

OCR (B) Chemistry A-level

Storyline 4: The Ozone Story

Detailed Notes

This work by [PMT Education](https://www.pmt.education) is licensed under [CC BY-NC-ND 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/)



Bonding and Structure

Electronegativity

Every atom has electronegativity, which is defined as:

The ability of an atom to attract the bonding electrons in a covalent bond towards itself.

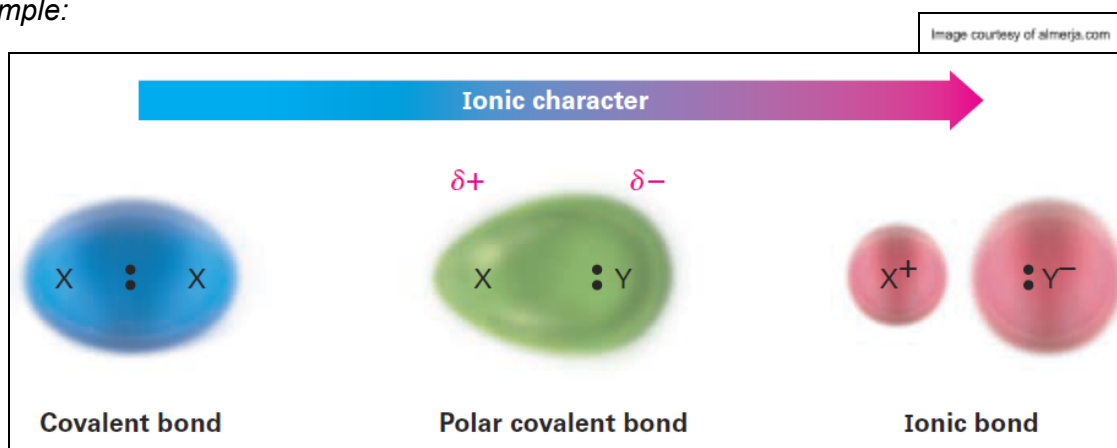
This 'power' is different for every atom depending on its **size and nuclear charge**.

- Electronegativity **increases along a period** as atomic radius decreases and charge density increases.
- Electronegativity **decreases down a group** as shielding increases and atomic radius increases so charge density decreases.

Pauling electronegativity values can be used to compare the electronegativity of atoms. A **higher value** on the Pauling scale indicates a **greater electronegativity**. Fluorine is the most electronegative atom and has a value of 4.0.

The Pauling values can be used to calculate **electronegativity differences** in a covalent bond. The greater the electronegativity difference, the greater the bond polarity. This leads to a greater degree of **ionic character**. Ionic and covalent bonding are the extremes in a continuous scale of bonding as shown below.

Example:



This bond polarity can be **permanent** or **induced**, depending on the molecule and how it interacts with things around it.

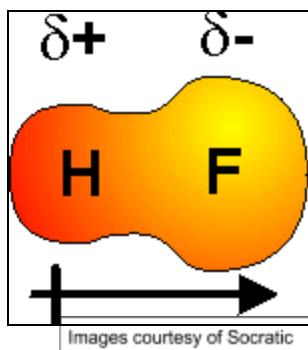
Permanent Dipole

If the two atoms that are bonded have sufficiently different electronegativities, a **polar bond** forms. The more electronegative atom **draws more of the negative charge towards itself** and away from the other atom, producing a δ^- region and a δ^+ region. This is a **permanent dipole**.





Example:

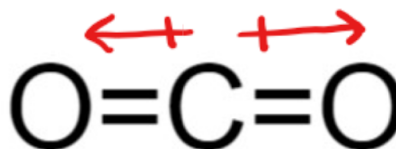
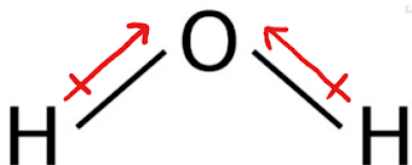


Hydrogen fluoride is a polar molecule as fluorine is a lot more electronegative than hydrogen. This means electrons are drawn towards the fluorine atom.

Polar molecules

Polar molecules arise when there is an **overall** difference in polarity **across the molecule**, due to the arrangement of polar bonds and the geometry of the molecule. Polar molecules must have polar bonds, however a molecule with polar bonds may not necessarily be a polar molecule.

Example:



CO₂ - the C=O bonds in CO₂ are polar, however the molecule is linear so the dipoles created by each polar bond cancel out.

H₂O - the O-H bonds in water are polar and the geometry of the molecule is bent, so overall there is a polarity and the molecule is polar.

Polar molecules with a permanent dipole can align to form a **lattice of molecules** similar to an ionic lattice.

Induced Dipole

An induced dipole can form when the electron orbitals around a molecule are **influenced by the distributions of electrons on another particle**.



Example:



[CC BY-NC-SA 3.0 US](https://creativecommons.org/licenses/by-nc-sa/3.0/us/), [Allison Soult, Chemistry LibreTexts](https://chem.libretexts.org/)

Intermolecular Forces

There are **three main types of intermolecular force**. Each one differs in strength and where they can arise.

Induced Dipole Bond (Van der Waals Forces)

Van der Waals forces are the **weakest** type of intermolecular force. They act as an **induced dipole** between molecules.

The strength of van der Waals forces varies depending on the M_r of the molecule and its shape. The **larger the M_r** of the molecule, the **stronger the intermolecular forces**.

Van der Waals forces act between organic **alkane chains** and are affected by the **chain length** and the presence of **branching**. As the chain length of the alkane increases, so does the M_r of the molecule. This results in **stronger** intermolecular forces between the chains and the compound has a **higher boiling point** as a result.

Branching of alkane chains weakens van der Waals forces between the chains as they are less able to **pack tightly** together. Therefore, the distance over which the intermolecular forces act is increased and the **attractive forces** are **weakened**. This means branched-chain alkanes have **lower boiling points** than straight-chain alkanes.

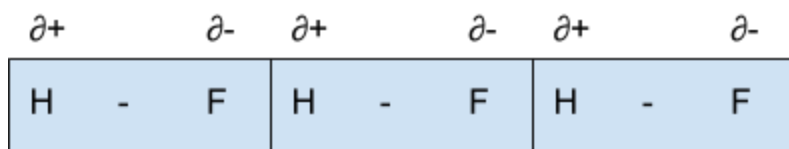
The Group 7 elements are **simple covalent molecules**, with weak **van der Waals** forces. The strength of these intermolecular forces increases as the relative atomic mass of the molecule increases, so the strength of the van der Waals forces **increases down the group**. This means **more energy** is required to overcome them, resulting in higher melting and boiling points. This is why **fluorine** is a **gas** at room temperature, whereas **iodine** is a **solid**.



Permanent Dipole

Permanent dipoles are a type of intermolecular force that acts between molecules with a **polar bond**. The δ^+ and δ^- regions on adjacent molecules attract each other and hold the molecules together in a **lattice-like structure**. These interactions are stronger than induced dipole-dipole interactions, so more energy is needed to overcome them, so melting and boiling points will be higher.

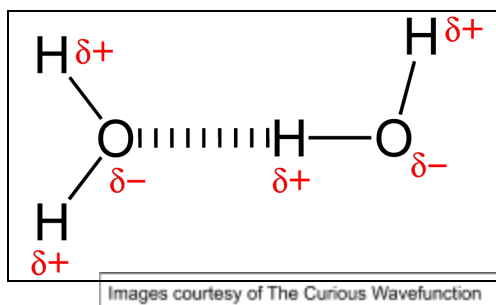
Example:



Hydrogen Bonding

Hydrogen bonds are the **strongest** type of intermolecular force. Hydrogen bonds only act between hydrogen and the three most electronegative atoms: **nitrogen, oxygen and fluorine**. The **lone pair** of electrons on these electronegative atoms forms a bond with the δ^+ hydrogen atom from another molecule. As seen in the diagram below, the hydrogen bond is often shown by a **dotted line**.

Example:



Molecules held together with hydrogen bonds have **much higher melting and boiling points** compared to similar-sized molecules without hydrogen bonding. This shows how the type of intermolecular force heavily influences the **physical properties** of a substance.

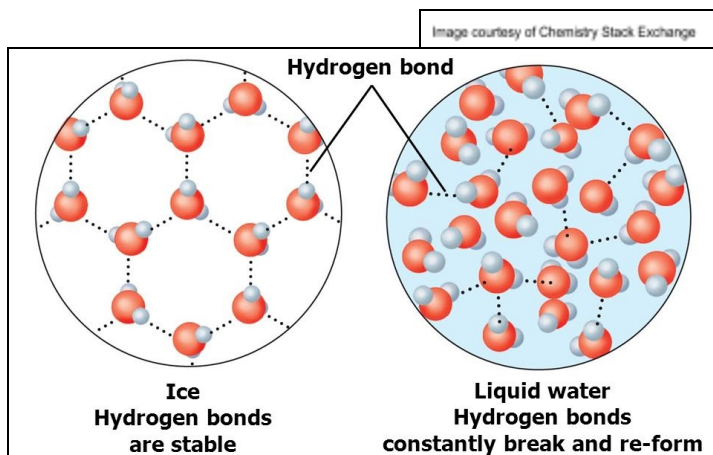
Water has a simple molecular structure but has **unusually high melting and boiling points** for the size of the molecule due to the presence of hydrogen bonds.

The hydrogen bonds in water also result in **ice** having a much **lower density** than liquid water, as they hold the molecules in a **rigid structure** with a lot of **air gaps**.



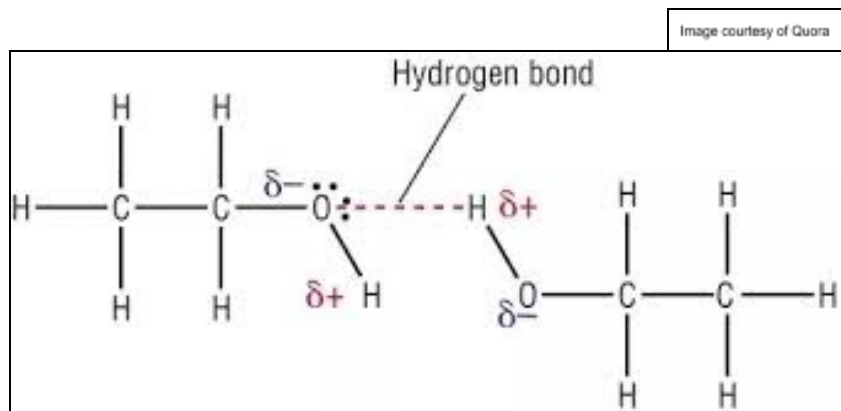


Example: Diagram indicating how the hydrogen bonds affect the density of ice



Hydrogen bonding is also why **alcohols** have **much higher boiling points** than alkanes with a similar Mr value. This is because the lone electron pair on the oxygen atom is able to form **hydrogen bonds** with a hydrogen atom on the hydroxyl group of a neighbouring alcohol molecule.

Example: Hydrogen bonds between ethanol molecules



This same property makes alcohols and water **good solvents** for compounds that are able to form hydrogen bonds in solution. However, alcohols and water can be poor solvents for dissolving some **polar molecules** such as halogenoalkanes which cannot form hydrogen bonds.

Kinetics

Activation Energy

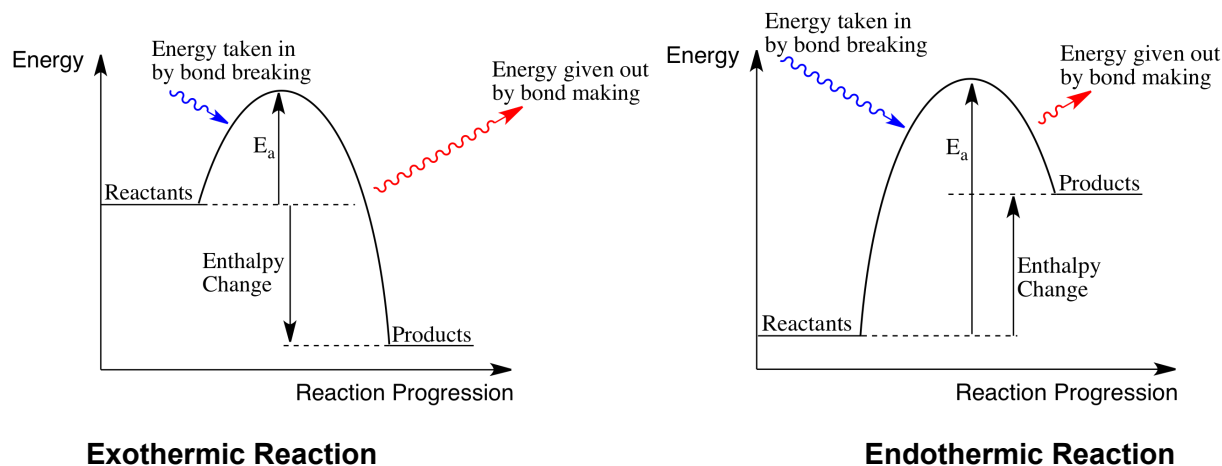
Activation energy is the **minimum energy** required for a reaction to take place between two colliding reactant particles.





Enthalpy changes are shown on an **enthalpy profile diagram**. **Activation energy** is the difference between the reactants and the top of the hump on an enthalpy profile diagram and is represented by the symbol E_a .

Example:



Rates of Reaction

Chemical reactions occur when reactant particles **collide**. For a reaction to occur successfully, these collisions must have energy greater than or equal to the **activation energy** of the reaction, and the **reacting particles' orientation** must be correct. The activation energy is the minimum amount of energy required for two particles to react.

The conditions of a reaction impact the collisions of the particles and can be altered to give the particles **more energy**. Therefore, the conditions can be changed to increase the likelihood of a collision occurring with **sufficient energy** to react. This will lead to a greater **rate of reaction**.

On a **concentration-time graph**, the rate of reaction is equal to the gradient of the curve at a given point. Therefore, the graph can be used to find the **rate** at a certain time by drawing a **tangent** to the curve at this given time and calculating the **gradient** of the tangent.

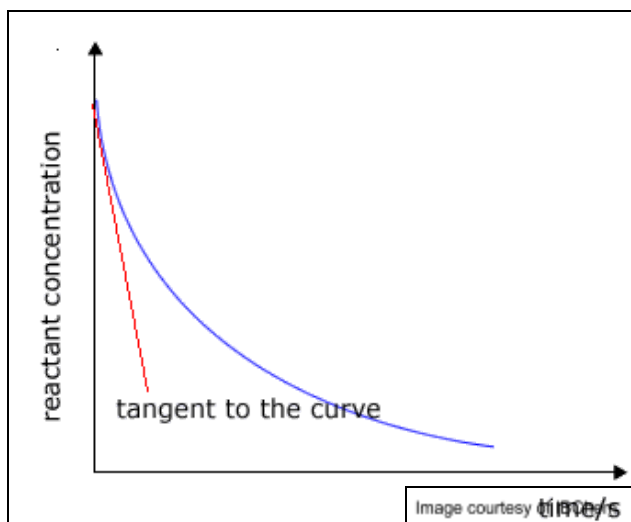
$$\text{Gradient} = (\text{change in } y) \div (\text{change in } x)$$

Drawing a **tangent** to the curve when **time = 0** finds the **initial rate** of reaction. The tangent at any other position finds the rate of reaction at that moment in time. The units of rate calculated in this way are generally **mol dm⁻³s⁻¹**.





Example:



Suitable **physical quantities** to **measure** to find the rate of a reaction include concentration, gas volume, and mass.

Effect of Concentration and Pressure

When the concentration of a species is increased, there are more molecules of the substance in the same volume, meaning they are **packed closer together**. Therefore, collisions between molecules become **more likely** and the probability of a collision occurring with energy greater than or equal to the activation energy increases. As a result, the rate of reaction increases.

Increasing the **pressure** of a gas has a similar effect as molecules are **packed closer together** into a smaller volume.

Effect of Temperature

When a substance is heated, **thermal energy** is transferred to it. This energy is converted to **kinetic energy** and the molecules of the substance move **faster and further**. Increased movement of the molecules means **collisions occur more often** and with **greater energy**. As a result, more collisions have energy greater than the activation energy and result in a reaction.

Therefore, **increasing the reaction temperature will increase the rate of reaction** as there are more frequent successful collisions.

Effect of a Catalyst

A catalyst is a substance that **increases the rate of reaction without being used up** in the reaction. It works by providing an **alternative reaction path** with a **lower activation energy**.

Catalysts are used in industry because they **lower the energy costs** of the reaction process. They allow lower temperatures and pressures to be used, whilst still achieving the same rate of reaction. They can also give a **higher atom economy**. Hence, they are economically important.

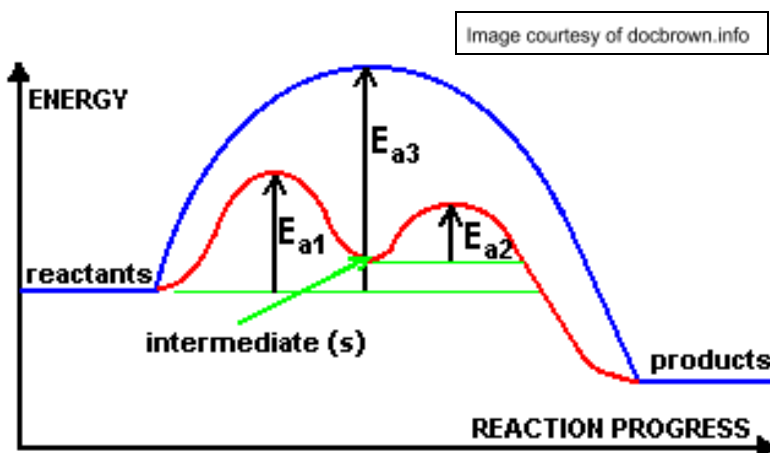




They also increase the **sustainability** of a reaction by lowering temperatures and reducing the energy demand from the combustion of fossil fuels. This results in a **reduction of CO₂ emissions**. These benefits to the environment of improved sustainability must be weighed against the negative effect of the toxicity of some catalysts.

The Reaction Profile of a Catalysed Reaction

The red line shows the pathway for a catalysed reaction, while the blue line shows the pathway for when the reaction occurs without a catalyst.



There is a **dip** in the **energy profile** for the catalysed reaction. This represents the **intermediate** formed during the reaction. The intermediate is **less stable** (and therefore higher in energy) than the reactants and products.

Homogeneous Catalysts

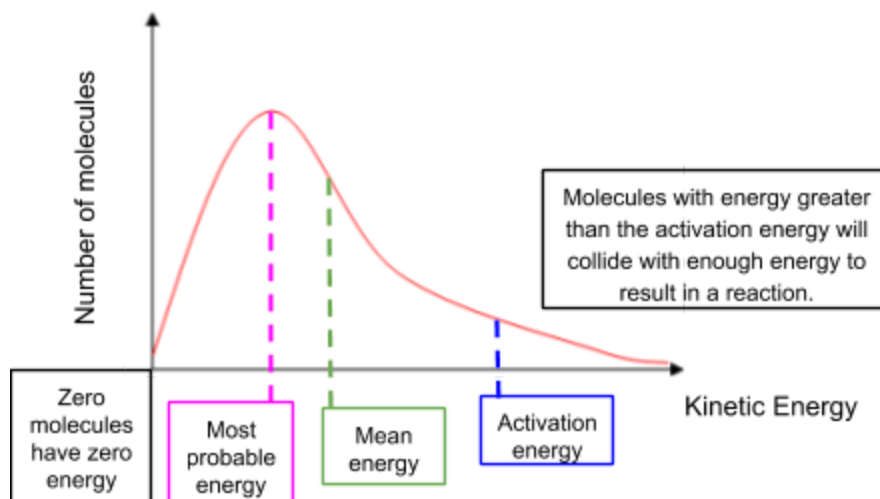
Homogeneous catalysts are catalysts that are in the **same phase** as the reactants and products.

The Boltzmann Distribution

Not all molecules in a substance have the same amount of energy. Their energies are **distributed** in a pattern called the **Maxwell-Boltzmann distribution**. This is a plot of the number of molecules against kinetic energy.

The **peak** is the **most probable energy** of a molecule. The **mean** energy is just to the right of this and divides the area below the graph into two equal halves. The curve is **asymptotic** - it doesn't quite reach the x axis. This is because there is no maximum value for the kinetic energy of a molecule.



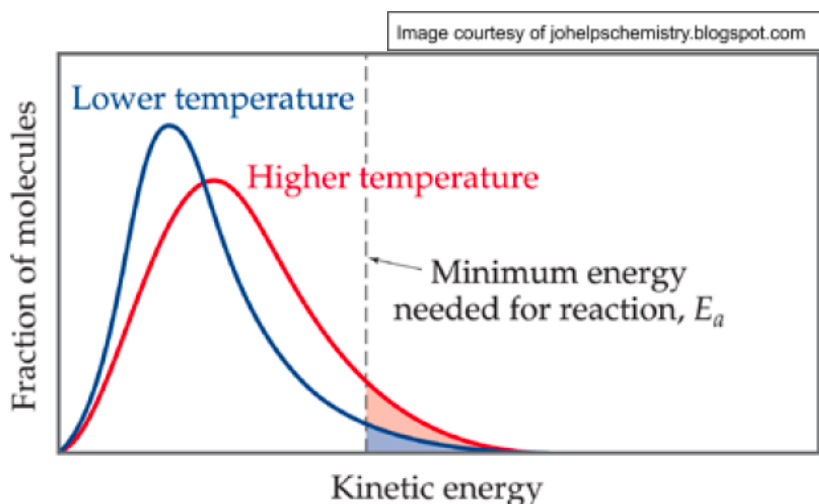


Changing the reaction conditions will **alter the shape of the curve**, because the number of particles with energy equal to or greater than the activation energy changes. The total **area under the curve** represents the **total number of molecules** in the sample, and so this area **must remain constant**.

Effect of Temperature

The Maxwell-Boltzmann distribution **shifts to the right** when the **temperature** is **increased** because a **greater proportion** of molecules have greater kinetic energy. As a result, a greater proportion of molecules will have energy greater than or equal to the activation energy.

Example:



Effect of Concentration, Pressure and Surface Area

Increasing the **concentration**, **pressure** or **surface area** of reactants means that successful collisions occur more frequently, however, the **energy** of the **individual particles is unchanged**. Therefore, the shape of the Maxwell-Boltzmann distribution **does not change**.

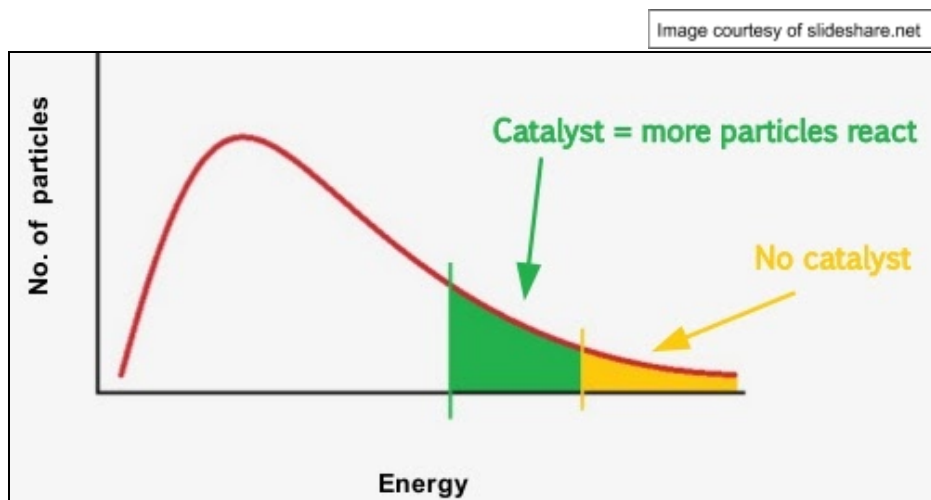




Effect of Catalysts

On the addition of a catalyst, the Maxwell-Boltzmann distribution curve is **unchanged in shape** but the **position of the activation energy is shifted to the left** so that a greater proportion of molecules have sufficient energy to react.

Example:



Inorganic Chemistry and the Periodic Table

Volumes of Gases

The **total volume** of a mixture of gases equals the **sum** of all of the individual partial volumes of the mixture.

Parts per million (ppm)

Concentration can be given in **parts per million (ppm)**. This gives the units of mass of that particular species within 1,000,000 total units of mass. It is most commonly used to represent the **concentrations of gases**.

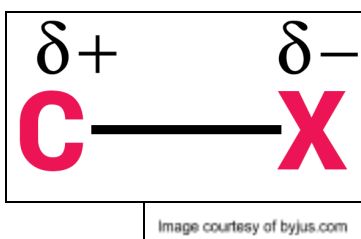
Organic Functional Groups

Introduction to Haloalkanes

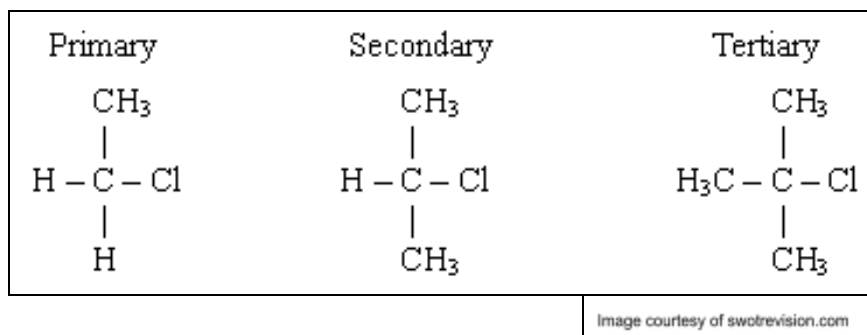
Haloalkanes contain **polar bonds** since halogen atoms are more **electronegative** than the carbon atom. This means electron density is drawn towards the halogen, forming **δ^+ and δ^- regions**.

Example: The electronegative carbon-halogen bond here X indicates the halogen atom.





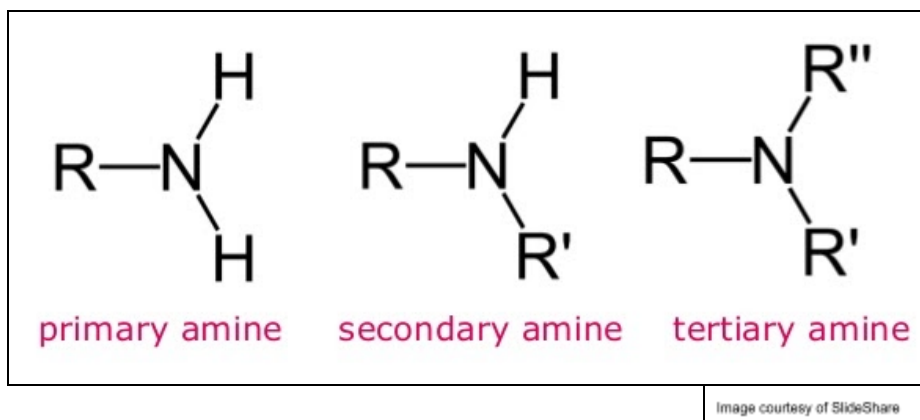
Haloalkanes can be classed as **primary, secondary or tertiary** haloalkanes depending on the position of the halogen within the carbon chain.



Introduction to Amines

Amines are produced when one or more of the hydrogen atoms in ammonia is **replaced with an alkyl group**. They can be classified as **primary, secondary or tertiary amines**, depending on how many alkyl groups are bonded to the nitrogen atom.

Example: Classification of amines



Organic Reactions

Relative Boiling Points of Haloalkanes





Van der Waals/induced dipole forces increase from fluoro- to iodo- haloalkanes due to the increase in the number of electrons. For the same reason, the boiling points also increase as the number of carbon atoms in the chain increases.

Relative Reactivity of Haloalkanes

Reactivity varies depending on the halogen present in the molecule. **Electronegativity** of the halogens **decreases down the group**, meaning that a carbon-fluorine bond is much more **polar** than a carbon-iodine bond. This polarity produces an electron deficient carbon atom which is what attracts the nucleophile in a nucleophilic substitution reaction. So you would expect the fluoroalkanes to be the most reactive.

However, the **greater the Mr** of the halogen in the polar bond, the **lower the bond enthalpy**. A lower bond enthalpy means the bond can be **broken** more easily. Therefore, the **rate of reaction actually increases** for haloalkanes as you move **down** the group, as the carbon-iodine bonds are the easiest to break.

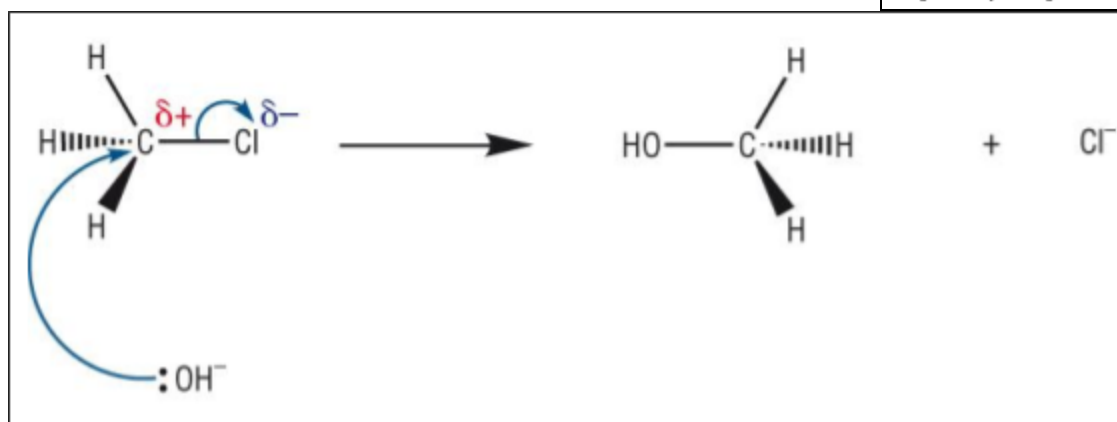
Nucleophilic Substitution Mechanism

Substitution - one functional group is **replaced** by a **different functional group**.

Nucleophile - an electron donor.

Nucleophilic substitution is the reaction mechanism that shows how **nucleophiles** attack haloalkanes. Haloalkanes can react with a variety of reagents to produce a variety of different products. Aqueous potassium hydroxide is used to produce **alcohols**, potassium cyanide is used to produce **nitriles** and ammonia is used to produce **amines**.

Mechanism - Producing Alcohols



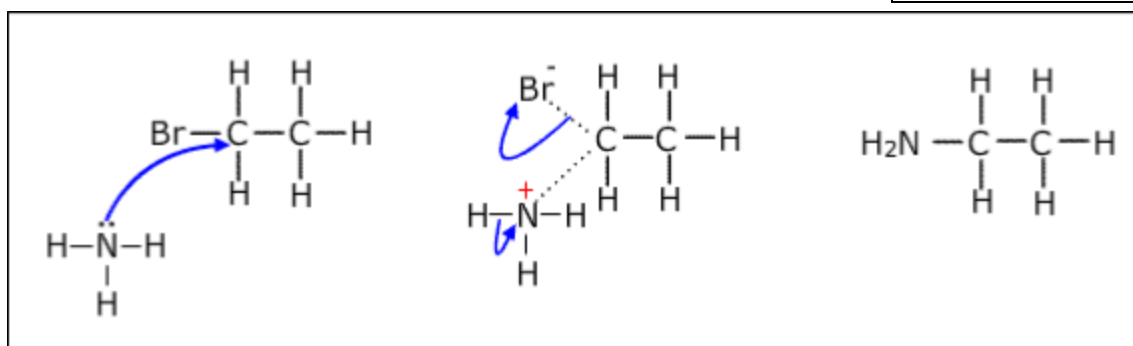
The nucleophile attacks the δ^+ carbon and the electrons are transferred to the chlorine.





Mechanism - Producing Amines

Image courtesy of IBChem.com



*The intermediate has a positively charged nitrogen (N^+).
Electrons are transferred to the nitrogen by the loss of a hydrogen atom.*

Breaking Bonds

In **homolytic fission**, each bonding atom receives one electron from the bonded pair, forming two **radicals**. Movement of one electron is shown by a single-headed curly arrow.



In **heterolytic fission**, one bonding atom receives both electrons from the bonded pair. This leads to the formation of a **positive and negative ion**. Movement of two electrons is shown by a double-headed curly arrow. Most mechanisms involve heterolytic fission.



A **radical** is a species with an unpaired electron. Radicals are represented by a dot, as shown above in the homolytic fission of Cl_2 .

Radicals

Alkanes react with halogens in the presence of **UV light** to produce **haloalkanes**. The UV light breaks down the halogen bonds (homolytic fission), producing reactive intermediates called **free radicals**.

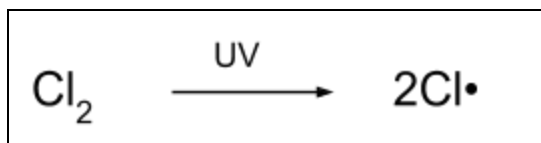
Free radicals are species containing an **unpaired electron** which is shown using a single dot. These attack the alkanes, resulting in a series of reactions: **initiation, propagation and termination**.





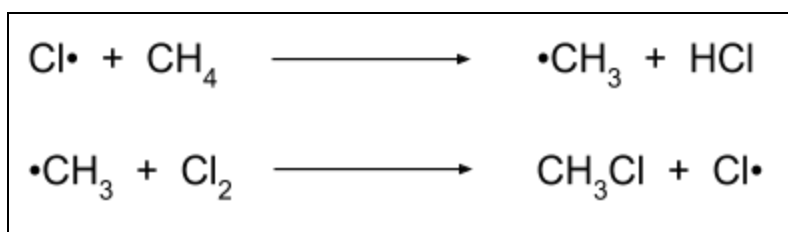
Example:

1. **Initiation** - the halogen is broken down.

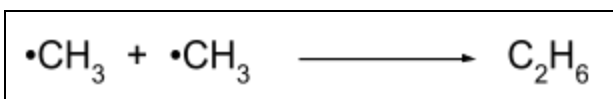


Free radicals are shown using a dot.

2. **Propagation** - a hydrogen is replaced and the $\text{Cl}\cdot$ radical is reformed as a catalyst.



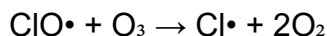
3. **Termination** - two radicals join to end the chain reaction and form a stable product.



The propagation step can continue many times to result in **multiple substitutions** - this is a **chain reaction**. The **conditions** of the reaction can be altered to favour the termination step and limit the number of substitutions, however, termination could also occur at different positions in the carbon chain. The nature of this reaction to produce **multiple products** limits its use in organic synthesis.

Environmental Impact of Haloalkanes

Ultraviolet (UV) radiation in the upper atmosphere can cause **CFCs** to produce halogen **radicals**. These radicals catalyse the breakdown of the Earth's protective **ozone** layer. CFCs are **chlorofluorocarbons** - haloalkanes containing carbon, hydrogen, chlorine and fluorine atoms only. The radical mechanism for the breakdown of ozone, O_3 , is shown below.



The overall equation for the breakdown of ozone: $2\text{O}_3 \rightarrow 3\text{O}_2$





The chlorine radical is **regenerated** in the second propagation step, so is **catalytic** in the breakdown of ozone. This means a small amount of CFC released can cause a lot of damage.

Sustainability

Most of the ozone in the atmosphere is found in the **stratosphere**. Humans rely on this ozone layer as it **absorbs ultraviolet rays**, which in excess can cause skin cancer and genetic damage. Ozone acts as a natural **sunscreen**. Ozone depletion is largely due to greenhouse gases and other pollutants being released into the atmosphere, including CFCs.

Photochemical smog is made by sunlight (this type of smog is more prevalent in sunny built-up cities) reacting with nitrogen oxides, other vehicle emissions and ozone.

Energy and Matter

The Electromagnetic Spectrum.

The **electromagnetic spectrum** (EM) is a range of radiation, the radiation with the smallest wavelength being gamma rays and the largest wavelength radio waves. The region of the EM spectrum being studied here includes: **ultraviolet, visible and infrared**.

Electrons orbitals have different energies, which **increase** as they move away from the nucleus. The most **stable arrangement** of electrons is in their lowest possible energy orbitals. However, electrons can be **promoted** from their lowest energy orbital to an empty higher level orbital when the correct energy of light is absorbed (usually ultraviolet or visible). This light must be the same energy as the **energy gap** between the orbitals.

The equation used to calculate the frequency using the energy of the wave is below:

$$E = h\nu$$

E- energy of the light

h- Planks constant

ν- frequency of the light

The equation used to calculate the wavelength using the frequency of the wave is below:

$$\lambda = c / \nu$$

λ- wavelength

c- speed of light

ν- frequency

