

Atomic Structure

Atoms are made from protons, neutrons, and electrons. Protons and neutrons are known as nucleons.

Electrons have a negligible mass compared to protons and neutrons which both have a relative mass of 1. Protons and electrons have equal and opposite magnitudes of charge, $1+$, $1-$.

MASS NUMBER – Total number of protons and neutrons in the nucleus

ATOMIC NUMBER – The number of protons in the nucleus of an atom.

Ions are formed when atoms lose or gain electrons.

ISOTOPE – An atom of the same element with a different number of neutrons.

Isotopes have the same chemical properties as they have the same electron configuration as one another. They have different physical properties to one another as this is due to the variance in mass.

The model of the atom has changed over time due to the increase in understanding:

- Dalton's model; Suggests that atoms are solid spheres and different spheres make up different elements
- Thomson's Model; Atoms are a positive charge with negatively charged particles in them.
- Rutherford's Model; Small positive nucleus in the centre of the nucleus and electrons surrounding it, mostly empty space
- Bohr's Model; Electrons exist in fixed orbitals and these have fixed energy.

RELATIVE ATOMIC MASS- Average mass of an atom of an element on a scale where $1/12^{\text{th}}$ of C^{12} is exactly 1.

Steps of mass spectrometer:

- **Ionisation**:
 - o Electrospray -> Sample dissolved in a highly volatile solvent and injected through a hypodermic needle that is attached to the positive terminal of a high voltage power supply. The particles gain H^+ and the solvent evaporates leaving gaseous positive ions.
 - o Electron impact -> high energy electrons are fired out of an electron gun which knocks out electrons from atoms.
- **Acceleration**: An negatively charged plate attracts electrons towards it and all ions are accelerated to the same kinetic energy.
- **Flight tube**: The ions drift through this region with the same speed as they left the electric field with
- **Detection**: Ions hit a plate and gain an electron causing a current to flow, the size of this current can be measured to determine the abundance of each of the isotopes.

Mass spectrometry can be used to identify elements in a sample.

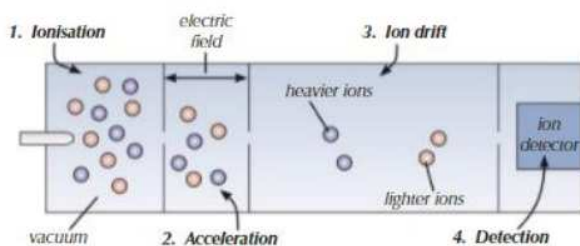


Figure 2: Diagram showing how a TOF mass spectrometer works.

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Electrons move around the nucleus in energy levels. Shells are divided up into subshells. s,p,d,f. Each sub shell will have a set number of orbitals. S -> 1, p -> 3, d -> 5, f -> 7. Electron configuration can be shown through sub shell notation, arrows in boxes representing orbitals, and energy level diagrams.

Electrons fill up lowest energy subshells first and full up orbitals singly before pairing p.

Chromium and copper both have a different electronic configuration in order for them to be stable.

Cr -> $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Cu -> $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

The periodic table is split up into blocks based on the outermost subshell that each element fills in it.

FIRST IONISATION ENERGY – The energy needed to remove 1 electron from each atom in 1 mole of gaseous atoms to form 1 moles of gaseous $1+$ ions.

Factors affecting ionization energy are:

- **Nuclear charge**; more protons in nucleus means that outermost electrons are more attracted to the nucleus.
- **Distance of outermost electrons from the nucleus**; Outermost electrons are more attracted to the nucleus if the atomic radius is smaller
- **Shielding**; Outermost electrons are more attracted to the nucleus if there are fewer inner electron shells.

First ionization energy of magnesium: $Mg(g) \rightarrow Mg(g)^+ + e^-$

Ionisation energy decreases down group two as there is more electron shielding as you go down the group as there are more electron shielding, so the outermost electrons are more attracted to the nucleus and less energy is required to remove them.

Ionisation energy generally increases across period three due to the increase in nuclear charge but there is no increase in shielding. There are several exceptions:

- Aluminium is lower than magnesium as a sub shell that is further from the nucleus is filled so the outermost electron is further from the nucleus
- Sulfur is lower than phosphorous; an electron is being removed from a paired 3p orbital so the electron repulsion means that it is easier to remove the electron.

Ionisation energy provides evidence for electron shells.

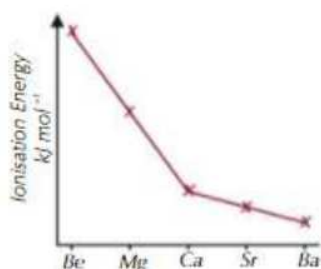


Figure 4: First ionisation energies of Group 2.

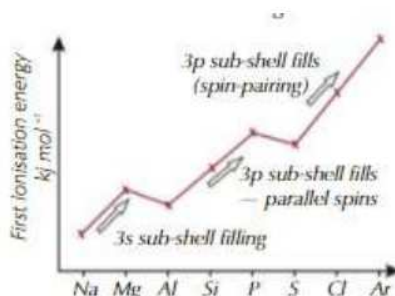


Figure 5: First ionisation energies of Period 3.

Amount of Substance

AVOGADROS CONSTANT – The number of atoms in 12g of carbon 12

The avogadros constant is equal to the number of molecules that are in a mole of any substance.

Mass of a substance can be calculated if you know its Mr and the number of moles you have of it. **Mass = Mr * Moles**

The number of moles in a solution can also be calculated using the formula $n = cv$, where n = number of moles, c = concentration of the solution in mol dm^{-3} and v = volume of the solution in dm^3 .

The ideal gas equation $\rightarrow pV = nRT$ where p = Pressure in Pa, V = volume in m^3 , n = number of moles, R = the ideal gas constant (8.31) and T = temperature in K

Ionic equations are reaction equations that show how the individual ions react in a reaction. Only the particles that react are included, meaning that all 'spectator ions' are removed.

MOLAR RATIO – The ratio moles of each reactant and product in a balanced chemical equation.

State symbols are used in an equation to show what state of matter things are when they react with one another.

EMPIRICAL FORMULA – The smallest whole number ratio of atoms of each element present in a compound

MOLECULAR FORMULA – The actual number of atoms of each element that are present in a molecule.

THEORETICAL YIELD – The mass of products that should be formed in a chemical reaction assuming no chemicals are lost in the process.

$$\text{Percentage yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

ATOM ECONOMY – A measure of the proportion of reactant atoms that have become part of the useful product in a reaction

Advantages of a high atom economy are:

- **Economic:**
 - o More efficient use of raw materials so less money must be spent on them
 - o Less waste to deal with, so less money needs to be spent on recycling
- **Environmental:**
 - o Fewer raw materials used is better for the environment
 - o Less harmful chemicals are produced as waste which is also better for the environment
 - o Processes with higher atom economies tend to be more sustainable

$$\text{atom economy \%} = \frac{\text{molecular mass of desired product}}{\text{sum of molecular masses of all reactants}} \times 100$$

Atom economy should always be calculated using a balanced equation.

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Bonding

Ions are formed from the electron transfer between two atoms so that they get a full outer shell of electrons. The number of electrons that an atom will lose or gain can be calculated through use of their group number in the periodic table. An atom in group 1 for example, will only lose 1 electron from their outer shell of electrons to form a stable ion.

Example of compound ions are:

- Ammonium – NH_4^+
- Carbonate – CO_3^{2-}
- Hydroxide – OH^-
- Nitrate – NO_3^-
- Sulfate – SO_4^{2-}

Ionic bonding is the strong electrostatic force of attraction between oppositely charged positive and negative ions that are held together in a giant ionic lattice.

Positive ions are cations and negative ions are anions.

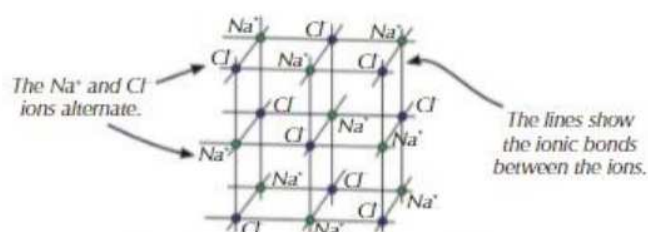


Figure 10: The structure of sodium chloride.

A **giant ionic lattice** is a giant regular structure that is made up of the same basic repeating unit. Ionic compounds can have different shaped structures however they are all ionic lattices. These ionic lattices are examples of a type of crystal structure.

Physical properties of ionic compounds :

- Conduct electricity when molten or dissolved in aqueous solution as the ions are free to move and carry a charge.
- High melting point due to the strong electrostatic forces of attraction that require a large amount of energy to overcome.
- Soluble in water due to the polar water molecules causing the lattice to dissociate into ions and these form intermolecular bonds with the polar water molecules

COVALENT BOND – A shared pair of electrons.

Molecules are formed when two or more atoms bond together. 1, 2 or 3 covalent bonds can form between two atoms.

Compounds made of many individual molecules that are held together by covalent bonds are called simple covalent compounds. The molecules are bonded to one another through weak intermolecular forces.

Physical properties of simple molecular compounds:

- Do not conduct electricity as there are no free charged particles to carry a charge.
- Low melting point due to weak intermolecular forces
- Soluble in water dependant on how polar the molecules are

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Giant covalent structures are known as macromolecular structures. They are held together by strong covalent bonds that extend throughout the structure. These bonds require a large amount of energy to overcome.

Graphite is an example of a macromolecular structure. The carbon atoms are arranged in sheets of flat hexagons that are covalently bonded with 3 other carbon atoms each. There is 1 delocalised electron per carbon atom. The layers are held together by weak van der Waals forces.

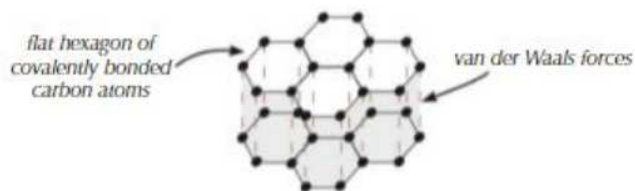


Figure 2: The structure of graphite.

Properties of graphite are:

- The layers can easily slide over one another due to the weak van der Waals forces between the layers. Therefore, graphite can be used as a lubricant
- An electric current can flow as it has delocalised electrons
- It has a low density due to its layers being spaced apart from one another
- It has a high melting point due to the strong covalent bonding
- It is insoluble as it isn't polar.

Diamond is another example of a substance with a macromolecular structure.

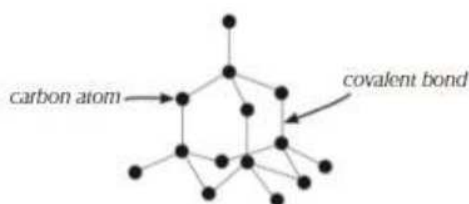


Figure 3: The structure of diamond.

Properties of diamond are:

- Very high melting point due to its strong covalent bonds that extend throughout the structure.
- It is very hard
- It is a good thermal conductor as vibrations can easily travel through the stiff lattice.
- It cannot conduct electricity
- It is not soluble.

A coordinate bond is where an atom with a lone pair of electrons provides both of the electrons required to form a covalent bond.

Electron pairs will always position themselves as far apart from one another as possible. Lone pair – lone pair is the greatest amount of repulsion that can occur. Bonding pair – bonding pair is the lowest amount of electron repulsion that can occur.

ELECTRONEGATIVITY – The power of an atom to draw the electron density of a covalent bond towards itself.

Electronegativity is measured on the Pauling scale. Covalent molecules with large differences in electronegativity can form polar bonds where there is a dipole where half of the molecule may have a partially positive charge and half of the

molecule with a partial negative charge. A molecule with several polar bonds can have those bonds cancel one another out so that the overall molecule is not considered to be polar.

Van der Waals forces are caused by temporary dipoles being created due to electrons constantly moving around in their orbitals. These temporary dipoles induce dipoles in the opposite direction on an atom that is near by, the opposite charges on these dipoles mean that they are attracted to one another.

Van der Waals forces are affected by:

- Number of electrons in an atom; more electrons means that the dipole will have a greater charge.
- The shape of molecules; planar molecules can lie flat and get closer to one another meaning that they are more attracted to one another than molecules with branched chains.

Van der Waals forces are weak and can easily be overcome by gentle heating.

Permanent dipole-dipole forces occur in molecules that have polar bonds, these forces act in the same way that vdw forces do, with the oppositely charged dipoles attracting one another, however, these forces are stronger than van der Waals forces as they act often.

Hydrogen bonding is the strongest type of intermolecular force and only occurs when hydrogen is covalently bonded to oxygen, nitrogen or fluorine as these are the three most electronegative elements in the periodic table. The bonds between these are very polar. Hydrogen has such a high charge density due to its small size so these hydrogen atoms form weak bonds with the lone pairs of electrons on O, N and fluorine atoms.

Hydrogen bonding has a large effect on the properties of a substance, meaning that they have much higher boiling and melting points than you would expect from the trends of the group that that element is in.

When water freezes and forms ice, hydrogen bonding arranges the water molecules in such a way that they have an open structure and this means that it has a lower density than water itself.

Metals exist in **giant metallic lattice structures**. The outermost electrons are delocalised and this forms a sea of free electrons which are strongly attracted to the positive metal ions due to electrostatic forces of attraction.

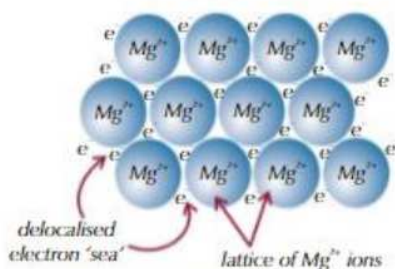


Figure 1: Metallic bonding in magnesium.

Physical properties of metals:

- High melting point due to the strong electrostatic forces of attraction between oppositely charged positive metal ions and negative electrons.
- Malleable and ductile as the metal ions are arranged into layers and the bonding stays the same strength when they have been shaped.

- Can conduct heat and electricity well due to the delocalised electrons which can pass through the structure and transfer kinetic energy as well as charge.
- Metals are insoluble.

Shapes of molecules:

Number of electron pairs	Name of shape	Bond angle	Diagram	Example
2	Linear	180		BeCl ₂
3	Trigonal Planar	120		BF ₃
4	Tetrahedral	109.5		CH ₄
	Trigonal Pyramidal	107		NH ₃
	Bent	104.5		H ₂ O
5	Trigonal Bipyramidal	90, 120		PCl ₅
	Seesaw	86.5, 102		SF ₄
	T-shaped	87.5		ClF ₃
6	Octahedral	90		SF ₆
	Square Pyramidal	90		ClF ₅
	Square Planar	90		XeF ₄

STANDARD CONDITIONS – 298K, 100kPa

ENTHALPY CHANGE – Heat energy transferred in a reaction at a constant pressure.

Exothermic reactions are those that give out heat energy to the surroundings. The enthalpy change is negative.

Endothermic reactions are those that take in heat energy overall from the surroundings and the enthalpy change is positive.

BOND ENTHALPY – Energy needed to break a bond.

When bonds are formed, energy is released and when bonds are made, energy is taken in from the surroundings.

MEAN BOND ENTHALPY – The average energy needed to break a certain type of bond measured over a range of different compounds.

Enthalpy change for a reaction = total energy absorbed – total energy released.

The total energy needed to break the bonds in the reactants is the total energy absorbed. The total energy needed to form the bonds in the products is the total energy that must be absorbed.

ENTHALPY OF FORMATION – Enthalpy change when 1 mole of a substance is formed from its elements with all products and reactants in their standard states under standard conditions.

ENTHALPY OF COMBUSTION – Enthalpy change when 1 mole of a substance is completely combusted in an excess of oxygen with all products and reactants in their standard states under standard conditions.

ENTHALPY OF REACTION – Enthalpy change when a reaction occurs in the molar quantities shown in the chemical equation under standard conditions with all products and reactants in their standard states.

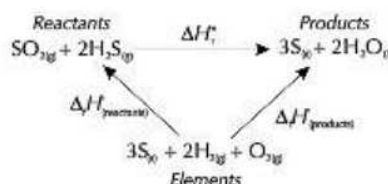
Enthalpy change can be calculated for a reaction by using the equation $q = mc\Delta T$.

HESS'S LAW – The total enthalpy change for a reaction is independent of the route taken to reach it.

Hess's law can be used to calculate the enthalpy change of a reaction that cannot be directly measured.

It can also be used to calculate enthalpy changes of formation using a thermochemical cycle:

So $\Delta H_r = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$.



A similar method can be used to calculate enthalpies of combustion.

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Collision theory states that a reaction cannot take place unless two particles collide with the correct orientation and energy that is greater than or equal to the activation energy.

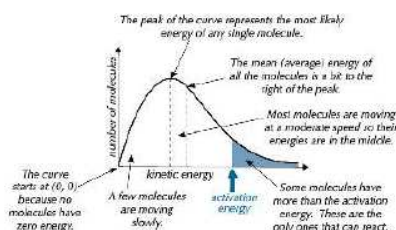


Figure 1: An enthalpy profile diagram.

ACTIVATION ENERGY – The minimum energy that is needed for a reaction to occur between two particles.

Activation energy is the energy that is used to break the bonds within the reactant particles and therefore start the reaction.

The Maxwell Boltzmann distribution below shows the energy distribution of particles in a reaction mixture. Increasing the temperature of the reaction mixture will shift the peak of this curve to the right as many more particles will have energy that is greater than or equal to the activation energy.



Many more particles will have energy that is greater than or equal to activation energy if the energy of a reaction mixture is increased, the frequency of collisions will also increase so there will be many more successful collisions so the rate of reaction will increase.

Increasing the concentration/pressure of a reaction mixture will increase the area under the curve and will increase the frequency of collisions as there will be more particles closer to one another available to react so the rate of successful collisions increases and so does the rate of reaction.

Catalysts increase the rate of reaction by providing an alternative reaction pathway that has a lower activation energy. They are not chemically changed at the end of the reaction. Using catalysts saves energy meaning that costs for an experiment are lower than they would be if a catalyst wasn't used. Many more particles will have energy that is greater than or equal to the activation energy if a catalyst is used in a reaction.

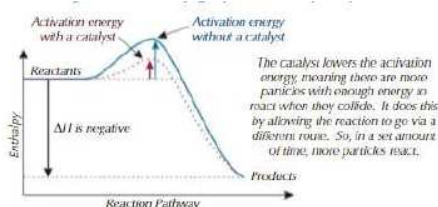


Figure 2: Enthalpy profile diagram for a reaction with and without a catalyst.

RATE OF REACTION - The change in the concentration of a product or reactant per unit time.

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Equilibria and Redox

In **dynamic equilibrium** the forward and reverse reactions are proceeding at the same rate as one another and there is no net change in the concentration of products or reactants. Dynamic equilibrium can only occur in a closed system where no products or reactants can get in and out.

Le Chatelier's principle states that equilibrium will shift to oppose changes that are made to it. For example, if pressure is increased, equilibrium will shift in the direction of the side of the reaction that has fewer moles on it.

Catalysts do not affect the position of equilibrium, they increase the rate of the forward and reverse reactions by the same amount.

The position of equilibrium can be detected in reactions where the forward and reverse reaction have products that have colours by seeing how the colour of the reaction mixture changes as you vary certain variables such as temperature, pressure etc.

Compromises must be made to reactions in industry to ensure that the rate of reaction is fast enough without the cost to run the reaction being too high.

K_c the equilibrium constant shows the ratio of concentrations of products and reactants at equilibrium.

For the reaction $aA + bB \rightarrow cC + dD$

$$K_c = \frac{[D]^d [C]^c}{[B]^b [A]^a}$$

K_c is only affected by **temperature**, it is not affected by catalysts as this increases the rate of the forward and reverse reaction by the same amount. It is also not affected by change in concentration of a substance as the concentrations of other substances will change to keep the ratio of them the same.

OXIDATION – A loss of electrons

REDUCTION – A gain of electrons

OXIDISING AGENT – A substance that accepts electrons and is reduced.

REDUCING AGENT – A substance that donates electrons and is oxidised.

OXIDATION STATE – The charge that an atom would have if it was not in the compound.

Oxidation state rules:

- Uncombined elements will have an oxidation state of 0
- Diatomic molecules have an oxidation state of 0
- Oxygen usually has an oxidation state of -2
- Hydrogen usually has an oxidation state of +1
- Halogens have an oxidation state of -1
- Group 1 metals have an oxidation state of +1

The oxidation state of a substance can be found from its systematic name e.g: sulfate(VI) ions has sulphur in an oxidation state of +6.

Half equations show oxidation and reduction and also so electrons so that charges balance. Half equations of oxidation and reduction can be combined to make full equations for redox reactions.

They must first be multiplied through to ensure that they have the same number of electrons in their reactions.

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Energy needed to break a bond between two ions is the same amount of energy that is given out when the bond is formed.

LATTICE FORMATION ENTHALPY – Enthalpy change when 1 mole of a solid ionic compound is formed from its gaseous ions.

LATTICE DISSOCIATION ENTHALPY – Enthalpy change when 1 mole of a solid ionic compound is completely dissociated into its gaseous ions.

Lattice enthalpy cannot be measured directly; enthalpies of different processes must first be calculated before it can be calculated.

ENTHALPY CHANGE OF FORMATION – Enthalpy change when 1 mole of a compound is formed from its elements in their standard states.

BOND DISSOCIATION ENTHALPY – Enthalpy change when all bonds of the same type in 1 mole of gaseous molecules are broken.

ENTHALPY CHANGE OF ATOMISATION OF AN ELEMENT – Enthalpy change when 1 mole of gaseous atoms is formed from an element in its standard state.

ENTHALPY CHANGE OF ATOMISATION OF A COMPOUND – Enthalpy change when 1 mole of a compound in its standard state is converted into gaseous atoms.

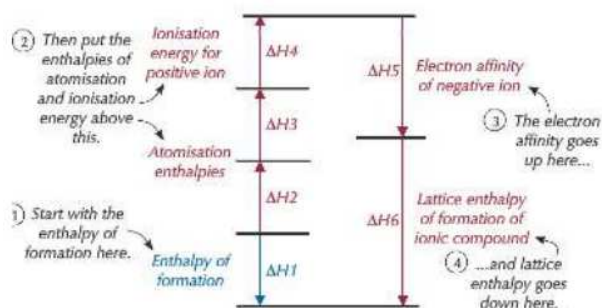
FIRST IONISATION ENERGY – Enthalpy change when 1 mole of gaseous 1+ ions is formed from 1 mole of gaseous atoms.

FIRST ELECTRON AFFINITY – Enthalpy change when 1 mole of gaseous 1- ions is made from 1 mole of gaseous atoms.

ENTHALPY CHANGE OF HYDRATION – Enthalpy change when 1 mole of aqueous ions is formed from gaseous ions.

ENTHALPY CHANGE OF SOLUTION – Enthalpy change when 1 mole of an ionic substance dissolves in enough solvent to form an infinitely dilute solution.

Born-Haber cycles can work out the enthalpy change for a reaction through using a less direct route. It follows Hess's law as the total enthalpy change of a reaction is always the same, independent of the route taken to reach it.

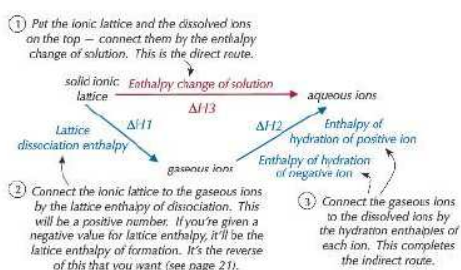


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The perfect ionic model assumes that all ions are spherical and have their charge evenly distributed around them, as well as having only ionic bonding without any covalent character. Different ions can be polarised to different extents based on whether the size of the ion is small or large. For example, a small positive ion will polarise a large negative ion, meaning that there will be some covalent character.

The value for **experimental enthalpy of lattice dissociation** may be different to the theoretical value as there may be some covalent character that the theoretical value does not account for as theoretical assumes that all bonding is perfectly ionic. If the two values are very different, it means that a compound will have a lot of **covalent character**.

Enthalpy change of solution can be calculated using a thermochemical cycle.



Entropy is a measure of the disorder of a substance. It is a measure of the number of ways that particles can be arranged and the ways that energy can be shared out within the particles.

Entropy is affected by the following factors:

- Physical state

- Solids are more ordered than gases are, this means that the entropy of gases is higher than solids as they are more disordered.

- Dissolution

- Dissolving a solid will increase its entropy as the particles are free to move.

- The number of particles

- More particles means that a substance will have more entropy as there are more ways that they can be arranged so their disorder is higher.

Entropy change can be calculated by:

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

Free energy change can be used to predict whether a reaction is feasible at a given temperature. A feasible reaction, once started, will carry on to completion without any energy being supplied to it. It is calculated by:

$$\Delta G = \Delta H - T\Delta S$$

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Thermodynamics

A reaction is **feasible** if ΔG is less than zero. If this value is less than zero, then a reaction still may not occur as the reaction may have a very high activation energy.

If a reaction is **exothermic with a positive entropy change**, then the reaction is feasible at any temperature. If a reaction is **endothermic with a negative entropy change** then the reaction is not feasible at any temperature.

The formula used to calculate free energy change can be mapped onto **$y = mx + c$** . The free energy change is on the y and temperature is on the x. The gradient is equal to minus the entropy change and the y intercept is equal to H. The x intercept is the temperature at which the reaction is just feasible.

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Rate Equations

RATE OF REACTION – The change in concentration of products or reactants per unit time.

The rate of reaction can be calculated from a **concentration-time graph**, it will be the gradient of the graph. From a curve, a tangent can be drawn to the curve at the point where you want to measure the rate of reaction, from this, you can then calculate the gradient of the tangent to calculate the rate of reaction at this point.

The rate equation shows how the rate of a reaction is affected by **varying the concentration of the reactants**.

$$\text{Rate} = k[A]^m[B]^n$$

The **order** of a reaction with respect to a reactant tells you how changing the concentration of that reactant will change the rate at which the reaction progresses:

- **0th order**; changing the concentration of the reactant will have no effect on the rate of reaction
- **1st order**; doubling the concentration of the reactant will double the rate of reaction
- **2nd order**; doubling the concentration of the reactant will increase the rate of the reaction by 2²

The **overall order** of a reaction is the sum of the individual orders of reaction with respect to a certain reactant.

The rate constant links the concentration of the reactants to the rate of a reaction. A larger value means that the reaction will be faster. It will have the same value at all temperatures. Increasing temperature will increase the rate constant.

The initial rate of a reaction can be found by drawing a **tangent to t=0** on a concentration-time graph and working out the gradient of this. The method to find the order of reaction from drawing this graph is:

- Carry out the reaction and monitor progress and draw a concentration-time graph
- Repeat the experiment for another initial concentration and draw another graph
- Calculate the initial rate of reaction for each experiment
- Compare this to the initial concentration to see how this affects the rate of reaction

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Rate Equations

Rate-concentration graphs can be used to determine the order of a reaction, they are the gradient graphs (differential functions) of the concentration-time graphs:

- 0th order; gradient = 0
- 1st order; straight line through the origin
- 2nd order; rate is directly proportional to $[X]^2$

RATE DETERMINING STEP – The slowest step in the reaction which determines the overall rate of the reaction.

The rate equation can be used to work out the rate determining step for a reaction. The rate determining step will have the same number of molecules of each reactant in the rate equation as their reaction order. The reaction mechanism can be worked out using this rate determining step as it will be the slowest step and this can distinguish between all of the possible mechanisms for the reaction.

The Arrhenius equation shows how the rate constant varies with temperature and activation energy.

$$k = Ae^{-\frac{E_a}{RT}}$$

As activation energy increases, the rate constant decreases so the rate of reaction decreases. This is because fewer of the particles in the reaction mixture will have the activation energy so there will be fewer successful collisions.

As temperature increases, so does the rate equation. This is because, many more particles will have the activation energy needed to react, so there will be many more successful collisions.

A straight line can be plotted from the Arrhenius equation by taking logarithms of both sides. A graph of $\ln(k) - 1/T$ can be plotted to find a gradient of $-E_a/R$. This allows us to find the activation energy of the reaction.

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Equilibrium K_p

In a mixture of gases, each gas will exert its own pressure called its partial pressure. The partial pressures will be the same if the gases are present in the same quantities. The total pressure of a gas mixture is the sum of the partial pressures of the individual gases.

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MOLE FRACTION – The proportion of a gas mixture that is made up of a particular gas.

$$\text{Mole fraction} = \frac{\text{number of moles of gas}}{\text{total number of moles of gas in the mixture}}$$

$$\text{Partial pressure in a mixture} = (\text{mole fraction}) \times (\text{total pressure of mixture})$$

K_p is the equilibrium constant for a gas reaction. For the equilibrium $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{(pD)^d (pC)^c}{(pB)^b (pA)^a}$$

Increasing **the temperature** of a reaction will shift equilibrium in the **endothermic** direction. Changing temperature will affect the value of K_p depending upon which way the equilibrium shifts.

Changing pressure in a reversible gaseous reaction will shift equilibrium in a way that the partial pressure of each of the reactants and products at the new equilibrium position keep K_p **constant**.

Catalysts have no effect on the position of equilibrium or the value of K_p as they increase the rate of the forward and reverse reaction by the same amount so the position of equilibrium remains the same. They do decrease the time taken to reach equilibrium.

Electrochemistry

Electrochemical cells can be made from two different metals that are dipped in aqueous salts of that metal. Oxidation and reduction reactions occur in these cells meaning that it is a redox process. The two cells are connected by a salt bridge which is usually a piece of filter paper dipped in KNO_3 which allows ions to flow between the half cells. This completes the circuit.

Electrons flow from the most reactive metal to the least, a voltmeter connected in this external circuit will show the EMF of the cell which is also called the cell potential.

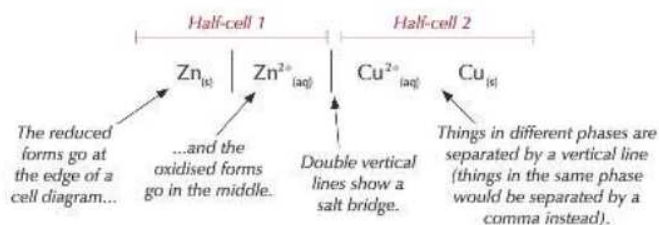
Half cells that contain solutions of two aqueous ions of the same element can also exist, a electrode such as platinum is necessary in these situations. Platinum is used as an electrode as it is a good conductor of electrons and therefore allows for them to be transferred easily. As well as this, it is inert which means it will not react with the solutions it is placed in.

Reactions occurring at each cell are **reversible and the direction in which the reaction occurs depends on how easily a metal loses its electrons** and is oxidized. A more negative electrode potentials means that a substance is more easily oxidized and is **a better reducing agent**.

The reaction that has the more negative electrode potential will go backwards and the reaction with the more positive electrode potential will go forwards.

For the following reactions: $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$ $E = -0.76\text{V}$ $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$ $E = +0.34\text{V}$

The copper equation will go forward and the positive electrode will be made of copper metal in a solution of copper ions. The zinc equation will go backwards as the electrode potential is more negative, the negative electrode will be made from zinc metal placed in a solution of zinc ions. The conventional representation of this cell is:



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Electrochemistry

The EMF, cell potential, of this cell can be calculated using the following equation.

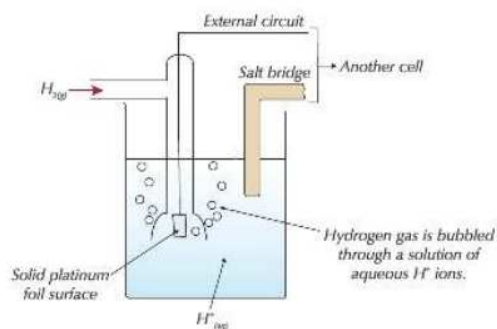
$$E^{\ominus} = E^{\ominus}_{\text{more positive}} - E^{\ominus}_{\text{more negative}}$$

The cell with the more positive value is in the direction of reduction and the cell with the less positive value is in the direction of oxidation.

As half cell equations are **reversible**, they are affected by factors that affect equilibrium. Changing the position of this equilibrium will change the cell potential so standard conditions are used to measure these electrode potentials. It is also measured against the standard hydrogen electrode which has a electrode potential of 0V.

The standard conditions used are:

- All solutions must have concentrations of 1 mol dm^{-3}
- Temperature of 298K
- Pressure of 100kPa



The **standard hydrogen electrode** is always on the left of the cell, regardless of whether the electrode potential of the cell being measured is greater or smaller.

The **electrochemical series** is a list of **electrode potentials** written in order from most negative to most positive. The more reactive a metal is, the more likely it is to lose electrons, so they are more likely to have a negative electrode potential. The more reactive a non-metal is, the more likely it is to gain electrons so it will have a more positive electrode potential.

A **feasible cell** will have a positive value for the cell potential. The reaction will not occur the other way around with this.

Non-rechargeable cells are used in devices that do not require lots of power and are only used for short periods of time. An example of this is a zinc-carbon dry cell alkaline battery. These equations do not have a reversible sign as it is not practical to reverse them. The reactions will reverse under the right conditions, but the electrode forms the casing of the battery meaning that it could be used up, causing the battery to leak.

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Electrochemistry

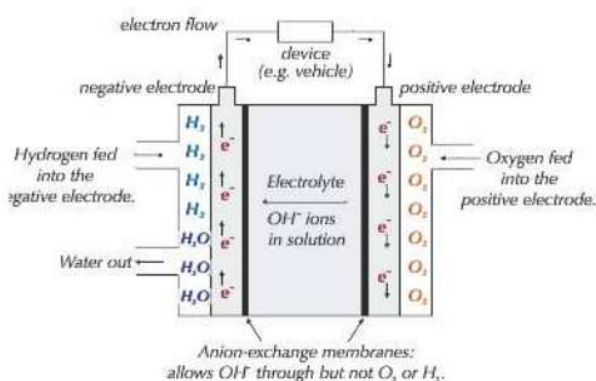
Rechargeable cells use reversible reactions and are used in mobile phones and other similar devices. An example is a lithium cell. This is made up of a LiCoO_2 electrode and a graphite electrode. The electrolyte is a lithium salt in an organic solvent.

The equations for this type of cell are:

- **Negative electrode:** $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
- **Positive electrode:** $\text{Li}^+ + \text{CoO}_2 + \text{e}^- \rightarrow \text{Li}[\text{CoO}_2]$

Other examples of rechargeable batteries are lead-acid and nickel-cadmium. To recharge these batteries, a current is supplied to force electrons to flow in the opposite direction around the circuit to reverse the reaction. None of the substances in these batteries escape or are used up, this means that the reverse reaction can occur.

Fuel cells generate electricity and store the chemicals used outside the cell and feed them in when electricity is required. An example of a fuel cell like this is the hydrogen-oxygen fuel cell that operates in alkaline conditions.



Hydrogen and oxygen are fed into platinum containing electrons which are made from porous ceramic materials with a thin layer of platinum to increase the surface area of the electrodes and reduce the cost needed to produce them.

The electrodes are separated by **an anion exchange membrane** which only allows anions and water to pass through so it will stop the gaseous substances from moving through too. The electrolyte used is aqueous alkaline, eg KOH . The equations for this fuel cell are:

- Negative electrode: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$
- Positive electrode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$
- Overall: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

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Advantages of fuel cells are:

- More efficient than internal combustion engine in cars
- Water is the only waste product so no CO_2 produced.
- Fuel cells don't need to be recharged unlike batteries

Disadvantages of fuel cells are:

- Constant supply of oxygen and hydrogen needed
- Hydrogen produced from electrolysis of water or the hydration of methane so fossil fuels required
- Hydrogen is flammable and explosive
- Infrastructure needed to provide fuel isn't ready yet.

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Acids and Bases

BRONSTED-LOWRY ACID – A proton donor

BRONSTED-LOWRY BASE – A proton acceptor.

Acids and bases dissociate in water, a strong acid/base will completely dissociate in water whereas a weak acid/base will only partially dissociate in water.

Acid base equilibrium involves the transfer of protons. This can be shown by a reaction equation such as: $\text{HA}_{(\text{aq})} + \text{B}_{(\text{aq})} \rightleftharpoons \text{BH}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$. In this equilibrium HA is the acid, A⁻ is the conjugate acid. B is the base and BH⁺ is the conjugate base.

Water also **dissociates into hydroxide and hydroxonium ions**. The simplified equation for this is:

$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. The equilibrium law can be used to write an expression for the equilibrium constant known as the ionic product of water, the ionic product of water is K_c multiplies by the concentration of water. So:

$$K_w = K_c \times [\text{H}_2\text{O}] = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \times [\text{H}_2\text{O}]$$

The $[\text{H}_2\text{O}]$ terms cancel leaving just $[\text{H}^+][\text{OH}^-]$. K_w has the same value for any aqueous solution at a given temperature. In pure water, $[\text{H}^+] = [\text{OH}^-]$.

The pH scale is a measure of the hydrogen ion concentration in a solution, as this can vary a large amount from solution to solution, a logarithmic scale must be used to analyse this. So pH can be calculated by:

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

MONOPROTIC – Each molecule of an acid will release one proton when it dissociates

DIPROTIC – Each molecule of acid will release two protons when it dissociates.

pH of strong bases can be calculated by using K_w to work out the concentration of $[\text{H}^+]$ ions from the concentration of OH^- ions.

Weak acids only dissociate slightly in solution so the concentration of hydrogen ions isn't the same as the concentration of the acid, which is the case in strong acids. The acid dissociation constant can be used to calculate the pH and various concentrations in a solution such as this.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

In a solution of only the weak acid in question, the concentration of A⁻ is equal to the concentration of H⁺. So the equation can be simplified.

pK_a is the logarithmic constant for K_a , it is calculated by:

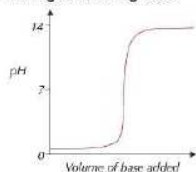
$$\text{p}K_a = -\log_{10}K_a$$

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Acids and Bases

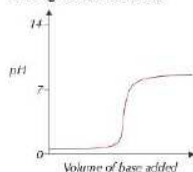
At the half neutralisation point of an acid, pK_a is equal to the pH of the acid.

Strong acid/strong base



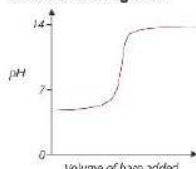
The pH starts around 1, as there's an excess of strong acid. It finishes up around pH 13, when you have an excess of strong base.

Strong acid/weak base



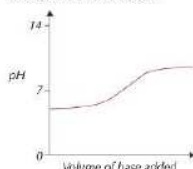
The pH starts around 1, as there's an excess of strong acid. It finishes up around pH 9, when you have an excess of weak base.

Weak acid/strong base



The pH starts around 5, as there's an excess of weak acid. It finishes up around pH 13, when you have an excess of strong base.

Weak acid/weak base



The pH starts around 5, as there's an excess of weak acid. It finishes up around pH 9, when you have an excess of weak base.

Titrations can be used to calculate the concentration of an unknown solution using a burette and a solution of known concentration in a conical flask. Using an indicator, this method can be used with acids and alkalis as they will neutralise one another and the indicator will change colour at a certain pH level.

pH curves can be plotted as a result of these titrations if a pH probe is used to continually measure the pH of the solution after a known volume has been added.

The **mid point** of the vertical section is the equivalence point and all of the acid has just been neutralised. An indicator cannot be used for a weak acid-weak base titration as there is not a sharp enough change in pH at any point during the reaction. Diprotic acids will have two equivalence points as the reaction happens in two stages due to the two protons being released at different times to one another.

The indicator for a reaction should be chosen so that it changes colour at the end point of the titration which is during the vertical region of the pH curve.

BUFFER SOLUTION – A solution that resists change to pH when small amounts of acid/alkali are added to it.

Acidic buffers contain a mixture of a weak acid with one of its salts, for example, ethanoic acid and sodium ethanoate can be used. The way that this buffer works for the equilibrium $HA \rightleftharpoons H^+ + A^-$, is:

- **Acid added:**
 - Concentration of H^+ increases
 - This excess H^+ combines with A^- and the equilibrium shifts to the left to oppose the increase in concentration of A^- .
 - So the concentration of H^+ decreases to close to its original value
 - pH remains almost constant
- **Base added:**
 - Concentration of OH^- increases
 - This combines with H^+ so the concentration of H^+ decreases.
 - The equilibrium shifts to the right to replace lost hydrogen ions
 - Concentration of H^+ increases to close to its original value.
 - pH remains almost constant.

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Acids and Bases

Both basic and acidic buffers can resist dilution. When a small amount of water is added, the water will slightly dissociate and the extra ions will push the equilibrium the same amount in both directions leaving it unchanged.

Applications of buffers include use in shampoos and in blood. In blood, a constant pH is required for the enzymes to work at their optimum conditions in our body.

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Periodicity

The periodic table is organised into periods and groups and the elements are organised by **ascending atomic number**.

All elements within a period have the **same number of electron shells** and all elements within a group have the same number of electrons in their outer shell.

The periodic table is split into the s, p, d and f block which identifies which sub shell the outermost electron from that element is in.

The image shows a standard periodic table with the following blocks highlighted:

- s block:** Groups 1 and 2, plus Hydrogen (H) and Helium (He).
- p block:** Groups 13 through 18.
- d block:** The transition metal series, groups 3 through 10.
- f block:** The lanthanide and actinide series, shown below the main table.

Figure 6: The periodic table showing the s block, p block, d block and f block.

Atomic radius decreases across a period. As the nuclear charge of the elements increases the attraction between the electrons and the nucleus increases so the electrons are closer to the nucleus meaning that the atomic radius for the element is smaller. The amount of shielding across a period does not increase by much so it does not affect the amount that the electrons are attracted to the nucleus.

There is no clear trend in the way that **melting points** change as you go across period 3.

- From **sodium to aluminium**, melting point increases:
 - o The charge on each of the positive metal ions increases so there are more delocalised electrons per each atom from Na – Al so the electrostatic forces of attraction between oppositely charged free electrons and positive metal ions increases meaning that more energy is needed to overcome these forces.
- **Silicon** has a very high melting point:
 - o Silicon has a macromolecular structure meaning that there are strong covalent bonds that extend throughout its structure which require a large amount of energy to overcome.
- **Phosphorous -> Argon**
 - o Sulfur has the highest melting point in this group as it forms S₈ molecules meaning that the van der Waals forces between molecules are greater. Phosphorous and chlorine both form smaller molecules and argon is monatomic so it has very weak van der Waals forces between molecules.

First ionisation energy increases across a period as the nuclear charge increases but the amount of shielding remains very similar so the outermost electron is more attracted to the nucleus and more energy is needed to overcome this attraction.

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Group 2

Atomic radius of elements down group 2 increases due to the increase in the amount of electron shielding despite the increase in nuclear charge too.

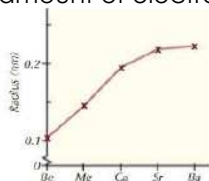


Figure 2: Atomic radii of the first five elements in Group 2.

First ionisation energy of elements down group 2 decreases due to this increase in shielding as it means that the outermost electron is less attracted to the nucleus of the atom so less energy is needed to overcome this attraction. Reactivity of the elements increases down the group due to this reason as it is easier for them to lose electrons.

Melting point general decreases down the group as the free electrons cannot get as close to the nucleus of the positive ions so they are not as attracted to the positive metal ions and less energy is needed to overcome their attraction.

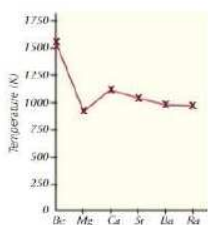


Figure 9: Melting points of Group 2 elements.

Group 2 elements react with water and are oxidised to 2+. They give a metal hydroxide and hydrogen.

The **solubility** of group 2 hydroxides increases down the group and the solubility of group 2 sulfates decreases down the group. Magnesium hydroxide is sparingly soluble and barium sulfate is insoluble.

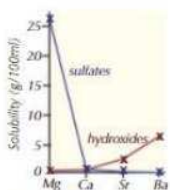
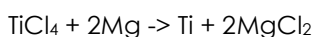
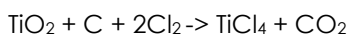


Figure 3: Solubilities of Group 2 compounds at room temperature and pressure.

The insolubility of barium sulfate makes it useful in medicine, it is used in barium meals which show soft tissue on xrays, this is not possible without the barium meal. It is safe to use as it is insoluble.

Magnesium is used to extract titanium:



Calcium oxide and calcium carbonate can be used to neutralise flue gases and remove sulphur dioxide from them.

Calcium hydroxide is used in agriculture to neutralise acidic soils and magnesium hydroxide is used in indigestion tablets to neutralise excess stomach acid.

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Group 7

The **boiling point** of halogens increases down the group due to the increase in the strength of van der Waals forces as the number of electrons on each atom increases.

The **electronegativity** of halogens decreases down the group as the number of electrons in each atom increases so there is more electron shielding and this means that the electron pair in the covalent bond is less attracted to the nucleus of the atom.

Halogens are **oxidising agents** and become less reactive down the group as there is more electron shielding so the nucleus cannot attract an electron as easily. Halogens can displace halide ions dependant on their relative positions in group 7. Chlorine can displace bromide and iodide ions and bromide can displace iodide ions.

These displacement reactions can be used to identify which halide ions are present in a solution. The colour of the solution produced is an indicator. If an orange solution is produced then bromide ions were present and if a brown solution was produced then iodide ions are present.

A reaction of chlorine gas with cold NaOH is a disproportionation reaction and produces NaClO which kills bacteria and acts as bleach. $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}$.

A reaction of chlorine and water is another disproportionation reaction and is reversible. $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$

Chlorine can decompose water in sunlight to form chloride ions.

Chlorate(I) ions kill bacteria and can be used in water supplies if it is used in small enough quantities so that the benefit outweighs the risk. Chlorine can irritate the respiratory system if breathed in and can cause chemical burns as well as reacting with substances that can create carcinogens.

Halide ions are reducing agents and their reducing power increases as the attraction between the nucleus and the outermost electrons decreases so it is easier for them to lose an electron and form halogens.

All halogens react with concentrated sulphuric acid, however, the extent to which the reaction progresses depends upon the reducing power of the halide ion present.

Chlorine and fluorine do not undergo a redox reaction as they are not strong enough reducing agents to reduce the concentrated sulphuric acid. $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$

White misty fumes are produced when the HCl comes into contact with air.

Sodium bromide undergoes the same reaction but goes a step further. $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$

Choking fumes of sulphur dioxide are produced as well as orange fumes of bromine as it is vaporised due to the heat produced from this exothermic reaction.

Sodium iodide goes another step further in its reaction with sulphuric acid. $6\text{HI} + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 3\text{I}_2 + 2\text{H}_2\text{O}$

The observations for all three of the iodine reactions are: white misty fumes, black solid iodine, purple gas from the iodine vapors, choking sulphur dioxide and bad egg smell from hydrogen sulphide.

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Period 3

Sodium and magnesium both react with water. Sodium is more reactive than magnesium as less energy is required for it to lose an electron than to lose two, meaning that more energy is needed for magnesium to react.

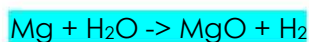
When sodium reacts with **cold** water, a molten ball is formed on the surface, there is **fizzing as H₂ gas is produced**. Sodium hydroxide is produced so the solution is strongly alkaline and has a pH of around 14.



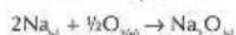
Magnesium reacts slowly with cold water and forms a weakly alkaline solution with pH 10 as the magnesium hydroxide produced is sparingly soluble in water.



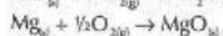
The reaction with steam is much faster as there is more energy for the reaction to occur, magnesium oxide is formed in this reaction and an alkaline solution is produced again due to the presence of the basic O²⁻ ions which can accept protons from the water molecules. So when MgO and Na₂O are dissolved in water, they form alkaline solutions.



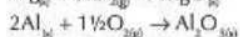
All period 3 elements react with oxygen to form oxides and they can be oxidised to their highest oxidation states. Sulfur is the only one that is not oxidised to its highest oxidation state initially, a high temperature and a catalyst is needed for this to occur.



sodium oxide



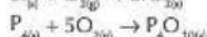
magnesium oxide



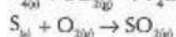
aluminium oxide



silicon dioxide



phosphorus(V) oxide



sulfur dioxide

Sodium forms a **yellow flame** when burnt in oxygen, magnesium and phosphorous both produce a bright **white flame** and sulphur produces a **blue flame**. Therefore, flame tests can be used to identify them. The reaction of silicon and aluminium in air are both slow and therefore there is no flame.

The difference in the melting points of period 3 oxides is due to the differences in their structure and bonding:

- Metal oxides form giant ionic lattice with high melting points due to the strong forces of electrostatic attraction between oppositely charged positive metal ions and negative oxygen ions
- Silicon forms a macromolecular structure with strong covalent bonds that extend throughout the structure and require a large amount of energy to overcome.

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Period 3

- Phosphorous and silver both form covalent molecules with low melting points due to their weak intermolecular forces which require little energy to overcome.

Reaction of non-metal Period 3 oxide with water	Acid formed	Dissociation of Period 3 acid in water
$\text{P}_4\text{O}_{10(s)} + 6\text{H}_2\text{O}_{(l)} \rightarrow 4\text{H}_3\text{PO}_{4(aq)}$	phosphoric(V) acid	$\text{H}_3\text{PO}_{4(aq)} \rightarrow 3\text{H}^+_{(aq)} + \text{PO}_4^{3-}_{(aq)}$
$\text{SO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{3(aq)}$	sulfurous acid (or sulfuric(IV) acid)	$\text{H}_2\text{SO}_{3(aq)} \rightarrow 2\text{H}^+_{(aq)} + \text{SO}_3^{2-}_{(aq)}$
$\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$	sulfuric(VI) acid	$\text{H}_2\text{SO}_{4(aq)} \rightarrow 2\text{H}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)}$

The **simple covalent oxides** of phosphorus and sulphur both form strongly **acidic** solutions with a low Ph and will dissociate in solution to form a conjugate base.

Silicon dioxide is not soluble in water as it has a **giant covalent structure**, it reacts with bases and therefore can still be considered to be acidic.

Aluminium oxide which has ionic bonding and covalent character is insoluble with water but reacts with both acids and bases and can be considered **amphoteric**.

Sodium and magnesium oxide can both **neutralise bases** and silicon, phosphorous and sulphur oxides can **neutralise bases**. Aluminium oxides can do both as they are **amphoteric**.

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Transition Metals

Transition metals are contained within the d block of the periodic table as their outermost electron is in the d sub shell.

TRANSITION METAL – A metal that can form one or more stable ions with an incomplete d sub-level.

Chromium and copper have electron configurations that are different to what would be expected, chromium has one electron in each 3d orbital but has only 1 electron in its 4s orbital. Copper has a full 3d orbital but only has 1 electron in its 4s electron. This **makes both of the atoms more stable**.

Scandium and zinc are not transition metals as they don't have incomplete 3d sub levels in their stable ions. Scandium 3+ has an empty 3d orbital and Zinc 2+ has a full 3d sub level. This occurs because the electrons are removed from the 4s orbital as this has a lower energy level than 3d.

Transition metals all have a **high density** and have **high melting and boiling points**. The chemical properties of transition metals are that they form complex ions, they form **coloured ions**, they are good as catalysts and can exist in variable oxidation states. Transition metals have variable oxidation states as the energies of the **4s and 3d** sub levels are similar, so different numbers of electrons can be gained or lost using similar amounts of energy.

The incomplete d sub level accounts for the chemical properties of transition metals.

COMPLEX ION – A metal ion surrounded by coordinately bonded ligands

COORDINATE BOND – A coordinate bond in which both electrons in the shared pair come from one atom

LIGAND – An atom, ion or molecule that donates a pair of electrons to a central metal ion

Ligands can form **varying numbers of coordinate bonds** with the central metal ion, dependent on the number of lone pairs that are on the molecule:

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Transition Metals

Examples of each of the type of ligand are:

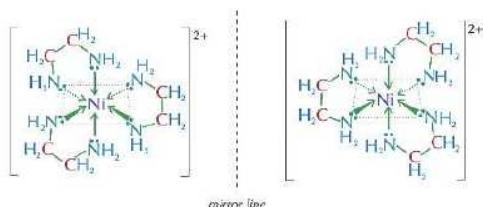
- Monodentate; Cl^- , NH_3 , H_2O
- Bidentate; (en) $\text{C}_2\text{O}_4^{2-}$
- Multidentate; EDTA^{4-}

The oxidation state of the transition metal ion can be calculated by taking the sum of the charges of the ligands from the total charge of the complex ion.

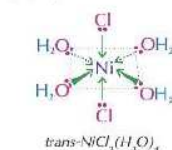
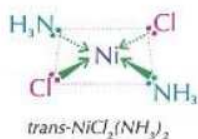
The shape of a complex ion depends on its coordination number which is the number of coordinate bonds that have been formed by ligands with the central metal ion.

- Molecules with 6 coordinate bonds have an octahedral shape with bond angles of 90°
- Molecules with 4 coordinate bonds have a tetrahedral shape with bond angles of 109.5° or a square planar shape with bond angles of 90°
- Molecules with 2 coordinate bonds have a linear shape with bond angles of 180° .

Optical isomerism can occur in octahedral complexes with 3 bidentate ligands bonded to the central metal ion. Two non-superimposable mirror images can be formed due to the arrangement of the bonding of the bidentate ligands.



Cis-trans isomerism can also occur in square planar and octahedral complexes, this is a form of stereoisomerism. When two paired ligands are directly opposite one another in a square planar complex, it is a trans-isomer, when they are next to one another, it is a cis-isomer. Cisplatin is an example of this in a square planar complex. Cis-trans isomerism in octahedral complexes can also be shown by the diagram.



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Transition Metals

When **ligands bond to transition metal** ions, the 3d orbitals split into two discrete energy levels with an energy gap. As electrons occupy the ground state, absorbing specific wavelengths of light can **excite** them. This allows them to go up to the higher energy level. So not all of the light incident on the sample **is reflected** meaning that the transition metal ions appear coloured.

The energy they **absorb** can be calculated using the equation:

$$E = hf = h\frac{c}{\lambda}$$

Transition metals can appear coloured due to **their lack of a full/empty 3d sub level**, this means that electrons can be excited. If an element has a full or empty 3d sub level then no energy can be absorbed as no electrons can jump to the next energy level.

Factors affecting the size of the energy gap and therefore the colour of the transition metal complex are:

- Oxidation state
- Coordination number
- Type of ligand

Spectroscopy can be used to determine the concentration of a coloured solution by determining how much light is absorbed by the solution. Light is shone through a filter which is chosen to only let light through that is absorbed by the substance. This light is then shone through the sample and then hits the colorimeter where it is detected. A calibration curve can be plotted by using this method for solutions of **known concentration**.

Advantages of **colorimetry** are that many readings can be taken in a short amount of time, as well as this, it does not interfere with the sample and very small changes in concentration can be detected.

Examples of the changes in **oxidation state** causing a change in colour for transition metals are seen in vanadium:

- +5 = Yellow
- +4 = Blue
- +3 = Green
- +2 = Violet

Vanadium is reduced by adding it to zinc metal in an acidic solution.

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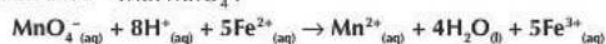
Transition Metals

The redox potential of an ion tells you how easily it is reduced to a lower oxidation state, the more positive it is, the more likely something is to be reduced. The type of ligand bonded affects the redox potential dependent on how well they bond to the metal ion in that oxidation state, the pH also affects it as sometimes H^+ ions are needed to reduce a solution.

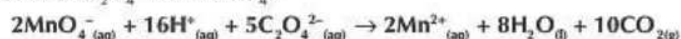
Tollens reagent is an example of a linear complex of silver. It is reduced from the complex to solid silver metal. The aldehyde is oxidized to a carboxylate anion when it is added to Tollens reagent. The formula for Tollens's is: $[\text{Ag}(\text{NH}_3)_2]^+$.

Titration can also be performed on transition metals to see how much oxidizing agent will react with a quantity of reducing agent. The variable oxidation state and colour changes of transition metal ions makes them useful for these titrations as they are **self-indicating**. The end point will be the first sign of permanent colour in the solution.

- Titration of Fe^{2+} with MnO_4^- :



- Titration of $\text{C}_2\text{O}_4^{2-}$ with MnO_4^- :



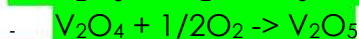
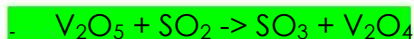
The solution turns purple at the end point of these reactions (see Figure 3).

Transition metals are useful catalysts as they can change oxidation states easily by losing or gaining electrons within their partially filled d orbitals.

CATALYST – A substance that increases the rate of a reaction without being chemically changed in the reaction

A catalyst increases the rate of a reaction by providing an alternate pathway for the reaction to occur on that has a lower activation energy. This can be done by providing an intermediate species.

The contact process uses a vanadium oxide catalyst to increase the rate of reaction, this process is used to produce sulfuric acid. The two steps in which this catalyst works are:



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Transition Metals

HETEROGENEOUS CATALYST – A catalyst that is in a different phase from the reactants.

Iron used in **the haber process** is an example of a heterogenous catalyst, this can be poisoned by sulfur impurities in the reaction mixture. Purifying the reaction mixture can reduce poisoning of catalysts.

An inert support medium can be used to put the catalyst on so that the surface area is increase, increasing the rate of reaction as more reactants can react at once. An example of this is the fine mesh that a rhodium catalyst is spread onto in catalytic conversion in cars. This catalyst can be poisoned by lead impurities in the fuel used.

HOMOGENEOUS CATALYST – A catalyst that is in the same phase as the reactants.

Homogeneous catalysts work **by forming an intermediate species** that has a lower activation energy, the enthalpy profile for this reaction will have two lumps, one for the activation energy for each of the intermediates formed.

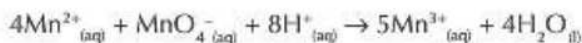
An example of a **homogeneous catalyst is Fe²⁺ ions**. They help S₂O₈²⁻ and I⁻ ions react more quickly. The activation energy for this reaction is particularly high as a collision between two negatively charged ions is required so as there is electrostatic repulsion between the two ions, more energy is needed to allow them to react. The two steps in the catalysis of this process are:

- $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$
- $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Fe}^{2+}$

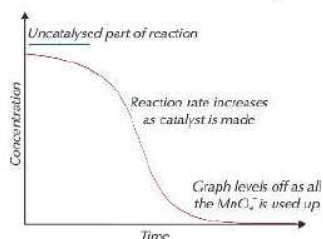
Another example of a **homogeneous catalyst is Mn²⁺** autocatalysing the reaction between MnO₄⁻ and C₂O₄²⁻. This reaction is autocatalysis as Mn²⁺ is produced as a product of this reaction. The equation is the same as the one above for the titration between these reagents.

The reaction is slow at the start as no Mn²⁺ is present. The rate of reaction increases as more of this is produced and eventually becomes zero as the reactants run out.

THE FULLY BALANCED EQUATION FOR THIS REACTION IS:



The Mn³⁺ ions are the intermediate. They then react with the C₂O₄²⁻ ions to make CO₂ and reform the Mn²⁺ catalyst:



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The functional group of an organic compound is responsible for its characteristic reactions.

MOLECULAR FORMULA – The actual number of atoms of each element that are present in a molecule.

EMPIRICAL FORMULA – Gives the simplest whole number ratio of atoms of each element that are present in a compound.

HOMOLOGOUS SERIES – A group of compounds with the same functional group and general formula but differ from each other by CH_2

A curly arrow in a reaction mechanism shows how electrons will move in a reaction.

STRUCTURAL ISOMERS – Compounds that have the same molecular formula but a different structural formula

CHAIN ISOMERS – Compounds with the same functional group as one another but the main carbon skeleton is arranged in a different way.

POSITION ISOMERS – Compounds that have the same molecular formula but the functional group is in a different position.

FUNCTIONAL GROUP ISOMERS – Compounds with the same molecular formula that have a different functional group.

STEREISOMERS – Molecules with the same molecular formula that differ in their arrangement of bonds in space.

Stereoisomerism occurs in alkenes as there is restricted rotation about the double bond. As well as this, the $\text{C}=\text{C}$ in the alkene is planar. E-isomers have the high priority group on the opposite side of the double bond and Z-isomers have their high priority groups on the same side of the double bond.



CIP priority rules govern whether a compound is an E or a Z isomer, these rules state that the way to determine this is:

- Assign priority to the two atoms attached to each side of the double bond
- Atom with the higher atomic number has a higher priority
- If the atoms directly bonded to carbon are the same then the next atom in the group is checked and the same thing is done
- To see which isomer is present, look how the two high priority groups are arranged relative to one another.

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Alkanes and Halogenoalkanes

Alkanes are saturated hydrocarbons. Crude oil can be separated into fractions of alkanes with different boiling points through the process of fractional distillation, the steps are:

- Crude oil is vaporised
- The vapours rise up the column and the longest chain hydrocarbons go to the bottom of the column
- As the vapours reach the temperature at which they condense, they condense and are tapped off in their fractions.
- The column has a temperature gradient

Short chain hydrocarbons are used as fuels and longer chain hydrocarbons are used as **lubricants**.

Longer chain hydrocarbons are not as useful and therefore do not have as great of a demand, this means that they are **cracked** to make shorter chain hydrocarbons.

Thermal cracking occurs at 1200K and 7000kPa and the main product of it is alkenes which can be used to make polymers.

Catalytic cracking occurs at 700K and a slight pressure and uses a **zeolite** catalyst. The main products of this type of cracking are aromatic hydrocarbons and alkanes that can be used for motor fuels. This type of cracking is cheaper due to the reduced energy costs as a lower temperature and pressure can be used.

In complete combustion of a hydrocarbon, the only products are carbon dioxide and water. When incomplete combustion occurs due to there being a lack of oxygen present, the **poisonous gas carbon monoxide** can be produced as well as carbon.

Nitrogen oxides are produced by the reaction of oxygen and nitrogen at a high temperature and pressure, for example in the engine of a car. These oxides can produce acid rain due to nitric acid forming.

Unburnt hydrocarbons can also be problematic from cars engines, catalytic converters can be used to remove these from the atmosphere using a rhodium coated honeycomb allowing for the exhaust gases to pass through them. Unburnt hydrocarbons can produce ground level ozone which forms smog and can aggravate respiratory problems.

Sulfur dioxide is formed when the impurities in fossil fuels are combusted with oxygen. Sulfur dioxide can dissolve in the moisture in the air and form sulphuric acid which is acid rain. This acid rain can damage trees and acidify lakes.

Sulfur dioxide can be removed from flue gases by using calcium carbonate or calcium oxide.

Carbon dioxide which is produced from the **combustion** of fossil fuels is a greenhouse gas and this contributes to global warming. Water vapour also contributes to this effect.

Chloroalkanes are produced in photochemical reactions in the presence of UV light. They are free radical substitution reactions.

There are three steps, **initiation**, when the free radical halogen is produced, **propagation**, the chain reaction step, and **termination**, when two free radicals react together to form a molecule.

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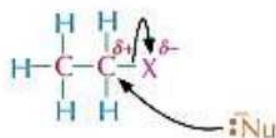
Chlorofluorocarbons are halogenoalkanes that have all of their hydrogen atoms replaced with chlorine or fluorine.

CFCs can damage the environment, particularly the ozone layer as the C-Cl bond breaks in the presence of UV light, forming a Cl free radical which can break down ozone in oxygen. This allows more UV radiation to reach us from the sun as the **ozone layer** usually stops this wavelength of radiation. UV radiation can cause skin cancer.

Safer alternatives to CFCs involve replacing the chlorine atoms with hydrogen or fluorine as uv light isn't energetic enough to break the bonds and form free radicals.

Halogenoalkanes are alkanes with at least one halogen atom in place of a hydrogen atom. They are polar as carbon-halogen bonds are polar. This means that they can be attacked by nucleophiles due to the presence of the partially positive carbon atom.

A nucleophile is an **electron pair donor**.



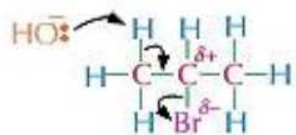
These reactions are called nucleophilic substitution.

Example of nucleophiles and their products from this reaction are:

- $\text{OH}^- \rightarrow$ Alcohol
- $\text{CN}^- \rightarrow$ A nitrile with an extra carbon on the chain.
- $\text{NH}_3 \rightarrow$ Amines

Faster nucleophilic substitution occurs when iodine is present in the molecule and not fluorine as the bond enthalpy is lower meaning that less energy is needed to break it.

Halogen elimination can occur when OH^- acts as a base. Alkenes are produced from these reactions. This reaction occurs instead of nucleophilic substitution when alcoholic conditions are used.



Alkenes and Alcohols

Alkenes have the general formula C_nH_{2n} and are unsaturated hydrocarbons with a carbon-carbon double bond. Addition reactions can occur, allowing for extra atoms to be added onto the molecule. An example of one of these reactions is electrophilic addition which occurs when an electrophile attacks the $C=C$

ELECTROPHILE - An electron pair acceptor.

In these electrophilic addition reactions, concentrated sulfuric acid must be used as a catalyst. A carbocation intermediate is formed. In unsymmetrical alkenes, the carbocation intermediate produced from the reaction will determine whether it will be a major or a minor product.

Carbocations are more stable when the positive carbon atom is attached to more alkyl groups due to the positive inductive effect which helps to stabilise this positive charge. So a tertiary carbocation intermediate which is more stable than a secondary carbocation intermediate will produce the major product of an electrophilic addition reaction.

Alkenes can be tested for by adding bromine water to them as it is added across the double bond and forms a colourless solution if double bonds are present.

Polymers are made up from long chains of monomers that have been joined together and they can be synthetic or natural.

Alkenes can form addition polymers when their double bonds open up and join together to form long chains of polyalkenes.

Alkene monomers are unsaturated but the polymer chains produced are saturated. The polymer chain is usually non-polar so polyalkenes are chemically inert. There are strong covalent bonds linking the chains together but there are only weak van der Waals forces between the polymer strands themselves. Polymers with less branched chains can pack together better meaning that their intermolecular forces are stronger.

PVC is formed from chloroethene monomers. The $C-Cl$ polar bond means that there are permanent dipole-dipole forces acting between the polymer chains. So PVC is hard and brittle and can be used in window frames and drain pipes.

Plasticisers can be added to polymers to reduce the strength of intermolecular forces between polymer chains as they get between polymer chains and increase the spacing between them. This makes the polymer itself more flexible. So plasticised PVC can be used in clothing and cable insulation.

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Alkenes and Alcohols

Alcohols have an OH group. Primary alcohols are attached to one alkyl group, secondary alcohols have the OH group attached to two alkyl groups and tertiary alcohols have their OH group attached to three alkyl groups.

Alcohols can be dehydrated when heated with concentrated sulfuric acid catalyst (MECHANISM). Dehydration of unsymmetrical alcohols results in more than one product. The product can be purified through use of distillation.

Alkenes can be hydrated to produce alcohols when heated with concentrated phosphoric acid under a pressure of 600kPa. These conditions are used to produce pure ethanol from ethene.

Ethanol can also be produced from the fermentation of glucose. The conditions needed for this reaction are anaerobic conditions with yeast at $30 < T < 40$. This temperature is necessary as it is the optimum temperature for the enzymes from yeast to work. When the solution of ethanol reaches 15% then the yeast die. So the product must be distilled.

Differences between the two methods of production:

- Hydration of ethene is much faster at producing ethanol than fermentation
- Pure ethanol is produced from ethene unlike from glucose.
- Ethene is not renewable unlike sugar which is
- Hydration of ethene is continuous unlike fermentation which is batch
- Fermentation has high labour costs but cheap equipment
- Hydration has expensive equipment costs but cheap labour.

Biofuels are made from dead biological material.

Advantages are:

- Renewable energy source
- Absorb the same amount of carbon dioxide as they produce when they are burnt

Disadvantages are:

- Land used to grow fuel instead of food
- Deforestation
- Fertilizers added which can pollute water
- Car engines cannot run off pure biofuel.

Ethanol is carbon neutral when looking at the equations for photosynthesis and combustion of the products, however, energy from fossil fuels must be used to transport the fuel around as well as distill it, so it cannot be considered to be truly carbon neutral.

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Alkenes and Alcohols

Alcohols can be oxidised to other organic products. Oxidation of **primary alcohols** will produce **aldehydes**. If you oxidise **aldehydes under reflux** and distill the final product you will produce **carboxylic acids**. Oxidation of **secondary alcohols** under reflux in acidic conditions will produce **ketones**.

A **strong oxidising agent** such as acidified potassium dichromate must be used for these reactions.

Tollens reagent can test for aldehydes and ketones. A silver mirror will be formed when added to an aldehyde and there will be no observed change when added to a ketone. **Fehlings solution** will also do the same, it will turn brick red in an aldehyde and there will be no observed change in a ketone.

Tertiary alcohols can only be oxidised by combustion.

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Organic Analysis

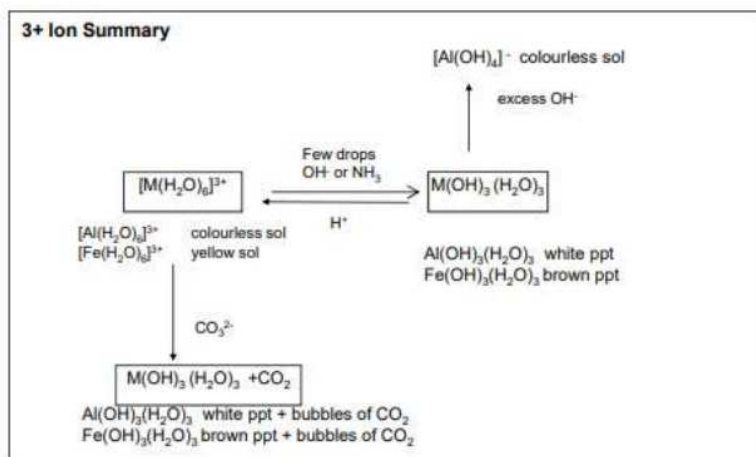
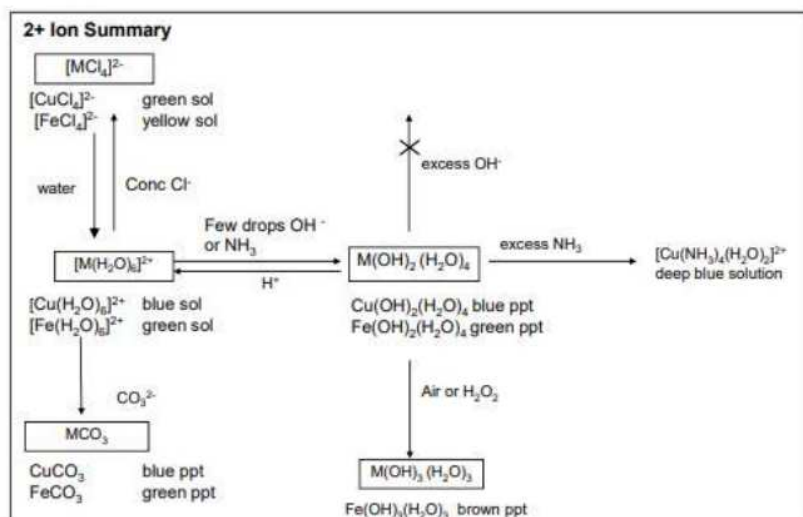
Carboxylic acids can be tested for by adding sodium hydrogencarbonate and then bubbling the products through lime water, if the limewater turns cloudy then the organic compound being tested is a carboxylic acid.

High resolution mass spectrometry can be used to identify compounds that appear to have the same M_r but actually are different compounds which will have different M_r s when measure to a higher resolution.

In infrared spectroscopy, a beam of infrared radiation is passed through a chemical sample, covalent bonds absorb different frequencies of this radiation so they can be identified by the frequency they absorb. The fingerprint region is unique to a particular compound and is located between 1000cm^{-1} and 1550cm^{-1}

Greenhouse gases such as carbon dioxide and water vapour are better at absorbing infrared radiation. So they can store this energy from the sun, causing the atmosphere to warm up.

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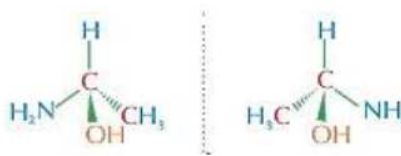


Isomerism and Carbonyl Compounds

STEREISOMERS – Molecules with the same structural formula but have a different arrangement of bonds in space.

CHIRAL CARBON – A carbon atom with four different groups attached to it.

ENANTIOMERS – Two optical isomers that are non-superimposable mirror images of each other.



Two optical isomers can be told apart by passing plane polarised light through the sample. Plane polarised light only oscillates in one plane. When it is passed through two separate samples of enantiomers, one sample will rotate the light in one direction and the other sample will rotate it in another.

RACEMATE – A mixture that contains equal amounts of each enantiomer

Racemic mixtures **do not show any optical activity** as there is no net rotation of plane polarised light when it is passed through the sample. When two molecules react, there is often an equal chance of forming each of the enantiomers. It can be difficult and expensive to form a reaction where only one enantiomer is formed.

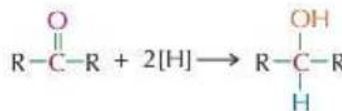
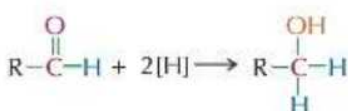
In medicine, only one enantiomer may be useful for its application in a drug, so a mixture of the two may make the drug less effective, or could mean that it doesn't work all together. So either a double dosage must be given to counteract this or the other, not useful, enantiomer can be removed from the mixture, this is more expensive to do.

Aldehydes and ketones are carbonyl compounds that both contain the planar C=O bond that is called a carbonyl group.

Aldehydes can be oxidised to carboxylic acids using an oxidising agent such as acidified potassium dichromate, ketones cannot be oxidised in this way. The only way to oxidise a ketone in this way is to break a carbon-carbon bond which is not easy to do. The reagent used is always reduced when the aldehyde is oxidised.

Tollens reagent can be used as a test for aldehydes and ketones, it will oxidise aldehydes to form a silver mirror as the silver complex has been reduced. There will be no visible reaction with a ketone. **Fehlings test** shows a similar change, copper $2+$ ions are reduced to copper $+$ ions and there is a colour change from blue to brick red.

Aldehydes and ketones can also be reduced using **NaBH_4** . It will reduce these compounds to primary and secondary alcohols respectively. It can be represented by $[\text{H}]$.



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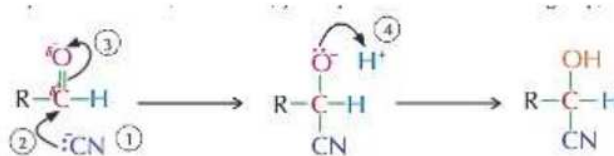
Isomerism and Carbonyl Compounds

The mechanism by which this occurs is called **nucleophilic addition** and it looks like this. It can be applied to both aldehydes and ketones.

Hydroxynitriles contain both an OH group and a nitrile group. The nitrile prefix takes highest importance and hence the alcohol group is called hydroxy in these compounds.

Hydroxynitriles can be produced **by reacting aldehydes and ketones with KCN and a dilute acid.** This is an example of nucleophilic addition. Hydrogen cyanide can also be used but this is much more dangerous as HCN gas can be evolved which is toxic and therefore this experiment must be done in a fume cupboard.

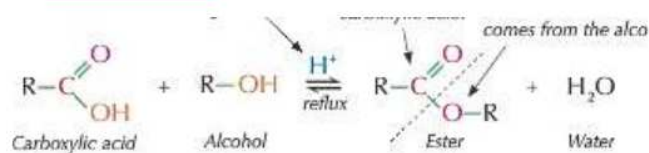
All the organic reagents used in this experiment are flammable so a water bath must be used to heat them instead of using a Bunsen burner.



The C=O bond is **planar**, this means that the nucleophile can attach from above or below the plane of the molecule, so each enantiomer is produced in equal amounts forming an optically inactive racemic mixture.

Carboxylic acids are weak acids and will **partially dissociate in water** to produce a H⁺ ion and a carboxylate ion. The reaction in which the acid dissociates is reversible but equilibrium lies to the left, so few molecules dissociate. Carboxylic acids react with carbonates as other acids do, a carboxylate salt is produced with water and carbon dioxide.

Heating a carboxylic acid with an alcohol in the presence of a strong acid catalyst such as sulphuric or phosphoric acid will produce an **ester** in an **esterification** reaction.



Esters can be used in many things such as:

- Perfumes and flavourings due to their sweet smell
- Solvents as they are polar, this allows polar organic compounds to dissolve in them.
- Plasticisers to make the plastics more flexible, these molecules escape over time causing the plastic molecule to become more brittle.

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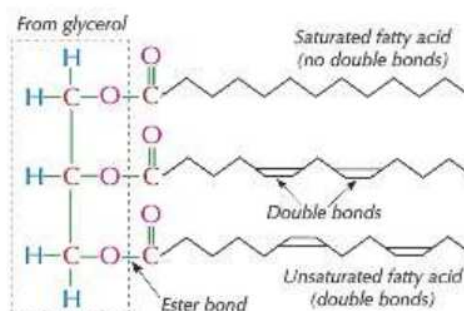
Isomerism and Carbonyl Compounds

The reverse reaction of esterification is **acid hydrolysis** and the ester can be split up into its constituent carboxylic acid and alcohol molecules. Using an **excess of water** pushes the **equilibrium** to the side to produce more carboxylic acid and alcohol. A strong **acid catalyst** must be used for this too.

Base hydrolysis can also be used to split up esters. The ester must be refluxed with a dilute alkali. A **carboxylate ion** and **alcohol** are produced from this reaction.

FATTY ACIDS – Long chain carboxylic acids.

Fatty acids can be **saturated or unsaturated**. Fats, which are solid at room temperature, have mainly saturated hydrocarbon chains which allow their molecules to pack together better meaning that the van der Waals forces between their molecules are stronger. Oils have more unsaturated chains with double bonds in them.



Combining fatty acids with **glycerol** makes these **fats and oils**. Glycerol's systematic name is **propane-1,2,3-triol**.

Fats and oils can be broken up using **base hydrolysis with sodium hydroxide**, this reaction produces glycerol and 3 sodium salts. These salts can be used for soap. The fatty acids that made up the fat can be reformed from these sodium salts by adding H^+ ions to the reaction mixture which will form the fatty acid.

Biodiesel can be formed by reacting a fat with methanol, this will form glycerol and 3 methyl esters. Biodiesel is not 100% carbon neutral as despite the fact that the same amount of carbon dioxide is absorbed by the plants as is released in their combustion, the energy used to transport these fuels comes from burning fossil fuels, which causes the emission of carbon dioxide into the atmosphere.

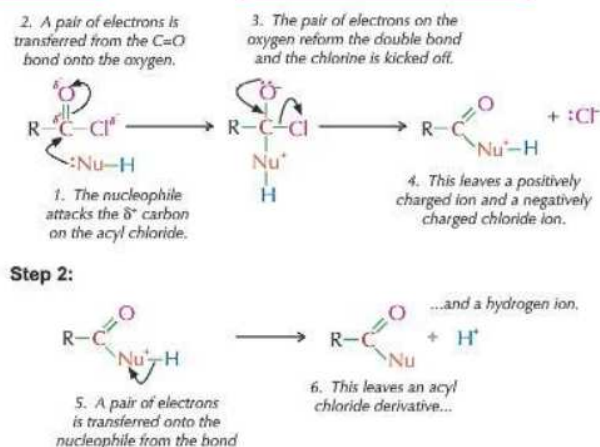
BIODIESEL – A mixture of methyl esters that can be used as a fuel.

Acyl chlorides react vigorously with cold water and alcohols, ammonia and primary amines at room temperature. All of these reactions produce HCl as one of their products, the other product is shown in the table below.

Reagent	Acyl Chloride	Acid Anhydride
Water	Carboxylic acid	Carboxylic acid
Alcohol	Ester	Ester
Ammonia	Amide	Amide
Primary Amine	N-Substituted amide	N-substituted amide

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The reactions of **acyl chlorides** occur by **nucleophilic addition-elimination**, the mechanism for this is below:



When acid anhydrides undergo the reactions above, they are much less **vigorous** and a carboxylic acid is produced as the second product instead of HCl.

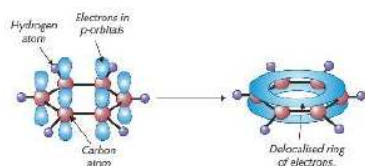
Advantages of acid anhydrides instead of acyl chlorides are:

- They are cheaper
- They are less corrosive
- They react much less slowly with water
- Dangerous HCl fumes are not evolved from acid anhydrides unlike acyl chlorides.

Aromatic Chemistry

The structure of benzene is:

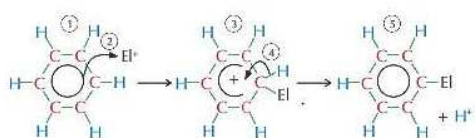
- Planar cyclic structure
- 6 carbon atoms and 6 hydrogen atoms
- Each carbon atom forms a single covalent bond with 1 hydrogen atom and 2 carbon atoms
- Each carbon atom has a delocalised p orbital electron.
- There is a ring of delocalised electrons above and below the plane of the molecule.
- Bond length is the same between all c-c, and the length is intermediate between a single bond and a double bond between carbon atoms.



Benzene is more stable than cyclohexa-1,3,5-triene. This can be seen by comparing enthalpy changes of hydrogenation between these compounds. If benzene had 3 double

bonds, you would expect its enthalpy of hydrogenation to be $-360, 3 \times -120$, however, its actual enthalpy of hydrogenation is -208 kJ mol^{-1} . As this is less exothermic than cyclohexatriene, it means that more energy must be supplied to break the bonds and therefore it is more stable. This extra energy required is due to the delocalised ring of electrons as the electron density is shared over more atoms, so the energy of the molecule is lowered and becomes more stable.

The benzene ring is a region of high electron density so electrophiles, electron pair acceptors, are attracted. Therefore, electrophilic substitution reactions can occur where one of the hydrogen groups on the ring are substituted for the electrophile.



Nitration of the benzene ring occurs by electrophilic substitution. To form the electrophile, concentrated nitric and concentrated sulphuric acid

must be reacted together. The equation for this is:



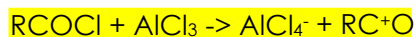
The ion formed that is the electrophile in this reaction is the nitronium ion and this reacts with benzene to form nitrobenzene. To ensure that only one nitronium ion is added to the benzene ring, the temperature of the reaction mixture must be kept below 55°C . The compounds formed in this reaction can be used to make dyes and medicines and can also be used as explosives as they violently decompose when heated.

Another example of an electrophilic substitution reaction is friedel-crafts acylation which adds an acyl group to a benzene ring. The reactants must be heated under reflux in a non-aqueous solvent for the reaction to occur.

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Aromatic Chemistry

An electrophile must have a large positive charge to be able to attack the benzene ring, they can be made into stronger electrophiles by using a catalyst called a halogen carrier such as AlCl_3 . In this acylation reaction, AlCl_3 accepts a pair of electrons from the acyl chloride, increasing the polarisation in the acyl chloride to form a carbocation. The equation for this is:



Aluminium chloride is reformed at the end of the reaction, showing that it acts as a catalyst. These compounds are useful as further groups can be added onto the acyl group using other mechanisms.

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Amines

Amines are formed when a hydrogen is replaced by an NH_2 group on an aromatic or alkyl group. A primary amine has 1 alkyl group, a secondary amine has two R groups, a tertiary amine has 3 alkyl groups.

Quaternary ammonium ions have a positive charge with four R groups attached to them. They can form salts with other negative ions.

SURFACTANTS – Compounds which are partially soluble and partially insoluble in water

Quaternary ammonium salts can be used as cationic surfactants, these are surfactants with a positive charge. These compounds must have at least 1 R group with a long hydrocarbon chain. This chain is **insoluble in water** as it is non-polar, therefore it will bind to other non-polar substances such as grease. The positive head is soluble in water as it can form intermolecular forces with the polar water molecules. They are useful in detergent as the non polar and polar ends will bind in different molecules and this allows grease and water to mix, allowing it to be washed away.

Amines act as **weak bases** as they accept protons, the lone pair of electrons on the nitrogen atom can form a coordinate bond with the proton. The strength of the base depends on how available the nitrogen's lone pair is. The availability depends on what group the nitrogen atom is bonded to.

A nitrogen atom bonded to an **alkyl group with have a lone pair** that is more available as the positive inductive effect means that the electron density on the lone pair of electrons is higher, making it easier for it to accept a proton.

If the nitrogen atom is bonded to an aromatic group such as a benzene ring, the lone pair of electrons will be **partially delocalized into the ring**, making it less available to accept a proton and reducing the base strength. Ammonia's base strength lies inbetween that of alkyl groups and aromatic groups.

Aliphatic amines are those that are not attached to an aromatic group.

Amides are carboxylic acid derivatives. The carbonyl group pulls electrons from the NH_2 group meaning that they do not behave in the same way as amines. N-substituted amides have one of the hydrogen atoms attached to the nitrogen **substituted with an alkyl group**.

Aliphatic amines can be formed from halogenoalkanes in nucleophilic substitution reactions. When a halogenoalkane is heated with **excess ammonia** in ethanol solution, a mixture of different amines are produced (primary, secondary...). More than one hydrogen is likely to be substituted when an excess of ammonia is used. Reducing the **concentration** of ammonia and increasing the concentration of the halogenoalkane will produce mainly primary amines.

Aliphatic amines can also be produced from **nitriles**. Using **a strong reducing agent such as LiAlH_4** can reduce these when a dilute acid is used too. A platinum/nickel catalyst can be used with high temperatures in this reaction in industry; this is **catalytic hydrogenation**.

In catalytic hydrogenation, a nickel catalyst is used with high temperature and pressure and hydrogen gas to reduce the nitrile compound to an aliphatic amine.

Acyl chlorides react with ammonia to form **primary amides** in nucleophilic addition-elimination.

Reducing a nitro compound can produce **aromatic amines**. Using tin metal and hydrochloric acid and heating under reflux with an alkali, an aromatic amine can be produced.

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Polymers

Condensation polymers are formed when two monomers that have at least two functional groups react together. Each functional group reacts with a group on another monomer to form a link, a small molecule is lost each time this occurs, and this is usually water.

Polyamides are formed from the reaction between dicarboxylic acids and diamines. An amide link is formed when this occurs and a water molecule is eliminated each time. Examples of polyamides are nylon 6,6 and Kevlar.

Nylon is strong and resistant to abrasion, so it is used to make clothing, carpet

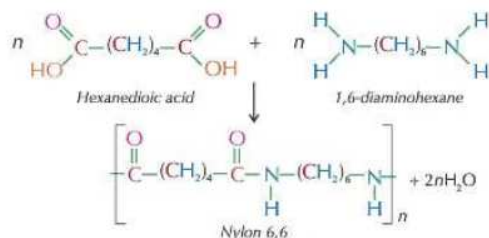


Figure 2: The formation of nylon 6,6.

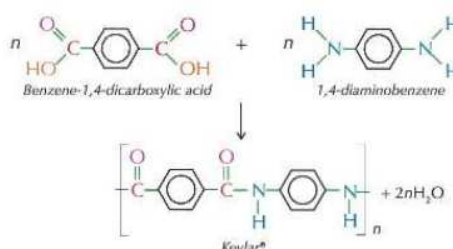


Figure 4: The formation of Kevlar®.

and rope. Kevlar is strong and light so it is used in bulletproof vests and sports equipment.

Amino acids contain a functional group and a carboxylic acid group and can be used to form peptides which are polyamides. This occurs due to a condensation polymerisation reaction.

Polyesters are formed from diols and dicarboxylic acids. Ester links are formed between the monomers. An example of a polyester is terylene which is stable at hot and cold temperatures, so can be used in food packaging.

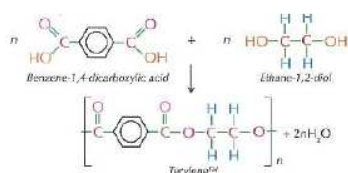


Figure 8: The formation Terylene®.

The ester or amide link in these condensation polymers can be broken in a hydrolysis reaction. This essentially reverses the condensation reaction that is used to form the polymers. The monomers that were used to form the polymers are produced as a result of this. Hydrolysis is too slow just with water so polyamides can be hydrolysed under acidic conditions more quickly and polyesters can be hydrolysed under basic conditions more easily.

Condensation polymers are more rigid than **addition polymers** due to the polar bonds in the chains so the intermolecular forces between the chains are much stronger than in addition polymers.

The polar bonds in condensation polymers also means that unlike polyalkenes, they are **biodegradable**. This is because they can easily be attacked by nucleophiles that can break them down.

Plastic can be difficult to dispose of carefully.

Despite landfill being cheap, it still has its disadvantages:

- Lots of land required
- Methane can be released as the waste decomposes
- Toxins can be released as the waste decomposes and this can be washed into our water supplies

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Polymers

Plastic can be burnt to release energy to power devices but, disadvantages of burning plastic are:

- Toxic gases, such as HCl, are produced, these must be removed
- Greenhouse gases can be produced such as carbon dioxide.

Advantages of recycling plastics are:

- Reduces amount of waste in landfill
- Saves raw materials
- Cost is cheaper than making plastic from scratch
- Produces fewer CO₂ emissions

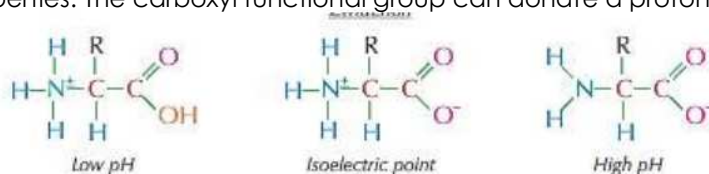
Disadvantages of recycling plastics are:

- Technically difficult
- Collecting and sorting is more expensive than burning or using landfill
- Cannot remake the plastic that you started with
- Plastic can easily be contaminated in the process.

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Amino Acids Proteins and DNA

Amino acids have two functional groups, an amine functional group and a carboxyl functional group. They all have the same structure apart from they differ on their organic side chain. These molecules are amphoteric and therefore have acidic and basic properties. The carboxyl functional group can donate a proton in basic conditions and the amine functional group can accept a proton in acidic conditions.



ZWITTERION – A dipolar ion with a positive and a negative charge

Amino acids can exist as a zwitterion at their isoelectric point which is the pH when the overall charge on an amino acid is zero. This is different for every amino acid as it depends on the R group of amino acids.

Amino acids can be separated using thin layer chromatography as the different R groups means that they will have different solubility in the same solvent as they will have different polarities. A locating agent must be used to find the amino acids on the chromatogram as they are colourless. Examples of this are:

- Ninhydrin
- Iodine crystal vapour
- UV light

Amino acids can be identified using their R_f value which can be calculated by dividing the distance travelled by the amino acid by the distance travelled by the solvent.

Proteins are condensation polymers of amino acids. They are made from amino acids joined by peptide links. They can be formed in condensation reactions and broken up into the constituent amino acids in hydrolysis reactions. Dipeptides are made from two amino acids.

Proteins can be hydrolysed by adding them to 6mol dm^{-3} HCl and refluxing the mixture for 24 hours.

Proteins have a primary, secondary and tertiary structure:

- **Primary:**
 - o Sequence of amino acids in the chain making up the protein
 - o Held together by covalent bonds
- **Secondary:**
 - o Peptide links form hydrogen bonds to form chains that are not a straight line. The shape can be an alpha helix or a beta pleated sheet, the shape is determined by the number of hydrogen bonds.
 - o Secondary structure formed by hydrogen bonds
- **Tertiary**
 - o The way that the chain of amino acids is coiled and folded together in characteristic ways, determining the protein itself.
 - o Tertiary structure formed by hydrogen bonds and disulphide bonds.

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Amino Acids Proteins and DNA

Intermolecular forces determine the shape of the protein and this determines how the protein will function. Hydrogen bonds form between **polar groups** with electronegative atoms that induce a positive charge on the hydrogen atom that cause the partially positive hydrogen to be attracted to a lone pair of electrons on one of the **more electronegative atoms**.

Disulphide bonding forms between cysteine molecules which contain the thiol group. These groups lose their H atom which allows them to form a S-S bond between thiol groups and cysteine molecules. **pH and temperature** can affect the formation of hydrogen bonds and disulphide bonds so this can affect the shape of proteins.

Enzymes are proteins that act as biological catalysts and increase the rate of biological reactions. The substrate fits into the active site of the enzyme. The active site is part of the tertiary structure of the enzyme.

Enzymes **are stereospecific** so will only work with one **enantiomer** of a certain substrate.

Drugs can act as enzyme inhibitors by having a similar shape to the active site of the enzyme. The relative concentration of the enzyme to the inhibitor can be used to determine how much inhibition will occur. The inhibitor can bind to the active site to prevent any substrates from fitting into it, when this occurs, they block the active site. The shape of these molecules can be designed using computers and adapted so that the scientists will know if they fit with the desired enzyme in the body.

DNA is made up from **nucleotides**. Each nucleotide contains a phosphate group, a pentose sugar and a base. DNA is made up from nucleotides containing a **phosphate group, deoxyribose sugar and a ACGT base**.

The nucleotides in DNA join up to form a polynucleotide chain. **Covalent bonds** form between the phosphate group of one nucleotide and the sugar of another, this forms the sugar phosphate backbone. This is formed by a condensation polymerisation reaction where a molecule of water is eliminated.

DNA is formed from **two polynucleotide strands which spiral to form a double helix**, held together by hydrogen bonds between complementary bases. CG and AT are complementary base pairs. Base pairs are complementary due to the arrangement of atoms in the molecules that can form hydrogen bonds. AT form 2 hydrogen bonds and CG form 3 hydrogen bonds. The DNA helix spirals in a way so that these can be correctly aligned.

Cisplatin is an anticancer drug made from the platinum complex **$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$** . The isomer transplatin will have different effects.

Cancer can spread due to the replication of cells, for this to happen, DNA must unwind to replicate. **Cisplatin prevents the DNA from unwinding** and therefore does not allow cancer to replicate. The process by which this occurs is:

- Nitrogen atom on guanine base forms a coordinate bond with platinum ion and replaces a chlorine ligand.
- The same happens with another guanine molecule and the second chlorine ion is replaced too.
- The cisplatin complex bound to the DNA causes the strands to kink meaning that they cannot unwind and replicate.

This drug has side effects as the same process can occur with healthy cells which means that the immune system can be suppressed and hair loss can also occur.

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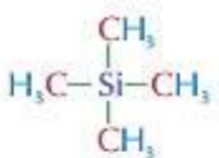
When chemists are designing synthetic routes, it is important that they choose ones that have high atom economies, produce few toxic chemicals and use little solvent. This means that the amount of waste is minimised as well as making the synthesis safe.

NMR tells you information about how the carbon and hydrogen atoms in a molecule are arranged. The nucleus of these atoms is shielded from the effects of a magnetic field by electrons, if there is less shielding due to the atom being attached to something electronegative such as oxygen, it means that less shielding occurs, so the nucleus will feel the effects of the magnetic field more.

NMR measures differences in the energy absorbed by nuclei in different environments relative to a standard substance, this difference is referred to as chemical shift. The standard substance that is used is TMS, tetramethylsilane. TMS has a chemical shift value of 0 and is added to many NMR spectra as a way to calibrate the system.

TMS is used as a standard because:

- It is inert
- It is non-toxic
- It is volatile, so it can easily be removed from the substance
- All the carbon and hydrogen atoms are in the same environment, so it produces one sharp absorption peak.



The number of peaks in carbon NMR tells you the number of carbon environments present in that molecule. The carbon atoms that are attached to more electronegative atoms will have less shielding and so will have a higher chemical shift value.

Each peak in a hydrogen NMR spectra is due to a hydrogen nuclei in a particular environment. The relative area under each peak tells you the number of H atoms in each environment. Integration traces can be used to show how many hydrogens are in an environment, the height of the peak is proportional to the areas of the peaks and therefore proportional to the number of hydrogens in that environment.

Peaks in H NMR are split into smaller peaks based on the number of hydrogens attached to the adjacent carbon atom. It follows the n+1 rule where if there are 3 hydrogens on the next atom then there will be a quartet splitting pattern on the peak.

H¹ free solvents must be used in these NMR spectra as otherwise they would appear on the spectrum, confusing the results. So deuterated solvents where H² atoms are used instead. Deuterium does not interact with the external magnetic field so it does not produce peaks on the spectra. Examples are CDCl₃, D₂O and CCl₄ which doesn't contain any hydrogen.

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NMR and Chromatography

Chromatography is used to separate and identify chemicals in mixtures, there is a mobile phase where the molecules are able to move, this is always a fluid. The stationary phase is where the molecules cannot move. The distance each substance moves depends on the solubility in the mobile phase and the retention by the stationary phase. Components more soluble in the mobile phase will travel further than components that are more strongly adsorbed onto the stationary phase. **The differences in solubility** help to separate the substances.

TLC uses a liquid solvent such as ethanol and a silicon dioxide plate. A pencil line should be used and the solvent is added to a level that is below this pencil line. A watch glass should be placed on top of the setup to prevent the evaporation of the solvent. The plate can be left in the fume cupboard to dry.

For colourless compounds, **locating agents must be used**. For example, fluorescent dye can be used on the plate and UV light shone over the plate. As well as this, iodine vapours can be used as they mark the spots as purple as the crystals **sublime**.

The substances can be identified by calculating their **R_f value** which is the ratio between the distance travelled by the spot and the distance travelled by the solvent. These values are properties of the material, so as long as conditions are kept the same, the value can be searched in the data book to find what substance is in the chromatogram.

If you are not sure what a substance is, a known substance can be placed alongside the unknown one to see whether they are the same once they separate in TLC.

Column chromatography can be used to purify organic products. It involves a glass column that is packed with a solid such as aluminium oxide coated with water. A solvent is poured through it and allowed to drain. The mixture separates out dependant on how soluble they are in the solvent and how much they are adsorbed onto **the stationary phase**.

The longer the component spends dissolved in the mobile phase, the quicker it will move through the chromatogram.

Gas chromatography can be used to separate a mixture of volatile liquids. A column is packed with a solid or with a solid coated by a liquid and a gas is passed through the column under pressure at a high temperature which vaporises the liquids as they are in an oven. The retention time is recorded by the chromatogram, under standard conditions, these can be compared to find out what a certain compound is. The area under each peak tells you the relative abundance of each compound.

Gas chromatography can be used to find the level of alcohol in blood to be used in court cases.

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Mass spectrometry can be used to identify the separated substances from gas chromatography. The spectrometer produces a mass spectrum for each component which can identify why the initial sample was made up from. The computers can match this up to compounds in a database so the process is automated. This means that compounds can be identified, as in GC, the retention times can sometimes be too similar so they cannot be identified from the chromatogram alone.

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