

Study Notes- HSC Chemistry

Production of Materials

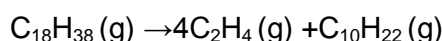
Polymers

Ethylene

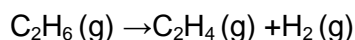
Industrial source of ethylene from petroleum:

Ethylene (C₂H₄) or ethene (systemic name) is produced from the cracking of crude oil fractions. Cracking is the chemical process of breaking large hydrocarbon molecules into smaller ones. There are two types of cracking:

- Catalytic cracking- Breaks down the heavier fractions of crude oil into shorter chain alkanes and small alkenes such as ethylene and propylene using a catalyst. The catalysts most commonly used are inorganic crystalline compounds of aluminium, silicon and oxygen (aluminosilicate) called zeolite. The reaction occurs at about 500°C in an air free environment. An example of catalytic cracking is:



- Thermal /steam cracking- Passes a mixture of alkanes with steam through very hot metal tubes (700°-1000°C) to decompose the alkanes completely into small alkenes such as ethylene, propene and butene as well as hydrogen. Often, the feedstock is a mixture of ethane and propane obtained from natural gas. The reaction for the cracking of ethane is:



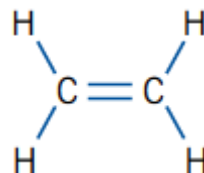
Uses of ethylene:

Saturated- Consisting of molecules that have only single bonds. They can undergo substitution reactions but not addition reactions

Unsaturated- Having double or triple bonds in its molecules. They can undergo addition as well as substitution reactions

Substitution reaction- A reaction in which an atom or molecule is replaced by another atom or molecule e.g. $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{l})$

Addition reactions- A reaction in which one atom or molecule adds to another. Two new atoms or groups of atoms are added across a double (or triple) bond, one to each atom. This also converts the double bond into a single bond (or the triple bond into a double bond).
e.g. $\text{CH}_2=\text{CH}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}(\text{g})$



Ethylene, as an unsaturated hydrocarbon, is very useful in the petrochemical industry as a result of its reactive C=C double bond. This allows it to readily combine with other compounds to form new compounds through addition reactions. For example, the halogenation of ethylene with chlorine gas to form 1, 2-dichloroethane as shown above. Products which can be produced from ethylene include ethanol (CH₃-CH₂-OH), vinyl chloride (CH₂=CH-Cl), styrene (C₆H₅-CH=CH₂) and vinyl acetate (CH₂=CH-O-CO-CH₃).

Reactions of Hydrocarbons with Bromine Water:

Aim: To observe the reactions of hydrocarbons with bromine water

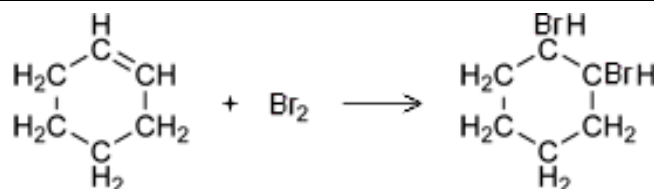
Risk analysis: Cyclohexane and cyclohexene are moderately toxic and highly flammable. Bromine water is toxic by all routes of exposure.

Method:

1. Drop 1mL of the hydrocarbon sample in a test tube
2. Drop a few drops of bromine water in the test tube
3. Place a stopper on the test tube and swirl around
4. Record observations

Results:

Hydrocarbon	Reaction with bromine water
Cyclohexane (C ₆ H ₁₂)	No reaction
Cyclohexene (C ₆ H ₁₀)	Orange to colourless
Toluene (C ₇ H ₈)	No reaction



Discussion:

- Bromine reacts with the C=C group through an addition reaction, turning the solution colourless
- With cyclohexene, the reaction was: C₆H₁₀ (l) + Br₂ (aq) → C₆H₁₀Br₂ (l)
- Another possible reaction where the bromine first reacts with water is:
C₆H₁₀ (l) + Br₂ (aq) + H₂O (l) → C₆H₁₀BrOH (l) + HBr (aq)
- Toluene, whilst containing a carbon double bond, does so in a benzene ring, which reacts differently from normal double bonds

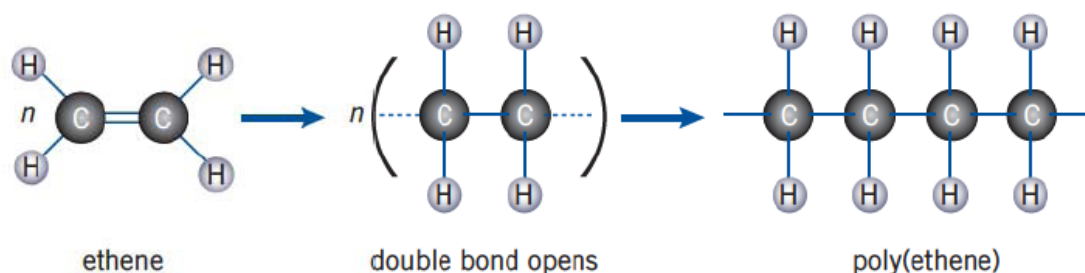
Conclusion: Hydrocarbons with carbon double bonds will react with bromine water through addition reactions and this can be used to distinguish saturated and unsaturated hydrocarbons

Addition Polymers:

Polymers- High molecular weight molecules formed from simple repeating units called monomers

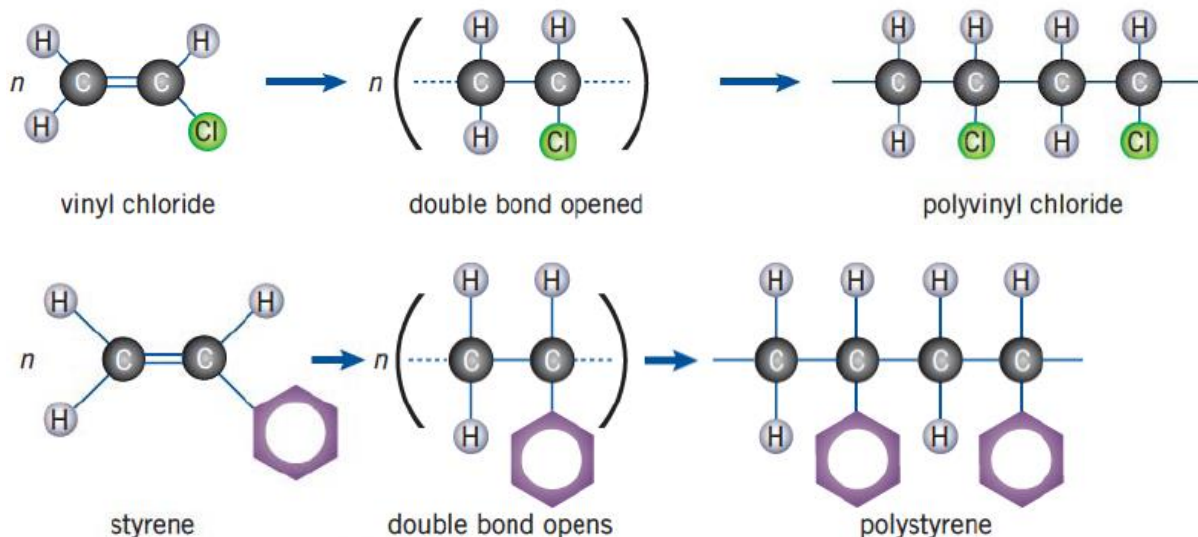
Addition polymers- Polymers formed by the combination of molecules without any loss of atoms

Polyethylene is an addition polymer formed from the combination of thousands of ethylene molecules. The double bonds in each molecule open as they join together to form long chains.



Two other commercially significant polymers are formed from vinyl-chloride and styrene:

Monomer			Polymer	
Common Name	Systematic name	Chemical Formula	Common name	Systematic Name
Ethylene	Ethene	$\text{CH}_2\text{-CH}_2$	Polyethylene	Polyethene
Vinyl chloride	Chloroethene	$\text{CH}_2\text{=CH-Cl}$	Poly (vinyl chloride)	Polychloroethene
Styrene	Ethenylbenzene	$\text{C}_6\text{H}_5\text{-CH=CH}_2$	Polystyrene	Polyethenylbenzene



Note that there are two types of polystyrene: crystalline polystyrene and polystyrene foam (Styrofoam) made by blowing gas through liquid polystyrene until it froths up into foam

Formation of polyethylene (polymerisation):

There are two types of polyethylene which form under different conditions. They are low-density polyethylene (LDPE) and high density polyethylene (HDPE).

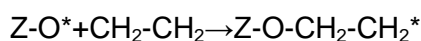
LDPE (shown schematically to the right) is formed under high pressure (1000atm), high temperatures (300°C) and uses an organic peroxide such as benzoyl peroxide ($\text{C}_6\text{H}_5\text{-C-CO-O-O-CO-C}_6\text{H}_5$ or simply Z-O-O-Z). This initiator becomes part of the polymer and forms free radicals (an atom or group of atoms with an unpaired valence electron, making it very reactive). There are three stages involved:



1. Initiation: Initiator forms free radicals which are highly reactive:



These attack the double bonds in ethylene, activating it:



This creates a monomer (ethylene) radical which attacks the double bonds in other ethylene molecule.

2. Propagation: The ethylene radical joins with more monomers to form a polymer (polyethylene) radical:

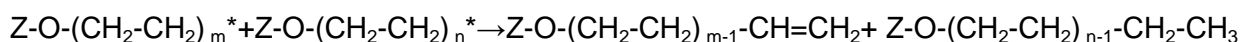


Some biting back may occur in which the radical end curls back and removes a hydrogen atom from the middle of the chain. This results in an unpaired electron within the chain from which a new chain can start. This is how branching occurs.

3. Termination: Two polyethylene radicals collide together and the active ends react to form one or two stable molecules. For example, they may join together as below:



Alternatively, they can exchange a hydrogen atom:



Each chain will have a different length, although the average molecular weight is 4.6×10^4 . Note that the polymerisation reaction is exothermic and so temperature monitoring is required.

HDPE (shown schematically to the right) is produced at around 2-3 atmospheres, 60°C and uses a mixture of compounds containing titanium (IV) chloride (TiCl_4) and triethylaluminium $\text{Al}_2(\text{C}_2\text{H}_5)_6$ as a catalyst called the Ziegler- Natta catalyst. The entire process is known as the Ziegler- Natta process. Ethylene monomers are added to the polymer on the surface of the catalyst which reduces branching, allowing the polyethylene molecules to pack together in an orderly fashion.



Factors affecting the properties of polymers:

- Length of chain (average molecular weight): The longer the length of chains in the polymer and the heavier each molecule is, the greater the dispersion forces between molecules. This makes the material stronger and gives it a higher melting/ softening point
- Degree of branching: Polymers with little branching are able to intertwine and align closely together, forming a crystalline structure. This material has a higher density, a higher melting point and is stronger and harder although less flexible than polymers with a high degree of branching which are more amorphous
- Substituents: Heavy or bulky substituents (an atom or group of atoms substituted in place of a hydrogen atom) in monomers restrict the movement of polymer molecules, making the polymer more rigid. Polar substituents also increase intermolecular forces between polymer molecules, increasing melting point and hardness
- Cross-linking: This is when the polymer chains are covalently joined, increasing melting point, hardness and elasticity. Polymers without cross-linking are thermoplastics (can be softened through heating) whilst polymers with cross-linking are thermo-setting (cannot be reformed after manufacture)
- Additives: Additives include pigments/ dye for colour, plasticisers to soften the material, stabilisers to increase the material's resistance to decomposition by heat/ UV rays and flame retardants to reduce flammability

Properties and uses of polyethylene, PVC and polystyrene

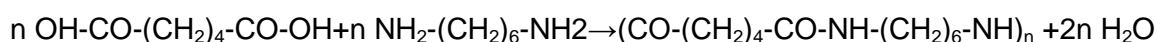
Polymer	Properties	Uses
LDPE	Soft, flexible, low MP Branching- non-crystalline- low density Shorter chains and lower strength than HDPE No substituents- non-polar No cross-linking- thermoplastic	Cling wrap, ice cream containers, garbage bags, electrical insulation, lining of cardboard milk containers
HDPE	Rigid, hard, strong, high MP Less branching- crystalline- higher density Longer chains and higher strength than LDPE No substituents- non-polar No cross-linking- thermoplastic	Bowls, buckets, milk cartons, wheelie bins, agricultural pipes, lunch boxes, playground equipment, children's toys
PVC	Hard, rigid and brittle Polar Cl substituent No cross-linking- thermoplastic Impermeable to water and flame resistant Can be made less brittle and more flexible depending on additives (plasticisers) C-Cl bond is vulnerable to UV- stabilisers are usually added to make it more resistant	Water pipes, guttering down pipes, electrical conduit, floor tiles, garden hoses, credit cards, furnishings, shower curtains, kitchen utensils
Polystyrene	Very hard and rigid Minimal branching- highly crystalline and transparent Bulky benzene substituent- makes polymer brittle but less dense than expected No cross-linking- thermoplastic Impermeable to water	CD cases, tool handles, clear drinking glasses, car batter cases, plastic furniture, toys
Styrofoam	Lightweight Shock absorber Heat insulator	Foam drink cups, foam packaging, bike helmet padding

Condensation Polymers

The need for alternative sources of compounds presently obtained by the petrochemical industry:

Petrochemicals are organic chemicals obtained from petroleum or natural gas. Petroleum (crude oil) is the main source of hydrocarbons that are used for making ethylene which can then be converted to useful substances such as polymers and ethanol. It is also used as a fuel to provide energy. Petroleum is a finite resource which will one day run out. As a result, alternative means will need to be developed to meet demand for energy and other useful substances such as polymers and ethanol.

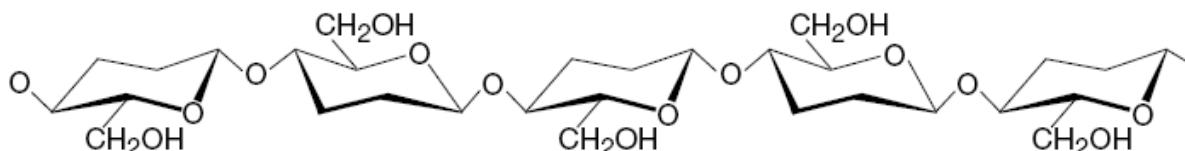
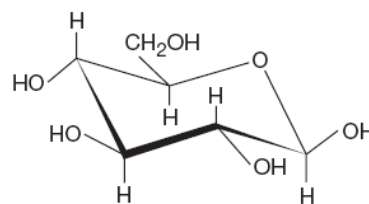
Condensation polymers: Polymers formed by a reaction between two different functional groups in which a small molecule (usually water) is eliminated and the two functional groups become linked together. For example:



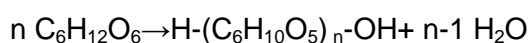
In the above reaction, the -OH groups of hexanedioic (adipic) acid react with hydrogen atoms from the -NH₂ groups of 1-6-hexanediamine, combining the two monomers in a long chain to form Nylon 6, 6 and water

Cellulose:

Cellulose is a condensation polymer formed from the monomer β -glucose (shown to the right). During polymerisation, the OH group attached to the carbon atom on the most left combines with the OH group of the carbon atom on the most right to join two glucose molecules with an oxygen atom whilst eliminating a water molecule. In cellulose, every second glucose molecule is inverted and this forms a linear chain as shown below:



The formula for polymerisation is:



Cellulose is the main constituent in plant cell walls and is the major structural component of wood and natural fibres such as cotton. Thus, cellulose is a major component of the world's biomass and is, in fact, the most abundant polymer in the biosphere.

Use of cellulose as a raw material:

Cellulose can be used to create a variety of biopolymers including:

- Rayon (viscose): This is made by treating cellulose with NaOH and CS₂ and then extruding the resultant substance into a solution of H₂SO₄ through a spinneret (a nozzle with numerous small holes). The fine threads of Rayon then harden and may be spun into fibres or woven into fabric
- Cellophane: When rayon is produced as a thin transparent film
- Cellulose nitrate: Made by replacing -OH groups with -ONO₂ groups. It was widely used as photographic film but was quickly replaced due to its flammability
- Cellulose acetate: Made by replacing -OH groups with -O-CO-CH₃. It is used for overhead projector slides
- Carboxymethyl cellulose (CMC): Made by replacing the -CH₂OH groups with -CH₂-COOH groups. It is used as a thickener in many foods

In addition, cellulose may be broken down into glucose by either:

- Digestion by cellulase enzymes: Involves treating finely ground cellulose containing materials with NaOH to swell up the fibres and then digesting them with cellulase enzymes to produce a solution of glucose
- Digestion by strong acid: Involves heating a suspension of cellulose containing materials with concentrated H₂SO₄ solution to break cellulose into glucose. Insoluble matter is filtered off and the solution neutralised to produce a solution of glucose

This in turn can be converted into ethanol through fermentation which can be dehydrated to form ethylene.

The advantages of using cellulose as a raw material are:

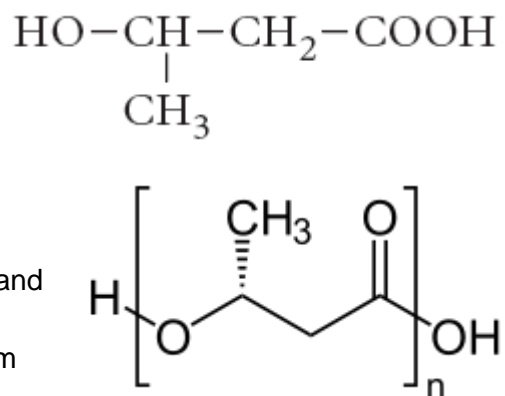
- Cellulose is renewable and abundant
- Polymers made out of cellulose are biodegradable, heavily reducing problems such as waste management hazards and wildlife ingesting plastics

Disadvantages of using cellulose as a raw material include:

- Processing cellulose to make materials is expensive and energy intensive as it requires a lot of energy to separate cellulose fibres
- Production of cellulose specifically for use as a raw material can reduce the amount of arable land available for growing crops for food, leading to possible food shortages
- Biomass, which usually exists as a solid, is harder to store and transport than oil which can easily travel through pipes

Biopolymer- poly-3-hydroxybutanoate/ polyhydroxybutyrate (PHB)

PHB (shown bottom right) is a type of polyhydroxyalkanoate (PHA) produced from the monomer 3-hydroxybutanoic acid (shown top right). It is formed by the bacteria *Cupriavidus metallidurans* (*Alcaligenes Eutrophus*) which is fed nutrients such as glucose and kept in a nitrogen-restricted environment at 30°C. The lack of nitrogen makes the bacteria unable to increase its population and so it instead produces PHB and stores it as a future energy source; PHB can make up to 80% of bacterium body mass. The PHB is harvested and milled to a powder.



Properties: Thermoplastic, stiff and brittle, thermally unstable, biodegradable, biocompatible

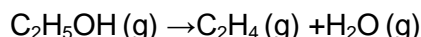
(Potential) Uses: Disposable nappies, packaging, bags, bottles, wrapping film, plates in fractured bones

PHB is more expensive to produce than oil based polymers and if energy costs for processing and transporting polymers made by bacteria are taken into account, actually takes more energy to produce. However, due to its uses as a biodegradable and biocompatible polymer, it may find use in niche markets where these things are a concern despite its higher cost.

A recent innovation which could reduce the cost of PHB is the use of genetic engineering to transfer genes for PHB production to *E. coli* which is able to grow faster, produces higher yields and has a more fragile membrane allowing for more convenient extraction. Still, with rising oil prices it is inevitable that PHB and other biopolymers will experience greater demand.

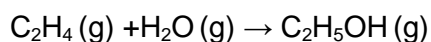
Ethanol

Dehydration of ethanol to ethylene:



This reaction takes place at 350°C and requires a catalyst. In the lab this is either concentrated H_2SO_4 or H_3PO_4 whilst porous ceramic catalysts are used in industry.

Hydration of ethylene to ethanol:



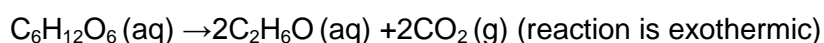
This reaction is carried out at 300°C using either dilute H_2SO_4 or H_3PO_4 as a catalyst. An acid catalyst is required as the water molecule will not attack the ethylene double bond itself.

Uses of ethanol:

- A common solvent for polar and non-polar substances such as cosmetics, flavourings, pharmaceuticals, perfumes and varnishes:
 - -OH end of the molecule is polar and dissolves polar substances by forming dipole dipole and hydrogen bonds with polar molecules
 - CH_3CH_2- (alkyl) part of the molecule is non-polar and dissolves non-polar substances through dispersion forces
- A fuel for combustion reactions to provide energy (mixed with petrol to form E10 fuel)
- Drinking and adding flavour to cooking

Fermentation:

(Alcoholic) fermentation is a biological process in which sugars are converted into cellular energy, producing ethanol and carbon dioxide in the process. In order for fermentation to occur, complex sugars such as starch and sucrose must be broken down into the fermentable sugars (monosaccharides) of glucose or fructose. This is done using enzymes e.g. invertase to break down sucrose into glucose. Other enzymes (zymase) then convert glucose into ethanol and carbon dioxide:



The following conditions promote fermentation:

- A suitable micro-organism such as yeast which produces enzymes is required. These enzymes act as catalysts to convert glucose to ethanol and carbon dioxide
- Temperature around 37°C
- Anaerobic conditions- airtight vessel
- Suitable grain or fruit to provide glucose
- Small amount of yeast nutrients such as phosphate salt
- Low pH of 3.7-4.6 to prevent the growth of pathogens

Fermentation continues until the concentration of alcohol reaches about 14-15% by volume. At this point, the yeast dies and fermentation stops. In order to achieve an ethanol concentration greater than 15%, fractional distillation is required where concentrations up to 95% can be obtained.

Production of ethanol from sugar cane:

Sugar production from sugar cane produces a large amount of molasses, sucrose rich syrup, as a by-product. Alcohol tolerant yeast is then added to the molasses which breaks down the sucrose into glucose and fructose. This then undergoes the fermentation reaction described above to produce ethanol and carbon dioxide.

Mass changes during fermentation:

Aim: To produce ethanol from glucose and monitor mass changes during the process

Risk assessment: Ethanol is flammable- avoid contact with naked flame

Method:

1. Place about 10g of glucose, 60mL of water and a spatula measure of yeast in a side arm conical flask. Stopper and agitate to mix the contents. Measure the weight of the conical flask. Position the delivery tube just under the surface of a beaker of limewater
2. Allow the mixture to ferment for one week, measuring its mass daily and recording observations in the limewater beaker

Results:

Mass of flask over time:

Days Passed	Mass (g)
0	411.69
1	407.58
2	407.44
3	407.32
4	407.22

Observations in limewater beaker: Limewater turned from clear to cloudy, indicating that carbon dioxide was produced by fermentation

Mass lost: $411.69 - 407.22 = 4.47\text{g}$

Mass CO_2 produced = 4.47g

Discussion:

- Carbon dioxide is produced by the fermentation of glucose
- Equation of fermentation is: $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g})$
- Moles CO_2 produced = 0.102mol
- Moles $\text{C}_2\text{H}_6\text{O}$ produced = 0.102mol
- Mass $\text{C}_2\text{H}_6\text{O}$ produced = 4.67g
- % Glucose used = $(4.47 + 4.67) / 10 = 91.4\%$

Conclusion: The mass of a flask in which fermentation is occurring decreases over time due to carbon dioxide being released.

Combustion of ethanol:

Molar heat of combustion- The heat liberated when one mole of a substance undergoes complete combustion with oxygen at standard atmospheric pressure with the final products being carbon dioxide gas and liquid water

It can be found by determining the amount of heat released by a certain amount of substance using a calorimeter and then converting the value into kilojoules per mole of fuel. Note that the molar heat of combustion is minus the enthalpy change:

$$\Delta H_c = -\Delta H = \frac{mC\Delta T}{n}$$

Where ΔH_c is molar heat of combustion (Jmol^{-1}), ΔH is change in enthalpy (Jmol^{-1}), m is mass of heat absorber (kg), C is specific heat capacity of heat absorber ($\text{JK}^{-1}\text{kg}^{-1}$), ΔT is change in temperature (K) and n is moles of fuel

Determining the heat of combustion of alcohols:

Aim: To determine the molar heat of combustion and heat of combustion per gram of alcohols of different carbon lengths

Risk analysis: Methanol, ethanol and 1-propanol are highly flammable and toxic except for ethanol which is only slightly toxic. Carbon monoxide and soot may also be produced. Take caution when burning, extinguishing the spirit burner by replacing cap

Method:

1. Measure the mass of a spirit burner full of ethanol
2. Attach a 250mL metal can to a retort stand with a boss and clamp for use as a calorimeter. Add 100mL of water to the metal can, place a thermometer in the water and record the temperature of the water. Place the spirit burner underneath the metal can
3. Light the spirit burner. Note the temperature of the water and extinguish the spirit burner when the temperature of the water increases by 10°C . Use this and the formula $\Delta H = -mC\Delta T$ to calculate the amount of heat absorbed
4. Measure the mass of the spirit burner and note the change in mass- this is the amount of fuel burnt. Use this and the amount of heat absorbed to find the molar heat of combustion
5. Repeat with methanol and propanol

Results:

Alcohol	Molar heat of combustion (Jmol^{-1})		Heat of combustion (Jg^{-1})	
	Obtained	Actual	Obtained	Actual
Methanol	2.88×10^5	7.25×10^5	9.00×10^3	2.27×10^4
Ethanol	6.22×10^5	1.367×10^6	1.35×10^4	2.97×10^4
1-Propanol	8.32×10^5	2.016×10^6	1.39×10^4	3.36×10^4

Molar heat of combustion increases with carbon chain length as more energy is released when breaking more bonds. Heat of combustion per gram also increases with carbon chain length although to a lesser extent than molar heat of combustion. This is because greater carbon chain length means greater molecular weight.

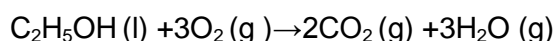
Discussion:

- Values obtained by this experiment deviated from their true accepted because:
 - Not all the heat was transferred to the tin can
 - Some of the heat might have escaped into the can and air
 - Incomplete combustion may have occurred
 - Test was not carried out under standard conditions
- Results for this experiment could be improved by:
 - Placing the spirit burner closer to the tin can
 - Using a more insulating material for the sides of the calorimeter and adding a lid
 - Ensuring there is sufficient oxygen for complete combustion

Conclusion: The molar heat of combustion of alcohols increases with the length of the carbon chain, as does the heat of combustion per gram although to a lesser extent

Potential of ethanol as an alternative fuel:

Ethanol burns with oxygen in the reaction:



This is able to be burnt as a fuel. For example, it can be used in camping as a portable fuel or mixed with petrol as a fuel extender. There is also potential for ethanol to be used as an alternative fuel for petrol in motor vehicles.

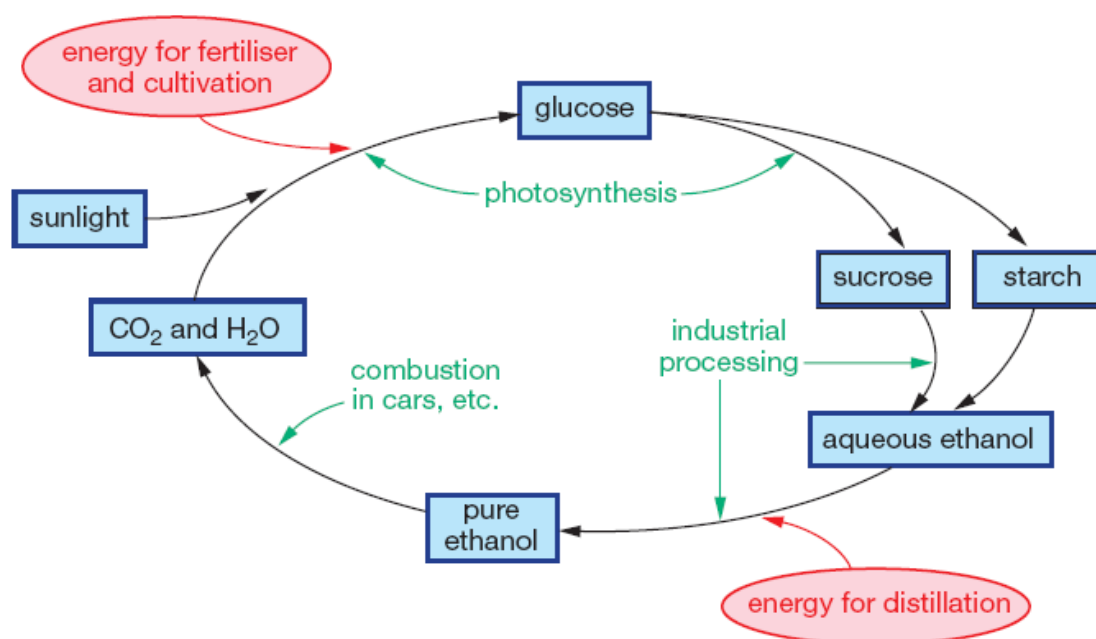
Advantages:

- Renewable resource- Ethanol can be produced from plants which can be grown indefinitely. The energy released by burning ethanol comes from the Sun whose energy is absorbed during photosynthesis
- Soluble in water and so is less toxic to marine life than oil spills
- As a liquid fuel, ethanol is easy to transport and with a higher flash point, is easier to store
- Burns more completely and efficiently due to its shorter carbon chain length producing less pollutants such as carbon monoxide and soot
- Oxygen present in ethanol means it burns more evenly than petrol and so toxic additives such as methyl tert-butyl-ether (MTBE) which are added to petrol are not needed
- Greenhouse neutral since carbon dioxide released by burning ethanol is equal to the amount absorbed by photosynthesis. However, this excludes the energy required to make fertiliser and to distil ethanol

Disadvantages:

- Large areas of agricultural land are required to grow crops that could otherwise be used to grow food
- Disposal of large amounts of smelly wastes produced by fermentation is required
- Produces less energy per gram than petrol
- Special engines are needed to use ethanol as a fuel in mixtures in concentrations greater than 10% due to the corrosive nature of ethanol
- Energy is still required to make fertiliser and for the distillation process

In Australia, government subsidies and excise concessions exist to encourage the production of ethanol for use as fuel. This is usually mixed with petrol to form E10 fuel with 10% ethanol, as is the case in other countries. However, due to the cost of infrastructure and engine modifications, concentrations greater than 10% are difficult to achieve. In Brazil, the government began a program to use ethanol as a fuel in order to reduce reliance on oil imports and boost employment. This required large amounts of government subsidies for ethanol production and engine modification, but was highly successful with over 90% cars in Brazil running on ethanol in the mid-1980s. However, the project was abandoned in the 1990s due to a shortage of ethanol and lower oil prices, leading to cars using petrol-ethanol mixtures instead. However, the ethanol industry was revitalised in 2003 with rising oil prices and the introduction of flex-fuel cars which can run on ethanol, petrol, or a mixture of both. Brazil's ethanol fuel program provides evidence of the practicality of ethanol as an alternative car fuel, especially in light of dwindling oil resources.



IUPAC nomenclature for naming alkanols:

Alcohols are organic compounds in which a hydroxyl functional group is bound to a carbon atom. Alkanols are a special subgroup of alcohols in which an alkane has one or more hydrogen atoms replaced by an -OH group. In naming straight-chain alkanols with only one -OH group, the alcohol is named by replacing the -e of the related alkane and replacing it with the -ol substance e.g. ethane \rightarrow ethanol. A number indicating the position of the -OH group is placed in the front e.g. 1-propanol is $\text{OH-CH}_2\text{-CH}_2\text{-CH}_3$

When there is more than one -OH group, the -diol , -triol etc. suffixes are added to the end of the related alkane (e is not dropped) and numbers indicating the positions of the -OH groups are placed in front e.g. 1-4 butanediol is $\text{OH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$

Note the following prefixes for the number of carbon atoms:

Meth-	1	Prop-	3	Pent-	5	Hept-	7
Eth-	2	But-	4	Hex-	6	Oct-	8

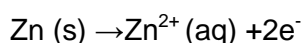
Electrochemistry

Displacement reactions:

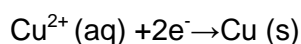
A displacement reaction is a reaction in which one element replaces another element in a compound. In metal displacement reactions, one metal displaces another metal in solution, turning metal ions into the neutral species by transferring some of its electrons. The displacing metal itself is transformed into ions which are dissolved in solution. Since the reaction involves the transfer of electrons, it is an oxidation-reduction (redox) reaction.

For example, when zinc Zn is placed in copper (II) sulphate CuSO_4 solution, the zinc displaces the copper ions in solution. This causes the solid zinc to reduce in size as it is dissolved in solution and for copper to form on the zinc. The solution also turns from blue to colourless as copper ions are removed from solution.

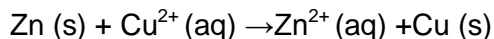
The zinc undergoes an oxidation half-reaction (loses electrons (to copper)), turning it into zinc ions:



Meanwhile, the copper undergoes a reduction half-reaction (gains electrons (from zinc)), turning it into the neutral species:



The total redox reaction is given by:



This reaction will only take place if the displacing metal is more active than the one in solution. For example, zinc placed in copper will result in a displacement reaction but copper placed in zinc will not. Zinc is considered to be a more active metal than copper as determined by the activity series of metals. As a result it has a greater tendency to lose electrons/ be oxidised than copper, allowing a displacement reaction to occur when it is placed in a solution of copper ions.

If the displacing metal is more active, or higher up in the activity series, than the metal in solution, a displacement reaction will occur. Conversely, if a displacement reaction occurs then the displacing metal is more active than the metal in solution and this can be used to determine the order of metals in the activity series of metals.

Oxidation State:

The oxidation state of an element in a compound is the number of electrons transferred from the neutral atom when a compound is formed. The following rules apply to oxidation states:

1. Substances in the elemental state have an oxidation state of 0
2. For monatomic ions, the oxidation state is the charge of the ion
3. The sum of oxidation states of all the atoms in neutral molecules or ionic compounds is 0
4. The sum of oxidation states of all atoms in a polyatomic ion is the charge of the ion
5. Combined oxygen has an oxidation state of -2 except in peroxides (-1) and F_2O (+2)
6. Combined hydrogen has an oxidation state of +1 except in metal hydrides (-1)

By finding the oxidation states of atoms in a reaction it is possible to determine whether the reaction is a redox reaction. It can also be used to determine which species have been oxidised or reduced and which species are neutral species.

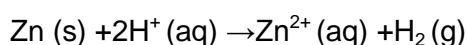
Oxidation- the loss of electrons, marked by an increase in oxidation state

Reduction- the gain of electrons, marked by a decrease in oxidation state

The oxidant in a redox reaction is the species that accepts electrons which is itself reduced.

The reductant in a redox reaction is the species that donates electrons which is itself oxidised.

For example, in the following reaction, zinc is oxidised from 0 to +2 whilst the two hydrogen ions are reduced from +1 to 0. Note that the total change in oxidation states is zero:



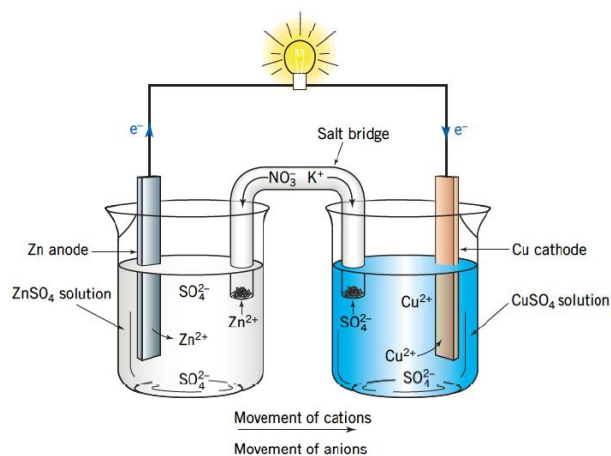
Galvanic Cells:

In a redox reaction, electrons flow from the reductant to the oxidant. If the reductant and oxidant are separated by a conductor, an electrical current will flow in the external circuit. A galvanic cell consists of two half cells each with a conductive metal or graphite, known as the electrode, in an electrolyte solution. These are connected by a salt bridge containing an electrolyte such as KNO_3 .

Electrode- The conductors of a cell which are connected to the external circuit

Anode- The electrode at which positive charge flows into a device; this is where oxidation occurs; in galvanic cells this electrode is negative

Cathode- The electrode at which negative charge flows into a device; this is where reduction occurs; in galvanic cells this electrode is positive



Electrolyte- A substance which in solution or molten conducts electricity

In the operation of the galvanic cell, electrons are released by an oxidation reaction at the anode and move through the external circuit to be absorbed by a reduction reaction at the cathode. In the anode half-cell the concentration of cations increases whilst in the cathode half-cell the concentration of cations decreases. In order to maintain electrical neutrality, anions from the salt bridge move into anode half-cell whilst cations from the salt bridge move into the cathode half-cell. Cations from the anode half-cell and anions from the cathode half-cell also move into the salt bridge.

The diagram above shows an example galvanic cell with zinc and copper electrodes. This cell can be expressed as $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$

Conditions under which a galvanic cell is produced:

Aim: To determine the conditions necessary for a galvanic cell

Method:

1. Place a clean 2 cent piece on top of a 20 cent piece and connect each of the terminals of a voltmeter. Note if a reading occurs; if not, reverse the polarity of the connections
2. Separate the coins and insert a small disc of filter paper between them and again test whether the combination gives a meter reading
3. Repeat this investigation with filter paper disks soaked in distilled water, methylated spirits, sucrose solution, NaCl solution and H₂SO₄ solution. In cases where a meter reading is produced, record the polarity of the connection
4. Repeat the investigation using a filter paper soaked in a liquid which produced a reading on the meter previously but with two 2 cent pieces and two 20 cent pieces

Results:

Coupling of 2 cent and 20 cent coins:

Coupling		Voltmeter reading (V)	Polarity
Direct		0	-
Through dry filter paper		0	-
Through filter paper soaked in	Distilled water	0	-
	Methylated spirit	0	-
	Sucrose solution	0	-
	NaCl solution	0.1	20 cent coin -ve
	H ₂ SO ₄ solution	0.1	20 cent coin -ve

Coupling of similar coins:

Voltaic couple	Voltmeter reading	Polarity
2 cent- 2 cent	0	-
20 cent- 20 cent	0	-

Discussion:

- The only couplings which produced a voltage were the coupling of 2 cent and 20 cent coins through NaCl solution and H₂SO₄ solution
- Different metals are needed for galvanic cells in order to produce a potential difference
- NaCl and H₂SO₄ are both electrolytes. The electrolytes allow current to flow between the two metals, completing the circuit
- Current only flows when there is a suitable connector between them

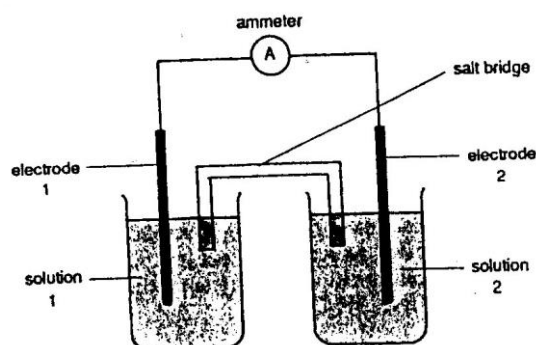
Conclusion: A galvanic cell requires two different metals, a salt bridge separating them and a conductor joining them

Potential differences of different combinations of metals in an electrolyte solution:

Aim: To determine the voltages of different galvanic cells

Method:

1. Set up a galvanic cell as shown in the diagram to the right
2. Record the solution present in each beaker and the type of electrodes. Connect up the circuit and record the voltage



Results:

Voltages produced by different galvanic cells and corresponding theoretical values

Cell	Voltage produced (V)	Theoretical voltage (V)
Mg Mg ²⁺ Cu ²⁺ Cu	0.20	2.23
Mg Mg ²⁺ Pb ²⁺ Pb	0.24	2.70
Zn Zn ²⁺ Cu ²⁺ Cu	0.20	1.10
Zn Zn ²⁺ Cu ²⁺ Cu	0.20	0.78
Zn Zn ²⁺ Cu ²⁺ Cu	0.10	0.63
Zn Zn ²⁺ Cu ²⁺ Cu	0.10	0.32

Discussion:

- Voltages produced were a lot less than the theoretical voltage as the concentration of the solutions was only 0.1M.
- However, it can still be seen that a greater difference in standard potentials will result in a greater voltage being produced
- This difference in standard potentials is related to the difference in reactivity

Conclusion: The greater the difference in reactivity of two metal in a galvanic cell, the more voltage that is produced

Comparison of commercial cells:

Criteria	Zinc- Carbon Dry Cell	Silver Oxide Button Cell
Diagram		

Criteria	Zinc-Carbon Dry Cell	Silver Oxide Button Cell
Anode	Zinc $\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$	Zinc $\text{Zn (s)} + 2(\text{OH})^- (\text{aq}) \rightarrow \text{ZnO (s)} + \text{H}_2\text{O (l)} + 2\text{e}^-$
Cathode	Carbon (inert) $2\text{MnO}_2 (\text{s}) + \text{NH}_4^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 (\text{s}) + 2\text{NH}_3 (\text{aq}) + \text{H}_2\text{O (l)}$	Silver oxide $\text{Ag}_2\text{O (s)} + \text{H}_2\text{O (l)} + 2\text{e}^- \rightarrow 2\text{Ag (s)} + 2\text{OH}^- (\text{aq})$
Electrolyte	NH_4Cl	NaOH/ KOH
Uses	Flashlights, portable radios, battery operated clocks, toys	Watches, hearing aids, calculators
Advantages	Cheap and easy to produce, store and use	Can provide considerable amounts of electricity at a very constant voltage over a long period of time
Disadvantages	Does not generate a very large amount of electricity for size Cannot deliver high currents Can develop leaks when flat	Expensive to produce
Relative cost	Cheap	Expensive due to silver content
Practicality	Small and easy to use Good for use in portable devices	Very small Good for use in portable devices
Impact on environment	Minimal environmental problems Manganese (III) readily oxidised to stable manganese (IV) oxide Small quantities of zinc no problem; ammonium salts and carbon are harmless	Until recently, silver oxide cells contained up to 0.2% mercury which becomes hazardous at the onset of leakage although mercury free cells are now being produced
Impact on society	Enabled the use of portable devices, making society more mobile	Enabled the use of portable devices, making society more mobile

Standard electrode potentials:

The standard electrode potential (E^\ominus) of an electrode is the potential of that electrode in its standard state relative to the standard hydrogen electrode. The standard state is 1.000M for solutes and 100.0kPa for gases. The standard hydrogen electrode consists of a piece of platinum immersed in a 1.000M solution of HCl with hydrogen gas being bubbled over the electrode at a pressure of 100.0kPa. Hydrogen ions in solution are reduced to hydrogen gas according to the reaction $2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$.

Standard electrode potentials are assigned to a particular reduction half reaction. For example, the standard potential of the reaction $\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Zn (s)}$ is -0.76V. The voltage of the corresponding oxidation half reaction would be minus the standard electrode potential. Thus, the voltage of the reaction $\text{Zn (s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^-$ would be +0.76V. The standard potentials also provide a measure of the relative activity of different metals, with metals with lower standard potentials being more active/ having greater reducing strength.

The total standard voltage of a reaction/ galvanic cell is the sum of the voltages of the oxidation and reduction reactions:

$$V_{\text{total}}^\ominus = V_{\text{reduction}}^\ominus + V_{\text{oxidation}}^\ominus = E_A^\ominus - E_B^\ominus$$

Note that multiplying half reactions so that both reactions have the same number of electrons does not alter the value of E^\ominus

Nuclear Chemistry

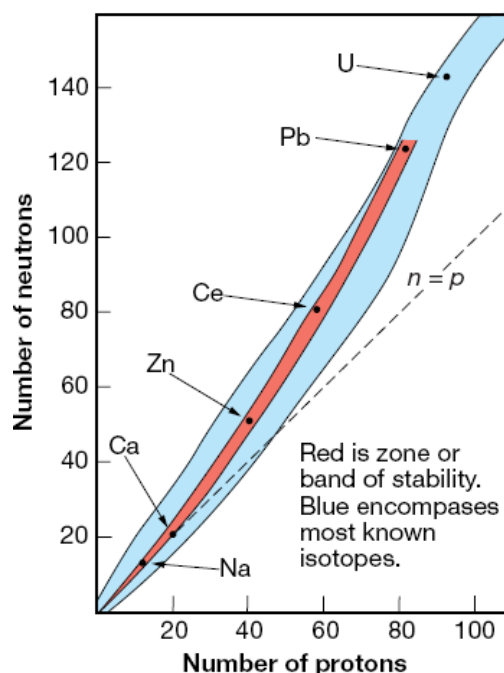
Stable and radioactive isotopes:

Isotope- Same number of protons and thus same atomic number but different number of neutrons and thus different mass number:



Where A is mass number, Z is atomic number and M is the element

Some isotopes are stable so its nucleus doesn't change. Radioactive isotopes have an unstable nucleus which releases particles or energy to become more stable. A nucleus is unstable if it has a neutron-proton ratio that is too high or too low for its atomic number (that is, it is outside the zone of stability as shown in the diagram to the right- N: P ratio of stable isotopes is 1:1 for lighter elements but increases with atomic number) or if the nucleus is too heavy- all isotopes with an atomic number greater than 83 (bismuth) are unstable. There are several types of radiation released by unstable nuclei:



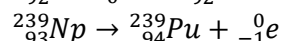
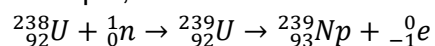
1. Alpha decay (α): This occurs when there are too many protons and neutrons (nucleus is too heavy). The nucleus loses mass by emitting an α particle which consists of two protons and neutrons (${}^4_2\text{He}$ nucleus), causing the mass number to decrease by 4 and the atomic number to decrease by 2, forming a new element
2. Beta decay (β^-): This occurs when there are too many neutrons for the number of protons present. A neutron decays into a proton and an electron (β^- particle), increasing the isotope's atomic number by 1 and forming a new element without a change in mass number
3. Positron emission (β^+): This occurs when there are too many protons for the number of neutrons present. A proton decays into a neutron and a positron (β^+ particle), decreasing the isotope's atomic number by 1 and forming a new element without a change in mass number
4. Electron capture: This occurs when there are too many protons for the number of neutrons present. One of the inner-orbital electrons is captured by the nucleus. A proton is converted into a neutron, decreasing the isotope's atomic number by 1 and forming a new element without a change in mass number
5. Gamma radiation (γ): This is the emission of high energy photons to enable the nucleus to lose excess energy and become more stable. Gamma radiation accompanies most other types of radioactive decay

Radiation	Alpha (α)	Beta (β)	Gamma (γ)
Composition	Helium nucleus ${}^4_2\text{He}$	Electron ${}^0_{-1}e$	Photons/ EMR
Mass	4AMU	5×10^{-4} AMU	0
Penetration	Stopped by a thin sheet of paper/ skin	Stopped by plastic, wood or aluminium	Dampened by lead or concrete
Speed	5% c (speed of light)	Up to 99% c	Travels at c
Charge	+2	-1	0

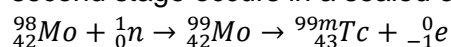
Production of transuranic elements and commercial radioisotopes:

Elements with atomic numbers greater than 92 and artificial radioisotopes are produced by bombarding the nucleus of atoms with neutrons or the nuclei of other atoms. This is done in nuclear reactors, accelerators and cyclotrons:

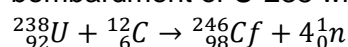
- Nuclear reactors: Neutron-induced transmutation occurs in nuclear reactors where a steady source of neutrons from the fission of U-235 is available. Since neutrons are uncharged, they don't need to be accelerated at high velocities to be absorbed. For example, neutron bombardment of U-238 is used to produce plutonium:



Neutron bombardment is used to produce neutron rich radioisotopes. For example, technetium-99m is produced from molybdenum-98 (first stage occurs in nuclear reactors, second stage occurs in a sealed on the way to hospitals)

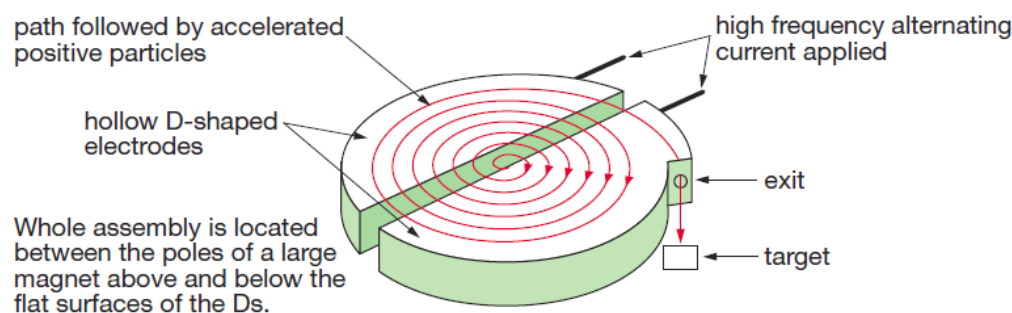
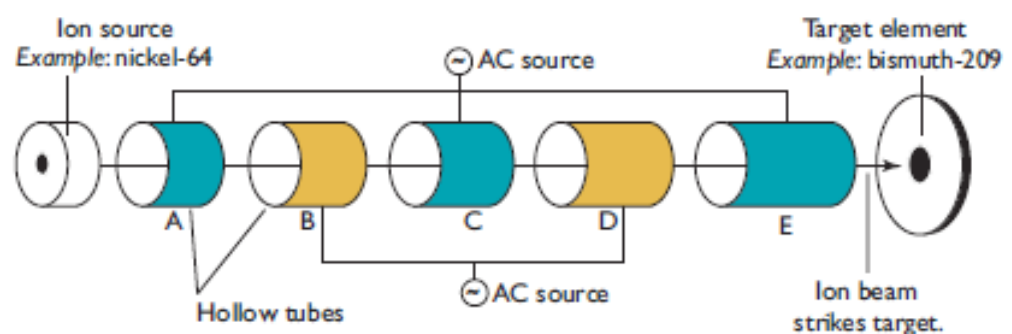
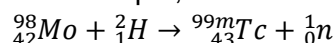


- Particle accelerators and cyclotrons: Since atomic nuclei are positively charged, they must be accelerated to high speeds in order to overcome electrostatic repulsion and be absorbed by the target nucleus. Particle accelerators consist of a series of cylindrical tubes made alternatively positive and negative by an AC power source which accelerates particles up to near-light speeds. Cyclotrons are a special type of accelerator in which particles are accelerated in a spiral path to take up less space. Alternating north and south magnetic fields are used to constrain particles onto the circular path. For example, bombardment of U-238 with a carbon-12 nucleus is used to produce californium:



Bombardment with charged particles is used to produce neutron-deficient radioisotopes.

For example, technetium-99m is produced by bombarding molybdenum-98 with deuterium:



Recent discoveries of elements:

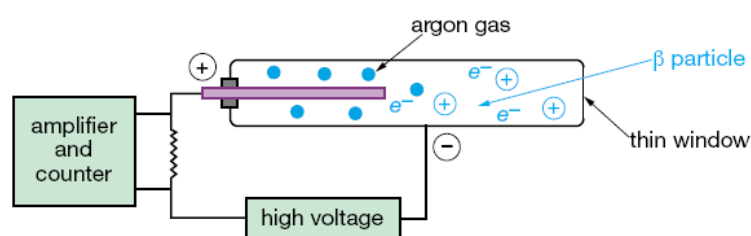
- Darmstadtium - Produced at the Lawrence Berkeley National Laboratory, USA in 1994
$$^{208}_{82}\text{Pb} + ^{64}_{28}\text{Ni} \rightarrow ^{271}_{110}\text{Ds} + ^1_0\text{n}$$
- Roentgenium- Produced at GSI in Darmstadt, Germany in 1996
$$^{209}_{83}\text{Bi} + ^{64}_{28}\text{Ni} \rightarrow ^{272}_{111}\text{Rg} + ^1_0\text{n}$$
- Copernicium - Produced at GSI in Darmstadt, Germany in 1994
$$^{208}_{82}\text{Pb} + ^{70}_{30}\text{Zn} \rightarrow ^{278}_{112}\text{Cn} \rightarrow ^{277}_{112}\text{Cn} + ^1_0\text{n}$$

Instruments used to detect radiation:

- Photographic film: Photographic film will darken upon exposure to radiation as a result of the decomposition of a silver halide into silver and a halide gas. The degree of darkening indicates the intensity of the radiation. It is used in radiation badges to monitor the exposure of workers exposed to radiation on a regular basis

- Geiger- Müller counter:

Radiation enters a thin window and ionises a gas (usually argon), knocking an electron out of it. The high voltage accelerates it to a central electrode and



as it gains speed it ionises more argon atoms. This causes an electrical pulse which is amplified and measured by the number of clicks produced by an audio amplifier or a digital counter. Positive argon ions move to the negative case to complete the circuit

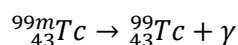
- Scintillation counter: These use certain materials such as ZnS_2 which emit a flash of light (scintillation) when struck by ionising radiation. These are electronically counted by a photomultiplier and digital counter to measure the amount of radiation
- Cloud chamber: This consists of a chamber filled with a supersaturated vapour of water or alcohol. When radiation passes through it, it ionises some of the air which acts as nuclei upon which droplets form. The type of path can be used to determine the type of radiation present:

- Alpha particles show up as thick and straight but short cloud trails
- Beta particle form thinner, longer, zigzag trails
- Gamma radiation generates long, wispy and weak trails

Cloud chambers may be used in conjunction with magnetic or electric fields as a means of verifying the type of radiation present by noting the deflection in trails

Uses of radioisotopes in industry and medicine:

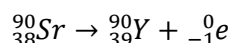
Technetium-99m $^{99m}_{43}\text{Tc}$ is used in medicine as a diagnostic tool. It decays into the more stable Tc-99, releasing gamma radiation in the process:



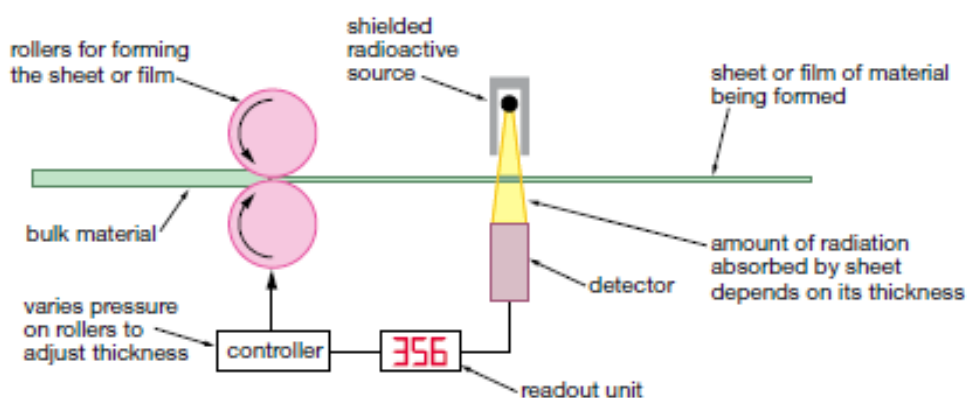
Tc-99m can be combined with other compounds and injected into different parts of the body. The gamma radiation produced by the isotope can then be detected using a scintillation counter in order to determine where in the body the injected technetium has travelled to. For example, by combining Tc-99m with a tin compound, it will bind to red blood cells when injected into the blood stream and travel throughout the circulatory system. This can be used to map blood flow in order to determine the location of blood clots, constrictions or other circulatory disorders. When combined with other substances it can be used to study the brain, kidney, bone, liver and spleen. For example, if it is combined with glucose it goes to areas high in glucose such as cysts and cancers

Tc-99m has a half-life of just 6 hours, minimising patient's exposure to radiation whilst providing ample time to scan the body. This property makes Tc-99m useful as a radioactive tracer.

Strontium-90 $^{90}_{38}\text{Sr}$ is used in industry as a thickness gauge. Sr-90 undergoes beta decay into Yttrium-90:



Sr-90 is placed one side of a sheet or film of material being formed. Some of the beta radiation that it emits is absorbed by the material and the remainder is detected by a radiation detector on the other side. The intensity of radiation that passes through is an indicator of the material's thickness, with thicker material absorbing more radiation. The thickness gauge can be built into a feedback loop to vary the pressure on rollers to adjust the material's thickness.



Sr-90's long half-life of 28 years makes it ideal for use as a thickness gauge as this means it does not have to be replaced very often. In addition, the low energy emission of Sr-90 allows most of the radiation to be absorbed by the material as well as minimising hazards to workers.

Benefits and problems associated with the use of radioisotopes:

Benefits:

- Enables more sensitive, precise and reliable monitoring equipment
- Enables sterilisation of food and medical supplies
- Provides a non-invasive diagnostic procedure for diseases
- Enabled radiation therapy as a treatment for cancer

Problems:

- Radiation from isotopes are harmful to people and may cause:
 - Tissue damage- shows immediately- skin burns, nausea, radiation sickness, death
 - Cancer- does not show up till 10-20 years after exposure- leukaemia and lung cancer
 - Genetic damage- leads to deformities in offspring

Harmful effects of radiation can be minimised by taking safety precautions such as:

- Storing radioactive materials in well-shielded containers
- Ensuring radiation is only directed where it is required
- Ensuring people using radioactive equipment or materials are well-trained
- Wearing appropriate safety clothing e.g. full protective body suits
- Wearing radiation badges to ensure cumulative radiation exposure is not too high
- Ensuring proper procedures for the safe storage and disposal of radioactive wastes
- Placing clear and unambiguous signs wherever radiation equipment or materials are stored

The Acidic Environment

Indicators

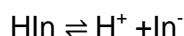
Acids- Corrosive, sour taste, $\text{pH} < 7$, conducts electricity in solution e.g. gastric juice, lemon juice, soft drinks, wine vinegar

Bases- Caustic, bitter taste, soapy feel, $\text{pH} > 7$, conducts electricity in solution e.g. baking soda, limewater, bleach

Neutral- Neither acidic or basic, $\text{pH} = 7$ e.g. distilled water

Common indicators:

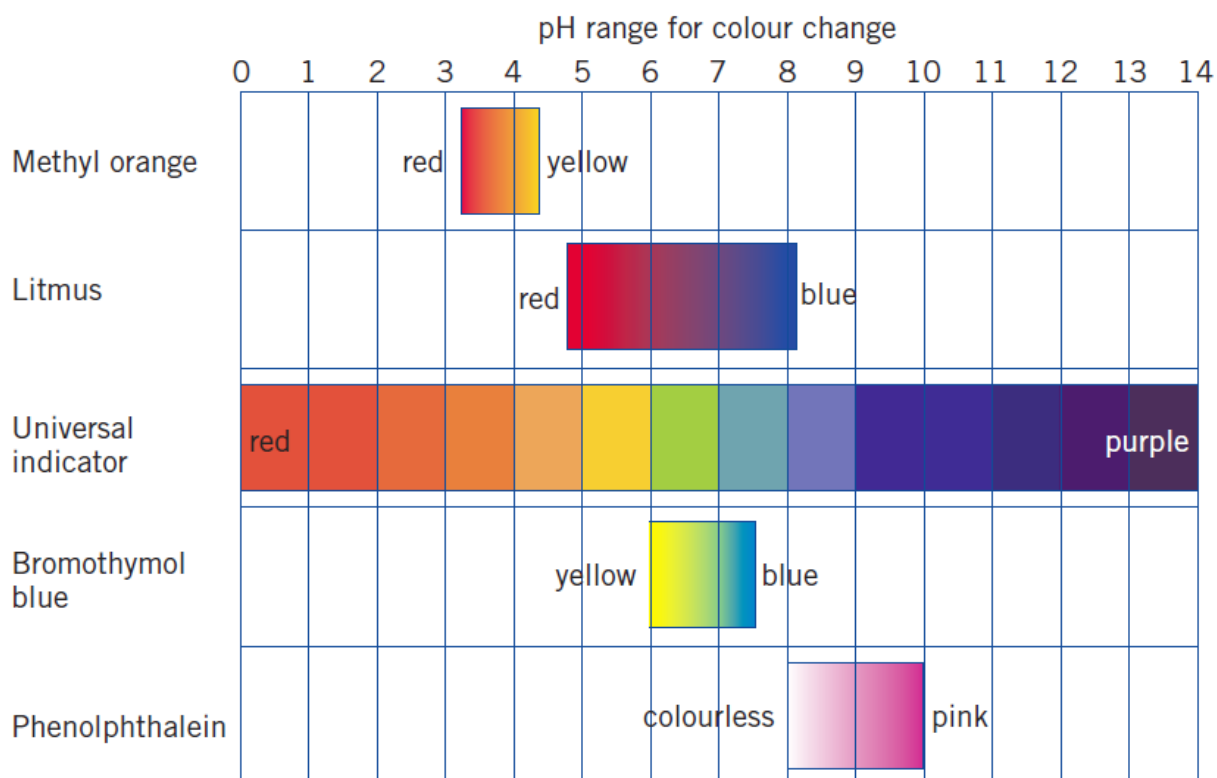
An indicator is an organic or synthetically made dye which has one colour in an acidic solution and a different colour in a basic solution. They are usually organic acids, represented by HIn where H represents a hydrogen atom that can be released as a hydrogen ion H^+ whilst In represents the rest of the organic molecule:



When conditions are acidic, the equilibrium is pushed to the left, producing more HIn . Basic conditions cause hydroxide ions to react with hydrogen ions, shifting the equilibrium to the right. HIn and In^- are typically different colours and thus varying the ratio of the two will alter the colour of the indicator

Common indicators include methyl orange, bromothymol blue, phenolphthalein and litmus. These only contain one indicator chemical and thus shift between two colours, with the change occurring over a range of pH. Universal indicator has many indicator chemicals and so has a gradual colour change over the entire pH scale:

Indicator	Highly acidic	Slightly acidic	Neutral	Slightly basic	Highly basic	pH range of colour change
Methyl Orange	Red	Yellow	Yellow	Yellow	Yellow	3.1-4.4
Bromothymol Blue	Yellow	Yellow	Green	Blue	Blue	6.0-7.6
Phenolphthalein	Colourless	Colourless	Colourless	Colourless	Purple/pink	8.3-10.0
Litmus	Red	Red	Purple	Blue	Blue	5.0-8.0



Practical uses for indicators:

- Testing acidity and alkalinity of soils to ensure optimal growing conditions for plants (insoluble BaSO_4 is also added to provide a good white background for contrast)
- Testing home swimming pool water to ensure the comfort of swimmers
- Monitoring wastes from photographic processing (wastes are very alkaline and need to be neutralised)
- Testing aquarium water to ensure optimal conditions for fish
- Determining the reaction end-point in titration

Preparing and Testing of Red Cabbage Indicator

Aim: To prepare and test a natural indicator

Method:

1. Tear or slice red cabbage leaves into small pieces and place them into a beaker. Just cover the red cabbage with water
2. Boil for 10-15 mins over a Bunsen burner
3. Let the mixture cool until warm then remove the cabbage with the tablespoon
4. Add a small amount of the red cabbage solution to water, white vinegar solution and baking soda solution and record any colour changes

Results:

Colour when placed into different solutions:

Solution	Colour
Water	Purple
White vinegar	Red
Baking soda	Blue-green

Discussion:

When placed in a neutral solution (water), the red cabbage indicator turned purple. In an acidic solution (white vinegar), the indicator turned red whilst in a basic solution (baking soda), the indicator turned blue-green. Thus, red cabbage indicator is purple in neutral solutions, red in acidic solutions and blue-green in neutral solutions.

Red cabbage contains two main types of plant dyes; anthocyanin and flavanol. The anthocyanin pigments are red in strong acidic solutions, blue in neutral and weakly basic solutions and colourless in strongly basic solutions (anthocyanin is diprotic and so has 3 colours in its range). Weakly acidic solutions contain some of the red and blue form and thus appear purple. Flavanol pigments are colourless in acidic and neutral solutions and yellow in basic solutions. These two pigments are responsible for the range of colours of red cabbage indicator

Conclusion: It is possible to make an indicator in laboratory conditions and test its colour in acidic, neutral and basic solutions

Using indicators to classify household substances as acidic, neutral or basic

Aim: To classify some household substances as acidic, basic or neutral

Method: Put about 2mL of household substance in a test tube and add a few drops of universal indicator. Record the colour of the solution and refer to the pH card to estimate the pH. Classify the substances as acidic, basic or neutral

.

Results:

Classification of household substances:

Household substance	Colour in universal Indicator	Approx. pH using universal indicator	Classification
Hair conditioner	Pink-red	4.0	Acidic
Lemon Juice	Pink-red	4.0	Acidic
Vinegar	Pink-red	4.0	Acidic
Toilet Cleaner	Pink-red	4.0	Acidic
Soda Water	Orange	5.0	Acidic
Hand Soap	Red	5.0	Acidic
Shampoo	Peach	5.5	Acidic
Milk	Orange-yellow	6.0	Acidic
Washing Up Liquid	Orange	6.0	Acidic
Hand Sanitiser	Orange	6.0	Acidic
Dishwasher Liquid	Yellow	6.5	Acidic
Toothpaste	Apple Green	7.0	Neutral
Soap	Bottle-green	8.5	Basic
Bleach	Green	9.0	Basic

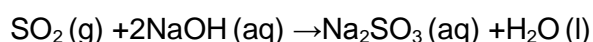
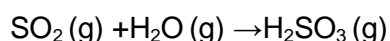
Discussion:

It was difficult to pinpoint the pH of these substances as the use of indicators gives only an approximate pH range. It appears that substances used for cleaning are more likely to be very acidic or basic whilst substances applied on skin or ingested tend to be more neutral or are usually diluted.

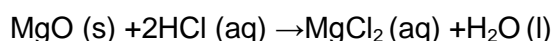
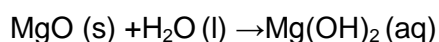
Conclusion: Indicators such as universal indicators can be used to classify household substances as acidic, basic or neutral

Acidic oxides

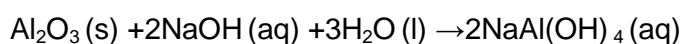
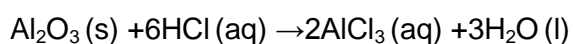
Acidic oxides- generally the oxides of non-metals such as SO_2 and CO_2 - these react with water to form an acid or with a base to form a salt:



Basic oxides- generally the oxides of metals such as MgO and Na_2O - these react with water to form a base or with an acid to form a salt:



Amphoteric oxides- oxides of certain elements near the semi-metals such as Al_2O_3 and ZnO - these can act as both an acid and a base:

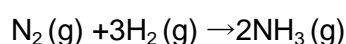
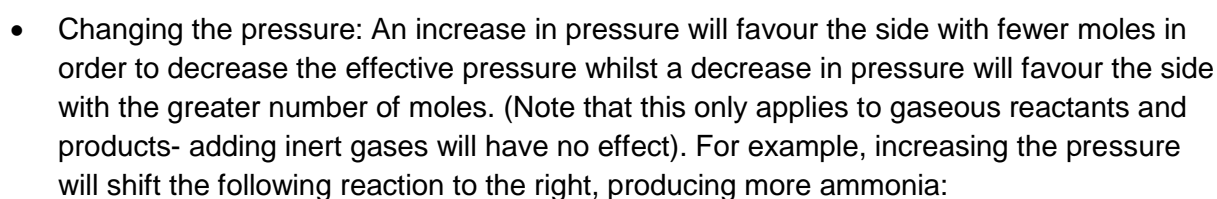
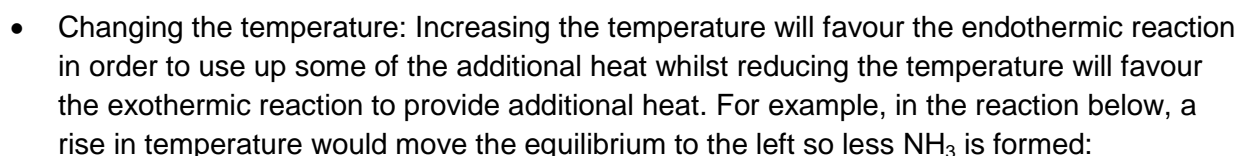


Neutral oxides- oxides of certain non-metals such as CO , NO and H_2O which are neutral

[illegible]

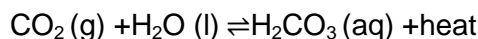
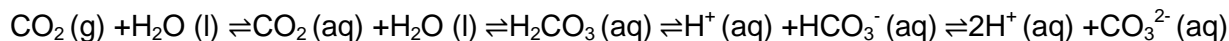
Le Chatalier's Principle:

- Changing the concentration: Increasing the concentration of a reactant will shift the equilibrium in the opposite direction in order to use up the additional amount. Likewise, reducing a reactant's concentration will shift equilibrium towards the side of the reactant in order to counteract the decrease. (Note that this only applies to dissolved and gaseous substances and adding a solid or pure liquid will not affect equilibrium). For example, adding more N_2 or H_2 to the following equation move the equilibrium to the right in order to use up the extra N_2 and H_2 :



Catalysts increase the rate of reaction by lowering activation energy. However, it does so equally in both directions, resulting in no change in equilibrium. It does, however, result in equilibrium being reached more quickly.

Equilibrium of carbon dioxide and water:



This above reaction shows the dissolution of carbon dioxide in water. A shift to the right is equivalent to an increase in the solubility of carbon dioxide. By Le Chatelier's Principle, a change in conditions will alter this reaction's equilibrium and affect the solubility of CO_2 :

- Changing pressure: Increasing pressure will favour the side with fewer moles of gas (the right). Increasing pressure would thus increase the solubility of CO_2
- Changing temperature: Increasing temperature will favour the endothermic reaction and shift the equilibrium to the left, releasing some CO_2
- Adding salt: The addition of salt uses some of the water in its dissolution, increasing the effective concentration of CO_2 and H_2CO_3 and moving the equilibrium to the left in order to counteract this. This will release a significant amount of CO_2
- Adding an acid or base: The addition of an acid increases the concentration of H^+ ions, shifting the equilibrium to the left and releasing some CO_2 . Adding a base will cause hydroxide ions to react with H^+ ions to form water, increasing the concentration of water and reducing the concentration of H^+ ions. This would shift the equilibrium to the right, absorbing some CO_2

Oxides of sulphur and nitrogen:

Natural sources of nitrogen oxides:

1. Lighting: $\text{O}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
2. Nitric oxide (NO) and nitrous oxide (N_2O) produced by soil bacteria
3. Action of sunlight on NO and O_2 : $\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

Industrial sources of nitrogen oxides:

1. High temperature environments of car engines and power plants: $\text{O}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
2. N_2O used as a sedative/ analgesic and as a fuel in racing cars

Natural sources of sulphur dioxide:

1. Some bacteria decompose organic matter to produce H_2S : $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
2. Volcanic eruptions and geysers
3. Bushfires

Industrial sources of sulphur dioxide:

1. Combustion of iron sulphide in coal: $4\text{FeS}_2(\text{s}) + 11\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 8\text{SO}_2(\text{g})$
2. Smelting of ores e.g. chalcophyrite: $\text{CuS}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Cu}(\text{s}) + \text{SO}_2(\text{g})$
3. Incineration of garbage
4. Manufacture of sulphuric acid and paper and food processing

Evidence of increases in atmospheric concentrations of oxides of sulphur and nitrogen:

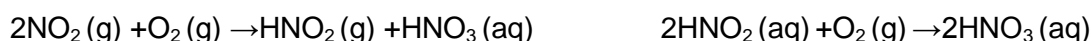
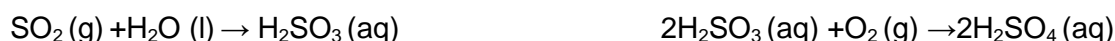
Concentrations of sulphur and nitrogen oxides have tended to increase in industrialised areas and cities since the start of the industrial revolution due to activities such as the combustion of fossil fuels, refining of metal ores and the running of automobiles. This has been evidenced through direct measurements of air quality levels, with concentrations of nitrogen and sulphur dioxide being much greater than that in normal air (although the equipment required to accurately measure this has only been available for the past 50 years). In addition, there is indirect evidence from environmental effects such as impacts on human, fauna and flora health, acid rain reducing the pH of water and damaging structures and visible photochemical smog.

Whilst concentrations of sulphur and nitrogen oxides have tended to increase in the past two centuries, many modern cities such as Sydney have shown a trend of reduced emissions of these oxides since the 1970s due to lower levels of heavy industry, tighter government controls, the use of low-sulphur coal, flue gas desulphurisation, trapping of sulphur dioxide to make sulphuric acid and catalytic converters in cars. However, this is not the case in cities of emerging economies such as Beijing where large amounts of heavy industry and lax environmental regulations have resulted in rapid increases in the concentrations of sulphur and nitrogen oxides. Mining towns such as Port Isa and Kalgoorlie also tend to have higher concentrations of these oxides

Emissions of sulphur and nitrogen oxides tend to get washed away by rain, and thus only affect the surrounding region (which can still be quite extensive). Another effect of this is that sulphur and nitrogen oxides do not stay in the atmosphere for long and so there appears to be no significant build-up of their concentrations over the past two centuries.

Formation of acid rain:

Oxides of sulphur and nitrogen disperse through larger volumes of air and dissolve in water droplets to form acid rain ($\text{pH} < 5$):



Effects of acid rain:

- Increased acidity of lakes- harms fish populations by preventing fish eggs from hatching, reducing calcium uptake in fish and leaching of heavy metals from soil
- Harms forests and vegetation e.g. Black Forest in Germany, maple forests in Quebec
- Damages steel and iron structures: $\text{Fe}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- Erodes marble buildings and statues: $\text{CaCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

Other harmful effects of sulphur and nitrogen oxides:

- Sulphur dioxide and nitrogen dioxide are respiratory irritants e.g. causes bronchitis
- Nitrogen dioxide, in the presence of hydrocarbons and oxygen and under the effect of sunlight, forms ozone, peroxyacylnitrates (PANs) and haze (photochemical smog):
 $\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{O}_3(\text{g})$

Decarbonation of soft drink:

Aim: To measure mass changes involved in the decarbonation of a soft drink bottle and measure the volume of gas released

Method: Weigh an unopened bottle of soft drink. Remove the cap to release the gas and reweigh. Replace the cap and shake the bottle for 30s, before releasing the gas and reweighing. Repeat until the soft drink no longer bubbles or a constant mass is reached

Results:

Initial mass of bottle= 341.23g

Final mass of bottle= 335.48g

Mass of CO₂ lost= 341.23-335.48= 5.75g

Moles of CO₂= 5.75/44.01= 0.13 moles

Volume of CO₂ at 25°C and 100kPa= 0.13X24.79= 3.2227L

Discussion: Manufacturers use high pressure CO₂ above the solution to increase the solubility of CO₂ in the drink. When a bottle is opened, the temperature above a solution drops dramatically from 400kPa to 100kPa, shifting the CO_{2(g)} + H₂O_(l) ⇌ H₂CO_{3(aq)} equilibrium to the left and causing CO₂ to bubble out to the surface. By shaking the bottle, CO₂ bubbles are allowed to form which rise to the surface.

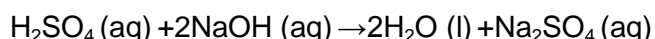
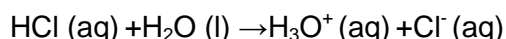
Soft drink can be decarbonated further by increasing temperature, adding an acid or adding a salt to the solution, all of which shift the carbonic acid equilibrium to the left

Conclusion: By measuring mass changes as a soft drink is decarbonised, the volume of gas (CO₂) released can be calculated

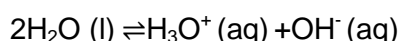
Ionisation of Acids

Acids as proton donors:

By the Brønsted- Lowry definition of acids and bases, acids are proton donors whilst bases are proton acceptors. When an acid reacts with water, it donates a proton to water to form a positive hydronium ion and an anion. In a neutralisation reaction, a proton is transferred from an acid to a base. For example:



Water self-ionises to a small degree:

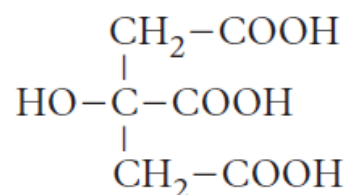


At a given temperature, the product of the concentrations of hydronium and hydroxide ions is a constant (K_w). At 25°C:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

Common acids:

- Acetic (ethanoic) acid: CH_3COOH
- Citric (2-hydroxypropane-1,2,3-tricarboxylic) acid: $\text{C}_6\text{H}_8\text{O}_7$
- Hydrochloric: HCl
- Sulphuric: H_2SO_4



pH scale:

The pH (power of hydrogen) scale is used to measure the acidity of a solution. It usually ranges from 0 to 14, with 7 being neutral and anything above and below being basic and acidic respectfully. pH is given by:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

A related scaled is the pOH (power of hydroxide):

$$\text{pOH} = -\log_{10}[\text{OH}^-] = 14 - \text{pH}$$

Note that pH is a logarithmic function and thus a change in pH of 1 results in a tenfold change in $[\text{H}^+]$. In recording the pH of a solution, the number of significant figures of the hydrogen concentration is the number of decimal places the pH is recorded up to.

Strong/ weak and concentrated/ dilute solutions:

Strong acid/ base- A species which (virtually) completely ionises in solution e.g. HCl , H_2SO_4 , HNO_3 , NaOH , KOH

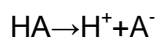
Weak acid/ base- A species which only partially ionises in solution e.g. H_2CO_3 , CH_3COO , $\text{C}_6\text{H}_8\text{O}_7$, NH_3 , CH_3NH_2

Concentrated solution- One in which the total concentration of solute species is high e.g. $>5\text{M}$

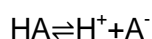
Dilute solution- One in which the total concentration of solute species is low e.g. $<2\text{M}$

The strength of acids is determined by their degree of ionisations. The greater the percentage ionisation of weak acids, the stronger the acid is considered. Note that there are no degrees of strongness for strong acids as they simply ionise completely.

In strong acids, since the acid ionises completely, its reaction with water is entirely forward:



However, in weak acids, there is an equilibrium reaction occurring:



Stronger acids will have equilibrium further to the right.

In strong acids, all hydrogen atoms which can ionise do so and if the concentration of the acid is known, the concentration of hydrogen ions and the pH of the solution can be determined. Weak acids will have a higher pH than strong acids of the same concentration and number of ionisable hydrogen atoms. pH can be used to determine the degree of ionisation of weak acids and their relative strength:

Acid (0.1M)	pH	$[H^+]$ (molL ⁻¹)	Theoretical $[H^+]$ (molL ⁻¹)	% Ionisation
Citric C ₆ H ₈ O ₇	2.1	0.008	0.3	2.7
Acetic CH ₃ COOH	3.0	0.001	0.1	1
Hydrochloric HCl	1.0	0.1	0.1	100

HCl is a strong acid as it ionises completely. In contrast citric and acetic acid are both weak acids as they only ionise partially, with citric acid being the stronger of the two. The three acids, in order from strongest to weakest, are: $HCl < C_6H_8O_7 < CH_3COOH$

Investigating the pH of equal concentrations of strong and weak acids and bases

Aim: To measure the pH of identical concentrations of strong and weak acids

Method:

1. Fill beakers with 0.1M solutions of various acids and bases
2. Measure the pH of these solutions using a pH meter/ data logger
3. Verify the result with universal indicator

Results- Measured pH:

Solution (0.1M)	pH (data logger)	Colour in universal indicator	pH using universal indicator
Sodium carbonate	11.31	Purple	11
Sodium hydroxide	12.77	Dark purple	13
Hydrochloric acid	1.11	Dark red	1
Ethanoic acid	3.16	Light red	3
Citric acid	2.02	Red	2

Acids (strongest-weakest): Hydrochloric, citric, ethanoic

Bases (strongest-weakest): Sodium hydroxide, sodium carbonate

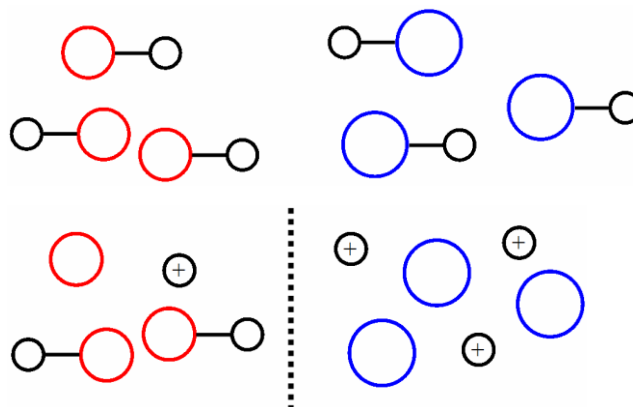
Discussion:

- Hydrochloric acid ionises completely and so would have a higher $[H^+]$ and lower pH compared to ethanoic and citric acid: $HCl(l) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
- Acetic and citric acid only partially ionise and so would have a lower $[H^+]$ and higher pH compared to hydrochloric acid: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$
- Citric acid has a lower pH than ethanoic acid as it is slightly stronger and has three hydrogen atoms which can ionise compared to one for ethanoic acid
- pH meters are more accurate but are expensive and need to be calibrated before use- it is non-destructive as it doesn't affect the solution
- Indicators are cheap and quick but are less accurate, only giving a pH range- destructive

Conclusion: Strong acids have a lower pH than weak acids of equivalent concentration due to a greater degree of ionisation (opposite for bases)

Modelling the molecular nature of acids

A molymod kit can be used to model strong/weak/concentrated/dilute acids. The hydrohalic acids HCl and HF were modelled. HF is a weak acid and ionises little in solution, while HCl has essentially complete ionisation. H is a black circle, F a red circle, and Cl blue. In their non-solution state they exist as molecular gases as above. In solution, however, they ionise to form H^+ ions and their conjugate base.



Note the differences between their degrees of ionisation – HCl, being a strong acid, completely ionises, while HF, as a weak acid, ionises to a small extent only. The evidence for this small extent of ionisation comes from testing pH using a pH meter – The pH of HF is higher than the pH of HCl at the same concentration, meaning that the HF solution has less H^+ ions, meaning it ionises less.

Acids in food additives:

Acids are added to foods in order to:

- Enhance taste (adds a sour taste) and flavour e.g. ethanoic acid in vinegar
- Preserve the food by lowering pH, making it more difficult for bacteria and fungi to grow e.g. SO_2 and ethanoic acid
- Improve nutritional value by adding vitamins e.g. ascorbic acid (vitamin C)

Naturally occurring acids and bases:

Common naturally occurring acids include:

- Acidic oxides such as CO_2 , SO_2 and NO_x found in the atmosphere
- Formic (methanoic) acid HCOOH found in bee stingers
- Acetic (ethanoic) acid CH_3COOH found in vinegar formed from the oxidation of ethanol
- Citric acid $\text{C}_6\text{H}_8\text{O}_7$ found in citrus fruits
- Carbonic acid H_2CO_3 found dissolved in waterways
- Lactic (2-hydroxypropanoic) acid $\text{C}_3\text{H}_6\text{O}_3$ found in milk

Common naturally occurring bases include:

- Calcium Oxide CaO or lime produced by roasting limestone- used in concrete
- Metallic oxides such as Fe_2O_3 and Ti_2O_3 found as ores
- Ammonia NH_3 produced by the decomposition of plant and animal matter
- Caffeine $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ found in coffee and caffeinated drinks
- Nicotine $\text{C}_8\text{H}_{14}\text{O}_2$ found in cigarettes

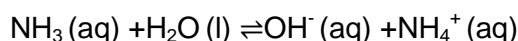
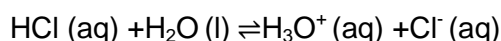
Theory of Acids

Historical developments of ideas about acids:

- Early ideas: Acids were defined by their properties such as their sour taste, their ability to react with metals and neutralise bases
- Antoine Lavoisier (c. 1780): First to define acids in terms of their chemical composition- hypothesised that acids were substances which contained oxygen-proven wrong since metallic oxides such as MgO were basic and some acids such as HCl lacked oxygen
- Humphry Davy (1815): Proposed that acids were substances that contained hydrogen rather than oxygen. However, some hydrogen containing substances such as methane were clearly not acidic and thus Davy's theory was flawed
- Justus Von Liebig (1838): Furthered Davy's theory by suggesting that acids were substances that contained replaceable hydrogen- hydrogen which could be partly or wholly replaced by a metal. Metals would react with acids to form a salt and hydrogen gas whilst bases would react with acids to form a salt and water. This provided a means for recognising acids but could not explain its properties
- Svante Arrhenius (1884): Suggested that acids were substances which ionised in aqueous solution to produce hydrogen ions whilst bases were substances which ionised in aqueous solution to produce hydroxide ions. This theory helped to define strong and weak acids and a neutralisation reaction as a reaction between hydrogen ions and hydroxide ions to form water. However, it did not take into account the role of the solvent (only applied to aqueous solutions), how acid- base reactions could occur even without ionisation and how some substances could act as both acids and bases. In addition, some substances such as MgO and Na₂CO₃ lacked hydroxide groups but were basic
- Brønsted- Lowry (1923): Defined acids as proton donors and bases as proton acceptors. For example, in water acids donate a proton (hydrogen atom), forming a hydronium ion. Bases take a proton from water, leaving behind a hydroxide ion. The acidity or basicity of a substance depends not only on the properties of the substance relative to the solvent. The theory also accounts for acid- base reactions in which ionisation does not occur e.g. $\text{HCl (g)} + \text{NH}_3 \text{ (g)} \rightarrow \text{NH}_4\text{Cl (s)}$. The Brønsted- Lowry theory can be thought of a generalisation of the Arrhenius theory for solvents other than water, although since most acid-base reactions occur in water, the Arrhenius theory is often used for convenience
- Lewis (1923): An even more general theory that defines acids as electron pair acceptors and bases as electron pair donors

Conjugate acids and bases:

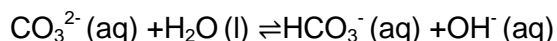
When an acid donates a proton, it forms a conjugate base which tends to accept a proton. Similarly, when a base accepts a proton, it forms a conjugate acid. For example:



In the above example, Cl⁻ is the conjugate base of HCl whilst NH₄⁺ is the conjugate acid of NH₃. Each of these forms a conjugate base pair. The strength of conjugate acids and bases is inversely related to the strength of the acid. A strong acid will produce a weak conjugate base whilst a weak acid will produce a strong conjugate base. This is also true for bases.

Acidic, basic and neutral salts:

Salts consist of an anion and a cation which dissociate in solution. These ions can be acidic, basic or neutral, depending on the acid or base which it was derived from. Strong acids and bases will produce neutral (very weakly acidic or basic) ions which do not react with water to any significant extent. Weak acids and bases will produce basic and acidic ions which hydrolyse to return to their original form, taking or releasing a proton from water in the process and altering the solution's pH. For example:



	Neutral	Acidic	Basic
Anions	Derived from strong acids e.g. Cl^{-} , NO_3^{-} , Br^{-} , I^{-}	Derived from some polyprotic acids ¹ e.g. HSO_4^{-} , $\text{H}_2\text{PO}_4^{-}$	Derived from weak acids and some polyprotic acids ¹ e.g. F^{-} , CO_3^{2-} , HCO_3^{-}
Cations	Derived from strong bases e.g. Na^{+} , K^{+} and other group I, II metals	Derived from weak bases ² e.g. NH_4^{+} , Fe^{3+} , Al^{3+}	None

¹Some amphiprotic ions are acidic whilst others are basic and this depends on the relative tendencies of the two possible hydrolysing reactions

²Small, highly charged metal ions form complexes with water which are able to donate protons e.g. $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$

Depending on the acid- base properties of the anion and cation, salts can be acidic, basic or neutral. For example, a neutral ion with a neutral ion will produce a neutral salt whilst an acidic ion with a neutral ion will produce an acidic salt. If a salt consists of both an acidic and a basic ion, then its acidity/ basicity will depend on the relative effects of each ion, with the hydrolysis reactions of each ion cancelling out. Thus, such salts tend to be close to neutral. As a general rule, the salt formed from different neutralisation reactions will be:

	Strong Base	Weak Base
Strong Acid	Neutral pH=7	Acidic pH<7
Weak Acid	Basic pH>7	Close to neutral pH≈7

Identifying the pH of a range of salt solutions

Aim: To measure the pH of a variety of salt solutions

Method: Pour 0.1M solutions of various salts into a beaker and measure the pH with a pH probe and with universal indicator solution

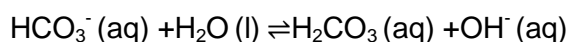
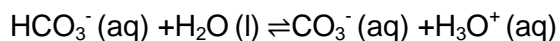
Results- pH of various salt solutions:

Solution 0.1M	pH (probe)	Colour in UI	pH (UI)
NaCl	7.4	Green	7
NaHCO ₃	8.8	Dark green	9
CH ₃ COONa	7.7	Green	8
Na ₂ CO ₃	11.2	Purple	11
NH ₄ Cl	5.1	Yellow	5

Conclusion: The pH of different salt solutions was measured and it was found that some hydrolysed, altering the pH of the solution

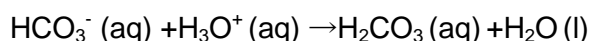
Amphiprotic substances:

Substances which can act as both proton donors and acceptors and thus according to the Brönsted- Lowry definition can act as both an acid and a base are amphiprotic. For example, HCO_3^- is amphiprotic:

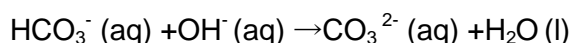


In the first equation, HCO_3^- acts as an acid whilst in the second equation it acts as a base. Both these reactions occur simultaneously when HCO_3^- is dissolved in water to a small extent.

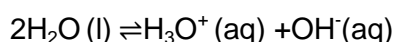
However, when HCO_3^- is placed within an acidic solution, it acts as a base, reacting with hydronium ions to form carbonic acid and water:



When HCO_3^- is placed within a basic solution, it acts as an acid, reacting with hydroxide ions to form carbonate ions and water:

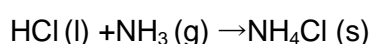
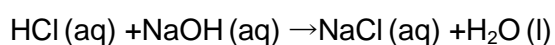


Other examples of amphiprotic substances include HSO_3^- , HPO_4^{2-} and H_2O . Water, as a solvent, can either donate protons to or accept protons from solvents depending on the relative tendency of the solute to gain or lose protons. For example, water acts as a base in HCl solution but as an acid in NH_3 solution. In addition, water can also self-ionise:



Neutralisation:

A neutralisation reaction is one in which an acid and a base react to form a salt. Water is often formed as well. They can be thought of as a proton transfer reaction in which a proton is transferred from the acid to the base. For example:



In the first reaction, a proton was transferred from HCl to the hydroxide ion, forming water whilst in the second reaction, a proton was transferred from HCl to NH_3 , forming NH_4^+ . Neutralisation is an exothermic reaction. ΔH is around -56kJ/mol with a few kJ/mol of variance depending on the strength and concentration of the acids and bases used.

Neutralisation reactions are used to deal with chemical spills involving acids and bases and to neutralise effluents. Na_2CO_3 is often used for the controlled neutralisation of acidic effluents whilst HCl or H_2SO_4 is often used for the neutralisation of basic effluents. For emergency spills, NaHCO_3 is used since it is a stable solid that is safe to store and handle, is readily and cheaply available and HCO_3^- is amphiprotic, allowing it to be used for both acid and base spills. It is also a weak acid/ base, so there is little danger if excess amounts are used.

Titration:

Volumetric analysis- A form of chemical analysis in which the concentration or amount of a substance A is determined by measuring the volume of a solution of known concentration of another substance B which is just sufficient to react with all of A

Equivalence point/ end point- The point at which the amounts of two reactants are just sufficient to cause the complete consumption of both reactants/ the observed point of complete reaction because of the effect of the indicator

Titration is a form of volumetric analysis in which a solution of known concentration (titrant) is added to a solution of unknown concentration from a burette until the equivalence point or end point is reached. In order to undertake titration, a standard solution must be prepared:

1. Dry solid in a desiccator or oven
2. Weigh on an analytical or electronic balance the exact mass of solid required. Dissolve the solid in a small amount of distilled water in a beaker
3. Using a filter funnel transfer the solution to a clean volumetric flask. Rinse the beaker with distilled water and add washings to the volumetric flask
4. Using distilled water make up the volume of the flask until the bottom of the meniscus is level with the etched mark on the flask
5. Shake and invert the flask roughly to ensure thorough mixing
6. Label solution

Primary standards are substances which have a concentration which can be known by dissolving a measured amount of solute in a certain volume of water. Substances suitable for making primary standards include Na_2CO_3 and oxalic acid $\text{H}_2\text{C}_2\text{O}_4$:

- Available in pure form
- Have an accurately known chemical formula,
- Chemically stable,
- Readily soluble in distilled water
- Of relatively high molecular mass to minimise weighing errors

Other substances such as HCl , H_2SO_4 and NaOH can be used to make secondary standard solutions which must be standardised against primary standards. These substances may not be used for primary standards because:

- HCl is volatile and may spontaneously release fumes
- H_2SO_4 and NaOH absorb water from the air
- NaOH reacts with CO_2 in the air to form Na_2CO_3

Once a standard solution has been prepared, it may be used for the titration process:

1. Using a filter funnel, fill a burette with a standard solution of known concentration (titrant) and record the initial level (remove filter funnel before reading)
2. Use a pipette to measure a set amount of the sample to be analysed (analyte) to be emptied into a conical flask. Add a few drops of a suitable indicator
3. Slowly run solution from the burette into the flask, swirling the flask constantly, until the indicator just changes colour (must persist for at least 10s)

- Record the final level of the burette and thus calculate the volume of titrant used
- Repeat the titration several times and use the average volume of the titres (omitting the first rough titre) to calculate the concentration of the analyte

The concentration of the analyte can be found using this formula:

$$c_a = \frac{c_t v_t M}{v_a}$$

Where c_a is concentration of the analyte (molL^{-1}), c_t is the concentration of the titrant (molL^{-1}), v_a is the volume of the analyte (L), v_t is the concentration of the titrant (L) and M is the stoichiometric ratio between the analyte and titrant

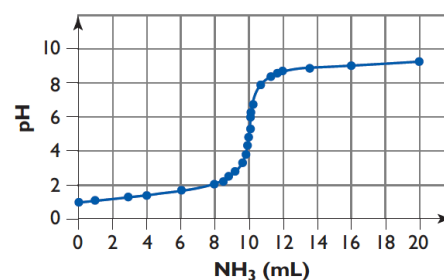
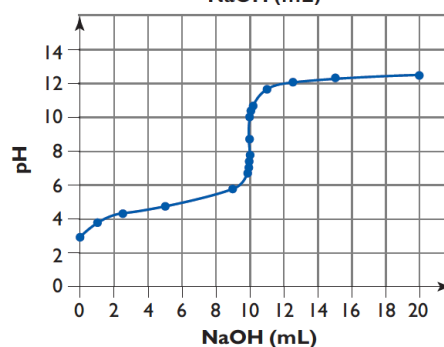
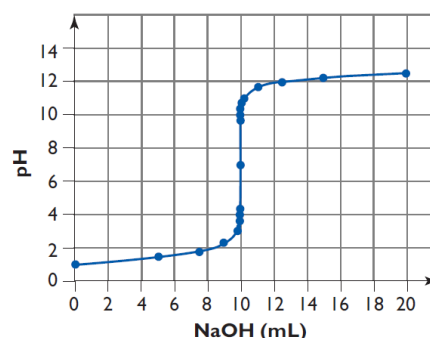
A few things should be noted during titration:

- The concentration of the titrant and analyte must be similar (within a factor of 10) and thus some dilution may be necessary
- Pipettes and burettes should be washed with distilled water and then with the solution to be measured before use
- Burette readings should be taken to one significant figure greater than that which is marked
- The positions of the titrant and analyte may be reversed

Titration curves:

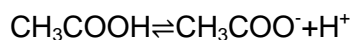
Titration curves graph the pH of the titrated solution over the volume of the titrant added. The shape of the titration curve will depend on the strength of the acid and base being used. The shape of the titration curve will also affect the indicator used. Ideally, an indicator would be used that changes colour around the equivalence point.

- Strong acid/ strong base: The titration curve is very steep around the equivalence point. The salt produced is neutral and thus the equivalence point occurs at $\text{pH}=7$. Suitable indicators for such titrations include litmus, bromothymol blue and phenol red
- Strong base/ weak acid: This titration curve is less steep but still rises significantly around the equivalence point. The salt produced is basic and thus the equivalence point occurs at $\text{pH}>7$. Suitable indicators for such titrations include phenolphthalein and thymol blue
- Strong acid/ weak base: Salt produced is acidic and thus the equivalence point occurs at $\text{pH}<7$. Suitable indicators for such titrations include methyl orange, methyl red, bromophenol blue and bromocresol green
- Weak acid/ weak base: Titrations of this type are generally not performed as there is no significant pH change around the equivalence point. Thus the colour change in the indicator occurs over several drops and thus it is not possible to accurately determine the amount of titrant used at the end point

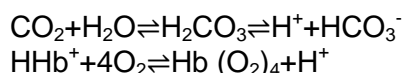


Buffers:

A buffer solution is a solution which contains comparable amounts of a weak acid and its conjugate base and is able to maintain a constant pH even when significant amounts of strong acid or base are added to it. For example:



When acid is added, the above equilibrium shifts to the left by Le Chetelier's Principle, countering the decrease in pH. When a base is added, hydroxide ions react with hydrogen ions, reducing the concentration of H^+ and moving the above equilibrium to the right, countering the increase in pH. Other examples of buffer systems include:



The first equilibrium is used in freshwater lakes in order to maintain a constant pH. H_2CO_3 is provided by the dissolving of carbon dioxide whilst HCO_3^- is provided by nearby rocks.

In the blood, the above equilibria are used to manage pH to around 7.35 and move oxygen and carbon dioxide through the circulatory system. When oxygen is taken in by the lungs, oxyhaemoglobin is formed, moving the second equilibrium to the right, increasing the concentration of hydrogen ions and lowering pH. The first equilibrium moves to the left by Le Chetelier's principle, increasing pH and releasing CO_2 which is then exhaled. In the cells, oxyhaemoglobin releases oxygen, moving the second equilibrium to the left, reducing the concentration of hydrogen ions and increasing pH. The first equilibrium then moves to the right by Le Chetelier's principle, decreasing pH and absorbing carbon dioxide to be transferred out of the body by the lungs through plasma in the bloodstream.

Esters

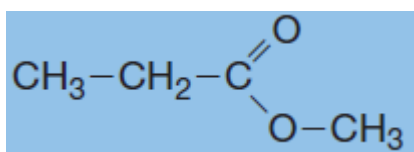
Alkanols- Alkanes with at least one hydrogen atom replaced with a hydroxyl functional group (-OH). Primary alkanols have the general structure R-OH where R is an alkyl group and the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$

Alkanoic acids- Alkanes with a carboxyl functional group (-COOH) at the end with the general structure R-COOH where R is an alkyl group and the general formula $\text{C}_{n-1}\text{H}_{2n-1}\text{COOH}$

Esters- Compounds containing a carbonyl functional group (-CO) adjacent to an ether linkage (-O-) with the general structure R-COO-R' where R and R' are alkyl groups and the general formula $\text{C}_{n-1}\text{H}_{2n-1}\text{COOC}_m\text{H}_{2m+1}$

Esters can be regarded as derivatives of alkanoic acids where the acidic hydrogen atom has been replaced by an alkyl group. The alkyl group bonded to the oxygen atom is named as a separate word and is followed by the acid name of the remainder of the molecule but with the suffix -oic acid becoming -oate i.e. alkyl alkanoate

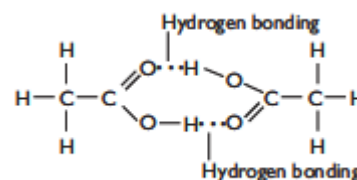
For example, methyl propanoate ($\text{C}_2\text{H}_5\text{COOCH}_3$) is:



Melting and boiling points of straight-chained alkanolic acids and straight- chained primary alkanols:

Both alkanols and alkanolic acids are polar and can form hydrogen bonds, although alkanolic acids are able to form a greater number of hydrogen bonds due to its carboxyl structure. Thus, alkanolic acids have higher melting and boiling points than alkanols of similar molecular mass or the same number of carbon atoms.

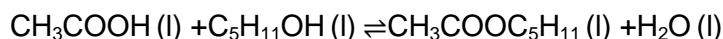
Alkanols in turn have higher melting and boiling points than alkanes of similar molecular mass or the same number of carbon atoms which have only dispersion forces between molecules. Melting and boiling points will also increase going down a homologous series due to greater dispersion forces.



Esterification:

Esterification is a reaction between a carboxylic acid and an alcohol to form an ester, eliminating water in the process:

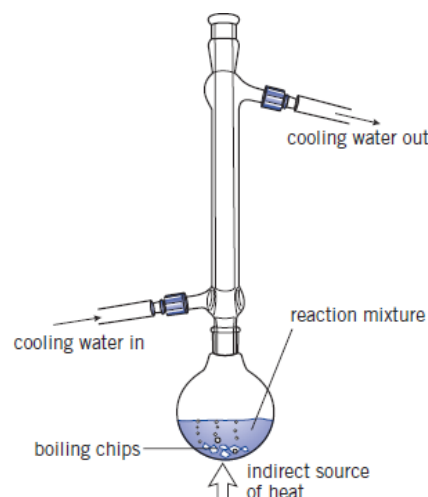
Alkanolic acid+ Alkanol \rightleftharpoons Ester+ Water



Acid is used as a catalyst in order to speed up the reaction by providing a lower energy reaction pathway. It also absorbs water from the products, thus shifting the above equilibrium to the right by Le Chatelier's principle and increasing the yield of the reaction. 18M H_2SO_4 is most commonly used.

Refluxing:

Refluxing involves heating a reaction mixture in a vessel with a cooling condenser attached. The open end of the reflux apparatus prevents pressure from building up in the flask due to the production of vapours whilst the condenser prevents volatile components from escaping. A water bath is often used instead of a naked flame from a Bunsen burner in order to reduce the risk of fire.



Occurrence, production and uses of esters:

- Esters have a sweet smell and are found naturally in nature in fruits. Due to these properties, esters are often manufactured in order to mimic natural odours for use in perfumes, cosmetics and artificial food flavourings. For example:
 - Pentyl ethanoate- banana
 - Octyl ethanoate- orange
 - Butyl ethanoate- raspberry
 - Ethyl butanoate- strawberry
- Natural fats and oils are also esters formed from triglycerides (glycerol and fatty acids)
- Used as solvents and coatings such as ethyl ethanoate in nail polish remover and propyl ethanoate in wood lacquers
- Phthalate esters used as plasticisers for PVC

Preparation of an ester using reflux

Aim: To prepare an ester, pentyl ethanoate, using reflux

Method:

1. Add 10mL of 1-pentanol, 12 mL of ethanoic acid and a few drops of concentrated H_2SO_4 into a distillation flask with ceramic boiling chips. Clamp the flask and immerse in a water bath over a Bunsen burner. Attach a reflux condenser over the flask and heat the mixture for 10-20 minutes
2. Allow mixture to cool and transfer to a separating funnel. Add 100mL of water, shake, and discard the lower layer
3. Add 50mL of 1M Na_2CO_3 to the separating funnel, shake and discard the lower layer
4. Transfer the remaining liquid to a test tube and add a few pellets of anhydrous CaCl_2 . Stopper, shake and then filter the remaining liquid
5. Use fractional distillation to obtain ester

Results: A small amount of a colourless, sweet smelling liquid was obtained

Conclusion: Refluxing of an alkanol and an alkanoic acid can be used to create an ester, with use of separating funnels and fractional distillation able to separate the ester from the resulting liquids

Chemical Monitoring and Management

Work of Chemists

Role of a chemist employed in a named industry:

A plant **analytical** chemist is employed by a major Australian chemical manufacturing company that makes ethylene from ethane and then polymerises it to polyethylene. The company is part of the **chemicals and polymer manufacturing industry**. It sells some of its ethylene to another company that uses it to make ethylene oxide and ethylene glycol, non-ionic surfactants and starting materials for making other polymers. Some of the chemists' roles include:

- Monitoring the quality of ethylene by determining the nature and amount of impurities
- Monitoring waste water to ensure it meets environmental requirements e.g. pH, suspended solids, sulphate, grease, hydrocarbons
- Monitoring gaseous emissions to ensure they do not contain particulates or polluting chemicals
- Collaborate with chemical engineers at the cracking furnace to adjust operating conditions in order to optimise yield levels
- Ensure that equipment operates properly and calibrate instruments
- Train shift workers in the use of instruments
- Perform analyses to ensure the reliability of results
- Find ways of improving the overall monitoring process

Such chemists generally work in a central lab for a large portion of the time to perform analyses. Many of these analyses use **gas chromatography** which determines what substances and how much of each are present in materials. A liquid or gaseous mixture is vaporised into a carrier gas such as helium which flows over a stationary phase.

The stationary phase is either a finely divided solid packed in long thin tube or column (gas solid chromatography) or liquid coated on the walls of the capillary tube (gas liquid chromatography- GLC).

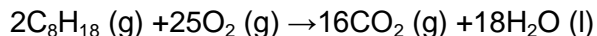
The stationary phase adsorbs (gas solid) or dissolves (GLC) the components at a different rate, causing different chemicals to pass through at different rates. These reach a detector which measures the amount of substance that passes different times, allowing the relative amounts of each component to be determined.

Need for collaboration between chemists:

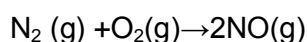
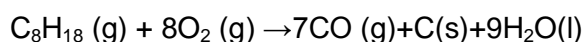
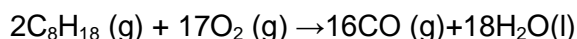
Chemical problems require expertise in more than one field of specialisation, especially in industry. Solving problems from wide-ranging and complex problems require input from chemists with different specialities, and therefore it is essential for chemists to work collaboratively and regularly interact and exchange different viewpoints. This means chemists need to have good communication skills to communicate aspects of their part skilfully and concisely. Collaboration and communication is key for quicker and more effective solutions, more reliable and accurate results, and to share new ideas, knowledge and resources.

Combustion:

In the combustion of hydrocarbons, different products are able to be formed under different conditions i.e. different levels of oxygen. When there is plentiful oxygen, complete combustion occurs and the reactants are completely converted to carbon dioxide and water:



However, there is often insufficient oxygen to achieve complete combustion and so incomplete combustion occurs. CO and soot (C) are formed which are dangerous as CO bonds to haemoglobin in place of oxygen, resulting in asphyxiation, and soot is carcinogenic. There is also potential to release other pollutants such as the acidic oxide NO:



Hence, it is important to monitor combustion in order to maximise energy output and efficiency and minimise the release of pollutants. This involves ensuring the correct fuel/oxygen mixture to ensure a plentiful supply of oxygen.

Variety of chemical occupations:

- Environmental: Collects, analyses and assesses environmental samples
- Metallurgical: Advises on the extraction of metals from ores and ways they could be combined with other materials such as polymers and ceramics, specialises in properties, applications and development of metals and alloys
- Industrial: Involved in the design of chemical processes and monitoring procedures in industry, study the structure and chemical reactions of materials used in industry

- Biochemist: Involved in the development of new medical, industrial or agricultural products, studying the chemical structure and functions of molecules in living things and studying the effects of new products on animals and plants in order to determine their potential toxicity
- Polymer: Involved in the production of new materials for industry or in the monitoring of manufacturing processes for these materials as well as investigating the properties of large polymeric molecules and manipulating their structure to produce new polymers
- Analytical: Monitors and controls the quality and quantity (yield) of products produced in industry

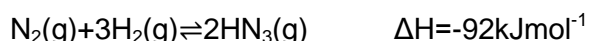
The Haber Process

Industrial uses of ammonia:

- Fertilisers (ammonium and nitrate salts)- contain usable nitrogen which plants need
- Fibres and polymers (rayon, acrylics, nylon)
- Nitric acid used to make fertiliser, dyes, fibres and polymers and explosives e.g. NH_4NO_3 , TNT and nitroglycerine
- Household cleaners
- Non-ionic detergents

Synthesis of ammonia:

Ammonia is formed from its component gases, nitrogen and hydrogen, in the reversible reaction:



Effect of temperature, on yield and reaction rate:

As seen above, the reaction of hydrogen with nitrogen is exothermic. Thus, by Le Chatelier's Principle, increasing temperature will shift the equilibrium to the left as the system tends to reduce temperature, hence reducing yield.

However, the rate of reaction increases with temperature as this increases the rate of collisions and the proportion of molecules with sufficient energy. The rate of reaction increases in both directions of a reversible reaction but the rate at which equilibrium is reached increases overall.

Thus, the temperature at which the reaction is made to occur is a compromise between yield and reaction rates in order to maximise the overall production of ammonia. This is approximately 400°C in industry. Note that this figure is affected by the use of a catalyst and the pressure at which the reaction occurs.

Effect of pressure on yield and reaction rates:

In the above reaction, the left side contains 4 moles of gas whilst the right contains 2 moles of gas. Thus, increasing the pressure of the reaction vessel will, by Le Chatelier's Principle shift the equilibrium to the right as the system tends to reduce pressure, increasing yield. In addition, increasing pressure increases the rate of reaction due to an increased rate of collisions between molecules. The rate of reaction increases in both directions but equilibrium is approached faster overall.

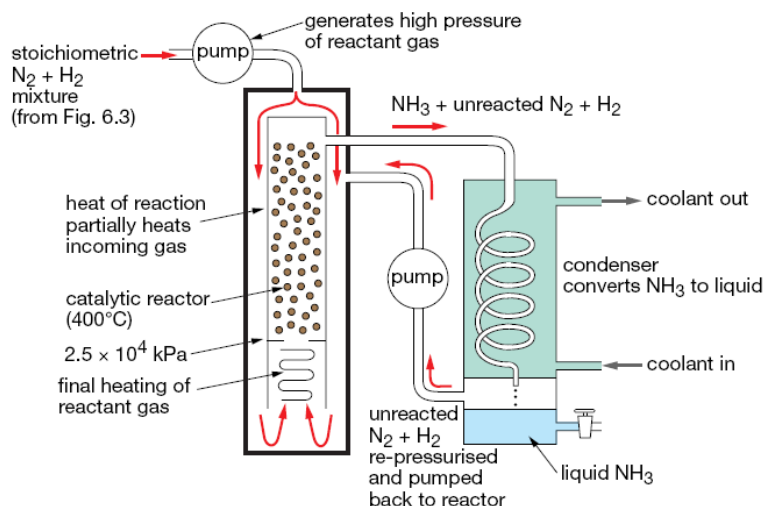
Hence, high pressures are used in order to maximise the rate of ammonia production. A pressure of $2.5 \times 10^4 \text{ kPa}$ (250 atm) is generally used.

Use of a catalyst:

A magnetite Fe_3O_4 catalyst (with the surface reduced to free iron) is used to increase the rate of reaction by providing a reaction pathway with a lower activation energy. Use of the catalyst increases the rate at which the reaction reaches equilibrium, although it does not affect equilibrium position. This also lowers the required reaction temperature, increasing yield and overall reaction rate as well as reducing the energy costs of the reaction.

Reaction process and monitoring:

Nitrogen and hydrogen in the stoichiometric ratio 1:3 are pumped into the reaction vessel and flow over the outside of the catalyst chamber, allowing the mixture to be heated by the heat of the reaction, reducing energy costs. It then flows into the catalyst chamber where some of it reacts to form ammonia. The equilibrium yield is generally 45% but this is usually not reached with yields of 30% being more common.



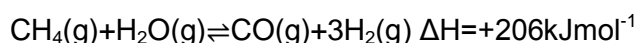
The ammonia and unreacted nitrogen and hydrogen are then pumped into a condenser which liquifies the ammonia to be pumped away. The unreacted nitrogen and hydrogen are then re-pressurised and pumped back to the reactor so that they are mixed with new incoming gases. In this way, no reactants are wasted and all reactants are used up eventually.

During the reaction process several factors have to be monitored:

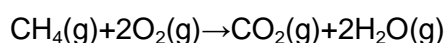
- Temperature: This should be kept in the range of optimum conversion from reactants to products. Excessive temperature can also damage the catalyst
- Pressure: This should be kept in the range of optimum reaction rates
- Ratio of H_2 to N_2 in the incoming gas stream: This should be kept in the ratio 3:1 to avoid the build up of one reactant
- Concentrations of O_2 , CO and CO_2 and sulfur compounds in the incoming gas stream: Oxygen creates the risk of explosions whilst CO , CO_2 and sulphur compounds can poison the catalyst
- Concentration of argon and methane in the reaction vessel: Any build up of these gases will lower the efficiency of the conversion process
- Purity of the ammonia product: Ensuring that no impurities contaminate the final product

Source of reactants:

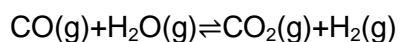
The reactants are obtained from normal air by removing oxygen and carbon dioxide and adding hydrogen. Hydrogen is produced by reacting steam with methane (or other natural gases) at a temperature of about 750°C over a nickel catalyst:



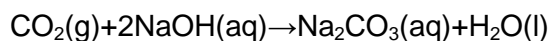
The methane also removes oxygen from the air:



Carbon monoxide is removed by a catalytic reaction with steam, using either Fe_3O_4 at 500°C or Cu at 250°C . Additional hydrogen is produced:



This leaves air with only nitrogen, hydrogen, carbon dioxide and trace gases. Carbon dioxide removed by passing the mixture over a base. For example:



This leaves only nitrogen, hydrogen and trace gases. By varying the amounts of steam and methane used, it is possible to obtain a 3:1 mixture of hydrogen and nitrogen. As this is the stoichiometric ratio of the reaction, there is no build up of either reactant. The removal of oxygen removes the risk of explosion whilst increasing the efficiency of the reaction.

Impact of the Haber Process on World History:

The Haber Process was developed in 1908 by Franz Haber and converted into a mass industrial process in 1914 by Carl Bosch in order to aid his nation's (Germany) war effort. This shielded Germany from the allied naval blockade during WWI that blocked imports of saltpeter from Chile which was necessary to produce fertiliser and explosives. With the Haber process, the Germans were able to maintain supplies of food and weapons. This prolonged the war and ironically, caused much starvation and suffering. However, since then the Haber process has allowed millions of farmers to fertilise their crops, providing a stable source of food for billions.

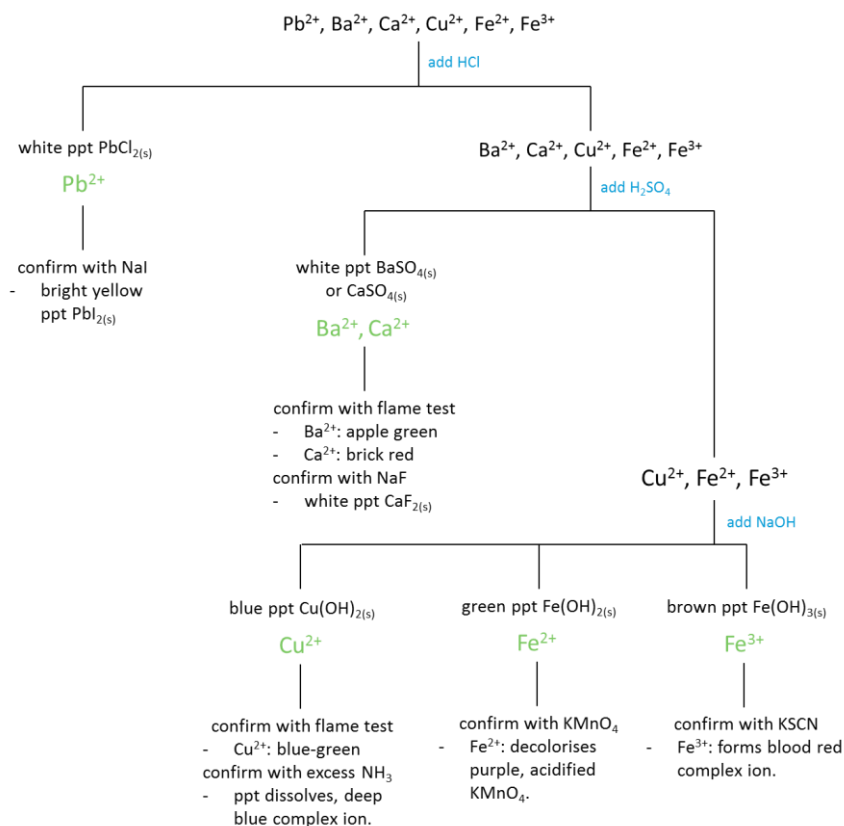
Analysis Techniques

Determining the presence of cations in solution:

- Colour of solution: Some cations generally appear as a certain colour in solution, such as copper (pale blue), iron (II) (pale green) and iron (III) (yellow). This is a useful preliminary step for seeing which cations may be present but cannot be taken as positive indication of a cation. In addition, most solutions of cations are colourless or are colourless in low concentrations, limiting its use
- Precipitation reactions: Cations will react with specific anions to form precipitates. Observing whether or not a precipitate forms with the addition of anions can be used to determine the presence of cations. Other times a precipitate doesn't form, but there is a change in colour, although this can be equally as useful. For example:
 - Pb^{2+} forms a white precipitate with Cl^- and a yellow precipitate with I^-
 - Ba^{2+} forms a white precipitate with SO_4^{2-}
 - Ca^{2+} forms a white precipitate with SO_4^{2-} and F^-
 - Cu^{2+} forms a blue precipitate with OH^- which dissolves in NH_3 to form a deep blue solution
 - Fe^{2+} forms a green precipitate with OH^- (may turn brown) and decolorises acidified dilute KMnO_4 solution
 - Fe^{3+} forms a brown precipitate with OH^- and forms a deep red solution with SCN^-
- Flame tests: A nichrome or platinum wire is dipped into a solution of the cation and placed into a bunsen flame. Each cation will give off a characteristic colour:
 - Ca^{2+} : Orange-red
 - Ba^{2+} : Green
 - Cu^{2+} : Blue-green

This is a useful confirmatory test for precipitation reactions but should not be the only method used as it only works for certain cations and some elements give off similar colours.

These tests can be combined to form a procedure for determining the presence of cations in solution. An example procedure is given below. Note that if multiple cations are present, steps must be taken to ensure that one cation does not interfere with tests for other cations. If a precipitate forms, it must be precipitated to excess (by adding excess anions) and then filtered. Further tests can then be performed on the filtrate.

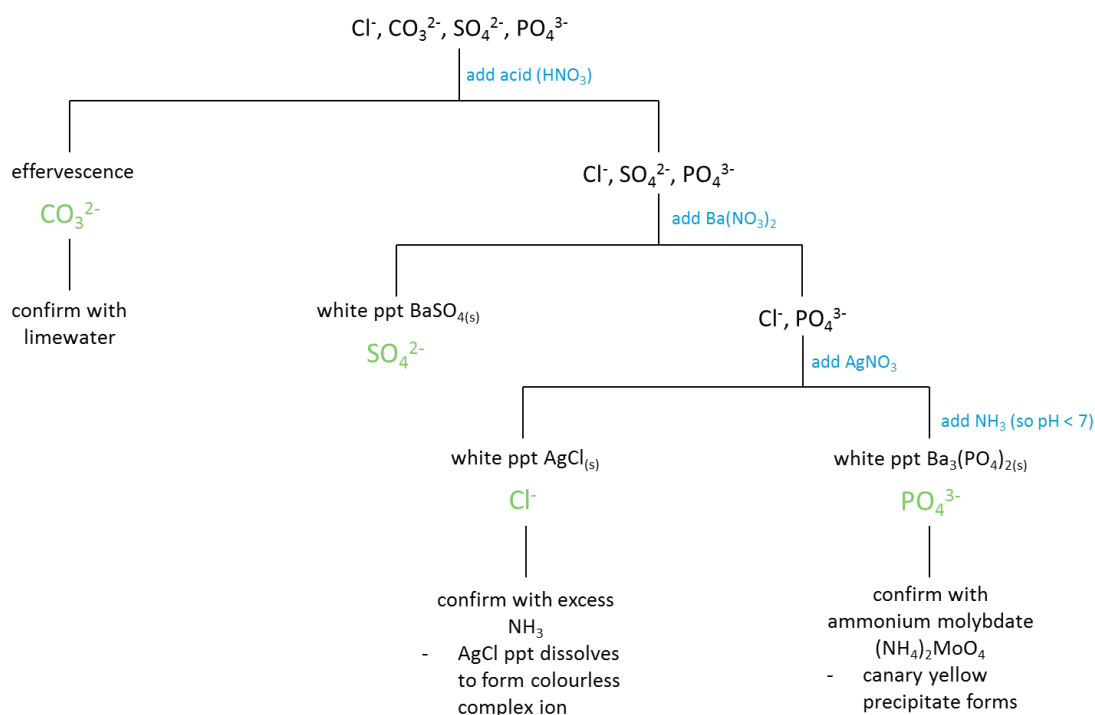


Determining the presence of anions in solution:

The presence of anions in solution can be determined by adding cations and observing whether or not a precipitate forms or by adding acid and seeing whether effervescence occurs. Specific tests for each anion include:

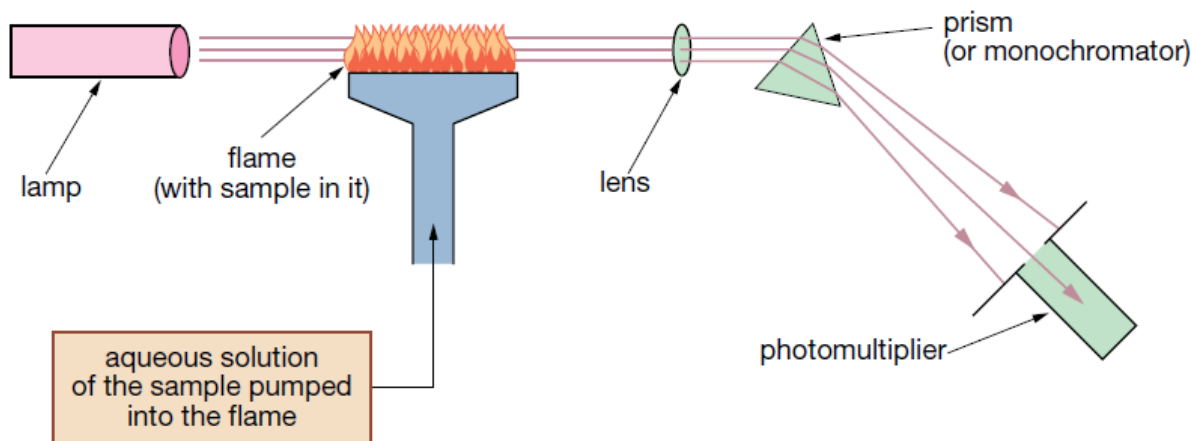
- Carbonate CO_3^{2-} :
 - Has a pH between 8 and 11
 - Addition of a dilute strong acid such as HNO_3 produces bubbles of CO_2 gas
- Sulphate SO_4^{2-} :
 - Addition of $\text{Ba}(\text{NO}_3)_2$ to an acidified solution produces a thick white precipitate
 - Acidification and addition of $\text{Pb}(\text{NO}_3)_2$ produces a white precipitate
- Phosphate PO_4^{3-} :
 - Addition of NH_3 and $\text{Ba}(\text{NO}_3)_2$ produces a white precipitate
 - Addition of Mg^{2+} in a $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer produces a white precipitate $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - Acidification with HNO_3 and addition of $(\text{NH}_4)_2\text{MoO}_4$ produces a yellow precipitate
- Chloride Cl^- :
 - Addition of AgNO_3 produces a white precipitate which dissolves in ammonia solution and darkens (breaks down) in sunlight (in acidic solutions Ag^+ will only form a precipitate with Cl^- , assuming SO_4^{2-} concentration is not too high)

Like with cations, the above tests can be combined to form a procedure for determining the presence of anions. If multiple anions are present, it is important to precipitate to excess if a precipitate forms and then filtering before performing additional tests. In the case of testing for CO_3^{2-} , acid should be added until no more effervescence is observed.



Atomic Absorption Spectroscopy (AAS):

This is a method for determining the concentration of ions, particularly metal ions, in solution. The sample to be analysed is fed into a flame which vaporises the sample. Light from an atomic emission lamp (of the same element as the one being analysed) is then passed through the flame. Atoms of the sample absorb the wavelengths of light given off by the atomic emission lamp, reducing the intensity of light. The light then passes through a prism or monochromator which selects the specific wavelength being measured and into a photomultiplier which measures the intensity of light. By comparing the intensities of light with and without the sample, absorbance (the base 10 logarithm of the ratio between the intensities of light without and with the sample) can be determined.



Absorbance is proportional to concentration of the element in the sample. Hence, the concentration of a substance can be determined by comparing it to a calibration curve obtained by calculating the absorbance of an element at known concentrations. AAS is very sensitive as measurements are made from absorption by nearly 100% of atoms in the sample and the wavelength of the light source exactly matches the wavelength absorbed by atoms in the sample. As a result it can measure very small concentrations quite accurately (as small as 0.01ppm). However, AAS requires expensive equipment and needs to be done in a laboratory. In addition, a different lamp is required for each element.

AAS is used to monitor small concentrations of metals in the environment, particularly the heavy metals such as Pb, Hg, Cd, Cr, Cu and Zn, concentrations of micro-nutrients in soils, contaminants in food, medicines and manufactures and the concentrations of elements in living organisms. The ability of AAS to measure very low concentrations of a wide variety of elements makes it extremely effective in monitoring pollution.

Due to AAS' ability to measure very small concentrations of elements, it has allowed a greater scientific understanding of the effects of trace elements, elements required by living organisms in very small amounts (1-100ppm) such as Zn, Co and Mo. Older analytical methods were slower, less accurate and unspecific and hence unable to identify trace elements in soils and organisms. AAS allowed these elements to be identified and connected to their biological role as well as disorders associated with their deficiency. For example, iron was found to be essential for haemoglobin function and production, with its deficiency resulting in anaemia.

The need to monitor ion concentrations:

Many ions present in the environment and in manufactured goods are harmless in small concentrations but are quite harmful in higher concentrations. Hence, it is important to measure ion concentrations to prevent damage to humans and the environment. For example, some potentially harmful ions include:

- Lead: Lead is a poisonous heavy metal which retards intellectual development in children, causes brain damage and leads to neurological disorders. Until recently it was a constituent in petrol and house paints, resulting in them becoming dispersed in the environment. Lead is also emitted by certain industries such as lead smelters and car battery manufacturers. Monitoring lead concentrations in soils (particularly near highways), waterways and the atmosphere in urban areas is important to ensure people are not exposed to harmful concentrations (blood levels should be <0.1ppm lead and drinking water should be <0.01ppm lead)
- Phosphate: Excess amounts of phosphate in waterways can trigger algal blooms (eutrophication) which covers the surface of water bodies, blocking sunlight and killing other aquatic life. Human activity such as agricultural run off can increase the risk of algal blooms by increasing the concentration of phosphates. Monitoring of phosphate levels can help prevent algal blooms and protect waterways

Determining the sulphate concentration of lawn fertiliser

Aim: To determine the sulphate concentration of lawn fertiliser using gravimetric analysis

Method:

1. Accurately weigh out a known mass of crushed fertiliser and dissolve in dilute HCl solution
2. Filter any insoluble matter
3. Heat the solution until almost boiling (>80°C) and add excess BaCl₂, stirring well
4. Allow solution to cool and filter the white BaSO₄ precipitate
5. Dry residue in an oven
6. Weigh filter paper and subtract mass of dry filter paper to determine precipitate mass

Results:

Mass of fertiliser: 1.00g

Mass of filter paper: 1.59g

Mass of filter paper+ BaSO₄: 3.14g

Mass of BaSO₄: 1.55g

$M(\text{BaSO}_4) = 233.392 \text{ g mol}^{-1}$

$M(\text{SO}_4^{2-}) = 96.065 \text{ g mol}^{-1}$

$n(\text{BaSO}_4) = n(\text{SO}_4^{2-})$

$m(\text{BaSO}_4) / M(\text{BaSO}_4) = m(\text{SO}_4^{2-}) / M(\text{SO}_4^{2-})$

$m(\text{SO}_4^{2-}) = m(\text{BaSO}_4) * (M(\text{SO}_4^{2-}) / M(\text{BaSO}_4)) = 1.55 * (96.065 / 233.392) = 0.638 \text{ g}$

$\% \text{SO}_4^{2-} = 0.638 / 1.00 = 63.8\%$

Discussion:

- Ba²⁺ forms a white precipitate with SO₄²⁻: $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4$
- Possible sources of error in the experiment include:
 - Some of the BaSO₄ may have been left in the beaker, resulting in an underestimation of sulphate content. This error can be reduced by transferring all the precipitate to the filter paper through multiple washings
 - Some BaSO₄ may have seeped through the filter due to the particles being very fine, resulting in an underestimation of sulphate content. This error could be reduced by cooling the solution before filtering to reduce solubility or by using a sintered glass crucible and vacuum filter pump
 - BaSO₄ may have been contaminated with adsorbed impurities. HCl was used to acidify the solution to prevent the precipitation of PO₄³⁻ and CO₃²⁻ which would have led to an overestimation of sulphate content
 - There may have been some moisture remaining in the filter paper, leading to an overestimation of results. This error could be reduced by drying the filter in a dessicator
- The experiment was reasonably reliable as the results agreed with those of other students. However, the reliability of the results could be improved by rectifying the errors described above using the suggested solutions

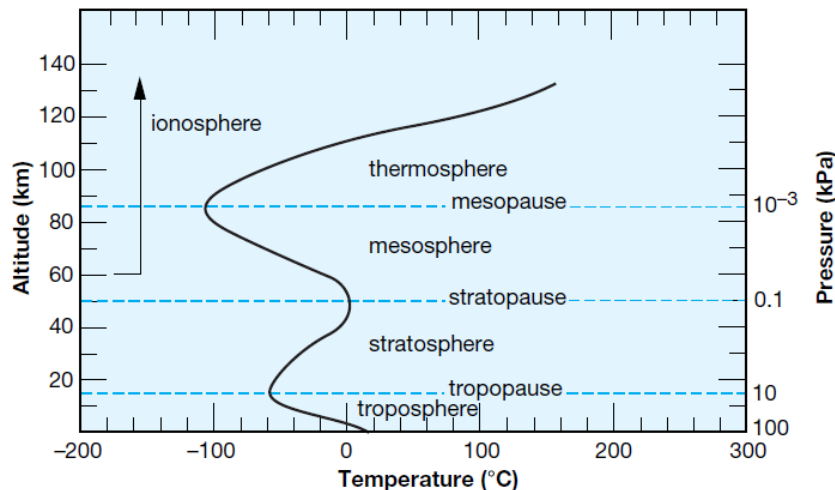
Conclusion: Gravimetric analysis can be used to determine the sulphate content of fertiliser

Atmospheric Chemistry

Layers and composition of the atmosphere:

The atmosphere is a layer of gas which surrounds the Earth. Pressure decreases consistently with altitude, whilst temperature both increases and decreases with altitude. The main layers of the atmosphere are:

- Troposphere (0-15km): Temperature decreases with altitude, resulting in convection patterns which mix gases well and allows weather patterns to occur
- Stratosphere (15-50km): Temperature increases with altitude, limiting the vertical mixing of gases due to a lack of convection currents, causing this layer to be very stable. Gases only diffuse very slowly across the tropopause. This layer also contains the ozone layer which is most concentrated at 25km
- Mesosphere (50-85km): Temperature decreases with altitude like in the troposphere. It contains part of the ionosphere in which solar radiation ionises atoms and molecules
- Thermosphere (85-600km): Temperature increases with altitude. This layer also contains a part of the ionosphere
- Exosphere (>600km): Particles are gravitationally bound to the Earth but it is not dense enough for them to act as a gas. Also contains part of the ionosphere



The atmosphere consists mainly of nitrogen, oxygen and argon, making up 78.08%, 20.95% and 0.93% of the atmosphere (v/v) respectively. In addition, there are a number of trace gases including:

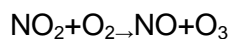
- | | |
|----------------------------|-------------------------------------------------|
| • CO ₂ (350ppm) | • N ₂ O (0.2ppm) |
| • Ne (18ppm) | • CO (0.1ppm) |
| • He (5ppm) | • O ₃ (0.02ppm) |
| • CH ₄ (1.5ppm) | • NO/NO ₂ (<0.01ppm) |
| • Kr (1ppm) | • NH ₃ (<0.01ppm) |
| • H (0.5ppm) | • SO ₂ /H ₂ S (<0.002ppm) |

Pollutants in the lower atmosphere:

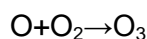
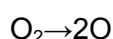
- Carbon dioxide CO₂: Produced from the combustion of fossil fuels in power plants and motor vehicles as well as deforestation. CO₂ results in respiratory problems in high concentrations and contributes to the enhanced greenhouse effect
- Carbon monoxide CO: Produced from the incomplete combustion of fossil fuels in motor vehicles, bushfires and cigarettes. CO is a respiratory irritant as it binds to haemoglobin in the blood, preventing O₂ absorption, and it contributes to the enhanced greenhouse effect
- Sulphur dioxide SO₂: Produced from combustion of sulphur impurities in fossil fuels in power plants and motor vehicles, metal extraction and some chemical industries. SO₂ is a respiratory irritant, and also results in acid rain
- Nitrogen oxides NO_x: Produced from lightning strikes and high temperature combustion in power stations. NO_x is a respiratory irritant, results in acid rain and in the presence of hydrocarbons and oxygen under the action of sunlight, forms photochemical smog
- Hydrocarbons/ volatile organic compounds (VOCs): Produced from unburnt fuels in motor vehicles as well as industrial and domestic solvents. They are carcinogenic and form photochemical smog
- Particulates: Includes small particles such as soot and asbestos. Produced from combustion, industrial processes, bushfires and demolition of old buildings containing asbestos. Results in respiratory diseases and photochemical smog
- CFCs/ halons: Produced from aerosols, refrigeration, air-conditioning, foam plastics and fire extinguishers (although none are produced anymore). They are very stable and cause little harm in the troposphere but result in the depletion of the ozone layer in the stratosphere
- Ozone O₃: Produced in photochemical smog. O₃ a respiratory irritant toxic to all living organisms as it is a strong oxidising agent is
- Lead: Produced from lead smelters, lead paint from old houses and, until recently, combustion of leaded petrol in cars. It is a direct poison, resulting in brain damage

Ozone:

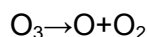
Ozone is an allotrope of oxygen with 3 oxygens in a molecule. In the troposphere, where ozone levels are usually 0.02ppm, it is considered a pollutant. Concentrations of 0.1ppm are harmful to one's health. It causes breathing difficulties, aggravates respiratory problems, and produces headaches and premature fatigue. Ozone is a major component of photochemical smog. Ozone is produced from the reaction of NO_2 (produced from cars) and oxygen:



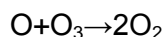
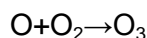
In the stratosphere however, ozone acts as a radiation shield, absorbing UV-B and UV-C so that they don't reach the Earth's surface. Ozone levels in the stratosphere typically range from 2-8ppm. When high energy short wavelength UV-C rays strike molecules of ordinary oxygen (O_2), they split the molecules into 2 free oxygen atoms. The two free oxygen atoms combine with oxygen molecules to form ozone:



When an ozone molecule absorbs medium energy UV-B radiation, it splits into an ordinary oxygen molecule and a free oxygen atom:



The free radical oxygen may combine with an oxygen molecule, creating another ozone molecule or take an oxygen atom from an existing ozone molecule to create two ordinary oxygen molecules:

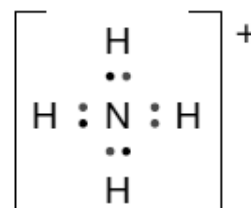
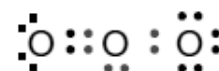


In this way, the formation and destruction of ozone is able to block out short wavelength UV radiation which damages living tissue and can lead to skin cancer, cataracts, reduced plant growth and damage to PVC. Note that ozone doesn't block out longer wavelength UV-A which is actually beneficial as it promotes photosynthesis and vitamin D production.

Coordinate covalent bonds:

A coordinate covalent bond is formed when one atom provides both shared electrons. These shared electrons come from a lone electron pair. Note that despite being formed differently from ordinary covalent bonds, coordinate covalent bonds are indistinguishable from ordinary covalent bonds once they are formed (all bonds are the same length). Species which contain coordinate covalent bonds include ozone, carbon monoxide and ammonium.

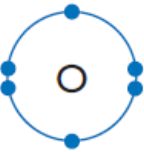
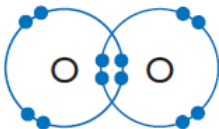
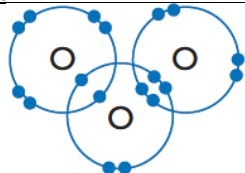
Note that in ozone, there are two possible single and double bond arrangements, with one possible Lewis Dot structure shown to the top right. The actual structure is an intermediate between these two structures known as a resonance hybrid, which is represented below.



Resonance hybrid

Comparison between allotropes of oxygen:

- Free oxygen is a free radical as it has an incomplete valence shell. Hence, it is extremely reactive and unstable, with oxygen atoms tending to react spontaneously with each other at room temperature to form diatomic oxygen
- Diatomic oxygen has a double bond, making it very reactive. It is also non-polar and hence has a low melting and boiling point and a low solubility in water
- Ozone is more reactive than diatomic oxygen as it has weaker bonds (the energy needed to split off one oxygen atom is less than the energy needed to break a double bond). However, it is less reactive than free oxygen and is a stable molecule. The ozone molecule is bent in order to minimise the repulsion between the bonding electron pairs and the lone electron pair on the central molecule. This asymmetric arrangement makes the ozone molecule polar, with the central atom positive and the single bonded atom negative. This polarity gives ozone a higher melting and boiling point and greater solubility in water

		Oxygen Radical	Oxygen Molecule	Ozone
Identity		O	O ₂	O ₃
Molecular Diagram				
Colour	Gas	n/a	Colourless	Pale Blue
	Liquid		Pale Blue	Deep Blue
	Solid		Pale Blue	Black-Violet
Boiling Point (°C)		n/a	-183	-111
Melting Point (°C)		n/a	-219	-193
Water Solubility		n/a	Partially soluble	Much more soluble
Stability		Unstable	Very Stable	Decomposes to O ₂
Bond Energy		n/a	498kJ/mol	106kJ/mol
Reactivity		Very High Strong Oxidant	Moderately High, Moderate Oxidant	High, Strong Oxidant
Density		-	~Air	~1.5x Air
Uses		-	Combustion, rocket fuel, life support.	Sterilisation, bleaching agent, disinfectant

Naming Haloalkanes:

Halons or haloalkanes are alkanes with at least one attached halogen.

In naming straight chained haloalkanes, the prefixes bromo-, chloro-, fluoro- and iodo- are added to the name of the alkane in alphabetical order. If there is more than one of each type of halogen the prefixes di-, tri- etc. should also be added and if multiple isomers (compounds with the same molecular formula but different structures with slightly different properties) are possible, their position along the carbon chain denoted. The numbering of carbon atoms should start from whichever side gives the smallest sum of numbers or, if multiple names are still possible, whichever side gives the smallest sum of numbers to the most electronegative element.

CFCs and Halons:

Chlorofluorocarbons (CFCs) are compounds containing chlorine, fluorine and carbon. CFCs have boiling points near room temperature, are very stable and inert, non-toxic and non-flammable, making them ideal for a number of purposes. Common CFCs which were in use included:

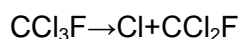
- Freon-11 (CFC-11): Trichlorofluoromethane CCl_3F - Used as a working fluid for refrigeration, a propellant in aerosol spray cans and a foaming agent in the manufacture of foam plastics such as polystyrene
- Freon-12 (CFC-12): Dichlorodifluoromethane CCl_2F_2 - Also used for the above purposes
- Freon-113 (CFC-113): 1,1,2-trichloro-1,2,2-trifluoroethane $\text{CCl}_2\text{FCClF}_2$ - Used for cleaning circuit boards

The use of CFCs in refrigeration, aerosols, foam plastics manufacture and circuit board cleaning cause them to be released into the atmosphere, either directly through the latter 3 uses or from the leaking of old refrigeration and air-conditioning units.

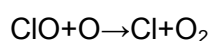
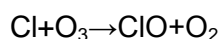
Halons are compounds of carbon, bromine and other halogens. They are dense, non-flammable liquids commonly used in fire extinguishers due to these properties and how it did little damage to nearby items. One commonly used halon is bromochlorodifluoromethane CBrClF_2 . The use of such halons caused them too to be released into the atmosphere.

Problems with CFCs in the atmosphere:

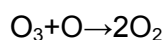
CFCs are not broken down by sunlight or oxygen in the lower atmosphere due to their stability and are not washed out by rain due to their insolubility with water. Hence, they remain in the troposphere for long periods of time (several decades), allowing them to slowly diffuse into the stratosphere where short wavelength UV radiation is able to break off a chlorine atom (free radical) from the CFC molecule:



The chlorine free radical then reacts with ozone, turning it back into diatomic oxygen:

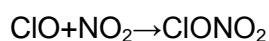
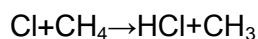


This gives a net reaction of:

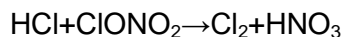


Hence chlorine free radicals derived from CFCs in the stratosphere is able to reduce the amount of ozone in the atmosphere, reducing its ability to block harmful UV radiation. This results in increased incidence of sunburn and skin cancer, increased risk of cataracts, lowered immune response, reduced plant growth and increased damage to many synthetic materials such as PVC.

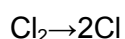
As chlorine is not used up in the above reaction, it is able to destroy thousands of ozone molecules in a chain reaction before being removed. Chlorine is removed from the cycle through reaction with the small amounts of methane and nitrogen dioxide which diffuse into the stratosphere:



The depletion of the ozone layer is especially problematic over Antarctica in spring. The Antarctic Winter is a period of continuous darkness. In addition, a polar vortex over Antarctica prevents Antarctic air from mixing with warmer air up North, keeping the stratosphere above Antarctica extremely cold. Under such conditions, certain solid particles form which are able to catalyse a reaction between HCl and ClONO₂



Molecular chlorine accumulates in the stratosphere during the winter until early spring. Sunlight is able to split chlorine molecules into chlorine free radicals:



These chlorine free radicals are able to destroy large amounts of ozone, resulting in a drastic depletion of the ozone layer. Ozone levels over the Antarctic have dropped between 50-90% in Spring compared to a 3-8% decrease worldwide.

Steps taken to alleviate ozone depletion:

- The 1987 Montreal Protocol (along with the 1990 London and 1992 Copenhagen Amendments) which involved:
 - Stopping the use of halons by the end of 1994
 - Ceasing the manufacture and use of CFCs by 1996
 - Phase out HCFCs by the early 21st century
 - Provide developing countries with financial assistance for the phasing out of CFCs
- CFC alternatives such as:
 - HCFCs- Hydrochlorofluorocarbons which contain a C-H bond susceptible to attack by radicals and atoms in the troposphere, causing most of it to be decomposed in the troposphere. Only a small portion reaches the stratosphere where it is able to destroy ozone and thus has less ozone destroying capability. However, as it still has some ability to destroy ozone it is only a temporary solution until better alternatives can be found. One HCFC is chlorodifluoromethane CHClF₂ used for air cans and refrigeration
 - HFCs- Hydrofluorocarbons lack chlorine and thus have no ozone destroying capacity. The C-H bond also means that it undergoes some decomposition in the atmosphere. One HFC is 1,1,1,2-Tetrafluoroethane CF₃CH₂F used as in refrigeration. It is however less efficient and more expensive than CFCs

Whilst these measures have been effective at reducing CFC and halon emissions into the atmosphere, it has not yet had a significant effect on ozone levels due to the large amount of CFCs already in the atmosphere released from the 1930s onwards. This takes a long time to diffuse into the stratosphere and be destroyed. It is estimated that it will take from 50-100 years for complete recovery of the ozone layer to occur.

Monitoring ozone levels:

Total stratospheric ozone above the Earth's surface is measured in Dobson units (DU). One DU corresponds to a 0.01mm thickness of pure ozone at atmospheric pressure. The normal amount of ozone in the atmosphere is around 300DU:

- UV spectrophotometers measure the intensity of light at a wavelength which ozone absorbs and wavelengths either side and compare these measurements to find the amount of ozone in the total column of air above the instrument
- Satellites carry OMI (ozone monitoring instrument) which work similarly and are able to measure ozone concentration as a function of altitude and geographic position over a large area
- Helium filled balloons carry instruments including UV spectrophotometers into the atmosphere which measure ozone as a function of altitude

Waterway Management

Measuring water quality:

Concentration of common ions:

- Water typically contains small amounts of dissolved ions including cations such as Ca^{2+} , Na^{2+} , Mg^{2+} , K^+ , Sr^{2+} and Fe^{2+} and anions such as HCO_3^- , SO_4^{2-} and Cl^-
- Concentration of cations is mainly determined by atomic absorption spectroscopy whilst anions are analysed either gravimetrically by precipitation or volumetrically by titration

Total dissolved solids (TDS):

- TDS is the mass of solids dissolved in unit volume of water- measured in mgL^{-1} or ppm
- These are usually dissolved ionic salts
- Total level of dissolved inorganic salts is referred to as salinity
- Fresh water contains a low TDS (<500ppm) whilst saline water has a salinity of >3000ppm. Sea water has a TDS of around 35000ppm
- TDS can be determined by two ways:
 - Evaporating water from a filtered sample and weighing the mass of the remaining solids
 - Measuring the electrical conductivity of water using a conductivity meter. The greater the conductivity, the higher the concentration of ions/ TDS

Hardness:

- Hard water does not lather with soap and leaves behind a grey scum
- Hard water contains high concentrations of Ca^{2+} and Mg^{2+} ions
- The stearate ions in sodium stearate $\text{C}_{17}\text{H}_{35}\text{COONa}$ (soap) form a precipitate with Ca^{2+} and Mg^{2+} ions. This removes soap from solution, reducing its cleaning power and leaves behind a grey scum which can stick to basins and settle on fabrics, discolouring them:
 - $\text{Ca}^{2+}(\text{aq}) + 2\text{C}_{17}\text{H}_{35}\text{COO}^-(\text{aq}) \rightarrow \text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2(\text{s})$
 - $\text{Mg}^{2+}(\text{aq}) + 2\text{C}_{17}\text{H}_{35}\text{COO}^-(\text{aq}) \rightarrow \text{Mg}(\text{C}_{17}\text{H}_{35}\text{COO})_2(\text{s})$
- Water hardness is measured by the concentration of Ca^{2+} and Mg^{2+} ions in terms of milligrams of CaCO_3 per litre- soft water has a CaCO_3 of under 60mgL^{-1}
- The concentration of Ca^{2+} and Mg^{2+} ions can be determined by volumetric analysis by titration with an ethylenediaminetetraacetate (EDTA) salt in an $\text{NH}_3/\text{NH}_4^+$ buffer solution with Eriochrome Black T indicator (turns from purple to blue at the equivalence point)

Turbidity:

- Turbidity is how cloudy water is- it is a measure of suspended solids in water
- High turbidity can give water an undesirable appearance and taste, block sunlight needed for photosynthesis whilst sediment can carry nutrients and pesticides into waterways
- Turbidity is measured by measuring the depth of water to render an object invisible
- This is done by pouring water into a long, narrow turbidity tube until a black cross at the bottom of the tube disappears or lowering a secchi disk into the water until it disappears
- The depth of water is converted into nephelometric turbidity units (NTU)
- Clean water has a turbidity of less than 3NTU whilst polluted water is greater than 20NTU
- Alternatively, turbidity can be measured by filtering off suspended masses and determining the mass of the filtrate

Acidity:

- The pH of water can be measured using a universal indicator solution or a pH meter
- The pH of clean water is typically between 6.5 and 8.5 with any values outside this range indicating that some form of pollution such as industrial waste or fertiliser run off has been discharged into the water

Dissolved oxygen/ biochemical oxygen demand:

- Dissolved oxygen in water comes from the absorption of oxygen from the atmosphere at the surface and from photosynthesis of aquatic plants
- Dissolved oxygen is consumed by the respiration of aquatic plants and animals and the decomposition of organic matter
- The concentration of oxygen in water is usually about 10ppm
- If dissolved oxygen falls below 5ppm many aquatic species will die or fail to reproduce
- Dissolved oxygen is measured by adding manganese hydroxide, iodide ions and acidifying the water. This results in a series of chemical reactions shown below in which each molecule of dissolved oxygen is associated with two molecules of iodine. The solution is then titrated with a sodium thiosulphate solution $\text{Na}_2\text{S}_2\text{O}_3$ with starch as an indicator (turns from blue to colourless at the equivalence point) to determine the concentration of iodine and hence dissolved oxygen concentration. This is known as the Winkler method:
 - $2\text{Mn}(\text{OH})_2(\text{s}) + \text{O}_2(\text{aq}) \rightarrow 2\text{MnO}(\text{OH})_2(\text{s})$
 - $\text{MnO}(\text{OH})_2(\text{s}) + 2\text{I}^-(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
 - $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$
- Alternatively, a dissolved oxygen sensor which makes use of the electrolysis of oxygen to determine the level of dissolved oxygen can be used
- Dissolved oxygen can be reduced through thermal pollution which reduces the solubility of oxygen in water or through the addition of organic wastes or eutrophication which increases biochemical oxygen demand (BOD)
- BOD is a measure of the concentration of dissolved oxygen that is needed for the complete breakdown of the organic matter in water by aerobic bacteria
- It is measured by allowing aerobic microorganisms to oxidise organic matter in a sealed, dark environment at 25°C over a five day period and measuring the difference in oxygen levels (as well as accounting for any added oxygen when BOD is high)
- A BOD greater than 4ppm indicates that the water is likely to be polluted

Factors affecting the concentrations of ions in bodies of water:

The concentration of ions present in water bodies depends on the sources which feed it. The primary source of all bodies of water is the rain which contains very few ions (small concentrations of carbonate from dissolved CO_2 and Na^+ , Cl^- and SO_4^{2-} from sea spray). However, as the rainwater moves through the land, it picks up dissolved salts which are carried into rivers, lakes and oceans. Rivers which are constantly being replenished with fresh water tend to have low salinity levels, as do most lakes. However, they do carry dissolved salts to the oceans, resulting in oceans having very high salinity levels.

Salinity levels in oceans are maintained by natural salt removing processes such as nutrient and waste exchange and the formation of coral and limestone reefs. Due to the ocean's large size the concentration of ions in the ocean remains relatively constant throughout a geological time period, although coastal waters can be affected by significant discharge as a result of human activity.

In addition to the type of water body, the TDS as well as the concentration of specific ions in water depends on:

- The pathway of the water:
 - If rain runs straight into streams, it dissolves very few solids (small amounts of nitrates, phosphates and Ca^{2+} and Mg^{2+} ions) with TDS below 50ppm
 - If rain runs into underground aquifers and then into a stream it will dissolve Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- and CO_3^{2-} ions from the soil with a TDS between 100 and 300ppm
 - If rain percolates down to deep underground aquifers and remains there for several centuries it will contain higher amounts of the previous ions as well as other cations such as Fe^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} with a TDS above 1000ppm
- PH of the rain: Acid rain with a pH below 5 will more readily leech certain cations such as Ca^{2+} , Mg^{2+} and Fe^{3+}
- Human activity:
 - Land clearing results in water running more rapidly across the land, increasing sediment loads and concentrations of a ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- and CO_3^{2-}
 - Agricultural (fertiliser) run off increases the concentration of NO_3^{2-} and PO_4^{3-} ions
- Effluent discharge: Sewage and storm water runoff can greatly increase the TDS of water (although effective water treatments can remove most suspended matter), BOD and level of pathogens. Industrial effluents can discharge heavy metal ions such as Pb^{2+} , Hg^{2+} , Cd^{2+} , Cr^{2+} , Cu^{2+} and Zn^{2+} if not carefully monitored and controlled
- Leaching from rubbish dumps: Rain and stormwater flow through poorly designed rubbish tips can leech harmful substances such as the cations Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+} and anions such as NO_3^- and PO_4^{3-}

Sanitation of mass water supplies:

Water for human consumption comes from a catchment area which is the area from which all the streams and rainfall drain into a city's water storage dam. The environment of this area is preserved as much as possible in order to ensure that the water flowing into the dam is relatively free of sediments and animal wastes. From the reservoir, it undergoes treatment involving clarifying and sanitising the water, before it is fed into a cities' mains water supply:

- Flocculation: This involves adding cations to the water such as Fe^{3+} in FeCl_3 or Al^{3+} in $\text{Al}_2(\text{SO}_4)_3$ as well as making the water slightly alkali by adding a base such as NaOH or $\text{Ca}(\text{OH})_2$. The cations react with hydroxide ions in the alkali water to form a gelatinous precipitate such as $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$. Suspended solids and some bacteria are adsorbed onto the precipitate which coagulates into larger particles
- Clarification and filtration: The water is left to stand in a settling tank with the flocculated particles setting as sludge at the bottom of the tank. The water is then passed through granular filters comprised of sand and anthracite coal to filter out any remaining particulate matter

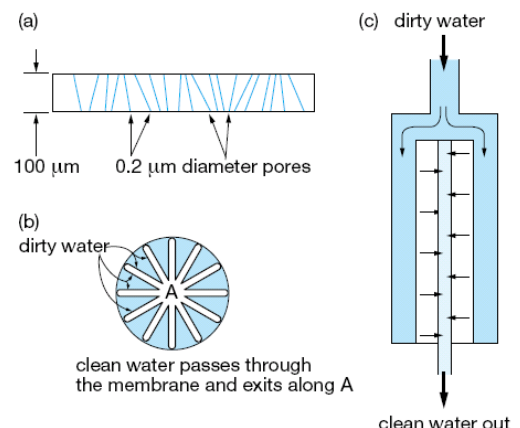
- Disinfection: This involves adding chemicals to water in order to kill any microorganisms and prevent the growth of algae in pipes. Chemicals commonly used are:
 - Chlorine added by reacting chlorine gas with water to form hypochlorous acid (HOCl) and Cl^- or by adding $\text{Ca}(\text{ClO})_2$ or NaClO to water. Sufficient chlorine is added to ensure that the concentration stays just above 1ppm until the water reaches the consumer
 - Chloramines added by adding chlorine and ammonia in water to form either NH_2Cl or NHCl_2
 - Ozone which is very effective and has a positive impact on the colour, odour and taste of water. It is produced on site by passing an electric spark through dry air or oxygen

The above method of water treatment which is commonly used in Australia is effective at producing a sufficient quantity of water to meet the demand of large cities in a cost effective matter. It also produces water that is tasteless, colourless and odourless and containing very low amounts of suspended solids and pathogens that can be harmful to humans. However, as evident by the 1998 Sydney water *Giardia* and *Cryptosporidium* scare in which such organisms were suspected of being present in the water supply, certain microorganisms can sometimes pass through water treatment.

In order to improve the quality of the water supply advanced sanitation techniques such as ozone sterilisation and membrane filters can be used, although at greater cost. Improving water quality of the catchment area may be a more cost effective method of improving water quality. Some people may also choose to install water filters in their homes or boil their water before drinking in order to further purify their water.

Microscopic membrane filters:

Membrane filters consist of a thin film of synthetic polymer, such as polypropylene, polytetrafluoroethylene and polysulphone, through which there are pores of fairly uniform size. These can either be pleated around a central rigid porous core and to be mounted in a water pipe to filter water flowing through it or by making the membranes into hollow capillaries. These capillaries typically have an outside diameter of $500\mu\text{m}$, an inside diameter of $200\mu\text{m}$ and a pore size of 0.2 to $0.5\mu\text{m}$. Dirty water, forced through by gravity, vacuum or pressure pumps or a centrifuge, flows from the outside to the inside of the capillary where it comes out as clean water. Large numbers of capillaries are bundled together to make a filtering unit with a large surface area. Membrane filters can be cleaned by blowing compressed air through the capillaries which blows away dirt to be flushed away.



Membrane filters differ from depth filters which consist of coarse material such as fibres in filter papers or granules in sand filters packed into a relatively thick bed. As a suspension flows through larger particles are blocked while smaller ones pass through. However, this process is much more refined in membrane filters with virtually all particles larger than the size of the pore being filtered out. Water will also pass through the thin membrane filters more quickly than depth filters. In membrane filters, high pressure can be used to speed up the process of filtration, a method which is ineffective with depth filters as this would simply push larger particles through the filter material. As a result, membrane filters will result in much cleaner water, although they are more expensive.

Heavy metal pollution of water:

The heavy metals are those with high atomic mass and generally includes the transition metals plus lead and sometimes arsenic. Certain heavy metals such as aluminium, cadmium, lead, manganese, mercury and silver can have detrimental effects on humans and thus it is important to determine their concentration in water. This is done through atomic absorption or atomic emission spectroscopy. Adding Na_2S to water can also be used to determine the presence of heavy metals in water as the metal cations will combine with the S^{2-} anions to form a precipitate e.g. PbS .

Algal blooms and eutrophication of waterways:

Algal blooms occur when waterways receive excess nutrients of nitrate NO_3^- and phosphate PO_4^{3-} which are essential for plant growth. Phosphate is usually in shorter supply so it is the limiting factor of plant growth. If there is an abundance of phosphate in water then algae begins to multiply rapidly, covering the water in a green scum. This increases the BOD of water and reduces sunlight penetration, killing off other plants and animals. This also results in a build-up of sediments in waterways and renders the water unsuitable for human consumption as the algae is too hard to filter out. In addition, the presence of other species such as cyanobacteria produces toxins which are harmful to humans and livestock.

Occasional algal blooms are reversed during the next flood or heavy rain. However, if this occurs too frequently without giving the waterway enough time to recover, sediments can build up, permanently degrading the waterway in a process known as eutrophication, the process in which a water body becomes lifeless as a result of receiving excess nutrients. This is usually a slow and natural process taking tens of thousands of years but is accelerated by human activity such as sewage discharge and fertiliser run off.

The likelihood of algal blooms can be determined by measuring the concentration of phosphate in water, since this is usually the limiting factor. This is done using a colorimetric test which measures the absorbance of a particular wavelength band of light by a coloured solution- the greater the absorbance, the greater the concentration. To prepare a sample for a colorimetric test, $(\text{NH}_4)_2\text{MoO}_4$ is added to form a yellow precipitate. Ascorbic acid is then added to produce an intense blue colour. A water body becomes eutrophic if phosphate concentration exceeds 0.05ppm in a dam or lake and 0.1ppm in a flowing river or stream.

Features of Sydney Water:

Catchment Area:

The primary catchment area for the Sydney metropolitan area is the Warragamba catchment, water from which flows into Warragamba dam. The catchment area covers an area of 9050km² and includes coal- fire stations to the North and grazing areas to the South which are possible sources of contamination. However, a 2600km² special and protected area helps to maintain water quality. Water from Warragamba dam is pumped to water filtration plants where it is clarified through flocculation and sedimentation and sanitised by chlorination. Water quality is monitored by Sydney Water both at the reservoirs and at various points in the customer supply system.

Chemical Additives:

Fluoridation occurs in Sydney's water supply in accordance with regulations by NSW Health. F^- ions are added to water in the form of compounds such as sodium hexafluorosilicate Na_2SiF_6 , fluorosilicic acid H_2SiF_6 and NaF. Fluoride is added to municipal water supplies to improve dental health since:

- Fluoride interacts with tooth enamel to produce a denser lattice that is stronger, more resistant and less soluble in low pHs
- Fluoride in plaque and saliva allows remineralisation of small defects in the tooth surface before cavities become permanent
- As a bactericide, fluoride interferes with bacteria that produce acid which speeds up the process of tooth decay

Chemistry of Art

Pigments

Sources of pigments in early history:

Pigments are coloured, insoluble, granular solids composed of very fine particles. In early history, pigments were derived from the minerals found in a variety of soft rocks or coloured earth. These minerals were readily available in the environment and did not require complex extraction processes. Such pigments included:

- Ochres: Natural earth of silica and clay which owes its colour to the presence of Iron (III) Oxide:
 - Yellow Ochre: goethite $Fe_2O_3 \cdot H_2O$
 - Red Ochre: Fe_2O_3 made by burning yellow ochre to drive off the water of hydration
 - Brown Ochre: limonite $FeO(OH)$
- Black pigments such as pyrolusite MnO_2 and charcoal C
- White pigments such as kaolin $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ chalk $CaCO_3$ and gypsum $CaSO_4 \cdot 2H_2O$

Insolubility of pigments:

Pigments need to be insoluble in most substances because:

- It allows their colour to be retained as the medium dries up
- It allows them to be preserved for a longer period of time e.g. rock and cave paintings are not washed away by rain and cosmetics are not dissolved by sweat

Early uses of pigments:

Cave paintings:

Pigments were used for cave paintings over 15000 years ago as evidenced through Aboriginal Australian Rock Art and the Lascaux cave paintings in France. Red and yellow ochre, charcoal, pyrolusite, chalk, gypsum and kaolin clay were used for the red, yellow, black and white pigments. These were mixed with orchard juice, egg yolks, resins, saliva and blood to make paints, usually applied with fingers, animal furs, feathers and the chewed and frayed ends of twigs.

Self- decoration and cosmetics:

Pigments were also used for decorative purposes in different cultures. For example:

- Aboriginal Australians used red, white, yellow and black paints on their bodies for ceremonial dances and rituals such as the Coroboree and coming of age
- The Ancient Egyptians, Greeks and Romans used pigments such as white lead for face powder, cinnabar for lipstick, malachite and azurite for body paint and eye shadow and kohl for mascara/ eyeliner

Preparation of the dead for burial:

- Ancient Egyptians used colours of white, red, yellow and ultramarine blue in their tombs
- Ancient Mayans used red ochre to soak the bodies and preserve them

Composition of Paints:

Paints consist of a pigment and a liquid to carry the pigment known as a medium:

Pigments:

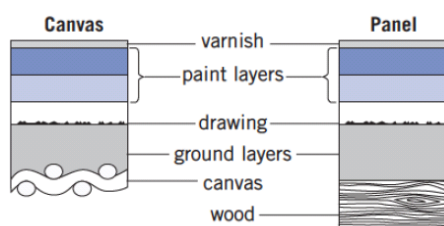
- Granular solids consisting of very fine particles
- Provides the paint's colour by absorbing certain wavelengths of light and reflecting others
- May also provide opacity, strength/ adhesion, durability/ weathering properties and corrosion resistance
- Lakes are a special class of pigments derived from vegetable dyes dissolved in water and then fixed onto an insoluble white powder such as chalk or gypsum which could be extracted and dried e.g. red alizarin $C_{14}H_9O_4$. However, being water soluble they will run if wet and fade over time

Medium:

- Liquid in which the pigment is suspended in
- Should be viscous enough to hold particles in suspension whilst being sufficiently fluid to allow the artist to easily apply the paint
- Disperses the pigment evenly across the surface and eventually forms a dry, adherent film that protects the pigment and makes colours last longer
- Has the ability to wet the pigment particles, increase the pigment's adhesiveness and form a protective film on the surface being treated
- Mediums used throughout history include egg yolk, blood, saliva, urine, tree and plant gums with natural and synthetic oils being used more recently

Paints and coloured glass:

Colour is able to be obtained by spreading paints over a surface layer. In early paintings this surface layer was either timber (pine, oak or poplar) or canvas prepared with a ground layer to reduce its roughness and absorbency. Ground layers consist of gesso, a mixture of gypsum or chalk with animal glue which sets to a brittle creamy layer to be scraped off and rubbed smooth. The artist then outlines details for the painting using charcoal before adding various paint layers to achieve a variety of colour effects. Paints were mainly added in their pure form, although white lead was used to lighten colours. Afterwards the painting was covered with a layer of clear varnish to protect the paint layers and give the colours clarity and depth of separation.



Colour can also be obtained by mixing pigments with the bulk of materials such as with coloured glass. This was made by adding finely powdered pigments to the glass mixture before melting. Flashing was also used to lighten the colours of glass and involved coating clear glass with a layer of coloured glass. By scratching or abrading the glass complex patterns could be formed. Another method of colouring glass was through staining. This involved painting glass with silver nitrate then firing it in an oven. This produced stained glass of a range of yellow tones; depending on how many times the glass was fired.

Chemistry of and processes used to prepare and attach pigments to a medieval artwork- Madonna and Child with Saints Jerome, John the Baptist, Bernadino and Bartholomew by Sano di Pietro (1405-1481) (Italy):

Preparing the timber for painting:

1. Liner attached to the timber with animal glue
2. Gesso grosso, a coarser thicker first layer of calcium sulphate or chalk attached to the timber with animal glue
3. Gesso sottile, a smooth hard white enamel like finish added
4. Underdrawing done using charcoal

The medium used for this painting was egg tempera, egg yolk mixed with water. This painting also featured a significant amount of gold gilding. This was either done by painting over the gold and then etching the paint away to reveal the gold underneath (sgraffito) or by attaching the gold over the paint layers (mordant gilding). Oil, varnish or garlic juice was used to attach the gold leaf to the surface of the painting.



Pigments used in this painting include:

Pigment	Colour	Chemical composition
Vermillion	Red	HgS_2
Ultramarine	Blue	$3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{Na}_2\text{S}$
Lead Carbonate	White	PbCO_3
Orpiment	Yellow	As_2S_3
Ochre	Brown	$\text{FeO}(\text{OH})$

Discovery of new mineral deposits and new pigments:

Over time, artists gained access to more minerals from which new pigments could be extracted. For example, the discovery of Lapis Lazuli in the Kokcha River Valley, Afghanistan- this contains the mineral Lazurite $(\text{Na, Ca})_8[(\text{S, Cl, SO}_4, \text{OH})_2](\text{Al}_6\text{Si}_6\text{O}_{24})$ from which the blue ultramarine $\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$ could be extracted. Another example is the discovery of vast Chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ deposits in the United States, allowing many chromium compounds to be synthesised such as chrome yellow PbCrO_4 and chrome red $\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$.

Metallic components of pigments and their colour:

The colour of pigments depends mainly on the metallic component of the pigment and its position in the periodic table. All pigments of a certain metal will have a similar colour range. For example, iron is usually associated with colours in the red- yellow range, copper in the blue- green range and cobalt in the yellow- violet range. Most of the metals in pigments are transition metals and the colours which these metals produce depend on their electron configuration.

Chemical composition of Egyptian and Roman cosmetics and their health risks:

Name		Chemical Composition	Cosmetic uses	Health Risks
White Lead		$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	Face powder	Inhalation and ingestion hazardous, skin eye and respiratory irritant, brain damage in children
Red Lead/ Minium		$\text{PbO}_2 \cdot \text{PbO}$	Face and body colouring	
Cinnabar		HgS	Lipstick	Toxic if ingested or inhaled, skin contact hazardous, eye irritant, organ damage
Malachite		$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Eye shadow, body paint	Eye irritant, toxic fumes, harmful if ingested- may cause gastrointestinal discomfort
Azurite		$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$		
Kohl	Stibnite	Sb_2S_3	Eyeliner, mascara	Skin and eye contact, inhalation and ingestion hazardous, kidney/ liver damage, skin burns
	Pyrolusite	MnO_2		Ingestion/ inhalation hazardous, lung damage, CNS impairment, reduced fertility in men
Orpiment		As_2S_3	Eye shadow, body paint	Toxic if ingested, inhaled or absorbed through skin, carcinogenic, reproductive disorders
Realgar		As_4S_4		

Additional pigment examples:

	Natural	Manufactured
Organic	Indigo $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$	(Red) Pararot $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3$
Inorganic	Red ochre FeO_3	Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Spectra

Emission spectra:

When metal ions are heated, for example by spraying them into a flame, some of the ion's electrons become excited and jump up to higher energy levels. As they move back down to a lower energy level, they release a photon of energy equal to the difference in energy levels. Since these photons have a fixed energy, they have a fixed frequency (due to Planck's equation $E=hf$) and thus appear as a certain colour (if within the range of the visible spectrum). In addition, since electrons of an atom occupy discrete energy levels, there are a set number of possible energy level gaps and thus frequencies which an excited atom could emit. Thus, metal ions emit distinct colours when placed into a flame.

Investigating the flame colours of metal ions

Aim: To observe the flame colours emitted by some metal ions

Method:

1. Take a piece of nichrome or platinum wire and clean by dipping in concentrated HCl
2. Heat wire over a hot Bunsen flame
3. Place the wire in the test solution- a metal salt
4. Heat wire over flame and note colour
5. Use a spectroscope to note the emission spectra of the metal ions

Results- Flame colours of metal ions

Solution	Metal Ion	Colour
NaNO ₃	Na ⁺	Yellow
KNO ₃	K ⁺	Violet
Ca(NO ₃) ₂	Ca ²⁺	Orange-red
Ba(NO ₃) ₂	Ba ²⁺	Green
Sr(NO ₃) ₂	Sr ²⁺	Red
Cu(NO ₃) ₂	Cu ²⁺	Blue- green

Conclusion: Some cations can be identified using a flame test, assuming the metal has spectral lines within the visible spectrum

Spectral lines, emission spectra, absorption spectra and reflectance spectra:

Spectral line- A dark or bright line in an otherwise uniform and continuous spectrum due to certain frequencies/ wavelengths of light being absorbed or emitted by atoms

Emission spectrum- Atoms are excited and thus emit photons of a certain frequency/ wavelength. Light from these atoms are then split using a spectrometer into different wavelengths to obtain bright spectral lines on a black background

Absorption spectrum- EMR is passed through atoms in a vapour phase which absorbs certain frequencies/ wavelengths of light. This is then split using a spectrometer into different wavelengths to obtain dark spectral lines in a continuous spectrum- an element's absorption spectrum is the reverse of its emission spectrum

However, the absorption spectrum of molecules and complex ions is more complex. It consists of broad bands rather than discrete wavelengths. The intensity of absorption varies with wavelength, and thus absorbance can be plotted against wavelength to obtain a substance's absorption spectrum.

Reflectance spectrum- Light is shone upon a surface, some wavelengths of which are absorbed and others reflected. The reflected light is split using a spectrometer and the intensity at different wavelengths is measured. Thus, the reflectance spectrum of a substance can be obtained, featuring a plot of reflectance against wavelength. This is the reverse of its absorption spectrum

Bohr model of the atom:

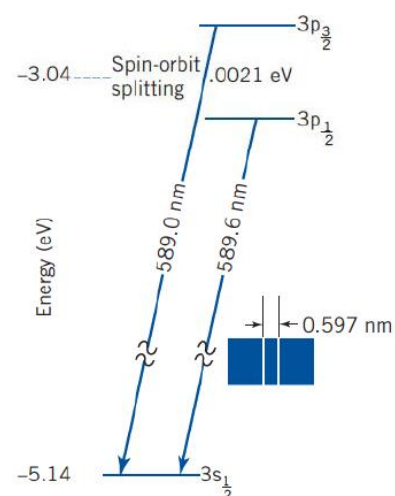
- Atoms with electrons in fixed orbits with definite and discrete energy levels which corresponded to a fixed, circular electron shell with a certain radii
- Electrons may only occupy these energy levels- they are stable and don't radiate energy
- Each energy level could be identified in terms of a principal quantum level n , with the energy level closest to the nucleus having $n=1$, the next $n=2$ etc.
- Energy levels increase as n increases, although the energy levels become closer higher up
- When electrons absorb energy, they move to higher energy levels
- When excited electrons return to their ground state, they emit a quanta of energy (photon) equal to the difference of energies of the two states in the form of EMR
- These photons have a certain wavelength which humans may detect as a specific colour
- Bohr used this model of the atom to explain the emission spectrum of the hydrogen atom

Merits and limitations of the Bohr model:

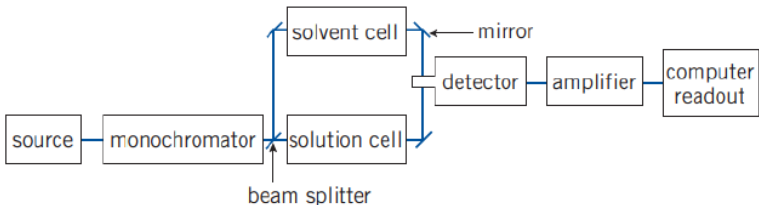
- Bohr was able to explain the spectral lines emitted by the hydrogen atom as the release of a photon of specific frequency when an electron transitions between energy levels
- By quantising electron orbits into allowable energy states, Bohr was able to explain how negative electrons were able to orbit the positive nucleus without collapsing into it, one of the failings of the Rutherford model
- However, the Bohr model failed to explain the emission spectra for other elements which had more electrons and more complex spectra
- Bohr could not explain how only a restricted number of energy levels existed or why accelerating electrons did not lose energy
- Bohr could not explain the relative intensity of different spectral lines i.e. how some transitions were more preferred than others
- Bohr could not explain the existence of hyperfine lines- upon closer inspection; some single spectral lines were composed of multiple closely spaced lines. These could be split even further apart in a magnetic field in a phenomenon known as the Zeeman effect
- Despite these shortcomings, Bohr's atomic model was a significant leap forward

Emission spectrum of sodium- the sodium doublet:

The 3p level of sodium is split into two different energy levels by the magnetic energy of the electron spin in the presence of the internal magnetic field due to the electron's orbital motion. This effect is called the spin orbit effect. An additional external magnetic field causes further splitting known as the Zeeman Effect. The visible light spectrum of excited sodium atoms is dominated by a pair of closely spaced yellow lines known as a doublet which appear at 590.0nm and 589.6nm. These two lines represent the transition of electrons within the $n=3$ shell from the 3p energy level to the 3s energy level.



Analytical techniques for identifying pigments:

- **UV-visible absorption spectroscopy:** This is a destructive test that involves dissolving a small amount of the pigment in a solution. Electrons in the sample become excited as they absorb certain wavelengths of the light. A double beam absorption spectrophotometer is used to find the absorbance at different wavelengths. Radiation, obtained from a tungsten lamp or a deuterium discharge tube, is split into two paths. One is passed through the sample and the other through the solvent which is used as a reference. The detector, a photomultiplier tube, measures the intensity of the two paths of light in order to determine the absorbance plotted against wavelength. This can be compared to known absorbance spectra to identify the pigment and find its concentration. It is mainly used for identifying pigments containing metal ions
- 
- **Infrared absorption spectroscopy:** This is a destructive test similar to UV-visible absorption spectroscopy. Molecules in the sample undergo stretching and/or bending vibrations which become excited by infrared radiation, absorbing it in the process. These absorptions correspond to certain bonds/groups. Live UV-visible spectroscopy, this test uses a double beam absorption spectrophotometer except the source is a heated ceramic such as a silicon carbide rod and the detector is a thermocouple. A graph of transmittance plotted against wave number can be obtained and compared with known spectra to identify the pigment. It is used mostly for polar, organic molecules. It is also used to identify TiO_2 as this is not affected by UV
 - **Reflectance spectroscopy:** This is a non-destructive test that involves shining light onto a surface and measuring the radiation that is reflected. The reflectance spectrum obtained, a graph of reflectance against wavelength, is the complement of the absorption spectrum. It can be compared to known spectra in order to identify pigments. The advantages of reflectance are that it is non-destructive and can be done conveniently at the painting. Either visible, UV or infrared radiation can be used:
 - **Visible-** White light is shone on the surface of a painting and its reflectance measured. This is compared to the reflectance of a non-absorbing or white substance such as zinc oxide (Chinese white) to obtain a reflectance spectrum
 - **UV-** UV rays are shone on the painting's surface and its reflectance measured. This is compared with the reflectance from a material that does not absorb UV such as SiO_2
 - **Infrared-** Infrared radiation is shone upon a painting's surface and its reflectance compared with that of a material that does not absorb infrared radiation such as NaCl
 - **Laser microspectral analysis-** A high energy laser (light amplification by stimulated emission of radiation) vaporises the sample. The vapour is fed through a gap between two electrodes that sparks and excites the atoms and ions, producing emission spectra as excited electrons return to their ground state. This can be compared to known spectra to identify pigments. This is useful because it only results in the destruction of a small amount of sample, can identify many elements at a time and is highly sensitive. In addition to determining the authenticity of paintings, this technique may be used to identify the compositions of steels

Effect of infrared and UV radiation on zinc oxide and copper compounds:

- ZnO fluoresces yellow in UV
- ZnO changes from white to yellow in infrared radiation, returning to normal colour on cooling
- Green malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ fluoresces dirty mauve in UV
- Red copper (I) oxide, malachite and verdigris change permanently to black CuO in IR

Distribution of electrons within elements

The Pauli Exclusion Principle:

This is a quantum mechanical principle which states that no two identical fermions may occupy the same quantum state simultaneously. In the case of electrons, it means that no two electrons may occupy the same position- their four quantum numbers must be unique:

- Principle quantum number (n) - shell: The distinct energy levels in which electrons are located in- $n=1, 2, 3, 4, \dots$ each shell can hold up to $2n^2$ electrons
- Azimuthal quantum number (l) - subshell: Components of shells with slightly different energies corresponding to a certain shape- $l=0, 1, 2, 3$ (s, p, d, f) ($0 \leq l \leq n-1$)
- Magnetic quantum number (m_l) - orbital: A region of space around the nucleus through which an electron with a given orbital may move- $m_l=0, \pm 1, \pm 2, \dots$ ($-l \leq m_l \leq l$)
- Spin projection quantum number (m_s)- spin: Each orbital can contain at most two electrons which must be of opposite spin- $m_s=\frac{1}{2}, -\frac{1}{2}$

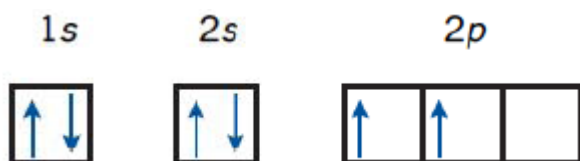
Order of filling subshells:

In an atom's ground state, electrons will occupy the lowest possible energy orbital. The order to filling is: $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 5f \rightarrow 6d$

[illegible]

In addition, if two or more orbitals with the same energy but different orientation are available, electrons will occupy them one at a time, keeping spins parallel until forced to pair by lack of additional empty orbitals. This is known as Hund's rule.

The electronic configuration of an atom can be described using subshell notation. For example, the electronic configuration of nickel is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$. Note that each subshell is listed in order of shell, not in order of filling. The electronic configuration of an atom can also be described using orbital diagrams, with each orbital represented by a box and each electron represented by an arrow pointing either up or down to represent opposite spins. For example, carbon, with an electronic configuration of $1s^2 2s^2 2p^2$ is represented as:



Whilst electrons in the ground state occupy the lowest possible orbitals, excited atoms have different electronic configurations as electrons jump up to higher energy levels. For example, an excited sodium atom may have electronic configurations of $1s^2 2s^2 2p^6 3d^1$ or $1s^2 2s^2 2p^6 4p^1$

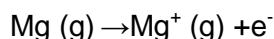
Trends in electronegativity:

Electronegativity is a measure of an atom in a molecule's ability to attract electrons to itself in a chemical bond. It is related to, but different to its ionisation energy since the energy needed to remove an electron is a measure of how strongly it is attracted to the nucleus. Electronegativity is expressed on a relative scale with the most electronegative element, fluorine, being assigned a value of 4.0. The noble gases have an electronegativity of zero. Electronegativity:

- Increases going across a period (and thus with more electrons in the outer shell): Increased nuclear attraction due to greater nuclear charge from more protons (whilst additional electrons are placed in the same energy level) and reduced atomic radii
- Decreases going down a group: Reduced nuclear attraction due to greater atomic radii and shielding of the outermost electrons by the inner electrons

Trends in ionisation energy:

The ionisation energy, I , of an atom or ion is the amount of energy needed to remove the outermost electron from one mole of the gaseous atom or ion. For example:



The first ionisation energy of an element, I_1 , is the energy needed to remove an electron from the neutral atom per mole. The second ionisation energy, I_2 , is the energy needed to remove a second electron per mole and so on. Like electronegativity, first ionisation energies:

- Increase going across a period due to more protons and thus greater nuclear charge and reduced atomic radii increasing nuclear attraction for the outermost electrons
- Decrease going down a group due to greater atomic radii and shielding by the inner electrons reducing nuclear attraction for the outermost electrons

However, there are a few anomalies that buck this trend:

- Group 3 elements such as boron and aluminium have a lower first ionisation energy than expected because the first ionisation involves the removal an electron from the p subshell, which contains only one electron. This has a slightly higher energy than the s (or d) subshell and is well shielded by the electrons in the fully filled s (or d) subshell. Hence, less energy is required to remove this electron, giving boron and aluminium lower first ionisation energies than their respective group 2 elements, beryllium and magnesium
- Group 6 elements such as oxygen and sulphur also have a lower than expected first ionisation energy. The electronic configuration of such elements features 4 electrons in the p subshell with 2 orbitals having one electron each and the third having two electrons. The two electrons in the same orbital have a greater electrostatic repulsion, resulting in less energy needed to remove one. Thus, oxygen and sulphur have lower first ionisation energies than their respective group 5 elements, nitrogen and phosphorous
- In addition, first ionisation energies increase more slowly for the transition metals. This is because going across a period of the transition metal involves adding successive d electrons which are not removed by the first ionisation (the outer s shell electrons are) and thus, the difference between ionisation energies of transition elements are smaller

In successive ionisations, electrons are removed first from the valence shell, starting with the subshell with the highest energy. Subshells are emptied in the reverse order that they are filled. Successive ionisation energies increase gradually as the number of electrons decreases whilst nuclear charge remains the same, making it harder to remove electrons. However, there is a sharp increase in ionisation energy when removing an electron from a lower energy level as it takes substantially more energy to remove electrons from energy levels closer to the nucleus. By analysing successive ionisation energies to see where there is a sudden increase, we can predict the number of electrons in an element's valence shell.

Transition metals

A transition element (or metal since all transition elements are metals) is one that forms at least one ion with a partially filled subshell of d electrons. They occupy the d block of the periodic table, which corresponds to the filling of the d subshell. Note that this definition does not include scandium, whose only ion Sc^{3+} has no electrons in the d-sub-shell and zinc, whose only ion Zn^{2+} has a completely filled d subshell.

Exception to Hund's rule- copper and chromium

Filling of the d sub-shell generally follows Hund's rule with the exception of chromium and copper. Chromium would normally be expected to have 4 electrons in the 3d subshell and 2 electrons in the 4s subshell. However, having 5 electrons in the 3d subshell, thus filling every orbital with one electron, is a more stable electronic configuration. Thus, the 4s subshell of chromium only has 1 electron whilst the 3d subshell has 5. Similarly, copper would normally be expected to have 9 electrons in the 3d subshell and 2 electrons in the 4s subshell, but the increased stability of a fully filled 3d subshell means that copper only has 1 electron in the 4s subshell and 10 electrons in the 3d subshell. This is allowed through the very close energy levels of the 3d and 4s subshells.

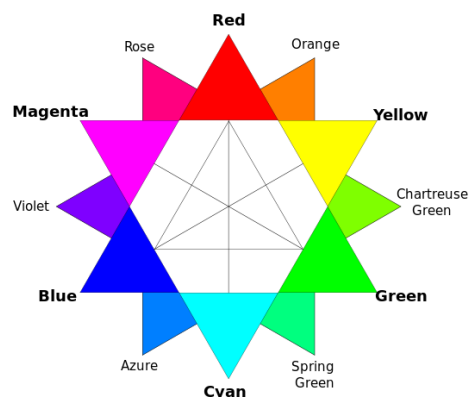
Oxidation states of transition metals:

Transition metals may have multiple oxidation states because they may lose electrons from both their outermost s subshell and the d subshell in the second highest energy level. This is because these two subshells have very similar energies. The +2 oxidation state in nearly all transition metals occurs with the loss of the two s subshell electrons (with the exception of copper and chromium). Higher oxidation states may be obtained from losing electrons from the d subshell. The number of possible oxidation states of a transition metal increases going across a group, peaking at the group containing manganese with a maximum oxidation state of +7. From there, the maximum oxidation states decrease with +2 and +3 becoming the most common.

Colour changes in transition metals:

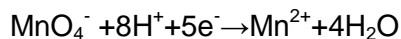
Transition metals ions can be a variety of colours due to the slight energy differences of electrons in the d orbital when it is incompletely filled (ions with empty or fully filled d orbitals are colourless as no electrons can move up within d orbitals). Electrons are able to move up to a slighter energy within the d orbital, absorbing a photon with an energy corresponding to the frequency of visible light. Thus, transition metal ions are able to absorb certain wavelengths of visible light and will appear as the colour of the wavelengths which aren't absorbed (see diagram).

The energy required exciting d electrons to higher energy states and hence the wavelengths of light absorbed also depend on the ion's oxidation state. This is because different oxidation states will have different numbers of electrons in the d orbital. Hence, the colour of transition metal ions can change with oxidation state, resulting in colour changes of transition metal compounds in redox reactions.



Oxidising power of species containing transition metals in a high oxidation state:

Transition metals with a high oxidation state have a smaller radius as they have had a large number of electrons removed. This gives them a greater attraction for electrons, making transition metal oxides such as $\text{Cr}_2\text{O}_7^{2+}$ (+6), MnO_4^- (+7) and FeO_4^{2+} (+6) strong oxidising agents in acidified solutions. Note that H^+ ions are used in the reduction of these species. For example:



The strong oxidising strength of these species can be seen through the high E^\ominus values of the associated reduction reactions.

Investigating colour changes of Vanadium as it changes oxidation states

Aim: To investigate the colour changes of Vanadium as it changes oxygen state

Method:

1. In a 250mL conical flask dissolve 3 grams of ammonium vanadate NH_4VO_3 in 100mL of 1M NaOH
2. Acidify the solution by adding 75mL of 2M H_2SO_4
3. Pour off about 20mL of the yellow solution into a large test tube
4. Add about 6-8 granules of zinc into the conical flask and stopper with a rubber bung
5. Swirl the solution gently until it becomes blue. Save about 20mL in a test tube
6. Swirl the flask again until the solution becomes green. Save another 20mL in a test tube
7. Swirl the flask vigorously until the solution becomes violet. Save about 20mL in a test tube

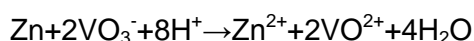
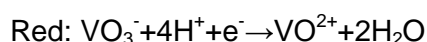
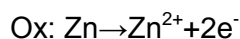
Results:

As the solution was swirled it changed colour from yellow to green to blue and finally violet

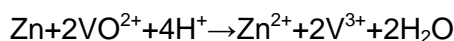
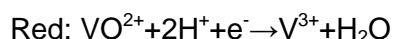
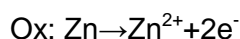
Discussion:

As the solution was reduced, the vanadium became reduced in a series of redox reactions:

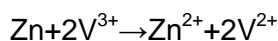
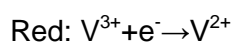
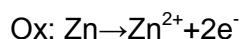
1. +5 (yellow) to +4 (blue):



2. +4 (blue) to +3 (blue-green):



3. +3 (blue-green) to +2 (violet):



Conclusion: Metal ions of different oxidation states may have a variety of colours

Investigating the oxidising strength of KMnO_4^-

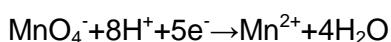
Aim: To investigate the oxidising strength of KMnO_4

Method:

1. Add equal quantities of 0.01M KMnO_4 and 1M H_2SO_4 to use as a test solution
2. Add 2-3 drops of KMnO_4 to various test solutions including KCl, KBr and KI and various metals including Zn, Mg, Cu, Sn, and Fe. Record the colour change of the solution

Results/ discussion:

The KMnO_4 solution turned from pink to colourless with all samples, indicating the manganese in pink MnO_4^- (+7) had been reduced to the colourless Mn^{2+} (+2):



Since MnO_4^- was able to be reduced by all the tested substances, it has strong oxidising strength. This is revealed through the high E° of the above reaction.

Conclusion:

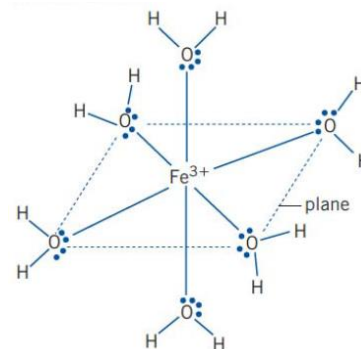
KMnO_4 is a strong oxidising agent, able to oxidise a large number of substances

Complex ions of transition metals

Hydrated ions in solution:

An ion is said to be hydrated if it is surrounded by water molecules. For example, when ionic compounds dissociate they become hydrated. Water molecules have their positively charged (hydrogen) ends directed towards anions and their negatively charged (oxygen) ends directed towards cations.

For many metal cations, the ion is surrounded by a fixed number of water molecules which bond to the cation via a coordinate covalent bond. A lone pair in the water molecule's oxygen atom fills vacant hybridised orbitals (where a set of orbitals are mixed to form a new set of orbitals with the same electron capacity and with energy levels intermediate between the original orbitals). Examples of hydrated ions include hexaaquairon (III) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, tetraaquacopper (II) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and diaquasilver (I) $[\text{Ag}(\text{H}_2\text{O})_2]^+$.



Coordination complexes:

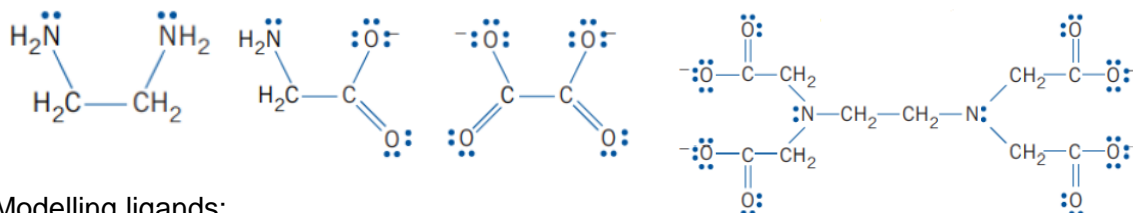
A coordination complex (or complex ion) consists of a central atom or ion (usually metallic) surrounded by an array of ions or atoms known as ligands. Hydrated metal ions described above are an example of coordination complexes. Examples of hydrated coordination complexes include Cobalt (II) chloride hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, magnesium sulphate heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and sodium tetraborate decahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Ligands:

Ligands bond to the central atom or ion via a coordinate bond, in which both shared atoms are provided by one atom. Ligands must thus have at least one atom with a lone pair of electrons in order to bond with the central atom or ion. Ligands are Lewis bases (electron pair donor) whilst the metal ion is a Lewis acid (electron pair acceptor). When a ligand bonds to the central metal ion, it donates an electron pair to the central ion in a Lewis acid- Lewis base interaction to form a coordinate covalent bond (one atom provides both shared electrons).

Chelated ligands:

Ligands which bond using the electron pair of a single donor atom such as H_2O , NH_3 , CO , F^- , Cl^- , CN^- and OH^- are monodentate ligands. Ligands which bond using the electron pairs of more than one donor atoms are polydentate ligands, otherwise known as chelated ligands or chelating agents. The donor atoms of chelated ligands bond simultaneously to the central ion. Examples of chelated ligands include ethylenediamine (en), the glycinate ion (gly $^-$), oxalate and the ethylenediaminetetraacetate ion (edta).



Modelling ligands:

It is impossible to see how ligands and chelated ligands bond in coordination complexes because of their small size and complex nature. As a result, we rely on two dimensional drawings such as drawings and three dimensional models such as computer models and modelling kits in order to gain an understanding their nature. Such models are useful in visualising the geometry of coordination complexes and explaining their structure and bonding. However, these models have several limitations; for example they do not show:

- Electrons or transitions in their orbitals
- Energy changes involved
- The rate at which interactions occur and what initiates them
- The mobility and flexibility of chemical bonds

Nevertheless, they are still useful for illustrating what happens at the micro-level in order to explain observations at the macro-level obtained from experiment.

Colours of transition metal complexes:

Transition metals in different ion complexes can exhibit a wide range of colours. This can be explained by crystal field theory. When ligands bond with an ion, the repulsion between the electrons and the ligand, the crystal field, increases the energy levels of outer electron orbitals. Due to the geometry of the complex, the crystal field increases the energy of d orbitals by different amounts, splitting the 5 d orbitals into 2 or more degenerate groups. This produces an energy gap Δ which allows coordination complexes to absorb certain wavelengths of light and hence appear as a certain colour. The degree of d-orbital splitting depends on the geometry of the complex (octahedral arrangements, for example, result in greater splitting than tetrahedral arrangements) and the ligand attached, with some ligands resulting in greater d-orbital splitting than others. The effect of d-orbital splitting by ligands is in addition to the effect of the various oxidation states of transition metals. Hence, transition metals are able to exhibit different colours depending on the number of ligands it is bonded to in a complex and the nature of those ligands. For example, chromium displays a wide range of colours in different complexes:

- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ - Blue
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ - Violet
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ - Green
- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ - Green
- $[\text{Cr}(\text{OH})_6]^{3-}$ - Green
- $[\text{Cr}(\text{OH})_4]^-$ - Deep green
- $[\text{Cr}(\text{NH}_3)_6]^{3+}$ - Violet

Data Sheet

Avogadro constant, N_A : $6.022 \times 10^{23} \text{ mol}^{-1}$

Volume of 1 mole ideal gas at 100kPa:

- at 0°C (273.15 K): 22.71 L
- at 25°C (298.15 K): 24.79 L

Ionisation constant for water at 25°C (298.15 K), K_w : 1.0×10^{-14}

Specific heat capacity of water: $4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$

Standard Potentials:

$\text{K}^+ + \text{e}^-$	\rightleftharpoons	K (s)	-2.94V	$\text{Cu}^{2+} + 2\text{e}^-$	\rightleftharpoons	Cu (s)	0.34V
$\text{Ba}^{2+} + 2\text{e}^-$	\rightleftharpoons	Ba (s)	-2.91V	$1/2\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	\rightleftharpoons	2OH^-	0.40V
$\text{Ca}^{2+} + 2\text{e}^-$	\rightleftharpoons	Ca (s)	-2.97V	$\text{Cu}^+ + \text{e}^-$	\rightleftharpoons	Cu (s)	0.52V
$\text{Na}^+ + \text{e}^-$	\rightleftharpoons	Na (s)	-2.71V	$1/2\text{I}_2(\text{s}) + \text{e}^-$	\rightleftharpoons	I^-	0.54V
$\text{Mg}^{2+} + 2\text{e}^-$	\rightleftharpoons	Mg (s)	-2.36V	$1/2\text{I}_2(\text{aq}) + \text{e}^-$	\rightleftharpoons	I^-	0.62V
$\text{Al}^{3+} + 3\text{e}^-$	\rightleftharpoons	Al (s)	-1.68V	$\text{Fe}^{3+} + 3\text{e}^-$	\rightleftharpoons	Fe (s)	0.77V
$\text{Mn}^{2+} + 2\text{e}^-$	\rightleftharpoons	Mn (s)	-1.18V	$\text{Ag}^+ + \text{e}^-$	\rightleftharpoons	Ag (s)	0.80V
$\text{H}_2\text{O} + \text{e}^-$	\rightleftharpoons	$1/2\text{H}_2(\text{g}) + \text{OH}^-$	-0.83V	$1/2\text{Br}_2(\text{l}) + \text{e}^-$	\rightleftharpoons	Br^-	1.08V
$\text{Zn}^{2+} + 2\text{e}^-$	\rightleftharpoons	Zn (s)	-0.76V	$1/2\text{Br}_2(\text{aq}) + \text{e}^-$	\rightleftharpoons	Br^-	1.10V
$\text{Fe}^{2+} + 2\text{e}^-$	\rightleftharpoons	Fe (s)	-0.44V	$1/2\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	\rightleftharpoons	H_2O	1.23V
$\text{Ni}^{2+} + 2\text{e}^-$	\rightleftharpoons	Ni (s)	-0.24V	$1/2\text{Cl}_2(\text{g}) + \text{e}^-$	\rightleftharpoons	Cl^-	1.36V
$\text{Sn}^{2+} + 2\text{e}^-$	\rightleftharpoons	Sn (s)	-0.14V	$1/2\text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ + 3\text{e}^-$	\rightleftharpoons	$\text{Cr}^{3+} + 7/2\text{H}_2\text{O}(\text{l})$	1.36V
$\text{Pb}^{2+} + 2\text{e}^-$	\rightleftharpoons	Pb (s)	-0.03V	$1/2\text{Cl}_2(\text{aq}) + \text{e}^-$	\rightleftharpoons	Cl^-	1.40V
$\text{H}^+ + \text{e}^-$	\rightleftharpoons	$1/2\text{H}_2(\text{g})$	0.00V	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-$	\rightleftharpoons	$\text{Mn}^{2+} + 4\text{H}_2\text{O}(\text{l})$	1.51V
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$	\rightleftharpoons	$\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}$	0.16V	$1/2\text{F}_2(\text{g}) + \text{e}^-$	\rightleftharpoons	F^-	2.89V

PERIODIC TABLE OF THE ELEMENTS																		2
1 H 1.008 Hydrogen																	He 4.003 Helium	
<div>3 Li 6.941 Lithium</div> <div>4 Be 9.012 Beryllium</div>		<div>Atomic Number</div> <div>Symbol</div> <div>Standard Atomic Weight</div> <div>79 Au 197.0 Gold</div>										5	6	7	8	9	10	
												B	C	N	O	F	Ne	
<div>11 Na 22.99 Sodium</div> <div>12 Mg 24.31 Magnesium</div>												13	14	15	16	17	18	
												Al	Si	P	S	Cl	Ar	
<div>19 K 39.10 Potassium</div> <div>20 Ca 40.08 Calcium</div>												21	22	23	24	25	26	
												Sc	Ti	V	Cr	Mn	Fe	
<div>37 Rb 85.47 Rubidium</div> <div>38 Sr 87.61 Strontium</div>												39	40	41	42	43	44	
												Y	Zr	Nb	Mo	Tc	Ru	
<div>55 Cs 132.9 Caesium</div> <div>56 Ba 137.3 Barium</div>												57–71	72	73	74	75	76	
												Lanthanoids	Hf	Ta	W	Re	Os	
<div>87 Fr</div> <div>88 Ra</div>												89–103	104	105	106	107	108	
												Actinoids	Rf	Db	Sg	Bh	Hs	
												109	110	111	112			
												Mt	Ds	Rg	Cn			
												Aluminium	Silicon	Phosphorus	Sulfur	Chlorine	Argon	
												Ga	Ge	As	Se	Br	Kr	
												In	Sn	Sb	Te	I	Xe	
												Cd	Pb	Bi	Po	At	Rn	
												Ag	Hg	Tl	Pb	Bi	Po	
												Cu	Zn	Ga	Ge	As	Se	
												Ni	Cu	Zn	Ga	Ge	As	
												Co	Ni	Cu	Zn	Ga	Ge	
												Fe	Co	Ni	Cu	Zn	Ga	
												Mn	Fe	Co	Ni	Cu	Zn	
												Cr	Mn	Fe	Co	Ni	Cu	
												V	Cr	Mn	Fe	Co	Ni	
												Ti	V	Cr	Mn	Fe	Co	
												Sc	Ti	V	Cr	Mn	Fe	
												Ca	Sc	Ti	V	Cr	Mn	
												Na	Ca	Sc	Ti	V	Cr	
												Mg	Na	Ca	Sc	Ti	V	
												Al	Mg	Na	Ca	Sc	Ti	
												Si	Al	Mg	Na	Ca	Sc	
												P	Si	Al	Mg	Na	Ca	
												S	P	Si	Al	Mg	Na	
												Cl	S	P	Si	Al	Mg	
												Ar	Cl	S	P	Si	Al	
												K	Ar	Cl	S	P	Si	
												Ca	K	Ar	Cl	S	P	
												Sc	Ca	K	Ar	Cl	S	
												Ti	Sc	Ca	K	Ar	Cl	
												V	Ti	Sc	Ca	K	Ar	
												Cr	V	Ti	Sc	Ca	K	
												Mn	Cr	V	Ti	Sc	Ca	
												Fe	Mn	Cr	V	Ti	Sc	
												Co	Fe	Mn	Cr	V	Ti	
												Ni	Co	Fe	Mn	Cr	V	
												Cu	Ni	Co	Fe	Mn	Cr	
												Zn	Cu	Ni	Co	Fe	Mn	
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												Se	As	Ge	Ga	Zn	Cu	
												Br	Se	As	Ge	Ga	Zn	
												Kr	Br	Se	As	Ge	Ga	
												Rb	Kr	Br	Se	As	Ge	
												Sr	Rb	Kr	Br	Se	As	
												Y	Sr	Rb	Kr	Br	Se	
												Zr	Y	Sr	Rb	Kr	Br	
												Nb	Zr	Y	Sr	Rb	Kr	
												Mo	Nb	Zr	Y	Sr	Rb	
												Tc	Mo	Nb	Zr	Y	Sr	
												Ru	Tc	Mo	Nb	Zr	Y	
												Rh	Ru	Tc	Mo	Nb	Zr	
												Pd	Rh	Ru	Tc	Mo	Nb	
												Ag	Pd	Rh	Ru	Tc	Mo	
												Cd	Ag	Pd	Rh	Ru	Tc	
												In	Cd	Ag	Pd	Rh	Ru	
												Sn	In	Cd	Ag	Pd	Rh	
												Sb	Sn	In	Cd	Ag	Pd	
												Te	Sb	Sn	In	Cd	Ag	
												I	Te	Sb	Sn	In	Cd	
												Xe	I	Te	Sb	Sn	In	
												Fr	Xe	I	Te	Sb	Sn	
												Ra	Fr	Xe	I	Te	Sb	
												Ac	Ra	Fr	Xe	I	Te	
												Th	Ac	Ra	Fr	Xe	I	
												Pa	Th	Ac	Ra	Fr	Xe	
												U	Pa	Th	Ac	Ra	Fr	
												Np	U	Pa	Th	Ac	Ra	
												Pu	Np	U	Pa	Th	Ac	
												Am	Pu	Np	U	Pa	Th	
												Cm	Am	Pu	Np	U	Pa	
												Bk	Cm	Am	Pu	Np	U	
												Cf	Bk	Cm	Am	Pu	Np	
												Es	Cf	Bk	Cm	Am	Pu	
												Fm	Es	Cf	Bk	Cm	Am	
												Md	Fm	Es	Cf	Bk	Cm	
												No	Md	Fm	Es	Cf	Bk	
												Lr	No	Md	Fm	Es	Cf	
													Lr	No	Md	Fm	Es	
														Lr	No	Md	Fm	
															Lr	No	Md	
																Lr	No	
																	Lr	

Elements with atomic numbers 113 and above have been reported but not fully authenticated.

Standard atomic weights are abridged to four significant figures.

Elements with no reported values in the table have no stable nuclides.

The International Union of Pure and Applied Chemistry Periodic Table of the Elements (February 2010 version) is the principal source of data. Some data may have been modified.