Chemistry (Chains, Energy & Resources)

Hydrocarbons

- The **Empirical formula** of a molecule is the simplest whole number ratio of its atoms
- The **Molecular formula** is the total number atoms in a molecule
- The **General formula** is the general algebraic formula for all molecules in a homologous series
- The **Structure formula** shows the arrangement of the atoms in a molecule through their symbols
- The **Display formula** shows the positions of the atoms in a molecule and the bonds connecting them
- The **Skeletal formula** shows the structure of a molecule while removing the hydrogen from chains
- A **homologous series** is a group of molecules that share the same functional group and differ each other by the number of carbons
- A **functional group** is a group of atoms responsible for the chemical properties of a molecule eg. OH or COOH
- First ten naming prefixes:

Prefix	**Number of Carbons in Chain**
Meth-	1
Eth-	2
Prop-	3
But-	4
Pent-	5
Hex-	6
Hept-	7
Oct-	8
Non-	9
Dec-	10

- **Structural isomers** are molecules that have the same number of atoms of each element but different structural formulas
- **Stereoisomers** are molecules with the same structural formula but different an arrangement in space
- An example of stereoisomers is E/Z isomerism

- E/Z isomerism occurs across a double bond because the bond can not rotate and so molecules with functional groups in different positions relative to the bond will react in different ways
- Cis-Trans isomerism is a specific type of E/Z isomerism in which the functional groups are the same
- A covalent bond can break in two ways:
  - In **Homolytic Fission** each atom gets one electron from the shared pair forming two radicals
  - In **Heterolytic Fission** one atom gets both electrons from the pair while the other gets none, forming a cation and anion
- A curly arrow is used to show the movement of electrons during these processes
- Atom economy can be calculated using the equation:

$$\frac{Mr\ of\ the\ desired\ products}{Sum\ of\ the\ Mrs\ of\ the\ products} \times 100$$

- Addition reactions have an atom economy of 100% whereas substitution reactions often have lower percentages
- Reactions with high atom economies are desirable as they have less waste to be disposed of
- Percentage yield and atom economy are different, one being high does not mean the other will

<u>Alkanes</u>

- A **hydrocarbon** is a molecule made mostly out of Carbon and Hydrogen
- Hydrocarbons are obtained from crude oil, which is separated via fractional distillation.
- Different lengths of carbon chain rise and fall to different areas in the tower so that different hydrocarbons can extracted
- Alkanes and cycloalkanes are saturated hydrocarbons, they have only single bonds
- Atoms bonded to a carbon make a tetrahedral shape
- As the length of the carbon chain increase so to does its boiling point, because with more atoms there are more electrons and so stronger Van der Waals' forces
- Octane is added to petrol
- Alkanes either combust completely or incompletely:
  - Complete combustion of alkanes
    - Occurs when alkanes burn in a plentiful supply of oxygen
    - Give off a lot of energy when burnt, therefore used as a fuel
    - Reacts to form CO_2 and H_2O

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(l)}$$

  - Incomplete combustion of alkanes
    - Occurs when alkanes burn in a limited supply of oxygen
    - Reacts to form H_2O and CO

$$C_8H_{18(l)} + 8\frac{1}{2}O_{2(g)} \rightarrow 8CO_{(g)} + 9H_2O_{(l)}$$

    - Carbon Monoxide (CO) is produced, it is an odourless, colourless gas
    - It is very toxic and causes the hemoglobin to not bind with oxygen, starving the tissues of oxygen, this can be fatal

            - Incomplete reactions of alkanes can occur due to faulty domestic heating systems
- Short alkanes are formed through cracking
    - Long chained alkanes are broken randomly, forming an alkene and an alkane
    - After fractional distillation there is too much long chain alkanes, because short chain alkanes are used in:
        - Fuels
        - Polymer production
    - **Catalysts** are used in the cracking to make it more efficient
        - Currently a zeolite catalyst is used at 450ºC
- The petroleum industry converts straight chained alkanes into branched and cycloalkanes
    - This is done because they are more efficient when combusted
    - Branched alkanes are produced through **Isomerisation**, where a straight alkane forms a branched isomer
    - Cycloalkanes and aromatic hydrocarbons (those containing benzene) are produced through reforming, where straight alkane is reacted to form a cyclic or aromatic hydrocarbon and hydrogen gas
- Fossil fuels are used to provide energy and raw materials however they also
    - Are unreliable or non-renewable, consequently we must develop renewable plant-based fuels
    - Increase the amount of CO_2 in the atmosphere when combusted, this leads to global warming
- A radical is a species with an unpaired electron
- In the presence of ultraviolet radiation or at 300ºC **halogens** and **alkanes** will react
    - This is the process of radical substitution
    - A hydrogen atom is substituted by a halogen atom
    - The reaction has the equation (where X is a halogen)

$$C_nH_{2n+2} + X_2 \rightarrow C_nH_{2n+1}X + HX$$

    - It has the following mechanism (eg. CH_4 & Cl_2)
        - **Initiation**
            - The Cl-Cl bond is broken by homolytic fission, forming two chlorine radicals
            - The energy is provided by ultraviolet light

$$Cl\text{-}Cl \rightarrow Cl^{\cdot} + Cl^{\cdot}$$

        - **Propagation**
            - In the first propagation step methane reacts with the the chlorine radical,

$$CH_4 + Cl^{\cdot} \rightarrow {}^{\cdot}CH_3 + HCl$$

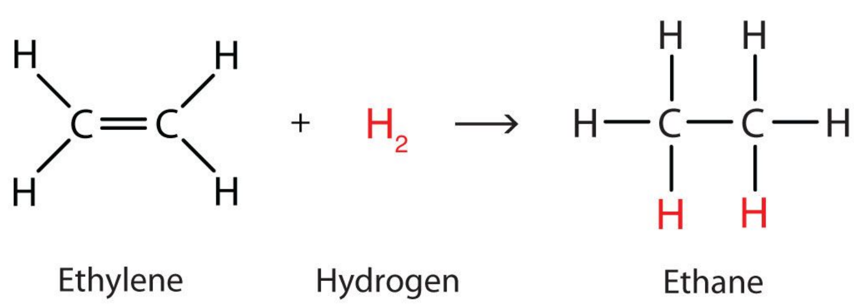
            - In the second propagation step the methyl radical reacts with chlorine

$${}^{\cdot}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$$

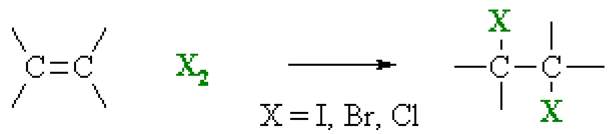
            - The propagation step will continue as a chain reaction, although a chlorine radical is used in the first step, another is formed in step 2
        - **Termination**
            - In this step two radicals combine to form a molecule
            - A number of different termination steps can occur as there are a large number of radicals that can form in the propagation step
    - Because of the number of propagation step possible and further substitution this process is unreliable when forming specific molecules

<u>Alkenes</u>

- Alkanes and cycloalkanes are unsaturated hydrocarbons, with one or more double bonds
- The double bond is made up of two parts
    - A sigma bond (**σ** bond) - Forms directly between the atoms by overlapping orbitals, each atom donates an electron
    - A pi bond (π bond) - Forms above and below the plane of the carbons atoms by sideways overlap of P-orbitals, each contributes one electron from a p-orbital to the electron pair
- Pi bonds fixes the carbons on each end of the bond, so that no rotation can occur
- In alkenes:
    - Three of each carbon's electrons are used to form three sigma bonds
    - One of each carbon's electrons is used to form one pi bond
- In a double bonded carbon:
    - Three regions of electron density surround each carbon, these repel so are at 120° from each other (largest distance)
- Alkenes typically take part in addition reactions, a small molecule added across the double bond, breaking the pi-bond
    - Two reactants form one product
    - Unsaturated hydrocarbon becomes a saturated molecule
- Addition of Hydrogen (**hydrogenation**)
    - A gaseous mixture is passed over a nickel catalyst is used at 150°C
    - Hydrogen adds across the double bond and an alkane is formed

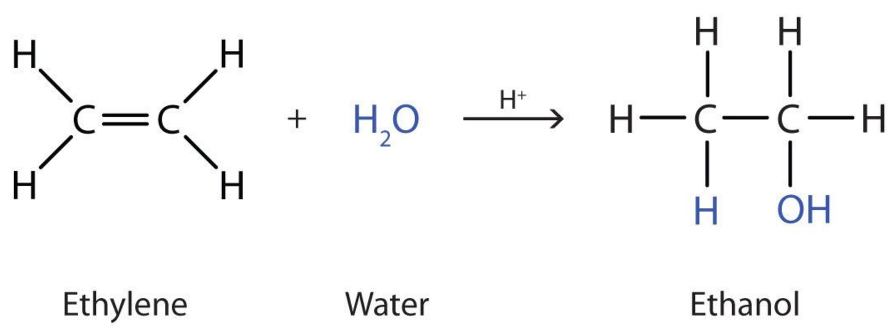


- Addition of halogens (**halogenation)**
    - The halogen adds across the double bond to give a di-substituted halogenoalkane

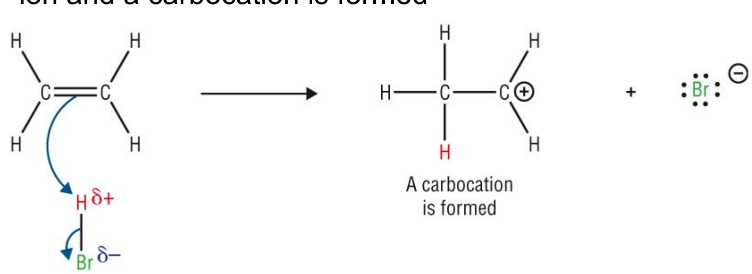


- When bromine is added to alkene the colour changes from orange to colourless,
- Used to test for saturation

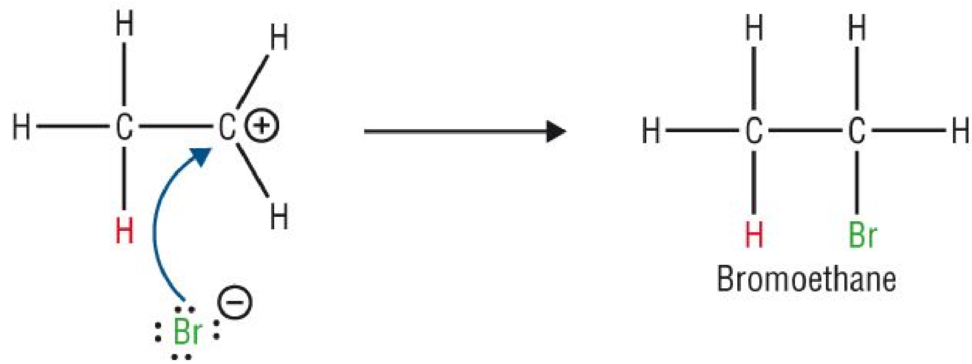
- Addition of Hydrogen Halides
    - Hydrogen halides add across the bond to produce a halogenoalkane
    - Hydrogen halides include HCl, HBr and HI
    - The gaseous hydrogen halides are bubbled through liquid alkenes
- Addition of Steam (**Hydration)**
    - Widely used in industry to produce alcohols
    - Steam and gaseous alkene are heated to a high temperature and pressure in the presence of a phosphoric acid catalyst



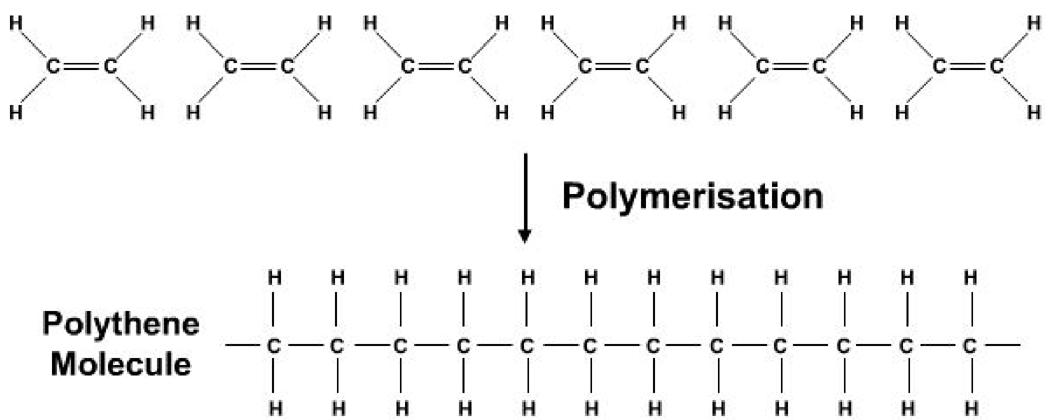
- Addition to unsymmetrical alkenes
    - A mixture of products will form each isomers of one and other
    - More of one product will be formed compared to the other
- An **electrophile** is an atom that is attracted to an electron-rich centre or atom, where it **accepts a pair of electrons** to form a new covalent bond
- **Electrophilic Addition (eg. hydrogen bromide)**
    - The hydrogen bromide has a dipole, $H^{\delta+}$-$Br^{\delta-}$
    - Electron pair in the π-bond is attracted to the δ+ of the hydrogen atom, causing the double bond to break
    - New bond forms between one of the carbon atoms and the hydrogen atom
    - The H-Br bond breaks by **heterolytic fission**, with the electron pair going to the bromine
    - A Br^- ion and a carbocation is formed



- The unstable carbocation reacts with the bromide ion to form an organic product



- In a non-polar molecule (eg. Br_2) the electrons in pi-bond induce a temporary diploe in the molecule and the above process occurs
- **Curly arrows** represent the movement of a pair of electrons
- Alkenes can be added together to form polymers, long chains of monomers (single alkenes)
    - Monomers are unsaturated, with a double bond
    - Addition polymers have saturated chains
- Addition polymers are made of one type of monomer only (eg. polyethene)



- Addition polymerisation occurs in two different processes
    - **Radical Polymerisation**
        - Requires high temperature and pressure
        - Leads to branching polymer chains and the production of polymer mixtures
    - **The Ziegler-Natta Process**
        - Requires a specialist catalyst, eg. $TiCl_3$ and $Al(C_2H_5)_2Cl$ at 60°C
        - The alkene is passed over the catalyst, the conversion is low so the unreacted alkene is recycled, repeating the process
        - Most common process for forming non-branched polyethene
- Alkenes are used in the production of margarine
    - The oils are hydrogenated, hydrogen put across their double bonds

    - This solidifies the oil, by altering the number of double bonds that are hydrogenated how hard the margarine is can be changed
    - Partial hydrogenation can cause **cis** double bonds to become **trans**, these are thought to be more unhealthy
    - Because hydrogenation is used a nickel catalyst is used
- Teflon is formed from a tetrafloroethene monomer
- Recycling of polymers involves two stages
    - **Sorting**
        - Different polymers must be separated otherwise they will contaminate samples
        - Identification codes are used to show the type of polymer in the object
    - **Reclamation**
        - The objects are chopped into flakes and washed to remove impurities
        - The flakes are melted down, turned into pellets and remoulded
- Polymers can be burnt to produce heat, from this electricity is produced
- A process is being developed to convert polymers into hydrogen and carbon monoxide, these could then be used to make other useful organic molecules
- **PVC** is dangerous to recycle by heating as HCl is formed, a new method is used to dissolve the PVC in a solvent and then precipitate it out
- **Bioplastics** are plastics that are biodegradable or compostable
    - Decompose into carbon dioxide, water, inorganic compounds and biomass
    - Supermarket bags are made of plant starch
    - Disposable tableware made from sugar cane fibre
    - Cold-drink cups made from lactic-acid

<u>Alcohols</u>

- Alcohols have a relatively high melting and boiling point because of hydrogen bonds between the alcohol molecule
    - This causes the molecules to have a lower volatility than alkanes with a similar Mr
- Alcohols dissolve in water because of the hydrogen bonds and the polar water molecule
    - Solubility decrease as chain length increases because
        - A larger part of the alcohol molecule is made up of the non-polar carbon chain
        - The carbon chain does not form hydrogen bonds with the water
- Alcohols can be put into three groups
    - **Primary Alcohols**
        - The -OH group is bonded to a carbon with no or one alkyl group
    - **Secondary Alcohols**
        - The -OH group is bonded to a carbon with two alkyl groups bonded onto it
    - **Tertiary Alcohols**
        - The -OH group is bonded to a carbons with three alkyl groups bonded onto it
- Ethanol is made in one of two ways

- **Hydration of Ethene**
  - Ethene and steam are passed through a phosphoric acid (H_3PO_4) catalyst
  - This is done at a 300°C and 60 atm

    $$H_2C{=}{=}{=}CH_{2\,(g)} + H_2O_{\,(g)} \rightarrow CH_3CH_2OH_{\,(l)}$$
  - The reaction is reversible so only 5% is converted, the rest is recycled, overall 95% conversion
- **Fermentation**
  - Carbohydrates (often glucose) converted into ethanol by yeast
  - The reaction slows below 25°C and the enzymes begin to denature above 37°C
  - The concentration of alcohol is limited to 14% as above this the yeast dies because of the toxicity
  - Must occur in the absence of oxygen as the process is anaerobic

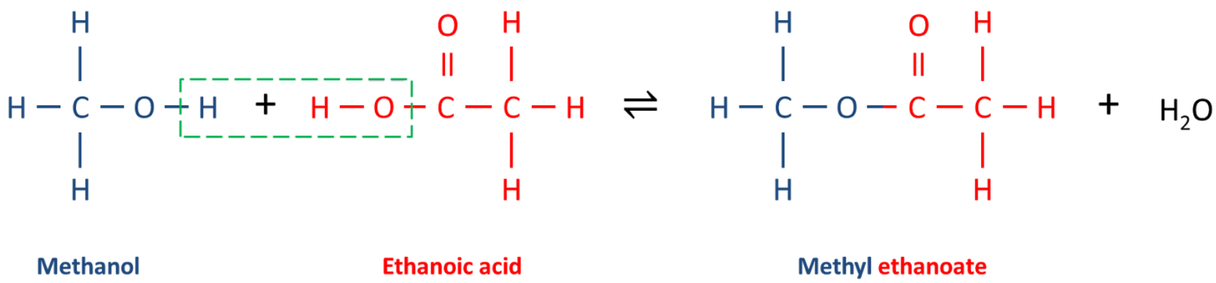
    $$C_6H_{12}O_{6\,(aq)} \rightarrow 2CH_3CH_2OH_{\,(aq)} + 2CO_{2\,(aq)}$$

- Uses of ethanol
  - Used in alcoholic drinks
  - Added to petrol to increase the octane rating, makes it cleaner burning
    - Made from renewable resources
  - Mixed with methanol and a dye, toxic and exempt from tax so is less expensive than ethanol, used for:
    - Burning in camp stoves
    - As a solvent for paint and ink stains
- Uses of Methanol
  - Used as a clean burning fuel, added to high-performance cars
  - Highly toxic
  - Feedstock of the chemical industry, used to make ethanoic acid and methanal
- Combustion of alcohols
  - In a plentiful supply of oxygen alcohols burn to give carbon dioxide and water

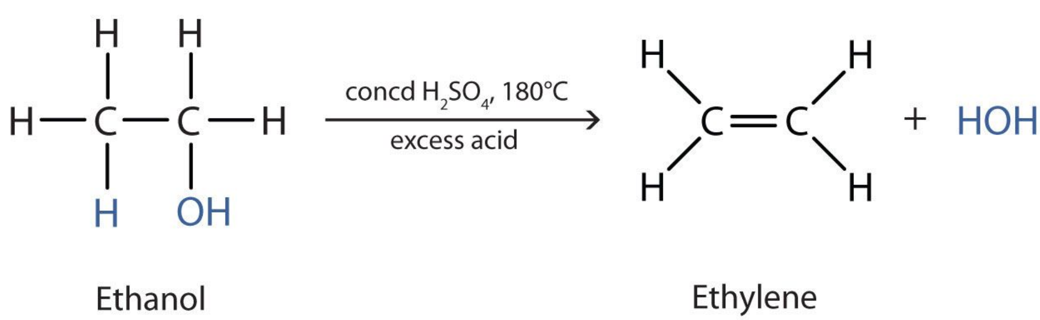
    $$C_2H_5OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{(l)}$$
- Oxidation of Alcohols
  - Primary and Secondary alcohols can be oxidised using an oxidising agent
  - A suitable agent is a solution containing acidified dichromate ions ($H^+/Cr_2O_7^{2-}$)
  - Oxidising mixture made from potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4)
  - During the reaction the acidified potassium dichromate changes colour from orange to green
- Oxidation of **Primary Alcohols**
  - Gentle heating, using distillation will form an aldehyde and water
  - Stronger heating, using **reflux** will form a carboxylic acid and water, the aldehyde formed above is oxidised
  - The oxidising agent will go green
- Oxidation of **Secondary Alcohols**
  - Only ketones and water are produced

- The oxidising agent will turn green
- Further heating has no effect

- Oxidation of **Tertiary Alcohols**
  - Tertiary alcohols do not oxidised
  - The oxidising agent remains orange
- **Esterification**
  - Alcohol is warmed with a carboxylic acid in the presence of an acid catalyst
  - Concentrated sulphuric acid is often used
  - The O-H bond in alcohol is broken during and water is formed



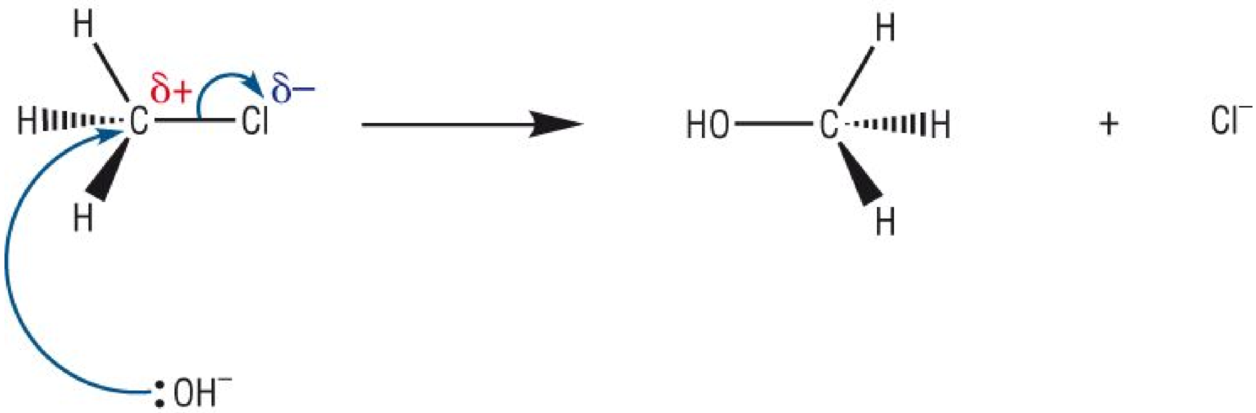
- **Dehydration of Alcohol**
  - When an alcohol is heated with an acid catalyst it will form an alkene and water
  - This is an elimination reaction
  - Concentrated phosphoric acid (H_3PO_4) or concentrated sulfuric acid (H_2SO_4) are suitable acid catalysts
  - The alcohol is heated for about 40 minutes under reflux



<u>Halogenoalkanes</u>

- **Nucleophile -** An atom that is attracted to an electron-deficient centre or atom, where it donates a pair of electrons to form a new covalent bond
- Because of the dipole in the carbon-halogen bond nucleophiles (eg. H_2O, OH^- & HN_3) are attracted to the electron-deficient carbon atom
- **Nucleophilic Substitution Reactions**
  - An atom or group of atoms is replaced by a nucleophile
- **Hydrolysis of halogenoalkanes**
  - When halogenoalkanes react with an aqueous solution of hot hydroxide ions under reflux, an alcohol is formed

- ○ The OH^- ion has a lone pair of electrons, these are attracted and donated to the electron-deficient carbon atom in the halogenoalkane, this is nucleophilic attack
- ○ The donation of the electron pair leads to a covalent bond forming between the oxygen and the carbon
- ○ The carbon-halogen bond breaks by heterolytic fission, both electrons going to the halogen forming a halide ion



- ○ This is a **nucleophilic substitution** - A substitution in which a nucleophile donates a pair of electrons to an electron-deficient centre or atom, forming a covalent bond
- ○ Aqueous sodium hydroxide is often used but any aqueous hydroxide is suitable

$$CH_3CH_2CH_2CH_2Cl_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3CH_2CH_2OH_{(aq)} + Cl^-_{(aq)}$$

- The rate of hydrolysis can be determined by:
    - ○ The halogenoalkane is heated with aqueous silver nitrate and ethanol
        - ■ Water is the nucleophile
        - ■ Ethanol is the common solvent, ensuring that the reactants mix
    - ○ In the hydrolysis reaction halide ions form
    - ○ These then reacts with the silver nitrate and form a precipitate
    - ○ The rate is calculated by 1/time taken for the precipitate to form
    - ○ For the experiment
        - ■ Heat to 50ºC
    - ○ Two factors **affect the rate of hydrolysis**
        - ■ **Polarity**
        - ■ **Bond Enthalpy**
    - ○ Bond enthalpy is **more** important than polarity
    - ○ The rate **increase** as you move down the group
- **Teflon, PTFE** (polytetrafluoroethene)
    - ○ Uses a tetrafluoroethene CF_4 monomer
    - ○ Strong carbon-flourine bonds
    - ○ Chemically inert, resistant to chemical attack
- **PVC, (Polyvinyl Chloride) or Polychloroethene**
    - ○ Uses a chloroethene monomer
- **CFCs (Chlorofluorocarbons)**

- Used in refrigeration, aerosols and air-conditioning
- Inert and non-toxic
- Causes environmental damage to the ozone layer, they are being phased out of use
- Being replaced by HCFCs (hydrochlorofluorocarbons) about ten times less effective on the ozone layer

Modern Analytical Techniques

- **Infrared Spectroscopy**
  - When molecules absorb infrared radiation they vibrate
  - How much they vibrate depends on
    - The bond strength
    - The bond length
    - The mass of each atom involved in the bond
  - Most bonds vibrate at frequencies between 300 and 4000 cm^{-1}
  - Most organic molecules produce a peak at 3000 cm^{-1} due to the absorption of C-H bonds
  - In modern breathalysers ethanol is measured on the breath using infrared spectroscopy
- **Mass Spectrometry**
  - Uses:
    - Determining the relative atomic mass of an element
    - Identifying elements, on space probes and measuring pollution levels
  - A mass spectra is a graph showing percentage abundance on the y-axis and mass:charge on the x-axis
    - Mass:charge is shown as m/z, m is the mass and z the charge
    - Each peak is an isotope
  - The molecular ion (M^+) is the positive ion formed in mass spectrometry when a molecule loses an electron
    - M^+ is the peak with the largest m/z value
    - Read the m/z to find the molecular mass of the molecule being tested
  - Excess energy from the process can cause the bonds to vibrate and break, this is fragmentation, these fragment ions are also detected by the mass spectrometer

$$C_2H_5OH^+ \longrightarrow CH_3 + CH_2OH^+$$

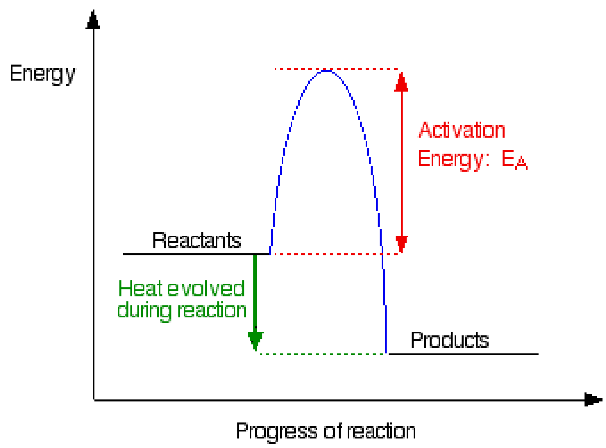
  - Isomers can be identified from fragmentation patterns, although M^+ will be the same different fragments will form
  - The mass spectrum is unique to each molecule and can be used to query a database, to identify the molecule

Enthalpy Changes

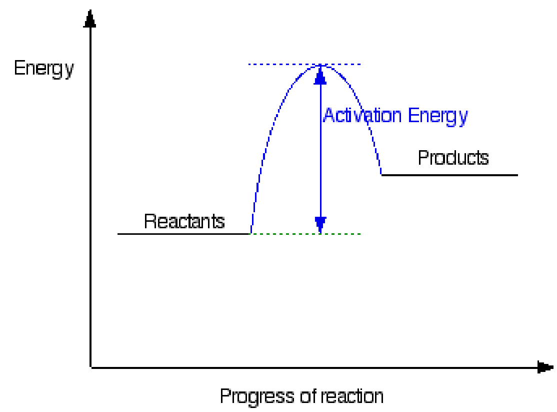
- **Enthalpy (H) -** is the heat content that is stored in a chemical system
- No energy is lost in a system, the ΔH is equal to the heat released
- Reaction can be **endothermic** or **exothermic**

- **Endothermic** - A reaction in which the enthalpy of the products is greater than the enthalpy of the reactants, resulting in heat being taken in from the surrounding (ΔH +ve)
- **Exothermic** - A reaction in which the enthalpy of the products is less than the enthalpy of the reactants, resulting in heat being lost to the surroundings (ΔH -ve)

- The oxidation of fuels is an exothermic reaction, in both the combustion of fuels and respiration of sugars
- Endothermic reactions require heat energy to be inputted
  - eg. The thermal decomposition of calcium carbonate
  - The products have a higher enthalpy than the reactants
- Activation energy is the energy required to break the bonds in the reactants to begin the reaction



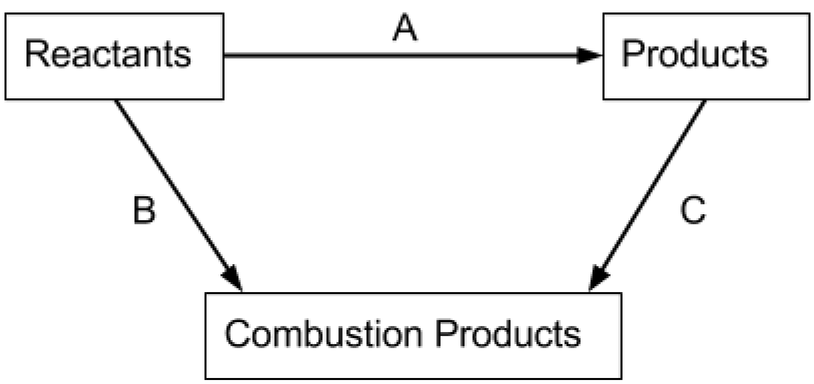
Exothermic Reaction



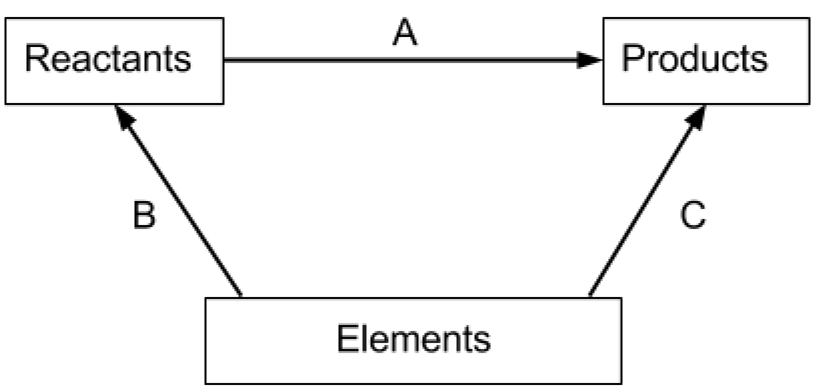
Endothermic Reaction

- **Standard Conditions ($^{\ominus}$) are:**
  - **100 kPa** of pressure
  - **298K** (25°C) is usually used
  - a concentration of 1 mol dm^{-3} (for aqueous solutions)
- **Standard States**
  - For a standard enthalpy change any substance must be in its standard state
  - The standard state is the state the substance is in at standard conditions
- **Standard Enthalpy Change of Reaction ($\Delta H_r^{\ominus}$)**
  - Is the enthalpy change that accompanies a reaction in the molar quantities of the equation, under standard conditions, all products and reactants in the standard states
- **Standard Enthalpy Change of Combustion ($\Delta H_c^{\ominus}$)**
  - Is the enthalpy change that takes place when one mole of a substance reacts completely with oxygen, at standard conditions and states
- **Standard Enthalpy Change of Formation ($\Delta H_f^{\ominus}$)**
  - Is the enthalpy change that takes place when one mole of a compound is formed from its constituent elements, at standard conditions and states
  - The $\Delta H_f^{\ominus}$ of an element is defined as 0 KJ mol^{-1}

- The energy required to heat a substance is given using the formula:
  - **$E = mc\Delta T$**
- Breaking bonds is an endothermic reaction
- Making bonds in an exothermic reaction
- The **difference** between the energy inputted to break the bonds and the energy outputted in forming new bonds is the **enthalpy change in the reaction.**
- **Bond Enthalpy** - The enthalpy change that takes place when breaking by homolytic fission 1 mol of a given bond in the molecules of a gaseous species
- **Average Bond Enthalpy** - The average enthalpy change that takes place when breaking by homolytic fission 1 mol of a given type of bond in the molecules of a gaseous species
- **Hess' Law** - If a reaction can take place by more than one route and the initial and final conditions are the same, the total enthalpy change is the same for each route
- Sometime it is not possible to measure the enthalpy change for a reaction, for example if
  - There is a high activation energy
  - It is a slow reaction
  - If more than one reaction occurs
- When using $\Delta H_c^{\ominus}$ values



  - A + C = B
  - ∴ A = B - C
- Using $\Delta H_f^{\ominus}$ values

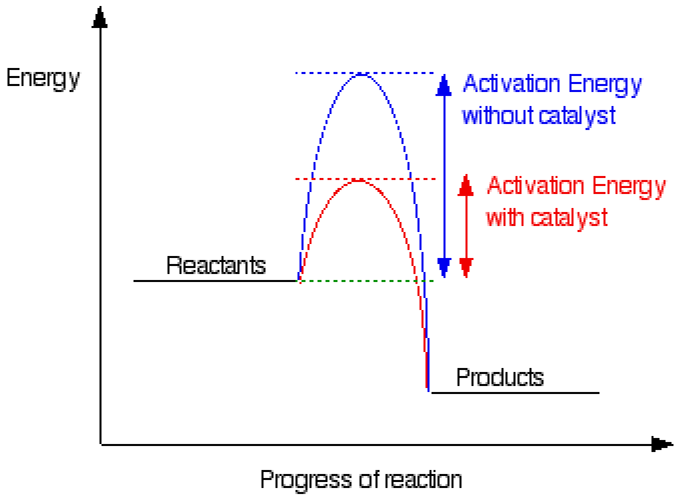


  - B + A = C

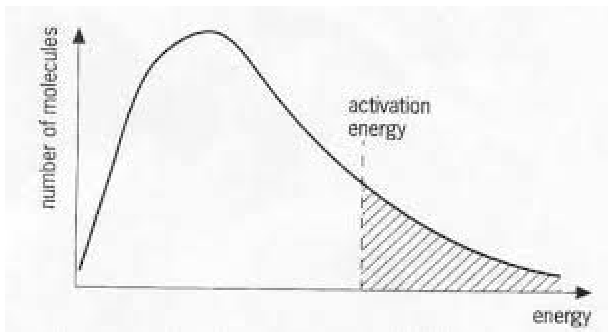
- ∴ A = C - B

Rates and Equilibrium

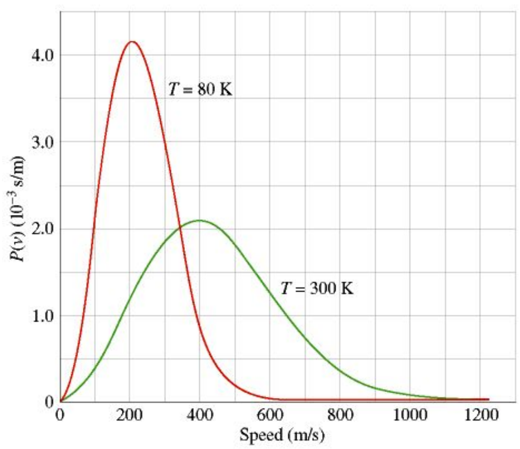
- Factors that affect the rate of a chemical reaction
    - Temperature
    - Pressure (in gaseous reactants)
    - Concentration
    - Surface area
    - Adding a catalyst
- An **increase in concentration** increases the rate of a reaction
    - Means more molecules in a given volume
    - Closer molecules means a greater chance of collisions
    - Collisions more frequent so more with energy greater than activation energy
- An **increase in pressure** increases the rate of a reaction
    - Same number of molecules occupy a smaller volume
    - For a gaseous reaction increasing pressure is the same are increasing concentration
- A **catalyst** speeds up a reaction without being consumed by the overall reaction
- Examples of catalysts:
    - **Iron** in the Haber process for NH_3 production
    - $\mathbf{V_2O_5}$ in the contact process within H_2SO_4 production
    - **Ni** in the hydrogenation of margarine
- Catalysts:
    - Enable reactions to occur at lower temperatures, less fossil fuels used
    - Enable different reactions to be used that may have better atom economies
    - Are often enzymes, generating specific products and operating at room temperature and pressure
    - Important in processes
        - Iron in the haber process
        - Ziegler-Natta catalyst in the production of polyethene
        - Platinum/ palladium/ rhodium in catalytic converters
    - Catalysts lower the activation energy of a reaction



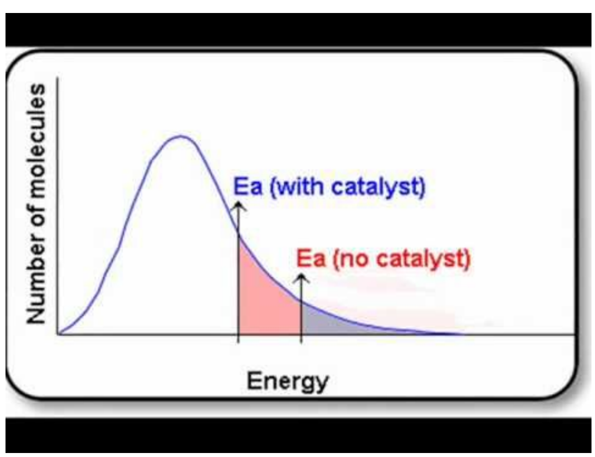
- **Heterogeneous Catalysis -** The catalysis of a reaction in which the catalyst has a different physical state from the reactants, often a solid catalyses a gaseous reaction
- **Homogeneous Catalysis** - The catalysis of a reaction in which the catalyst and reactants are in the same state
- The **Boltzmann distribution** is the distribution of energies of molecules at a particular temperature, often graphed
- The area under the curve is the number of molecules in the sample
- No molecules have zero energy, so the line passes through the origin
- Molecule with energies greater than E_a react



- With an increase in temperature, more molecules have energies larger than E_a



- With a catalyst E_a is lowered so more molecules are above it



- **Dynamic Equilibrium** - Is the equilibrium that exist in a closed system when the rate of the forward reaction is equal to that of the backward reaction
  - The concentration of reactants and products remains the same
- **Le Chatelier's Principle** - When a system in dynamic equilibrium is subject to change, the position of equilibrium will shift to minimise the change
  - Increase in pressure equilibrium will change so there are fewer molecules
- A catalyst will not alter the equilibrium, just increase the rate of the reaction
- In the chemical industry compromise is important
  - Compromise between rate of reaction and yeild

<u>Chemistry of the Air</u>

- In greenhouse gases (H_2O, CO_2 & CH_4) infrared radiation is absorbed by the bonds
  - In water the O-H bond
  - In carbon dioxide the C=O bond
  - In methane the C-H bond
- This absorption causes the bonds to vibrate
- The molecule then emits this energy as infrared radiation
- The global warming effect of a molecule is based on its
  - Concentration in the atmosphere
  - How able it is at absorbing infrared radiation
- The **Global Warming Potential (GWP)** of a gas is how able the gas is to cause global warming
  - Based on lifetime in the atmosphere
  - effectiveness at absorbing infrared radiation
- Climate change must be controlled because:
  - Rivers will flood due to increased rainfall and melting glaciers
  - Drought and disease cause disastrous harvest
  - Storms and hurricanes are becoming more extreme
  - Floods due to rising sea levels
- Role of chemists
  - Should provide evidence that global warming is occurring
  - Monitor the progress towards governmental targets (eg. the Kyoto Protocol)
  - Investigate solutions
- **Carbon Capture Storage (CCS)**
  - Captures CO_2 from power stations and stores it safely in old oil fields or porous rock
  - Decarbonised fuel
    - Hydrogen is used as a clean fuel
    - Formed by:

$$CH_{4\,(g)} + 2H_2O_{(l)} \rightarrow CO_{2\,(g)} + 4H_{2\,(g)}$$

    - The carbon dioxide would be collected and stored
- Storage as carbonates
  - Carbon dioxide reacts with metal oxide eg.

$$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)}$$

  - For the reaction to be fast enough to be economically viable a lot of energy is required
- **Ozone (O_3)**
  - Close to ground, harmful to animal's respiratory systems
  - In Stratosphere, protects organisms from UV radiation reaching them
  - Ozone layer is about 10 to 50 km up
    - Absorbs shorter wavelength UV radiation
- Types of UV
  - **UV-A**
    - Less energetic than other types
    - Does not cause much harm
    - About 5% absorbed by ozone layer
  - **UV-B**
    - Less energetic than UV-C but more so than UV-A
    - Causes sunburn and long term exposure can cause cancer
    - About 95% absorbed by ozone layer
  - **UV-C**
    - Highly energetic
    - Entirely screened by the ozone layer
- **Formation of ozone**
  - O_2 absorbs high energy UV forms 2O atoms

$$O_2 + (\text{radiation} < 240\text{nm}) \rightarrow 2O$$

  - O atoms react with O_2

$$O_2 + O \rightarrow O_3 + \text{HEAT}$$

- **How the Ozone Layer Absorbs UV**
  - Ozone absorbs UV and forms O_2 and O atom

$$O_3 \rightarrow O_2 + O$$

  - The O atom immediately reacts with an O_2 to form O_3 and heat

$$O_2 + O \rightarrow O_3 + \text{HEAT}$$

  - The overall effect is that the UV is converted into heat
  - The reactions that occur are the forward and backward reactions of

$$O_2 + O \rightleftharpoons O_3$$

- **Removal of Ozone**
  - The reaction for ozone removal is

$$O_3 + O \rightarrow 2O_2$$

  - The rate of this is low as the concentration of O atoms is low
- Chlorine radicals disturb the oxygen-ozone balance
  - Chlorine radicals are released by human activity
  - Chlorine radicals are mainly produced from CFCs and only form with extremely energetic UV radiation
  - When UV strikes a CFC molecule the C-Cl bond breaks

$$CFCl_3 \rightarrow Cl\bullet + \bullet CFCl_2$$

  - The radicals react with O_3

        - $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
        - $ClO\bullet + O \rightarrow Cl\bullet + O_2$
        - Overall reaction: $\{O_3 + O \rightarrow 2O_2\}$
    - A single CFC molecule can destroy 100 000 ozone molecules
- Another radical is Nitrogen Oxide •NO, from lightning and aircraft engines
    - The radicals react with O_3
        - $\bullet NO + O_3 \rightarrow \bullet NO_2 + O_2$
        - $\bullet NO_2 + O \rightarrow \bullet NO + O_2$
        - Overall reaction: $\{O_3 + O \rightarrow 2O_2\}$
- In general for radicals (where R is Cl• or •NO)
    - $\bullet R + O_3 \rightarrow \bullet RO + O_2$
    - $\bullet RO + O \rightarrow \bullet R + O_2$
- **Carbon Monoxide (CO)**
    - Toxic, bonds with haemoglobin, reduces the amount of oxygen to organs
        - Causes drowsiness, reduced dexterity and an inability to perform complex tasks
    - Can exist in the atmosphere for about a month before being oxidised into CO_2
    - Formed from incomplete combustion of hydrocarbons
        - From traffic (esp. in urban areas)
- **Oxides of Nitrogen (NO_x)**
    - Are respiratory irritants
    - In atmosphere form nitric acid and low level ozone
    - Formed in combustion engines
        - In high heat of cylinders the nitrogen in air is oxidised by oxygen in the air
        - NO and NO_2 are formed
- **Unburnt Hydrocarbons**
    - **Volatile Organic Compounds (VOC)** are released in vehicle exhausts usually from unburnt fuel
    - Benzene and buta-1,3-diene are human carcinogens
    - Unburnt hydrocarbons react with nitrogen oxides to form low-level ozone
        - Causes breathing difficulties and increase susceptibility to infection
        - Energy for this reaction comes from sunlight
- **Catalytic Converters** are fitted to engines to convert harmful gases into less harmful ones
- There are two types
    - **Oxidation** - Fitted to diesel engines, reactions are:
        - $2CO + O_2 \rightarrow 2CO_2$
        - $C_{12}H_{26} + 18\frac{1}{2}O_2 \rightarrow 12CO_2 + 13H_2O$
    - **Three-Way Catalyst** - Fitted to petrol engines
        - The reaction is:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

        - NO and CO diffuse over the catalytic surface of the metal, some molecules are held in place by absorption

        - **Absorption** - A gas, liquid or solute is held to a solid's surface
            - Temporary bonds form between the surface and gas molecules these hold the molecules in the correct position on the surface to react
            - After they react the molecules deabsorb and diffuse away
            - Bonds must be weak enough for absorption and deabsorption but strong enough to hold the molecules and weaken the bonds
- Infrared spectroscopy is used to monitor the amount of pollutants in the air

<u>Green Chemistry</u>

- Suitability is developing processes to prevent the depletion of natural resources
- Chemists should develop processes
    - That use fewer chemicals
    - That use no hazardous chemicals
    - With high atom economy
    - Using renewable resources
    - That use alternative energy sources (eg. solar)
    - Ensure that no waste products are toxic and are recyclable and biodegradable
- Apparent benefits from a process may be negated by unexpected side effects
- Hazardous chemicals can spread across the world so many countries sign international agreements to stop their production