonding forces.*

7. *Iodine, bromine and chlorine are all non-polar molecules and so only have dispersion forces. Dispersion forces increase with increasing molar mass. Iodine has the highest molar mass (253.8 gmol^{-1}), followed by bromine (159.8 gmol^{-1}) and then chlorine (79.90 gmol^{-1}). More heat energy is required to break stronger dispersion forces.*

8.

(a) *Nitrogen - dispersion forces*
Hydrogen - dispersion forces
Ammonia - hydrogen bonding

(b) *Ammonia has hydrogen bonding whereas nitrogen and hydrogen have only weak dispersion forces. As its boiling point is much higher it condenses at lower temperatures.*

Chapter 8. Chromatography

Set 1

1. *Chromatography is used to separate mixtures of substances into their COMPONENTS and to detect them within a mixture. All methods of chromatography work on the same principle. They all have a STATIONARY phase which is typically a solid or a liquid supported on a solid, and a moving or MOBILE phase which is a liquid or a GAS. The mobile phase flows through the stationary phase, carrying the components of the mixture with it. Components move through the stationary phase and are separated out based on their POLARITY.*

The distance that a component moves through the stationary phase depends upon its ability to form INTERMOLECULAR bonds with the material of the stationary phase and/or the mobile phase.

As the mixture moves through the stationary phase there are two processes occurring. Adsorption is where components from a mixture ADHERE to (bond with) the STATIONARY phase and DESORPTION where the components dissolve into (bond with) the MOBILE phase.

The rate of movement of any component depends upon how well it adsorbs onto the stationary phase and how well it dissolves into the mobile phase.

Different components travel at different RATES through the stationary phase, depending upon the POLARITY of the components in the mixture and the polarities of the stationary and mobile phases.

2. *Qualitative analysis can identify what substances are present whereas quantitative analysis can determine the relative amounts of substances that are present.*

3. *Paper chromatography and thin layer chromatography are purely qualitative.*

4. *In paper chromatography the mobile phase utilises capillary action to move up through the stationary phase, whereas in column chromatography the mobile phase moves down through the stationary phase via gravity.*

5.

	Stationary phase	Mobile phase
Paper chromatography	Absorbent paper	Liquid solvent e.g. H_2O or ethanol
TLC	Silica gel or aluminium oxide	Liquid solvent e.g. H_2O or ethanol
Column chromatography	Silica gel or aluminium oxide	Liquid solvent e.g. H_2O or ethanol
HPLC	Polar silica beads when a non-polar mobile phase is used, or silica beads that have been coated so as to be non-polar when a polar mobile phase is used	Non-polar solvents like chloroform or hexane, or a mixture of polar solvents like H_2O or methanol
GC	Polar solid such as silica or alumina, or a porous solid coated with a non-polar high boiling point liquid hydrocarbon	Unreactive gas such as helium or nitrogen

6. *Gas chromatography coupled with a mass spectrometer as a detector (GC-MS) can be used for small samples. The long column in GC allows for very effective separation and the MS is highly sensitive.*

7. *Gas chromatography can't be used for analysing compounds that decompose on heating, as the sample is heated to vaporise it as it is injected into the column.*

8. *TLC is often carried out in a closed container. The space inside the container is saturated with solvent vapour to prevent the solvent from evaporating. It is important for good separation that the only process occurring in the chamber is the movement of the sample up the plate via capillary action, and not evaporation.*
9. *The retention factor is a value that can be assigned to each component in a sample once a chromatogram is developed. It is a ratio expressing how far the component moved from the origin relative to how far the solvent front moved.*

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}$$

10.
(a) *A was eluted first as it has the shortest retention time.*
(b) *C is the most polar as it had the longest retention time, staying on the polar stationary phase the longest.*

11. *B will have the greatest retention time as it is the least polar of the four substances and so will adsorb onto, or bond with, the non-polar stationary phase most effectively. The other three substances all contain polar functional groups (-OH and –NH_2) that can desorb into, or bond with, the mobile phase.*
12. *A, since it will have the same retention time but double the abundance, or quantity.*
13.
(a) *0.77, phenylalanine*
(b) *0.37, aspartic acid*

14.
(a) *The blue ink is a mixture of light blue and dark blue ink components.*
(b) *The mobile phase is the polar ethanol solvent.*
(c) *The light blue ink was most attracted to the stationary phase.*
(d) R_f *for light blue = 12.7/19.1 = 0.66*
R_f *for dark blue = 16.9/19.1 = 0.88*
(e) R_f *for X = 14.7/20.9 = 0.70*
R_f *for Y = 13.9/20.9 = 0.66*
R_f *for Z = 12.7/20.9 = 0.61*
So component Y is very likely present in the black ink as it has the same R_f.

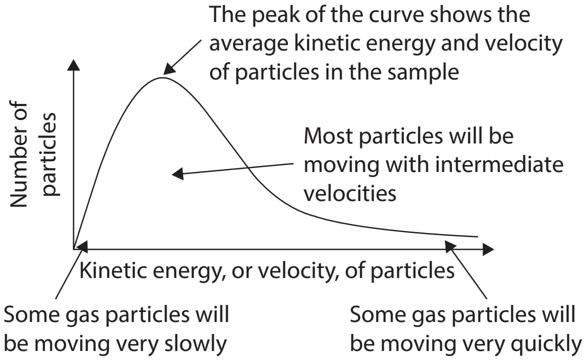
Chapter 9.
Kinetic Theory of Gases

Set 1

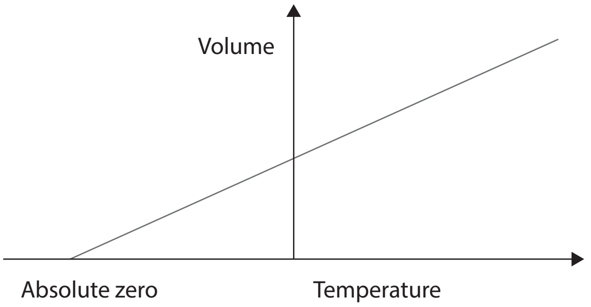
1.

- *Gases consist of particles called MOLECULES, except for the NOBLE GASES which consist of atoms.*
- *The average distance between the molecules of a gas is LARGE compared to the size of each molecule.*
- *The molecules of a gas move in RAPID, RANDOM straight line-motion. They collide with each other and the sides of their container.*
- *The molecules of a gas exert NEGLIGIBLE attractive or repulsive forces on one another.*
- *Collisions between gas molecules are perfectly ELASTIC. There is no overall energy loss during collisions.*
- *The average kinetic energy of the molecules INCREASES as the temperature of the gas increases.*

2.



3. *D, the total number of molecules present.*
4. *A*
5. *C Increasing the temperature of the gas.*
6.



7.
(a) *The area under both curves is the same, as it represents the same sample of oxygen gas with the same number of particles.*
The peak of each curve shows the average kinetic energy and average speeds of the particles. The peak for 1000 K corresponds to higher average speeds than the peak for 273 K since at the higher temperature the kinetic energy and speed of particles increases.
The peak of the curve for at 1000 K is lower than that of the curve for 273 K. This is because the area under the curve is the same for both but the curve at 1000 K represents a greater distribution and higher speeds so is more spread out along the horizontal axis.

b. The area under both curves is the same, as they represent equal moles of oxygen and hydrogen at 273 K.
The peak of the each curve shows the average kinetic energy and average speeds of the particles. Since they are at the same temperature the total kinetic energy of both samples is the same. The lighter of the two gases will have molecules of less mass and therefore must be moving quicker at the same temperature if the average kinetic energies are the same since $E_k = ½ mv^2$.
The peak of the curve for hydrogen is lower than that of the curve for oxygen at the same temperature. The area under the curve is the same for both but the curve for hydrogen represents a greater distribution and higher speeds so is more spread out along the horizontal axis.

8. P_1 = 110.0 kPa
V_1 = 50.5 L
P_2 = 130.0 kPa
V_2 = ?
$V_2 = P_1 \times V_1 / P_2$
= 110.0 × 50.5 / 130.0
= 42.7 L

9. V_1 = 0.0200 L
T_1 = 30.0°C = 303.15 K
V_2 = ?
T_2 = 15.0°C = 288.15 K
$V_2 = V_1 \times T_2 / T_1$
= 0.0200 × 288.15 / 303.15
= 0.0190 L

10. P_1 = 25.0 atm
T_1 = 20.0°C = 293.15 K
P_2 = ?
T_2 = 40.0°C = 313.15 K
$P_2 = P_1 \times T_2 / T_1$
= 25.0 × 313.15 / 293.15
= 26.7 atm

11. $n(CO_2) = PV/RT$
= 25.0 × 25.0 / 8.314 × 293.15
= 0.256 mol

12.
(a) $n(HCl) = PV/RT$
= 100.0 × 35.0 / 8.314 × (30.0 + 273.15)
= 1.39 mol
$n(HCl) = m/M$
$m(HCl) = n \times M$
$M(HCl)$ = 36.458 gmol^{-1}
= 1.39 × 36.458
= 50.6 g
(b) $P_2 = P_1 \times T_2 / T_1$
= 100.0 × 373.15 / 303.15
= 123.1 kPa

13.

	N_2	:	H_2
Stoichiometric ratio	1	:	3
Volume ratio	7.50	:	3.75

So limiting reagent is H_2
$V(NH_3) = 2/3 \times V(H_2)$
= 2.50 L
The answer is C.

14.
(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(b) $V(O_2) = ½ \times V(SO_2)$
= 25 kL
$V(SO_3) = 2/2 \times V(SO_2)$
= 50 kL

15. Intermolecular forces between particles in a real gas will result in attraction between particles and so the molar volume at STP will differ from 22.71 L. Hydrogen is a non-polar molecule with a low molar mass and has only very weak dispersion forces so its molar volume is very close to that of the ideal gas. Carbon dioxide is a larger non-polar molecule and so has stronger dispersion forces. This results in a smaller molar volume than hydrogen. Ammonia is a polar molecule and has strong hydrogen bonding and so its molar volume is even smaller.

16. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
$M(H_2O)$ = 18.016
$n(H_2O)$ = 145/18.016
= 8.048 mol
$n(H_2) = 2/2 \times n(H_2O)$
= 8.048 mol
$V(H_2) = n \times 22.71$
= 182.78 L
$n(O_2) = ½ \times n(H_2O)$
= 4.024 mol
$V(O_2) = n \times 22.71$
= 91.39 L

17. $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$
(a) $n(K)$ = 7.60 / 39.10
= 0.1943 mol
$n(H_2) = ½ \times n(K)$
= 0.09719 mol
$V(H_2) = n \times 22.71$
= 2.21 L
(b) $V(H_2) = nRT/P$
= 0.09719 × 8.314 × (25 + 273.15) / 108.0
= 2.23 L

18. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
(a) $n(CO) = PV/RT$
= 103.0 × 4.50 × 10^3 / 8.314 × 1773.15
= 31.44 mol
$n(Fe) = 2/3 \times n(CO)$
= 20.96 mol

$m(Fe) = n \times M$
$= 20.96 \times 55.85$
$= 1170$ g (3 s.f.)

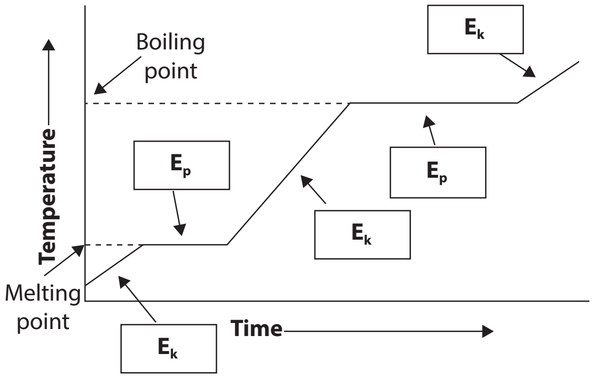
(b) Since $n(CO_2) = n(CO)$
$V(CO_2) = V(CO)$
$= 4.50$ kL

19. $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$
$n(H_2) = PV / RT$
$= 101.0 \times 13.2 / 8.314 \times (28.0 + 273.15)$
$= 0.532$ mol
$n(Fe) = n(H_2)$
$= 0.532$ mol
$m(Fe) = n \times M$
$= 0.532 \times 55.85$
$= 29.74$ g
$m(C) = 30.6 - 29.74$
$= 0.8610$
$\%C = (0.8610 / 30.6) \times 100$
$= 2.81\ \%$

20. $P(N_2) = 125.0 \times 10.0 / 35.0$
$= 35.71$ kPa
$P(O_2) = 250.0 \times 25.0 / 35.0$
$= 178.6$ kPa
Total pressure $= P(N_2) + P(O_2) = 214.3$ kPa

Set 2

1.



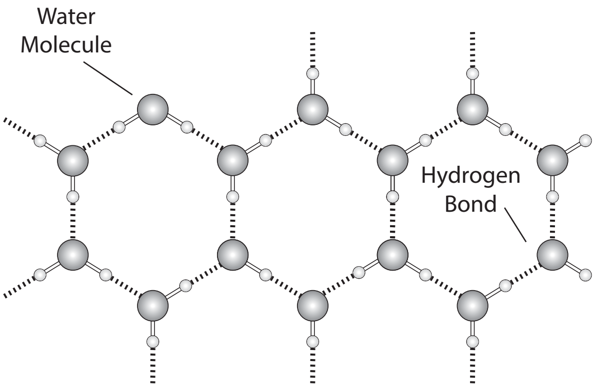
2. *The temperature remains constant during boiling because the energy added is being used to break bonds and increase potential energy rather than increase kinetic energy, or temperature.*
3. *Both steam and water will release energy equivalent to a 100°C burn, but steam, in addition, will also condense, releasing the latent heat of vaporisation to the skin.*
4. *The boiling point of a substance is the temperature at which it changes from a liquid to a gas at atmospheric pressure. For bubbles of gas to form they need to have an internal (vapour) pressure equal to atmospheric pressure. Evaporation is the change from liquid to gas at a temperature below the boiling point of that liquid. Unlike boiling, it occurs at the surface of a liquid. Particles with sufficient energy can escape into the air as some of the molecules are moving faster than the average.*
5. *In a glass of water below boiling point the particles have a wide range of velocities. Some near the surface will have enough energy and be moving in the right direction to break free from the liquid and escape into the air.*
6. *If the water warms up to room temperature more particles will have sufficient energy to turn from liquid to gas and the vapour pressure will increase. This evaporation would cause the level of liquid water to drop.*
7. *Melting is an endothermic process, as energy is required by the system to break bonds.*

Chapter 10.
Water and Aqueous Solutions

Set 1

1. *Water has relatively high melting and boiling points when compared to other covalent molecular compounds of similar molar mass due to the strong hydrogen bonding that must be overcome in order for it to change state from solid to liquid to gas. Most covalent molecular substances have only the weaker dipole-dipole or dispersion forces*
2.

(a)



(b) *As liquid water cools down it becomes denser, but when it begins to freeze it forms an open crystalline structure with each water molecule hydrogen bonded to four others. To enable this shape to form the molecules must move further apart than when they were liquid. They become less dense.*

3. *Capillary action is the ability of a liquid to flow in narrow spaces without the assistance of external forces. It occurs because the polar water molecules adhere to the walls of the tube at the edge and create an upward force on the water at the edges. Surface tension*

due to hydrogen bonding holds the surface together. Capillary action occurs when the adhesive force between the water molecules and the walls is greater than the bonding between the water molecules.

4. *The high specific heat capacity of water means that water takes longer to heat up and cool down than land. Sea breezes occur when the land heats up faster than the water in the daytime and this heats the air over the land more than the sea. This warmer air rises and cooler air from the sea moves in to take its place.*

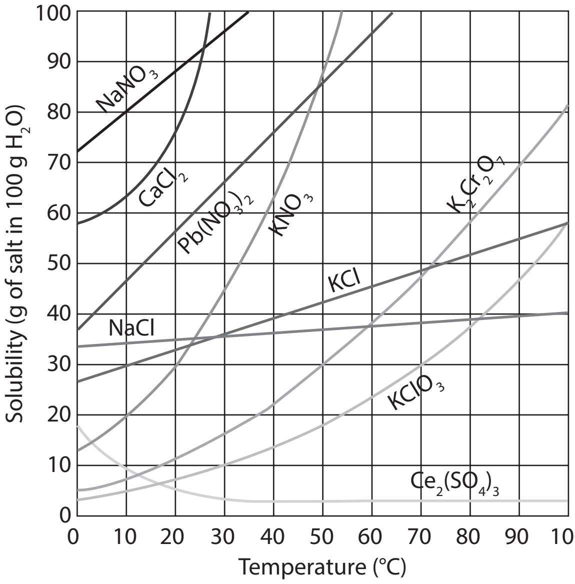
Set 2

1.

(a) *A* ***saturated solution*** *is a solution where no more solute will dissolve in a solvent at a particular temperature and pressure.*
An ***unsaturated solution*** *is a solution that contains less than the quantity needed to saturate it at a particular temperature and pressure.*
A ***supersaturated solution*** *is a solution that contains more than the quantity needed to saturate it at a particular temperature and pressure.*

(b) *Add some sodium chloride crystals to each of the solutions. If the crystals dissolve the solution is unsaturated. If they don't dissolve the solution is saturated. With the supersaturated solution, adding crystals will cause many crystals to precipitate out of solution.*

2.



(a) *~35 g*

(b) *~26 g*

(c) *Increasing the temperature increases the kinetic energy of all particles and this results in more collisions between sodium and nitrate ions, and the water solvent. The added kinetic energy of the sodium and nitrate ions enables them to more easily break free from the ionic bonding holding them together.*

(d) $Ce_2(SO_4)_3$

(e) *At 20°C approximately 57 g of potassium nitrate will dissolve in 100 g of water. To prepare a saturated solution one could add more than 57 g of potassium nitrate solid crystals to 100 g of water. Warm it gently and stir until all the crystals have dissolved. Then very carefully cool the solution back down to 20°C.*

(f) *80 – 66 = 14 g undissolved.*

(g) *solubility = 30 g in 100 g*
$n(K_2Cr_2O_7) = 30 / ((2 \times 39.10) + (2 \times 52) + (7 \times 16.00))$
$= 0.102$ mol
100 g water = 0.1 L
So solubility $= 0.102/0.1 = 1.02$ mol L^{-1}

3. *An increase in temperature decreases the solubility of a gas dissolved in a liquid. This is because the increased kinetic energy of dissolved gas molecules enables them to break free from the intermolecular forces that they have with the solvent.*

4. *Deep sea divers breathe gas that is at a higher pressure than at the surface and more nitrogen can dissolve in their blood at these pressures. As a diver ascends the pressure decreases so the nitrogen gas dissolved in their blood at higher pressure can now come out of solution in their blood and form bubbles at this lower pressure.*

5. *Methanol, sodium bromide, hydrogen chloride, sulfur dioxide*

6. *Ethanol and water are polar molecules, and both have hydrogen bonding as their predominant intermolecular force. Ethanol can dissolve in water because the hydrogen bonds that form between ethanol and water are similar in strength to those that need to break between ethanol molecules, and between water molecules. The energy given out when the new hydrogen bonds form is sufficient to break the hydrogen bonds between ethanol molecules, and between water molecules.*

7. *Acetone is a polar molecule and dipole-dipole interactions are its predominant intermolecular force. Water produces hydrogen bonding so they can form hydrogen bonds with each other. Acetone can dissolve in water because the hydrogen bonds that form between acetone and water are greater in strength to those that need to break between acetone molecules, and between water molecules. The energy given out*

when the new hydrogen bonds form between acetone and water molecules is sufficient to break the dipole-dipole interactions between acetone molecules, and the hydrogen bonds between water molecules.

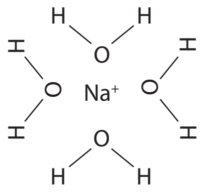
8. *Carbon tetrachloride and hexane are both non-polar molecules. Their predominant intermolecular forces are dispersion forces. Carbon tetrachloride can dissolve in hexane because the dispersion forces that form between them are similar in strength to those that need to break between carbon tetrachloride molecules, and between hexane molecules. The energy given out when the new dispersion forces form between carbon tetrachloride and hexane molecules is sufficient to break the dispersion forces between carbon tetrachloride molecules, and the dispersion forces between hexane molecules.*

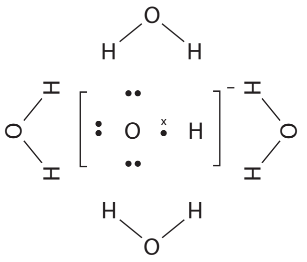
   The strongest bonds that can form between carbon tetrachloride and water molecules are dispersion forces, and these do not provide enough energy to break the hydrogen bonds between water molecules.

9. *For ionic substances to dissolve, ionic bonds between the positive cations and the negative anions need to break, and some hydrogen bonds between water molecules need to break. Ion-dipole forces between the ions and water molecules need to form. Ion-dipole forces are considered equivalent in strength to hydrogen bonds. The ion-dipole forces that form provide enough energy to overcome both the ionic bonding in the ionic lattice and the hydrogen bonding between water molecules, so the ionic substance dissolves.*

   Non-polar solvents cannot form ion-dipole bonds as they are not polar, and so not enough energy could be provided to break the ionic bonds.

10.





Set 3

1.

(a) *Both terms refer to a substance forming ions in solution. Dissociation is used for ionic substances that already contain ions. Ionisation is used for covalent molecular substances that do not already have ions as a molecule but produce ions in solution.*

(b) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
$HBr(g) \rightarrow H^+(aq) + Br^-(aq)$

2. *Strong electrolytes conduct well whereas weak electrolytes do not. Using a DC power source, electrodes and an ammeter one can test the acid's ability to conduct. A good conductor is potentially a strong electrolyte, a poor conductor is potentially a weak electrolyte.*

3.

	Strong/weak/non electrolyte	High/low/no conductivity
$C_6H_{12}O_6$	Non-electrolyte	No conductivity
LiBr	Strong electrolyte	High conductivity
H_2CO_3	Weak electrolyte	Low conductivity
$Ca(OH)_2$	Strong electrolyte	High conductivity
Br_2	Non-electrolyte	No conductivity
CH_3CH_2OH	Non-electrolyte	No conductivity
$Sr(NO_3)_2$	Strong electrolyte	High conductivity
HNO_3	Strong electrolyte	High conductivity

4. *$CrBr_3$ as it would contain the highest number of mobile charge carrying particles (0.4 moles of ions).*

5. *At high altitudes the atmospheric pressure is lower, so the vapour pressure within bubbles doesn't need to be as high for them to form and the boiling point is easier to achieve, at a lower temperature.*

   The boiling point will be elevated when salt is added because the dissolved ions result in a lower vapour pressure and therefore the water will need to be heated to a higher temperature in order for the vapour pressure to become equal to the atmospheric pressure and boil.

6. *(A) Ether, chloroform, ethanol.*

Set 4

1.

(a) *Total dissolved solids are anions and cations dissolved in water e.g Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{3+}, HCO_3^-, Cl^- and SO_4^{2-}, NO_3^- and PO_4^{3-} and also soluble organic matter. The TDS is the total concentration of ions found in the water sample.*

It is determined by testing the electrical conductivity of the sample, or by heating it to remove the water and leaving the salts that can be weighed.

TDS can find their way into water naturally. Water may dissolve ions as it percolates through rock to reach an underground aquifer. Mineral springs or sea water could run into water catchment areas. Human activity may also contribute to a high TDS result. Wastewater from industrial sources, *storm water run-off from urban areas and water containing high levels of fertilisers and pesticides from agricultural areas could end up in water catchments.*

(b) *Turbidity is a measure of the clarity or transparency of water. Material that contributes to turbidity includes microscopic organisms, soluble organic compounds, organic matter, clay and silt. Turbidity is determined by shining light through a water sample and using a light sensor to measure the amount of light scattered at right angles by the sample.*

(c) *Fe, Co, Zn, Mn, Cr, Ni, Cu, Ag, Cd, Hg and Pb.*
They can be removed from groundwater in many ways: They can be precipitated out if the pH is adjusted and some are removed through flocculation. It is also possible to use activated charcoal, filtration and ion-exchange methods.

(d) *Radon is dangerous as it is a radioactive gas and can cause cancers. It is removed from groundwater by aeration, or spraying the water into the air, where the radon gas dissipates.*

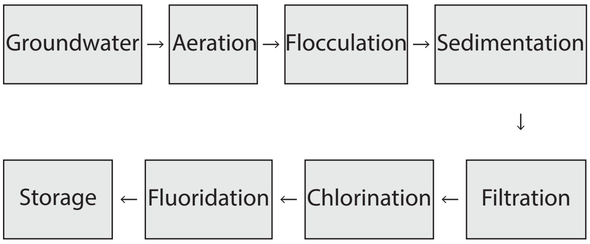
2.

(a) *Hardness in water is caused by the presence of ions such as* Ca^{2+}, Mg^{2+} *and* Fe^{3+}. *These ions dissolve into water as it makes its way to underground aquifers through rocks like sandstone or limestone, which contain* $CaCO_3$.

(b) $2\ CH_3(CH_2)_{16}COO^-Na^+ + Ca^{2+} \rightarrow (CH_3(CH_2)_{16}COO^-)_2Ca^{2+} + 2Na^+$

(c) *Hard water interferes with the cleaning action of soaps, preventing them from lathering and instead forming an insoluble scum. It can also cause precipitates like lime scale to form in kettles, hot water systems and pipes.*

3.



(a) *Groundwater is aerated to allow dissolved gases like radon, carbon dioxide and hydrogen sulphide to be released and also to oxygenate the water. Oxygenation reduces the solubility of dissolved organic compounds and any dissolved iron. These are then easier to remove in the flocculation and filtration processes.*

(b) *Flocculation is where small suspended particles in the water are made to clump together so that they become heavy enough to sink, or settle out of the water. Alum is added. The aluminium ions in the alum forms floc,* $Al(OH)_3$ *with the hydroxide ions in the water. The floc then traps suspended particles and these clump together and sink to the bottom.*
$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$

(c) *Water is left to stand in the sedimentation basin for a time to allow floc to settle. It forms a thick layer on the bottom, which is removed. The remaining water is then pumped to the filtration stage.*

(d) *The filtration step is where water is passed through a filter bed of anthracite and then progressively coarser sand and gravel. This removes any remaining suspended particles.*

(e) *Chlorine is added to water to kill any bacteria. It is thought that adding fluoride reduces tooth decay in the population.*

4. *Reverse osmosis (RO) and Multi-stage flash distillation (MSF)*

Set 5

1.

	Anion	Cation
Sample A	potassium	bromide
Sample B	iron (III)	chloride
Sample C	sodium	carbonate

2.

(a) $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
$Na_2CO_3(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2O(l) + CO_2(g)$
A white solid is added to a clear, colourless solution. The solid dissolves leaving a clear, colourless solution and producing bubbles of a colourless, odourless gas.

(b) $Cl_2(g) + 2KBr(aq) \rightarrow Br_2(aq) + 2KCl(aq)$
$Cl_2(g) + 2\ Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$
A pungent, green gas is bubbled through a clear, colourless solution producing an orange solution.

(c) $Ba(NO_3)_2(aq) + CuSO_4(aq) \rightarrow BaSO_4(s) + Cu(NO_3)_2(aq)$
$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
A clear, colourless solution is added to a clear, blue solution. A white precipitate forms and settles beneath a blue solution.

(d) $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$
$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$
A clear, colourless solution is added to a clear, colourless solution. No visible reaction is seen to occur.

(e) $Pb(NO_3)_2(aq) + K_2S(aq) \rightarrow PbS(s) + 2KNO_3(aq)$
$Pb^{2+}(aq) + S^{2-}(aq) \rightarrow PbS(s)$
A clear, colourless solution is added to a clear, colourless solution and a black precipitate is produced.

(f) $2Cr(NO_3)_3(aq) + 3Ba(OH)_2(aq) \rightarrow 2Cr(OH)_3(s) + 3Ba(NO_3)_2(aq)$
$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$
A clear, deep green solution is added to clear, colourless solution and a deep, green precipitate is produced.

(g) $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$
$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
A grey, metallic solid is added to a clear, colourless solution. The solid dissolves and bubbles of a colourless, odourless gas are produced. A clear, colourless solution remains.

(h) $Ag_2O(s) + 2HNO_3(aq) \rightarrow 2AgNO_3(aq) + H_2O(l)$
$Ag_2O(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2O(l)$
A brown/black solid is added to a clear, colourless solution. The solid dissolves leaving a clear, colourless solution.

(i) $Br_2(aq) + NaCl(aq) \rightarrow NR$
A clear, orange solution is added to a clear, colourless solution. No reaction is seen to occur.

(j) $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$
$CO_2(g) + Ca^{2+} + 2OH^-(aq) \rightarrow CaCO_3(s) + H_2O(l)$
A colourless, odourless gas is bubbled through a clear, colourless solution and a white precipitate is produced.

Set 6

1.

(a) $n(NaCl) = 0.113 / (22.99 + 35.45)$
$= 0.001934 \text{ mol}$
$n(Na^+) = 0.001934 \text{ mol}$
$c(Na^+) = 0.001934 / 0.750$
$= 0.00258 \text{ mol L}^{-1}$
$m(Na^+) = 22.99/(22.99 + 35.45) \times 0.113$
$= 0.0445 \text{ g}$
$c(Na^+) = 0.0445 / 0.750$
$= 0.0593 \text{ g L}^{-1}$

(b) $0.0593 \text{ g/L} = 0.0593 \text{ g/kg} = 0.0593 \times 1000 \text{ mg/kg} = 59.3 \text{ ppm}$

2. $n(MgSO_4) = c \times V$
$= 1.00 \times 60.0$
$= 60.0 \text{ mol}$
$m(MgSO_4) = n \times M$
$= 60.0 \times (24.31 + 32.07 + 64.00)$
$= 7222.8 \text{ g}$
$= 7.22 \times 10^3 \text{ g}$

3. $n(HCl) = c \times V$
$= 1.00 \times 0.150$
$= 0.150 \text{ mol}$
$V = n \times 22.71$
$= 0.150 \times 22.71$
$= 3.41 \text{ L}$

4. $c_1V_1 = c_2V_2$
$c_2 = 2.50 \times 0.250 / (0.125 + 0.250)$
$= 1.67 \text{ mol L}^{-1}$

5. $c_1V_1 = c_2V_2$
$V_2 = 2.00 \times 0.175 / 1.30$
$= 0.269 \text{ L}$
$V \text{ added} = 0.269 - 0.175 = 0.0942 \text{ L}$

6. $Na_2S(aq) + Cu(NO_3)_2(aq) \rightarrow CuS(s) + 2NaNO_3(aq)$
$n(Na_2S) = c \times V$
$= 0.100 \times 0.250$
$= 0.0250 \text{ mol}$
$n(CuS) = 1/1 \times n(Na_2S)$
$= 0.0250 \text{ mol}$
$m(CuS) = n \times M$
$= 0.0250 \times (63.55 + 32.07)$
$= 2.39 \text{ g}$

7. $4AgNO_3 + 2Cl_2 \rightarrow 2N_2O_5 + 4AgCl + O_2$

(a) $n(Cl_2) = V/22.71$
$= 3.00 / 22.71$
$= 0.1321 \text{ mol}$
$n(AgCl) = 4/2 \times n(Cl_2)$
$= 0.2642 \text{ mol}$
$m(AgCl) = n \times M$
$= 0.2642 \times (107.9 + 35.45)$
$= 37.9 \text{ g}$

(b) $n(O_2) = ½ \times n(Cl_2)$
$= 0.0661 \text{ mol}$
$V(O_2) = nRT/P$
$= 0.661 \times 8.314 \times (35.0 + 273.15) / 101.3$
$= 1.67 \text{ L}$

8.

(a) $Na_2SO_3 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O + SO_2$

(b) $n(Na_2SO_3) = 5.00 / ((2 \times 22.99) + 32.07 + (3 \times 16.00))$
$= 0.0397 \text{ mol}$
$n(HNO_3) = 0.500 \times 0.125$
$= 0.0625 \text{ mol}$

$$\begin{array}{lccc} & n(Na_2SO_3) & : & n(HNO_3) \\ \text{Stoichio:} & 1 & : & 2 \\ \text{actual:} & \dfrac{0.0397}{0.0397} & : & \dfrac{0.0625}{0.0397} \\ & 1 & : & 1.57 \end{array}$$

∴ *Limiting reagent is nitric acid*
$n(SO_2) = ½ \times n(HNO_3)$
$= 0.03125 \text{ mol}$
$V(SO_2) = n \times 22.71$
$= 0.03125 \times 22.71$
$= 0.710 \text{ L}$

(c) $n(Na_2SO_3)_{reacted} = \frac{1}{2} \times n(HNO_3)$
$= 0.03125$ mol
$n(Na_2SO_3)_{excess} = n(Na_2SO_3)_{initial} - n(Na_2SO_3)_{reacted}$
$= 0.0397 - 0.03125$
$= 0.008417$ mol
$m(Na_2SO_3)_{excess} = n \times M$
$= 0.008417 \times ((2 \times 22.99) + 32.07 + (3 \times 16.00))$
$= 1.06$ g

9. $SO_3 + H_2O \rightarrow H_2SO_4$
$n(SO_3) = PV/RT$
$= 110.0 \times 37.0 / 8.314 \times (15.0 + 273.15)$
$= 1.699$ mol
$n(H_2SO_4) = n(SO_3)$
$= 1.699$ mol
$c(H_2SO_4) = n/V$
$= 1.699 / 5.00$
$= 0.340$ mol L^{-1}

10. $2NaI(aq) + Pb(CH_3COO)_2(aq) \rightarrow PbI_2(s) + 2NaCH_3COO(aq)$
(a) $n(NaI) = 0.250 \times 0.350$
$= 0.0875$ mol
$n(Pb(CH_3COO)_2) = 0.450 \times 0.250$
$= 0.1125$ mol

$$\begin{array}{lccc} & n(NaI) & : & n(Pb(CH_3COO)_2) \\ \text{stoichio:} & 2 & : & 1 \\ \text{actual:} & \frac{0.0875}{0.0875} & : & \frac{0.1125}{0.0875} \\ & 1 & : & 1.29 \end{array}$$

$\therefore$ Limiting reagent is NaI
$n(PbI_2) = \frac{1}{2} \times n(NaI)$
$= 0.04375$ mol
$m(PbI_2) = n \times M$
$= 0.04375 \times (207.2 + (2 \times 126.9))$
$= 20.2$ g

(b) $n(Na^+) = 0.0875$ mol
$c(Na^+) = 0.0875 / 0.600$
$= 0.146$ mol L^{-1}
$n(CH_3COO^-) = 2 \times 0.1125$
$= 0.225$ mol
$c(CH_3COO^-) = 0.225 / 0.600$
$= 0.375$ mol L^{-1}
$n(Pb^{2+})_{excess} = n(Pb^{2+})_{initial} - n(Pb^{2+})_{reacted}$
$= 0.1125 - 0.04375$
$= 0.06875$ mol
$n(Pb^{2+}) = 0.06875$ mol
$c(Pb^{2+}) = 0.06875 / 0.600$
$= 0.115$ mol L^{-1}

Chapter 11.
Acid and Bases

Set 1

1. HCl, HNO_3, H_2SO_4

2. An acid is a substance that produces HYDROGEN IONS in solution. Acids are generally COVALENT MOLECULAR substances, and so when they are dissolved in water they IONISE, or produce ions in solution. An alkali is a soluble base and produces HYDROXIDE IONS in solution. Alkalis are generally IONIC substances, and so when they are dissolved in water they DISSOCIATE (or come apart) to produce ions in solution.

Acids and bases can be strong or weak depending upon the extent to which they ionise or dissociate in solution. Strong acids are COMPLETELY ionised in aqueous solution. Weak acids are PARTIALLY ionised in aqueous solution. Strong alkalis are completely DISSOCIATED into ions in aqueous solution. Weak alkalis are bases in which a SMALL proportion of the base species react with water to form hydroxide ions.

3.

(a) $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
A grey, metallic solid is added to a clear, colourless solution. The solid dissolves and bubbles of a colourless, odourless gas are produced. A clear, colourless solution remains.

(b) $MgCO_3(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l) + CO_2(g)$
$MgCO_3(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$
A white solid is added to a clear, colourless solution. The solid dissolves leaving a clear, colourless solution and producing bubbles of a colourless, odourless gas.

(c) $CuO(s) + 2HBr(aq) \rightarrow CuBr_2(aq) + H_2O(l)$
$CuO(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l)$
A black solid is added to a clear, colourless solution. The solid dissolves leaving a clear, blue solution.

(d) $H_2CO_3(aq) + 2KOH(aq) \rightarrow K_2CO_3(aq) + 2H_2O(l)$
$H_2CO_3(aq) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + 2H_2O(l)$
A clear, colourless solution is added to a clear, colourless solution. No visible reaction is seen to occur.

(e) $3NaHCO_3(s) + H_3PO_4(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l) + 3CO_2(g)$

$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + H_2O(l) + CO_2(g)$

A white solid is added to a clear, colourless solution. The solid dissolves leaving a clear, colourless solution and producing bubbles of a colourless, odourless gas.

(f) $Ag_2S(s) + 2HCl(aq) \rightarrow 2AgCl(s) + H_2S(g)$

$Ag_2S(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s) + H_2S(g)$

A black solid is added to a clear, colourless solution. It dissolves and a white precipitate is produced along with bubbles of a colourless, pungent gas.

(g) $CaSO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + SO_2(g)$

$CaSO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + SO_2(g)$

A white solid is added to a clear, colourless solution. The solid dissolves leaving a clear, colourless solution and producing bubbles of a colourless, pungent gas.

4.

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

Polyprotic acids have more than one ionisable hydrogen atom per molecule. Phosphoric acid is a triprotic acid. It contains three ionisable hydrogen atoms per molecule and this can be seen in the equation above, where three moles of NaOH are required to react with every mole of H_3PO_4.

(b) $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

(c) *HCl is a strong acid and ionises completely, so 1 mol* L^{-1} *HCl has 1 mol* L^{-1} H^+ *available to react with the magnesium. The reaction is vigorous.* H_3PO_4 *is a week acid and so most exists as* H_3PO_4 *molecules, with only a small proportion of* H^+ *available to react with the magnesium so the reaction is slow. As the* H^+ *from the* H_3PO_4 *reacts more ionisation will occur and eventually it will all react.*

5.

(a) > 5 mol L^{-1} NH_3

(b) < 1 mol L^{-1} HCl

(c) < 1 mol L^{-1} NaOH

(d) > 5 mol L^{-1} CH_3COOH

Set 2

1.

(a) $[OH^-] = 5.00 \times 10^{-15}$ mol L^{-1}

(b) $[OH^-] = 3.00$ mol L^{-1}

2.

(a) $[H^+] = 1.00$ mol L^{-1}

(b) $[H^+] = 5.00 \times 10^{-12}$ mol L^{-1}

3.

(a) $pH = 1.70$

(b) $pH = 13.7$

(c) $pH = 1.00$

(d) $pH = 9.30$

4.

(a) *acidic*

(b) *basic*

(c) *neutral*

(d) *acidic*

(e) *basic*

5. $ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

$ZnO + 2NaOH + 2H_2O \rightarrow Zn(OH)_4^{2-} + 2Na^+$

It can react with both acids and bases.

6.

		Colour in indicator				
Substance	Approx. pH	litmus	U.I.	phenolphthalein	Methyl orange	Red cabbage
Milk	6	red	yellow	colourless	yellow	purple
Toothpaste	9	blue	blue	pink	yellow	indigo/ blue
Lemon juice	2	red	red	colourless	red	pink
Household ammonia	11	blue	blue	pink	yellow	blue/ green

Set 3

1. $[H^+] = 6.30 \times 10^{-4}$ mol L^{-1}

$[OH^-] = 1.58 \times 10^{-11}$

$[NO_3^-] = 6.30 \times 10^{-4}$ mol L^{-1}

2. $[H^+] = 0.650$ mol L^{-1}

$[OH^-] = 1.54 \times 10^{-14}$ mol L^{-1}

$[Cl^-] = 0.650$ mol L^{-1}

$pH = 0.187$

3. $[Ba^{2+}] = 0.125$ mol L^{-1}

$[OH^-] = 2 \times 0.125$

$= 0.250$ mol L^{-1}

$[H^+] = 4.0 \times 10^{-14}$ mol L^{-1}

$pH = 13.39$

4. $[H^+] = 0.01$ mol L^{-1}

$c_1V_1 = c_2V_2$

$c_2 = c_1V_1 / V_2$

$= 0.01 \times 0.250 / 0.400$

$= 0.00625$ mol L^{-1}

$[H^+] = 0.00625$ mol L^{-1}

$pH = 2.20$

5. pH12

$[H^+] = 1.0 \times 10^{-12}$ mol L^{-1}

$[OH^-] = 0.01$ mol L^{-1}

pH10

$[H^+] = 1.0 \times 10^{-10}$ mol L^{-1}

$[OH^-] = 0.0001$ mol L^{-1}

$c_1V_1 = c_2V_2$
$V_2 = c_1V_1 / c_2$
$= 0.01 \times 0.500 / 0.0001$
$= 50.0\ L$
$V_{added} = 50.0 - 0.500 = 49.5\ L$

6. $[H^+] = 10^{-3.5}\ mol\ L^{-1}$
$= 0.000316227\ mol\ L^{-1}$
$n(H^+)_{initial} = 3.16 \times 10^{-4} \times 0.150$
$= 4.74 \times 10^{-5}\ mol$
$n(H^+)_{added} = 1.00 \times 0.200$
$= 0.200\ mol$
$n(H^+)_{total} = 4.74 \times 10^{-5} + 0.200$
$= 2.00047434 \times 10^{-1}\ mol$
$[H^+]_{final} = 2.00047434 \times 10^{-1} / 0.350$
$= 0.572\ mol\ L^{-1}$
$pH_{final} = 0.24$

7. $pH\ 5.00$
$[H^+] = 10^{-5}\ mol\ L^{-1}$
$n(H^+) = 10^{-5} \times 0.100 = 10^{-6}\ mol$
$pH\ 7.00$
$[H^+] = 10^{-7}\ mol\ L^{-1}$
$n(H^+) = 10^{-7} \times 0.100 = 10^{-8}\ mol$
$n(H^+)_{total} = 10^{-6} + 10^{-8}$
$= 1.01 \times 10^{-6}\ mol$
$[H^+]_{final} = 1.01 \times 10^{-6} / 0.200$
$= 5.05 \times 10^{-6}\ mol\ L^{-1}$
$pH = 5.30$

8. $pH\ 9.50$
$[H^+] = 10^{-9.5}\ mol\ L^{-1}$
$[OH^-] = 10^{-4.5}\ mol\ L^{-1}$
$pH\ 11.0$
$[H^+] = 10^{-11}\ mol\ L^{-1}$
$[OH^-] = 10^{-3}\ mol\ L^{-1}$
$\Delta[OH^-] = 10^{-3} - 10^{-4.5}$
$= 9.68 \times 10^{-4}\ mol\ L^{-1}$
$n(OH^-)_{added} = 9.68 \times 10^{-4} \times 0.250$
$= 2.42 \times 10^{-4}\ mol$
$n(KOH) = n(OH^-)$
$= 2.42 \times 10^{-4}\ mol$
$m(KOH) = n \times M$
$= 2.42 \times 10^{-4} \times (39.10 + 16.00 + 1.008)$
$= 0.0136\ g$

Set 4

1. $n(NaOH) = 0.100 \times 0.150$
$= 0.0150\ mol$
$[H^+] = 10^{-2.5}$
$n(HCl) = 10^{-2.5} \times 0.150$
$= 4.74341 \times 10^{-4}\ mol$
$n(NaOH) = 0.0150 - 4.74341 \times 10^{-4}$
$= 0.014525658\ mol$
$[OH^-] = 0.014525658 / 0.300$
$= 0.048418861\ mol\ L^{-1}$
$[H^+] = 1.0 \times 10^{-14} / 0.048418861$
$= 2.0653 \times 10^{-13}\ mol\ L^{-1}$
$pH = 12.69$

2. $Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$
$n(Ba(OH)_2) = 25.0 / (137.3 + 32.00 + 2.016)$
$= 0.1459\ mol$
$n(HCl) = 2.00 \times 0.250$
$= 0.500\ mol$
$n(Ba(OH)_2) : n(HCl)$
stoichio: $1 : 2$
actual: $\dfrac{0.1459}{0.1459} : \dfrac{0.500}{0.1459}$
$1 : 3.43$
$\therefore$ Limiting reagent is $Ba(OH)_2$
$n(HCl)_{reacted} = 2 \times n(Ba(OH)_2)$
$= 0.2919\ mol$
$n(HCl)_{excess} = 0.500 - 0.2919$
$= 0.2081\ mol$
$n(H^+) = 0.2081\ mol$
$[H^+] = 0.2081 / 0.250$
$= 0.8326\ mol\ L^{-1}$
$pH = 0.08$

3. $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$
$pH\ 2.50$
$[H^+] = 10^{-2.5}\ mol\ L^{-1}$
$n(H^+) = 10^{-2.5} \times 0.570$
$= 1.802 \times 10^{-3}\ mol$
$n(Na_2SO_3) = 0.100 / ((2 \times 22.99) + 32.07 + (3 \times 16.00))$
$= 7.93335 \times 10^{-4}\ mol$
$n(Na_2SO_3) : n(HCl)$
stoichio: $1 : 2$
actual: $\dfrac{7.93335 \times 10^{-4}}{7.93335 \times 10^{-4}} : \dfrac{1.802 \times 10^{-3}}{7.93335 \times 10^{-4}}$
$1 : 2.27$
$\therefore$ Limiting reagent is Na_2SO_3
$n(SO_2) = n(Na_2SO_3)$
$= 7.93335 \times 10^{-4}\ mol$
$V(SO_2) = nRT/P$
$= 7.93335 \times 10^{-4} \times 8.314 \times (20.0 + 273.15) / 110.0$
$= 0.0176\ L$

4. $CuS(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2S(g)$
$n(H_2S) = V/22.71$
$= 11.34 / 22.71$
$= 0.499\ mol$
$n(H_2SO_4) = n(H_2S)$
$= 0.499\ mol$
$V(H_2SO_4) = n/c$
$= 0.499 / 0.50$
$= 0.999\ L$

5. $pH\ 1.50$
$[H^+] = 10^{-1.5}\ mol\ L^{-1}$
$pH\ 7.00$
$[H^+] = 10^{-7}\ mol\ L^{-1}$
$\Delta\ [H^+] = 10^{-1.5} - 10^{-7}$
$= 3.162 \times 10^{-2}\ mol\ L^{-1}$
$\Delta\ n(H^+) = 3.162 \times 10^{-2} \times 0.500$
$= 1.581 \times 10^{-2}\ mol$

$CaO + 2HCl \rightarrow CaCl_2 + H_2O$
$n(CaO) = \tfrac{1}{2} \times n(HCl)$
$= 7.91 \times 10^{-3}\ mol$
$m(CaO) = n \times M$
$= 7.91 \times 10^{-3} \times (40.08 + 16.00)$
$= 0.443\ g$

6. $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$

(a) $m(CH_3COOH) = 3.97/100 \times 25.0$
$= 0.9925\ g$
$n(CH_3COOH) = 0.9925 / ((2 \times 12.01) + (4 \times 1.008) + (2 \times 16.00))$
$= 0.0165\ mol$
$n(NaOH) = 0.260 \times 0.150$
$= 0.039\ mol$
Excess NaOH so all CH_3COOH *will react.*
$[CH_3COOH] = n / V$
$= 0.0165 / (0.250 + 0.150)$
$= 0.0413\ mol\ L^{-1}$
$[CH_3COO^-] = 0.0413\ mol\ L^{-1}$

(b) $n(NaOH)_{unreacted} = 0.039 - 0.0165$
$= 0.0225\ mol$
$c(NaOH) = 0.0225 / 0.400$
$= 0.0562\ mol\ L^{-1}$
$[H^+] = 1.0 \times 10^{-14} / 0.0562$
$= 1.78 \times 10^{-13}\ mol\ L^{-1}$
$pH = 12.75$

7. $Cu_2CO_3(OH)_2 + 4HCl \rightarrow 2CuCl_2 + 3H_2O + CO_2$
$n(CO_2) = V / 22.71$
$= 9.00 / 22.71$
$= 0.3963\ mol$
$n(Cu_2CO_3(OH)_2) = n(CO_2)$
$= 0.3963\ mol$
$m(Cu_2CO_3(OH)_2) = n \times M$
$= 0.3963 \times ((2 \times 63.55) + 12.01 + (5 \times 16.00) + (2 \times 1.008))$
$= 87.6\ g$
$\%\ Cu_2CO_3(OH)_2 = 87.6 / 100 \times 100$
$= 87.6\ \%$

8. $KOH + HNO_3 \rightarrow KNO_3 + H_2O$
KOH:
$[OH^-] = 10^{-14} / 10^{-10}$
$= 1.0 \times 10^{-4}\ mol\ L^{-1}$
$n(OH^-) = c \times V$
$= 1.0 \times 10^{-4} \times 0.250$
$= 2.50 \times 10^{-5}\ mol$
HNO_3:
$[H^+] = 1.0 \times 10^{-3}\ mol\ L^{-1}$
$n(H^+) = c \times V$
$= 1.0 \times 10^{-3} \times 0.150$
$= 0.00015\ mol$
$n(H^+)_{unreacted} = 0.00015 - 2.50 \times 10^{-5}$
$= 0.000125\ mol$
$[H^+] = n / V$
$= 0.000125 / 0.400$
$= 0.0003125\ mol\ L^{-1}$
$pH = 3.51$

9.

(a) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
$n(H_2SO_4) = c \times V$
$= 0.325 \times 0.02275$
$= 0.00739375\ mol$
$n(NaOH) = 2 \times n(H_2SO_4)$
$= 0.0147875\ mol$
$n(NaOH)_{in\ 250\ mL} = 0.0147875 \times 250 / 20$
$= 0.18484375\ mol$
$c(NaOH)_{in\ 250\ mL} = 0.18484375 / 0.250$
$= 0.739\ mol\ L^{-1}$

(b) $[H^+] = 1.0 \times 10^{-14} / 0.739$
$= 1.35 \times 10^{-14}\ mol\ L^{-1}$
$pH = 13.9$

(c) $m(NaOH)_{in\ 250\ mL} = 0.18484375 \times (22.99 + 16.00 + 1.008)$
$= 7.39\ g$
$m(NaOH)_{in\ 500g} = 7.39 \times 500 / 15.0$
$= 246\ g$

10. pH 4.8
$[H^+] = 10^{-4.8}\ mol\ L^{-1}$
pH 6.8
$[H^+] = 10^{-6.8}\ mol\ L^{-1}$
$\Delta\ [H^+] = 1.569 \times 10^{-5}\ mol\ L^{-1}$
$n(H^+) = 1.569 \times 10^{-5} \times 3 \times 10^{6}$
$= 47.07\ mol$
$V(H^+) = n / c$
$= 47.07 / 2.00$
$= 23.5\ L$

11. $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
$n(NaOH) = 0.095 \times 0.01875$
$= 0.00178125\ mol$
$n(H_2SO_4)_{in\ 20\ mL} = \tfrac{1}{2} \times n(NaOH)$
$= 0.000890625\ mol$
$n(H_2SO_4)_{in\ 250\ mL} = 0.000890625 \times 250 / 20$
$= 0.011132812\ mol$
$n(H_2SO_4)_{in\ 2.5\ mL\ undiluted} = 0.011132812\ mol$
$c(H_2SO_4)_{in\ 2.5\ mL\ undiluted} = 0.011132812 / 0.0025$
$= 4.45\ mol\ L^{-1}$

12.

(a) *Solution 1:*
$n(KOH) = 20.00 / (39.10 + 16.00 + 1.008)$
$= 0.356\ mol$
$c(KOH) = 0.356 / 0.250$
$= 1.43\ mol\ L^{-1}$
Solution 2:
$c_1V_1 = c_2V_2$
$c(HNO_3) = 0.750 \times 0.100 / 0.250$
$= 0.300\ mol\ L^{-1}$

Solution 3:

$n(HCl) = PV/RT$
$= (100.0 \times 0.300) / (8.314 \times 293.15)$
$= 0.01231$ *mol*
$c(HCl) = 0.01231 / 0.250$
$= 0.0492$ *mol* L^{-1}

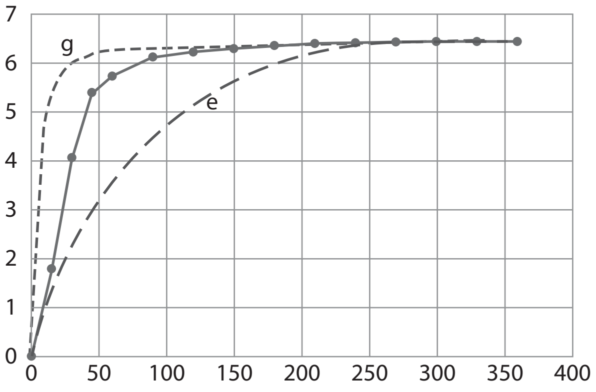
(b) $n(H^+)_{Solution\ 2} = c \times V$
$= 0.300 \times 0.050$
$= 0.015$ *mol*
$n(H^+)_{Solution\ 3} = c \times V$
$= 0.0492 \times 0.050$
$= 2.461791 \times 10^{-3}$ *mol*
$n(H^+)_{total} = 0.017461791$ *mol*
$[H^+] = 0.017461791 / 0.100$
$= 0.174617918$ *mol* L^{-1}
$pH = 0.76$

(c) $n(OH^-)_{required} = n(H^+)_{total}$
$= 0.017461791$ *mol*
$V(OH^-)_{required} = n / c$
$= 0.017461791 / 1.43$
$= 0.0122$ *L*

Chapter 12.
Rates of Chemical Reactions

Set 1

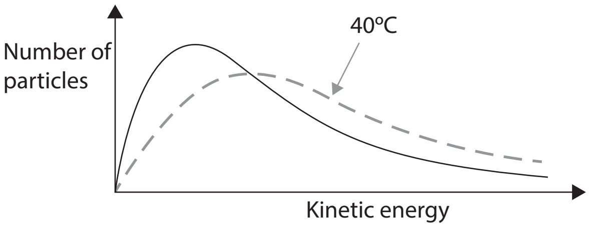
1. *Measure the volume of hydrogen gas produced with time. Collect the gas via downwards displacement of water. Rate = Volume / time*
   Measure the change in concentration of HCl, or pH, with time using a pH meter.
   Rate = Δc/time
   or
   Rate = ΔpH/time
2. *C would proceed at the fastest rate, since there is no complex bond rearrangement required.*
3. *Vaporising fuel increases its surface area, increasing the number of collisions between fuel and oxygen molecules. So the combustion reaction will have an increased rate and proceed more efficiently.*
4.



(a) *0 - 15 s*
(b) *i) 0.12 g/s*
ii) 0.003 g/s
(c) *The rate of this reaction decreases with time as the reactants are being used up. The concentration of nitric acid and the mass and surface area of sodium carbonate will decrease with time. Fewer collisions results in a lower rate.*
(d) *At 300 s the rate is zero, as the reaction is complete.*
(e) *see graph*
(f) *Large pieces of sodium carbonate would have less surface area. Decreased surface area would result in less collisions, less successful collisions and a lower rate.*
(g) *see graph*
(h) *If a higher concentration of nitric acid is used there will be more collisions, more successful collisions and therefore an increased rate.*

5.
(a) *Heterogeneous as the catalyst is solid and the reactants liquid.*
(b) *The hydrogen peroxide molecules adsorb onto the surface of the manganese dioxide catalyst. This weakens the bonds within the hydrogen peroxide molecules and provides an alternative reaction pathway with a lower activation energy. So more particles have sufficient energy for successful collisions and the rate increases.*

6.
(a) *Increasing the kinetic energy and velocity of the reactant particles has two effects. The frequency of collisions increases, which increases the number of successful collisions and this in turn increases the rate of reaction. The force/energy of the collisions increases, which increases the number of particles having high energy collisions, so more collisions have sufficient energy to overcome the E_a barrier. This also increases the rate of reaction.*
(b)



7. *When enzymes are heated they become denatured. This means that their shape changes and they are no longer able to act as a catalyst for certain reactions.*

8.

(a) $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

(b) *Increase the pressure of one or both of the gaseous reactants. This will increase the number of collisions between reacting particles and therefore the rate will increase. Increase the temperature. This will increase both the number of collisions and the energy of collisions, resulting in more successful collisions and an increased rate.*

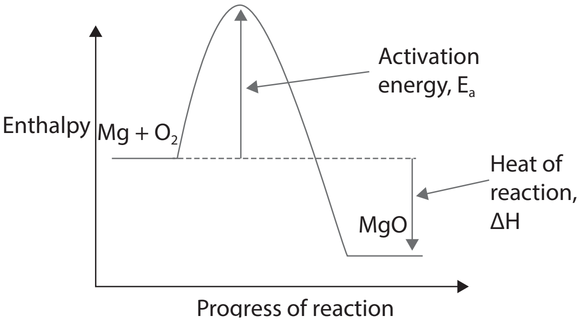
9.

(a) *Since a large input of energy initiates the reaction this suggests that the activation energy is quite large.*

(b) *Exothermic as lots of heat and light is released once the reaction begins.*

(c) *This reaction would have a large heat of reaction as it is very exothermic.*

(d) *Draw an energy level diagram for the reaction between magnesium and oxygen showing the reactants, products, ΔH and* E_a*. Label both axes.*



10.

(a) *Step 1: Combustion of sulphur*
$S(l) + O_2(g) \rightarrow SO_2(g)$
The sulphur is heated until molten. This increases temperature and increases the number and energy of collisions. Increasing the number of collisions increases the number of successful collisions and therefore the rate increases. Increasing the energy of collisions means that more collisions will be able to reach the activation energy required for a reaction to occur, hence the rate increases. The molten sulphur is sprayed as fine mist into the reaction chamber. This increases its surface area, meaning that there will be more collisions between reacting particles, increasing the number of successful collisions and therefore the rate increases.

(b) *Step 2: Production of sulphur trioxide*
$2SO_2(g) + O_2 \leftrightarrows 2SO_3(g) + heat$
A porous V_2O_5 *catalyst is used which provides an alternative reaction pathway with a lower* E_a*. This enables moderate pressures and temperatures to be used whilst still maintaining an economical rate.*

Chapter 13.
Data Analysis

1.

(i) *Experiment no. 5 looks faulty – the reading of 7 seconds seem far too low.*

(ii) *Neglect the 1st reading (7) and use the average of the other 2 readings = 8.15 s.*

(iii) *A systematic error – a fault with the method and not in reading the scale.*

(iv) *The acid would be diluted which would give consistently longer times.*

2.

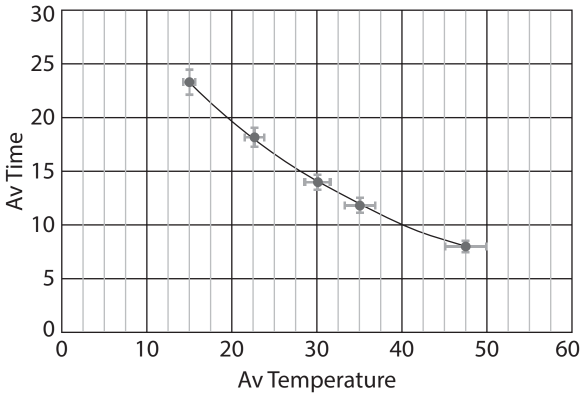
(i) *The 5th reading show the greatest variance and uncertainty.* $U_R = \frac{0.3}{8.0} \times 100 = 3.8\%$

3.

(i) *Predicted time for 5°C is about 30 seconds interpolated from the graph.*

(ii) *At a lower temperature the collision rate would be less, so the proportion of successful collisions would also be less. On the Maxwell- Boltzmann curve, there would be less particles with energy above the Activation Energy level.*

(iii)



Calculation of gradient:

At 20°C Time for cross to disappear= 19 s.
so average rate $1/19 = 0.053\ s^{-1}$
At 30°C Time for cross to disappear= 14 s.
so average rate $1/14 = 0.071\ s^{-1}$
Ratio $R_2/R_1 = 0.071/0.053 = 1.34$ *So reaction takes place 1.34 times faster at 30° than at 20°C.*

4.

(i) $U_R = \frac{0.05}{1.2} \times 100 = 4.2\%$

(ii) $U_R = \frac{0.1}{121.4} \times 100 = 0.08\%$

(iii) *Length:* $U_R = \frac{0.05}{27} \times 100 = 0.19\%$

Width: $U_R = \frac{0.05}{4} \times 100 = 1.25\%$

Total relative error (add %) = 1.44%

5.

(i) *Times are: 114 s, 103 s, 130 s, 119 s, 143 s.*
Average = 122 s (2 min 2 s)

(ii) *100/122 = 0.82 mL* s^{-1}.

(iv) *Variance in time is Largest value – average value = 143 - 122 = 21 s variance*
Which is 17% uncertainty. Rate will also have 17% uncertainty.

(iv) *17% of 0.82 = 0.14 absolute uncertainty*
Quoted value should be 0.82 ± 0.14 mL s^{-1}.

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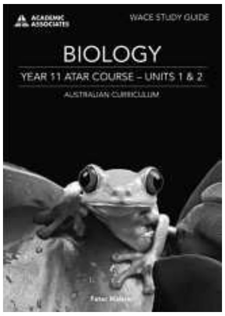

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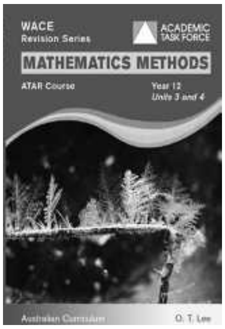

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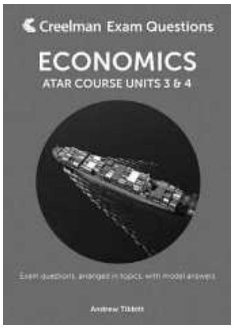

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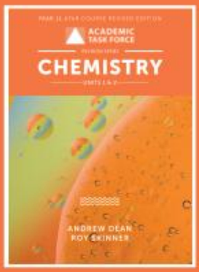

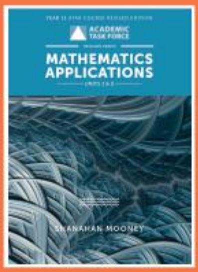

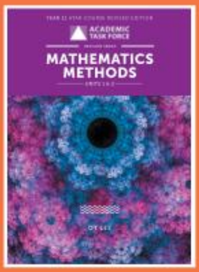

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