Equilibrium

Chemical Systems:

Open and Closed Systems:

An open system is a system that freely exchanges energy and matter with its surroundings.

- ➔ Matter can be exchanged simply by adding or removing matter.
- ➔ Energy can be exchanged via:
  - Heat
    - Energy can be induced through heat by bringing the system close to an object that dissipates heat.
  - Work
    - Carrying out any action against another force in the system.

A closed system is a system that exchanges only energy with its surroundings, not matter.

Non-Reversible and Reversible Systems:

Non-reversible reactions occur when reactions form products and these products cannot be converted back into the reactants.

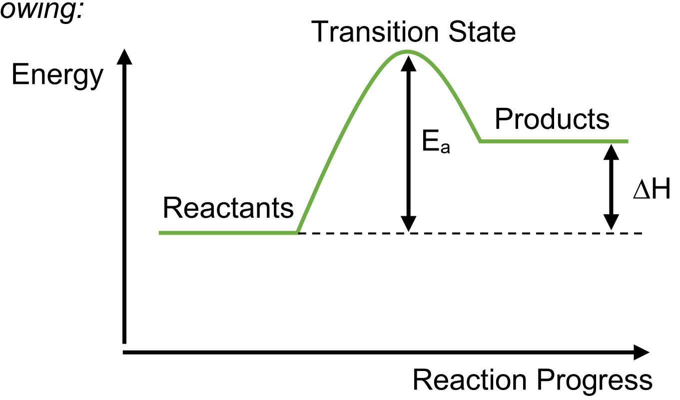
- ➔ Hence, these reactions only occur in one direction.
  - These reactions often occur in open systems, which allows matter and energy to be exchanged with the surroundings.

Reversible reactions come about when the reactants are in a constant state of forming products, whilst the products are in a constant state of re-forming the reactants.

- ➔ This is owing to the fact that product molecules collide with one another, and a chemical reaction that re-forms the reactants can take place.

Energy Profile Diagrams and Reversibility:

Consider the following:



The diagram above shows the energy profile diagram of an endothermic reaction.

- ➔ If we were to reproduce a mirror image of this diagram, it would show the reaction to be exothermic.
  - Therefore, if a forward reaction is exothermic or endothermic, then the reverse reaction must be endothermic or exothermic respectively.
    - To calculate the activation energy of the reverse – exothermic – reaction: $\textit{Activation Energy for the Endothermic Reaction} - \textit{magnitude of } \Delta H$

Dynamic Equilibrium:

The Dynamic State of Equilibrium:

Dynamic equilibrium occurs when the reaction rate of the forward reaction is equal to the reaction rate of the reverse reaction.

- ➔ Reactants are converted to products and products are converted to reactants at an equal and constant rate.
  - This does not mean, however, that the concentrations of reactants and products are equal.

Equilibrium is a state of equal and opposite rates but not equal concentrations.

The Extent of Reaction:

Not all reactions proceed to the same extent.

- ➔ Weak acids such as ethanoic acid, are good examples of reactions that reach equilibrium without any significant formation of product.
  - Almost all of the ethanoic acid molecules remain unreacted whilst only 1% of the molecules react with water to form hydronium.

$$\boxed{\mathbf{CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}}}$$

- ➔ Strong acids such as hydrochloric acid highlights the types of reactions that proceed to a significant extent.
  - Almost all hydrochloric acid molecules will react with water to form hydronium.

$$\boxed{\mathbf{HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}}}$$

The Equilibrium Law:

The Reaction Quotient and Equilibrium Constant:

The reaction quotient, *Q*, measures the relative amount of products and reactants present during a reaction at a particular point in time.

- ➔ *Q* functions in tandem with the *K* value to determine what direction a reaction is likely to proceed.

Q differs from the *K* value because it describes a reaction that is not at equilibrium, unlike *K*, which describes a reaction at equilibrium.

- ➔ However, the expression for both *Q* and *K* are the same.

The Expression for the Equilibrium Law:

$$\boxed{\mathbf{aA + bB \rightleftharpoons cC + dD}}$$

$$\boxed{\boldsymbol{Q = K = \frac{[C]^c[D]^d}{[A]^a[B]^b}}}$$

Note**: the equilibrium constant and reaction quotient only shows components in the gaseous or aqueous states.

The *K* value also stays constant with constant temperature.

Equilibria in Heterogeneous Reactions:

The difference between heterogeneous and homogenous reactions in terms of the *K* value is that pure liquids and solids have a fixed value of 1 in the *K* value expression.

Equilibrium Constants:

Q > K ; K < 1	The reaction favours the reactants; if Q > K, then this indicates that there are more products then there would be at equilibrium. LCP says that this is partially opposed, hence, the equilibrium shifts to favour the reverse reaction.
Q < K ; K > 1	The reaction favours the products; if Q < K, then there are more reactants than products at equilibrium, hence, the forward reaction is favoured according to LCP.
Q = K	The reaction is already at equilibrium and there is no tendency to form more reactants or products – there is no shift in equilibrium.

Changes to an Equilibrium System:

Le Chatelier's Principle:

"If an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change"

Adding a Reactant or Product:

If a chemical system is at equilibrium and we add a substance, the reaction will shift so as to reestablish equilibrium by consuming part of the added substance.

Conversely, removal of a substance will result in the reaction moving in the direction that forms more of the substance.

Adding a pure solid or pure liquid will not affect the equilibrium, as it would not make the reaction consume the added solid or liquid.

- ➔ If solid sodium chloride is at equilibrium with a saturated solution of sodium chloride, adding more pure sodium chloride will not cause additional dissolving.
- ➔ Removal of some of the solid sodium chloride which is at equilibrium with the saturated solution of sodium chloride will not cause further crystallizing of sodium chloride from the saturated solution.

Changing the Volume by Addition of Solvent:

Changing the volume effectively changes concentration – adding a solvent is essentially a dilution.

If the number of solute species on the reactant side is not the same as the product side, then volume changes can cause a shift in equilibrium.

- ➔ Increasing the volume favours the reaction with the lowest molecularity (sum of stoichiometric species for one side of the reaction).
  - Increasing the volume will cause the system to shift in the direction that increases the number of solute species. as

Changing the Pressure by Changing the Volume:

Pressure is inversely proportional to volume.

- ➔ If volume is decreased and subsequently the pressure is increased, the equilibrium will shift to the side of the equation that has few moles of substance, and hence lower pressure.

Volume ▲ = Pressure ▼= favours the side with the most gaseous molecules

Volume ▼ = Pressure ▲= favours the side with the least gaseous molecules

  - The *K* value stays constant because temperature is constant, hence it must return to its original level when equilibrium is reestablished.

Changing the Pressure by Adding an Inert Gas:

Adding an inert gas will increase the total pressure of the equilibrium system because the sum of the partial pressures will increase.

- ➔ However, it will not affect the rate nor the position of the equilibrium because the particle spacing remains the same.

Dilution:

When a solution is diluted, the reaction will go in the direction that will form the greater amount of particles

Changing the Temperature:

Temperature is a measure of average kinetic energy.

- ➔ As the temperature increases, the average kinetic energy of the particles increases.
  - This means that there will be an increased number of particles who are able to overcome the activation energy for a particular reaction.
    - Hence, the number of successful collisions increases.
  - Furthermore, because: $\boldsymbol{E_k = \frac{1}{2}mv^2}$, as the average kinetic energy increases and mass stays constant, the velocity of the particles must increase.
    - Hence, the number of collisions per second will increase as particle movement becomes faster and more rapid.

Temperature ▲ = favours the reaction that will decrease temp = endothermic

Temperature ▼ = favours the reaction that will increase temp = exothermic

The Influence of a Catalyst on an Equilibrium:

Catalysts are substances that increase the likelihood of successful collisions.

- ➔ They do this by offering an alternative pathway with lower activation energy for the reaction to occur, without getting consumed in the process.

Catalysts do not affect the equilibrium, however, it will increase the rate

Haber Process:

Raw Materials:

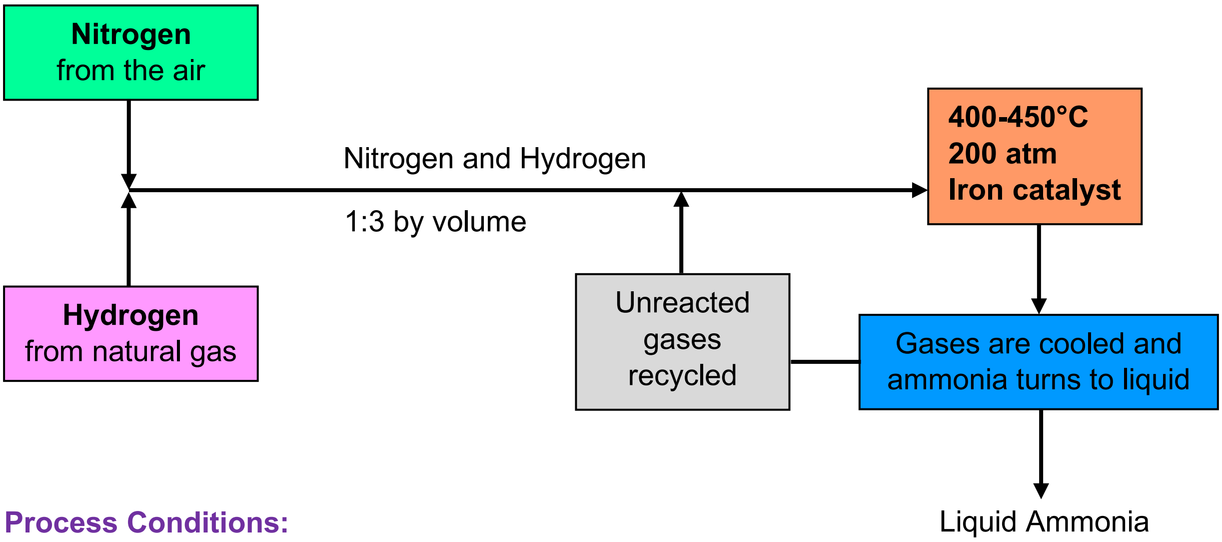
The Haber process requires nitrogen and hydrogen which react to form ammonia.

- ➔ The nitrogen comes from the air.
- ➔ The hydrogen is mainly derived from natural gas (methane).

Sometimes companies may decide to choose an excess of one of the reactants, to ensure another reactant is completely used up, perhaps due to it being expensive.

- ➔ However. If you have an excess of one of the reactants there is nothing for it to react with.
  - This wastes reactor space – particularly space on the surface of the catalyst.
    - Hence, only the proportions of 1:3 should be used for this reaction.

Process Flowchart:



Process Conditions:

To maximize the amount of ammonia produced, the equilibrium should be shifted as far right as possible. According to Le Chatelier's Principle (LCP), if the temperature is decreased the system will partially counteract this by favouring the forward reaction relative to the reverse and hence, more heat and yield is produced.

- ➔ A low temperature is ideal to optimize the amount of ammonia yield.

However, the lower the temperature used, the slower the reaction becomes. Ammonia decomposes more at higher temperatures and it would take a very long time to obtain a yield, even though it may have a very high proportion of ammonia.

- Hence, a compromise temperature of 400-450C is used, in conjunction with an iron catalyst to produce less yield, but at a higher rate → less product in a shorter time will give more product overall in a day.

There are 4 gas molecules on the left of the equation, and 2 on the right. According to Le Chatelier’s Principle, if we increase the pressure of the system the system will partially counteract this by favouring the side which produces fewer gas molecules – the right relative to the reverse.

- High pressures should be used to optimize the amount of ammonia yield.

However, although increasing the pressure will increase the number of particles collisions per unit volume and increasing their change of sticking to the surface where the catalyst acts, it is very expensive to produce high pressures. It is expensive to maintain and produce and also expensive equipment is required to withstand the high pressures.

- 200 atmospheres is the compromise temperature chosen on economic grounds.

Adding a catalyst does not impact the position of the equilibrium, rather, it provides an alternative reaction pathway with lower activation energy, which increases the number of successful collisions and hence, increases the reaction rate.

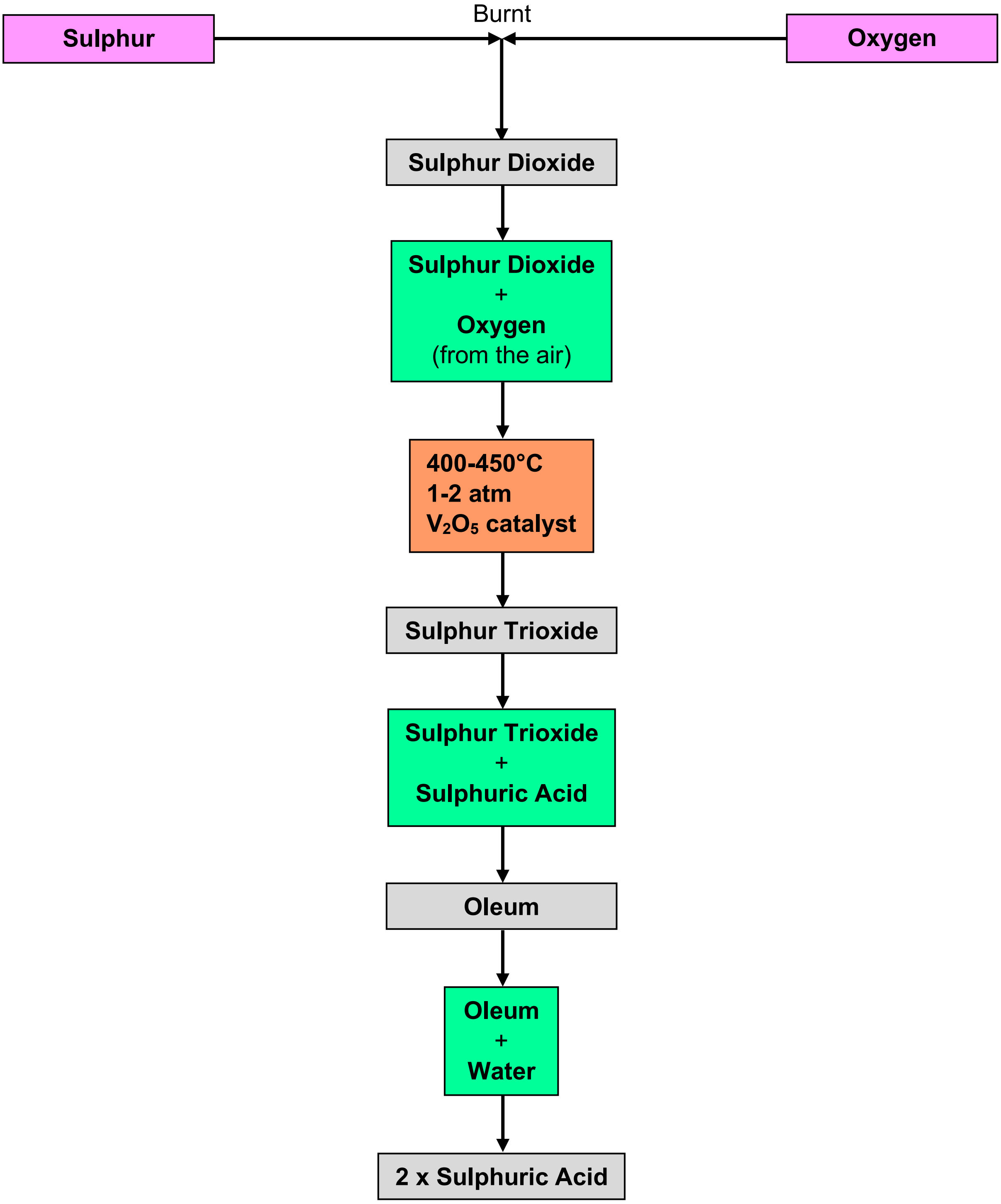
- Add more of the reactants.
- Remove the products as they form.
- Set and maintain pressure as necessary to produce a greater yield.
- Set and maintain temperature as necessary to produce the optimum yield.
- Use a suitable catalyst.

Contact Process:

Raw Materials:

Requires the sourcing of oxygen in air and sulphur, which is burned in the air.

Process Flowchart:



Reactions:

1. **Making sulphur dioxide:**

This can be done by burning sulphur in an excess of air.

- ➔ An excess of air is used so that the sulphur dioxide that is produced is already mixed with oxygen for the next stage of the Contact Process.

$$\boxed{\mathbf{S_{(l)} + O_{2(g)} \rightleftharpoons SO_{2(g)}}\ \Delta H=-196\text{kJ/mol}}$$

  - Molten sulphur is sprayed into the gaseous oxygen gas; this increases surface area and collisions.

2. **Converting sulphur dioxide into sulphur trioxide:**

Sulphur dioxide is oxidized to sulphur trioxide at high temperatures.

$$\boxed{\mathbf{2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}}}$$

3. **Converting sulphur trioxide into oleum, then sulphuric acid:**

This cannot be done simply by adding water. The reaction with sulphur trioxide and water is uncontrollable and creates a fog of sulphuric acid.

- ➔ The sulphur trioxide is instead dissolved in concentrated sulphuric acid.

$$\boxed{\mathbf{SO_{3(g)} + H_2SO_{4(l)} \rightleftharpoons H_2S_2O_{7(l)}}}$$

  - This process occurs under a variety of compromise conditions.

- ➔ Oleum (the product) can be reacted safely with water to produce concentrated sulphuric acid.
  - It produces twice as much sulphuric acid as originally used.

$$\boxed{\mathbf{H_2S_2O_{7(l)}} + \mathbf{H_2O_{(l)}} \rightleftharpoons \mathbf{2H_2SO_{4(aq)}}}$$

Process Conditions:

To get the maximum amount of sulphur trioxide, the equilibrium needs to be shifted as far right as possible. This reaction is exothermic, so according to Le Chatelier's Principle, if we decrease the temperature the system will partially counteract this imposed change and increase the heat produced, favouring the forward reaction relative to the reverse.

However, the lower the temperature used, the slower the reaction becomes. We want the gases to reach equilibrium within the very short time that they will be contact with the catalyst later.

- ➔ Hence, a compromise temperature of 400-450C is used.

There are three molecules on the left of the equation and two on the right. According to Le Chatelier's Principe, if the pressure is increased the system will favour the side which produces the least gaseous molecules – the forward reaction will be favoured relative to the reverse, producing more sulphur trioxide.

However, although increasing the pressure will increase the number of particles collisions per unit volume and increasing their change of sticking to the surface where the catalyst acts, it is very expensive to produce high pressures. It is expensive to maintain and produce and also expensive equipment is required to withstand the high pressures.

- ➔ 200 atmospheres is the compromise temperature chosen on economic grounds.

Adding a catalyst does not impact the position of the equilibrium, rather, it provides an alternative reaction pathway with lower activation energy, which increases the number of successful collisions and hence, increases the reaction rate.

- ➔ The catalyst ensures that the reaction is fast enough for a dynamic equilibrium to be set up within the very short time that the gases re actually in the reactor.

Carbon Dioxide in Nature:

Carbon Dioxide in the Atmosphere and Ocean:

Due to Greenhouse Gas emissions, the levels of carbon dioxide in our oceans is steadily rising.

- ➔ The carbonate ion content of the sea is important for the growth of coral reefs in Australian waters.

The formation of carbonate ions from carbon dioxide is shown by:

$$\boxed{\mathbf{CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + 2H^+_{(aq)}}}$$

Coral body is built from calcium carbonate when the carbonate ions combine with calcium ions in water.

$$\boxed{\mathbf{CO_{2(aq)} + Ca^{2+}{}_{(aq)} \rightleftharpoons CaCO_{3(s)}}}$$

Living coral polyps have a calcium carbonate skeleton and when they die these skeletons form part of the growing reef.

- ➔ Typically, sea water is slightly alkaline, with a pH of about 8.2 but as more CO_2 is absorbed as acidity rises, the carbonate/ hydrogen carbonate equilibrium is affected:

$$\boxed{\mathbf{HCO_3^-{}_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H^+_{(aq)}}}$$

As the ocean gets more acidic – this means the concentration of H^+ is increasing – the reverse reaction is favoured relative to the forward.

- ➔ This would remove carbonate ions from the water.
  - This stunts the growth of coral crops and the ability for coral polyp skeletons to form.

Coequally, with the rise of sea temperatures, the metabolism of polyps increases, thus increasing the growth of the coral reefs; we are yet to see what process comes out on top.

Acids and Bases

The Bronsted-Lowry Model:

Changing Ideas about the Nature of Acids and Bases:

Throughout the 18th century, acids and bases were defined on the basis of their constituent elements.

- ➔ Lavoisier hypothesized acidic properties to be due to the presence of oxygen.
  - This didn't explain why HCl was an acid.
- ➔ Davy later suggested that acid properties were associated with hydrogen and not oxygen.
  - This conclusion came about following an experiment between acids and metals to produce hydrogen gas.
    - Davy further suggested that acids react with bases to form salts and water.

In 1887, Arrhenius defined acids and bases as follows:

- ➔ Acids are substances that ionize in solution to produce hydrogen ions.
- ➔ Bases dissociate in solution to produce hydroxide ions.

The Bronsted-Lowry Model of Acids and Bases:

Essentially;

- ➔ Acids are proton donors.
- ➔ Bases are proton acceptors.

Unlike the Arrhenius theory, acid-base reactions were not restricted to aqueous solutions in the Bronsted-Lowry theory.

- ➔ A reaction between two gases can be an acid-base reaction too.

The Bronsted-Lowry theory is flawed in that it cannot be applied to the reaction between acid and basic oxides.

- ➔ Under certain conditions, for example, calcium oxide – a basic oxide – reacts with gaseous carbon dioxide – an acidic oxide – to produce the salt calcium carbonate.

Common Acids and Bases and their Strength:

Strong Acids	Weak Acids	Strong Bases	Weak Bases
Hydrochloric acid	Ethanoic acid	Sodium hydroxide	Ammonia
Sulphuric acid	Carbonic acid	Potassium hydroxide	Methylamine
Nitric acid	Phosphoric acid	Calcium hydroxide	
Hydrobromic acid	Hydrofluoric acid	Barium hydroxide	
Chloric acid	Hydrocyanic acid	Oxide ion	
	Hydrogen sulphate ion		

Conjugate Acid-Base Pairs:

Consider the following:

$$\mathbf{HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}}$$

- ➔ Because Cl^- can be formed from HCl by the loss of a single proton, it is called the conjugate base of HCl – this is because it is able to accept a proton to reform the HCl.
  - Similarly, HCl would be described as the conjugate acid of Cl^-.
    - HCl/ Cl^- are a conjugate acid-base pair – they differ by a proton.

Acidity of Solutions:

Amphiprotic Acids:

Some substances can donate or accept protons, depending on what they are reacting with.

- ➔ Therefore, they can behave as either acids or bases; they are amphiprotic.
  - Water is the most common amphiprotic substance, followed by HCO_3^- and HPO_4^{2-}
    - If the solute is a stronger acid than water, then water will react as a base.
    - If the solute is a stronger base than water, then water will react as an acid.

Polyprotic Acids:

Acids that can donate more than one proton from each molecule are said to be polyprotic.

- ➔ H_2SO_4 is a common polyprotic acid; it can donate two protons; hence, it is termed a diprotic acid more specifically.

Hydrolysis of Salts:

1. Strong Acid + Strong Base:
- ➔ A neutral solution will be produced.
  - Salt and water are produced, the cation and anion of the salt is not capable of hydrolyzing – it shows no acid-base properties.
2. Strong Acid + Weak Base:
- ➔ An acidic solution will be produced.
  - Salt and water are produced however, the cation is able to donate a proton and acts an acid.
  - The anion will show no acid-base properties – cannot hydrolyze.
3. Strong Base + Weak Acid:
- ➔ A basic solution will be produced.
  - Salt and water are produced however, the anion is able to accept a proton and acts as a base.
  - The cation will show no acid-base properties – cannot hydrolyze.
4. Weak Acid + Weak Base:
- ➔ We are unable to analyze the pH of the solution because there will be competing hydrolysis between the cation and anion.
  - The K value for each is needed to determine what dominates.

Forms an Acidic Solution	Sodium Hydrogensulphate, Sodium Dihydrogenphospate

Forms a Basic Solution	Sodium Hydrogencarbonate,

Acidity of Solutions:

Water molecules can self-ionize to a very small extent due to its amphiprotic nature.

- ➔ It will produce one hydronium ion for every hydroxide ion.

pH of Solutions:

the range of H^+ concentrations in solution is so great that the pH scale was developed to measure acidity. The pH of a solution is defined as:

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

This can be rearranged to give:

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

- ➔ The pH of a solution decreases as the concentration of hydrogen ions increases.

The ionization constant of water is defined as $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ at 25°C.

- ➔ If the temperature is not 25°C, then the value of K_w increases as the temperature increase.
  - This is due to the fact that the self-ionization of water is an endothermic equilibrium reaction.

The pH of pure water is only 7 at 25°C.

- ➔ It is misleading to believe that the pH of a neutral solution has a pH of 7.
  - A neutral solution is defined as when the hydronium and hydroxide ion concentrations are equal.

Acidity Constants:

- ➔ The lower the pK_a value, the stronger the acid.
  - The pK_a value allows you to compare acid strength and also base strength.
    - It is important to note that the stronger the conjugate acid, the weaker the conjugate base.

Indicators:

Indicators are either weak acids or weak bases.

- ➔ In solution, the acid form of the indicator is in equilibrium with its conjugate base:

$$\boxed{HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}}$$

  - The position of the equilibrium changes depending on the pH.
    - The colour of an acid form of an indicator and the colour of its conjugate base are different.

Bromothymol Blue	Acidic = yellow (0-6) ; Neutral = green (7) ; Basic = blue (7.6-14)
Methyl Orange	Acidic = red (0-3.1) ; Basic = yellow (4.4-14)

Phenolphthalein	Acidic = colourless (0-8.3) ; Basic = purple (8.3-14)

Buffers:

Understanding Buffers:

Buffer solutions are able to resist a change in pH when small amounts of acid or base are added.

A buffer consists of a mixture of either a weak acid and its weak conjugate base or a weak base and its weak conjugate acid.

- ➔ A buffer solution can be prepared by simply mixing the two together.
  - For example, ethanoic acid/ sodium ethanoate.

Buffer Capacity:

Buffer capacity is a measure of effectiveness of a buffer solution to resist a change in pH when either a strong acid or strong base is added.

- ➔ A buffer will reach a point where the addition of a strong acid or strong base consumes all the ions and the buffer system is no longer effective.
  - The buffer capacity is the greatest when:
    - There is a high concentration of the weak acid and its conjugate base.
      - ■ This means that the buffer requires more acid/ base to deplete the buffer.
    - The concentrations of the acid and its conjugate base are equal.
      - ■ This is because for the buffer to function in optimal capacity, pH = pKa.

Volumetric Analysis

Methods of Volumetric Analysis:

Primary Standards:

A pure substance whose concentration is known with a great precision.

- ➔ The substance must be so pure that the amount of substance, in moles, can be calculated accurately from their mass.
  - A primary standard should:
    - Be readily obtainable in pure form.
    - Have a known chemical formula.
    - Be easy to store without deteriorating or reacting with the atmosphere.
    - Have a high molar mass to minimize the effect of errors in weighing.
    - Be inexpensive.

Substances that are hydroscopic/ deliquescent cannot be used as primary standards as they absorb moisture from the atmosphere.

Standard Solutions:

A solution with an accurately known concentration. These are prepared by:

- ➔ Dissolving an accurately measured mass of a primary standard in an accurately measured volume or water, or
- ➔ Performing a titration with another standard solution in order to determine its exact concentration.

Preparing a Standard Solution from a Primary Standard:

1. Weigh the pure primary standard on an electric balance.
2. Transfer the solid into the volumetric flask using a clean, dry funnel.
3. Rinse any remaining solid particles into the flask using distilled water.
4. Half-fill the flask with distilled water, stopped and swirl vigorously to dissolve the solid, turn it upside-down too.
5. Add distilled water up to the calibration line on the on the neck of the flask.
    - The bottom of the meniscus of the solution of the solution should be on the mark when viewed at eye-level.
6. Stopper and shake the solution to ensure an even concentration throughout.

Your standard solution is now ready for titration.

Direct Titrations:

Volumetric analysis involves reacting a measured volume of a standard solution with a measured volume of another solution of unknown concentration.

The solutions are mixed until they have jut reacted completely in the mole ratio indicated by the balanced chemical equation.

- ➔ The equivalence point = the point at which the solutions have reacted completely in their mole ratio indicated by the balanced chemical equation.
- ➔ The end point = the point at which the indicator changes colour, denoting when chemical equivalence has been reached.

To perform a titration:

1. A known volume of one of the solutions is measured using a pipette.
    - This is then transferred into a conical flask.
        - The fixed volume of solution transferred by pipette is called an aliquot.
2. A few drops of an appropriate acid-base indicator are added so that a colour change will signal the point at which the titration should stop.
3. The other solution is dispensed slowly into the titration flask from a burette until the indicator colour changes permanently.
    - The volume of the solution delivered by the burette is known as the titre.

The titre is calculated by subtracting the final burette reading from the initial burette reading.

- ➔ To minimize errors, the titration is repeated several times and the average titre found.
    - Usually 3 concordant titres (titres that are within 0.10 mL of each other) are used to find the average.

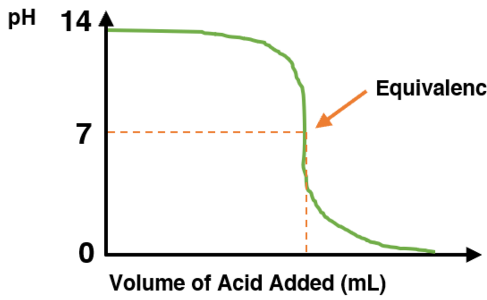
Indicators and Acid-Base Titrations:

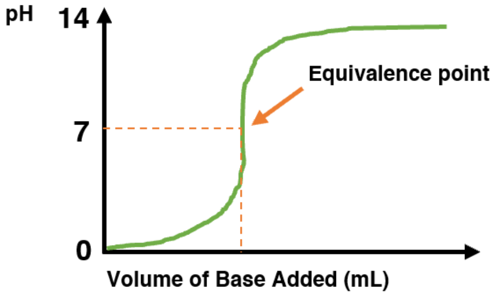
Using Acid-Base Indicators:

1. Strong Acids versus Strong Base Titration:

➔ Equivalence point will occur at pH = 7.

  - Bromothymol blue is the best indicator for this sort of titration.

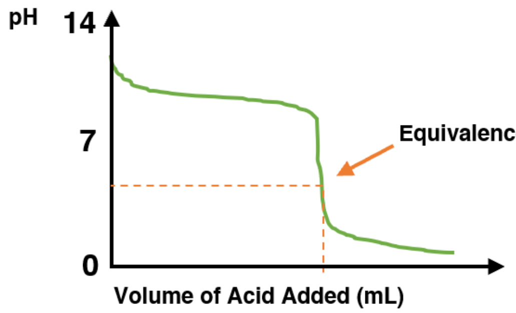


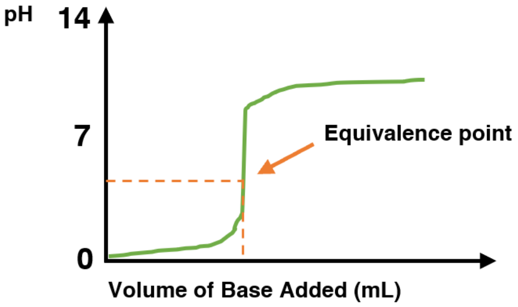


2. Strong Acid versus Weak Base Titration:

➔ Equivalence point will occur at pH < 7.

  - Methyl orange is the best indicator for this sort of titration.

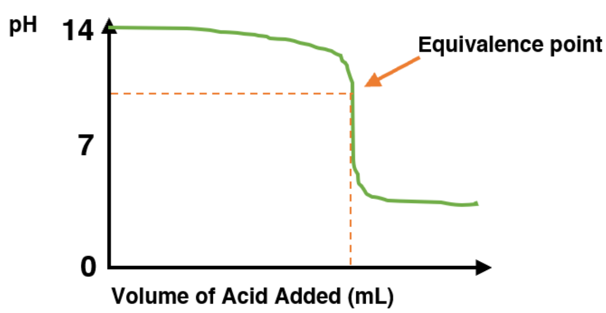


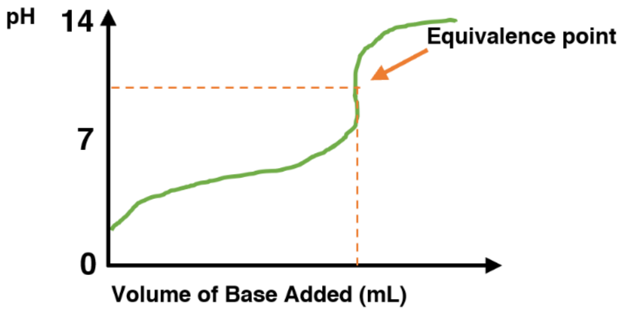


3. Weak Acid versus Strong Base Titration:

➔ Equivalence point will occur at pH > 7.

  - Phenolpthalein is the best indicator for this sort of titration.





Calculations in Volumetric Analysis – Titrations:

Precision and Accuracy:

Accuracy refers to the closeness of a measured value to a standard or known value.

Precision refers to the closeness of two or more measurements to each other.

➔ You can be precise but inaccurate.

➔ You can also be accurate but imprecise.

Redox

Oxidation and Reduction:

Redox (reduction-oxidation) reactions include all chemical reactions in which atoms have their oxidation states changed.

- ➔ Oxidation is the loss of electrons – or the increase in oxidation state – by a molecule, atom, or ion.
- ➔ Reduction is the gain of electrons – or the decrease in oxidation state – by a molecular, atom or ion.

Oxidation:

Oxidation is the loss of electrons.

Reducing Agent:

A substance that causes the reduction of another substance is called the reducing agent/ reductant.

- ➔ It is itself oxidized and so the electron donor.

Reduction:

Reduction is the gain of electrons.

Oxidizing Agents:

A substance that causes the oxidation of another substance is called an oxidizing agent/ oxidant.

- ➔ It is itself reduced and so it an electron acceptor.

Redox Equations:

To write the overall redox equation, we must combine the oxidation and reduction half-equations.

Since redox reactions involve electron transfer, the number of electrons donated by the species being oxidized must be equal to the number of electrons accepted by the species being reduced.

- ➔ We need to multiply one or both half-equations by a factor so that the numbers of electrons are the same in both equations.
  - Then the equations can be added.

Writing Redox Equations:

To write a half-equation:

- ➔ Balance the atoms being oxidized or reduced
  - Balance the charges using electrons.
    - Write in the physical states.

For complex half-equations:

1. Write down the reactants and products; include oxidation numbers.
2. Balance the number of atoms of the element being oxidized or reduced.

3. Balance the oxygen atoms on both sides by adding water to the side with the least amount of oxygen.
4. Balance the hydrogen atoms on both sides by adding H^+ to the side with the least amount of hydrogen.
5. Balance the charges by adding electrons to the side with the highest positive charge.
6. Check the balancing.
7. Write in the physical states.

Oxidation Numbers:

A number assigned to an element in chemical combination which represents the number of electrons lost (or gained, if the number is negative), by an atom of that element in the compound.

Oxidation Number Rules:

- The oxidation number of a free element is zero.
- The oxidation number of a simple ion is equal to the charge on the ion.
- Hydrogen has an oxidation number of +1 when it forms compounds with non-metals.
  - In metal hydrides, the oxidation number of hydrogen is -1.
    - This is because metals are better at losing electrons than hydrogen, hence hydrogen becomes negative instead of positive.
- Oxygen has an oxidation number of -2.
  - In compounds of fluorine, oxygen will have a positive oxidation number.
    - Oxygen becomes -1 in fluorine because fluorine is more electronegative than it, hence fluorine has a greater tendency to keep its electrons than oxygen and hence oxygen loses it.
    - In peroxides, oxygen has an oxidation number of -1.
      - Peroxide is a polyatomic ion and thus, oxygen needs an oxidation number of -1.
- The sum of the oxidation numbers in a neutral compound is zero.
- The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.

Using Oxidation Numbers:

The species that loses electrons is oxidized and its oxidation number increases.

The species that gains electrons is reduced and its oxidation number decreases.

Disproportionation:

When a substance is simultaneously oxidized and reduced.

- This occurs when hydrogen peroxide decomposes rapidly in the presence of manganese dioxide as a catalyst.

Galvanic Cells

Galvanic Cells:

A galvanic cell is an electrochemical cell which converts chemical energy into electrical energy.

The most common battery is the Daniell cell:

This cell produces an electric current that flows through the wire and light globe – this part of the cell is called the external circuit.

- ➔ The current flows because a chemical reaction is taking place in the cell.
  - Evidence of a reaction occurring within the cell is present in the corrosion of zinc and copper metal for example.
    - The copper metal becomes coated with a furry, dark brown deposit and the blue copper (II) sulphate solution loses some of its distinctive colour.

Electron flow within this specific galvanic cell reveals the electron flow from the zinc electrode, through the wire, to the copper electrode.

The salt bridge – typically made from filter paper or a hollow, U-shaped tube, which maintains the electrical neutrality of the cell by maintaining the flow of ions in the circuit.

Hence,

- ➔ The reaction in this cell is a redox reaction, because electrons are being transferred.
  - The zinc electrode corrodes, because the zinc metal forms zinc ions in solution: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
    - The oxidation of the zinc metal releases electrons, which flows through the wire to the copper electrode.
- ➔ Electrons are accepted by the copper ions in the solution where the ions collide with the copper electrode: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
  - The copper metal that is formed deposits on the electrode as a dark brown coating.

Galvanic cell reactions are spontaneous – a reaction that occurs naturally.

The Operation of a Galvanic Cell:

Galvanic cells are designed to ensure half-reactions occur in separate compartments of the cell.

- ➔ The oxidizing agent and reducing agent cannot come into direct contact with each other.
- ➔ Electrons can only be transferred by travelling through an external circuit connecting the negative and positive electrodes.

The Salt Bridge:

The salt bridge contains ions that are free to move so that they can balance charges formed in the two compartments.

Without a salt bridge:

- ➔ The solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would accumulate positive charge as the reaction proceeded.
  - This accumulation of charge would halt the reaction very quickly and prevent further reaction.

The salt bridge completes the circuit in the cell by providing ions.

- ➔ The positive ions move towards the cathode.
- ➔ The negative ions move towards the anode.

Half-Cells:

A galvanic cell consists of two half-cells. Each half-cell contains an electrode in contact with a solution.

- ➔ The species present in each half-cell forms a conjugate redox pair -an oxidizing agent and its corresponding reduced form – also known as a redox couple.

Oxidation = anode.

- ➔ Electrons are released here and is described as the negative terminal.

Reduction = cathode.

- ➔ Electrons are gained here and is described as the positive terminal.

If one member of the conjugate pair within a half-cell is a metal, typically it is used as the electrode.

- ➔ e.g. Br_2/ Br^- does not contain a pure metal, hence, an inert (unreactive) electrode, such as platinum or graphic is used.

The Reactivity of Metals:

Metals can be ranked in a list according to their reactivity.

- ➔ The lower down the table a metal is on the reactivity series, the more reactive it is.
  - The strongest oxidizing agents are at the top of the standard reduction potential table.
  - The strongest reducing agents are at the bottom of the standard reduction potential table.
    - Hence, it can be inferred that strong oxidizing agents are weak reducing agents and vice versa.

Metal Displacement Reactions:

A more reactive metal will be oxidized by, and donate its electrons to, the cation of a less reactive metal.

- ➔ The cation receives the electrons and is reduced.

For a spontaneous reaction to occur:

- ➔ the metal ions of one metal must be above the other in the reactivity series.
  - LEFT OVER RIGHT RULE.
    - The more reactive metal acts as a reducing agent, and the metal ions of the other metals acts as the oxidizing agent.

Halogen Displacement Reactions:

The halogens are some of the strongest oxidizing agents.

The oxidizing strength of fluorine can be explained by its atom's large core change and the proximity of the valence shell to the nucleus, due to the small size of fluorine atoms.

- ➔ A fluorine atom is able to attract an electron to its valence shell more effectively than any other atom.

As you move down group 17, the oxidizing strength of the halogens decreases.

- ➔ This is because the valence shell of the atoms gets further and further away from the nucleus and hence, they are less able to attract electrons.

Just like metal displacement reactions, a reducing agent can react spontaneously with an oxidizing agent that is higher than it in the series.

- ➔ e.g. when chlorine gas is bubbled through a colourless solution of iodide ions, orange-brown iodine will be observed as it is displaced from the iodide solution.

Combustion:

Combustion reactions involve the oxidation of a fuel by oxygen.

- ➔ When there is an abundance of oxygen, complete combustion occurs.
  - The products of this are carbon dioxide and water.
    - More energy is produced due to the larger increase in oxidation number.
- ➔ When there is limited oxygen, incomplete combustion occurs.
  - The products are carbon monoxide and water.
    - Results in less energy being produced because the increase in oxidation number is not as great.

Corrosion:

Direct reaction with oxygen in the air to form a metal oxide is known as dry corrosion or direct corrosion.

- Iron is much less reactive than sodium or aluminium; the rate of dry corrosion of iron is slow at normal temperatures.
- When iron does corrode, it forms a coating which flakes off readily, leaving the metal underneath exposed to further corrosion.

The presence of moisture accelerates the corrosion of iron. This process is known as wet corrosion.

- e.g. the formation of rust, the flaky brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. The factors affecting the rate at which corrosion occurs are:

- The presence of water.
- Impurities such as salt and acidic pollutants that dissolve in water.

The Wet Corrosion Process:

1. Iron is oxidized to form Fe^{2+} ions at one region on the iron surface:

$$\boxed{\mathbf{Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-}_{(aq)}}}$$

- At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions.

$$\boxed{\mathbf{O_{2(aq)} + 2H_2O_{(l)} + 4e^{-} \rightarrow 4OH^{-}_{(aq)}}}$$

Therefore, the overall equation is:

$$\boxed{\mathbf{2Fe_{(s)} + O_{2(aq)} + 2H_2O_{(l)} + 4e^{-} \rightarrow 4OH^{-}_{(aq)} + 2Fe^{2+}_{(aq)}}}$$

2. The formation of a precipitate of iron (II) hydroxide:

$$\boxed{\mathbf{Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)}}}$$

- During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs (called the anode) to the area where reduction occurs (the cathode).
  - Ions flow through the water droplets.

3. Further oxidation of iron (II) hydroxide occurs in the presence of oxygen and water to produce iron (III) hydroxide – a red-brown precipitate.

$$\boxed{\mathbf{4Fe(OH)_{2(s)} + O_{2(aq)} + 2H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)}}}$$

4. In air, the iron (III) hydroxide loses water to form hydrated iron (III) oxide: $Fe_2O_3xH_2O$

Galvanic and Electrolytic Cells

The Daniell Cell:

Uses:

The Daniell cell was the first practical and reliable electric battery.

- ➔ It was used extensively in telegraph and telephones as a source of electricity.
- ➔ The Gibbs Energy of the spontaneous redox reaction is converted into electrical energy which may be used for running a motor and other electrical gadgets like heaters, fans, geysers etc.
- ➔ These cells are often used as back-up systems to compensate for loss of electricity supply from the grid.
- ➔ These systems must be designed to close the supply gap for several hours and in some cases high power outputs must be available immediately or within minutes even if they are rarely put to use.

Description:

At the Anode:

- ➔ Anode is made of zinc metal.
- ➔ Electrolyte is $ZnSO_4$

At the anode (negative), zinc is oxidized into zinc ions.

- ➔ Zinc is a stronger reductant (reducing agent) than copper.
- ➔ The zinc anode disintegrates over time.
  - Over time, zing metal from the electrode is being converted to zinc ions, and these ions become part of the electrolyte solution.
  - Therefore, the mass of the zinc electrode will decrease.

At the Cathode:

- ➔ Cathode is made of copper metal.
- ➔ Electrolyte is $CuSO_4$

At the cathode (positive), copper ions are reduced to copper atoms.

- ➔ Reduction occurs at the cathode.
- ➔ At the cathode a species must gain electrons.
- ➔ Copper metal won't gain electrons, but copper (II) ions in the electrolyte solution can gain 2 electrons.

Copper is deposited on the copper cathode over time.

- ➔ Copper ions continue to gain 2 electrons to form solid copper.
  - This reaction occurs on the copper electrode.
    - The 'new' copper atoms stick to the 'old' copper atoms of the electrode
    - As the cell operates the mass of the copper electrode increases.

Electrons flow from the zinc anode to the copper cathode.

- ➔ Electrons are produced by the oxidation reaction occurring at the anode (zinc electrode).
  - These electrons flow through the conducting wire from the anode to the cathode.

- At the cathode (copper electrode) these electrons are used to reduce copper (II) ions to copper atoms.

Equations:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (ANNOX)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (REDCAT)

Therefore, $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Oxidation Numbers:

- Zinc is initially a pure element, so its oxidation number is 0. It then is oxidized and loses two electrons, therefore making its oxidation number +2.
- Copper initially exists in a compound with oxidation number +2 ($CuSO_4$), however it is reduced and gains two electrons, and its final oxidation number is 0.

Potential Different Produced:

- Reduction potential of oxidation of zinc = -0.7618 V.
- Reduction potential of reduction of copper = +0.340 V.
  - Therefore, potential difference = 0.340 + | 0.7618 | = 1.1018 V.

Environmental Considerations:

As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left out.

The Leclanche Cell:

Uses:

The leclanche cell saw use in:

- Low drain appliances such as radios, torches, liquid crystal calculators, toys.
- A good general-purpose cell/ battery but it can only produce small current and its voltage output drops with use.

It is different to the alkaline battery in that it can deliver three to five times the energy of the standard zinc-carbon dry cell of similar size.

- Alkaline batteries use alkaline electrolytes such as potassium hydroxide.
  - They are prone to leaking and can be unsafe.

Description:

Contains an electrolyte paste of MnO_2, NH_4Cl and C

- A salt bridge is not required since the thick paste prevents the contents mixing.
  - The manganese dioxide is mixed with carbon powder to increase the electrical conductivity.

At the Anode:

- Anode is made of zinc casing

Zinc atoms on the surface of the anode oxidize.

- They give up both their valence electrons to become positively charged Zn^{2+} ions.

- As the Zn^{2+} ions move away from the anode, leaving their electrons on its surface, the anode becomes more negatively charged than the cathode.
  - When the cell is connected in an external electrical circuit, the excess electrons on the zinc anode flow through the circuit to the carbon rod, the movement of electrons forming an electric current.

At the Cathode:

- ➔ Cathode is made of a central carbon rod.
  - The cathode is made of carbon because it is a practical conductor material because most common metals will quickly corrode away in the positive electrode in salt-based electrolyte.

When the electrons enter the cathode (carbon rod), they combine with manganese dioxide (MnO_2) and water (H_2O), which react with each other to produce manganese oxide (Mn_2O_3) and negatively charged hydroxide ions (OH^-).

- ➔ This is accompanied by a secondary acid-base reaction in which the hydroxide (OH^-) accepts a proton (H^+) from the ammonium ions present in the ammonium chloride electrolyte to produce molecules of ammonia and water.

Equations:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (ANNOX)

$2MnO_{2(s)}+2NH_4^+{}_{(aq)}+2e^-\rightarrow Mn_2O_{3(s)}+2NH_{3(aq)}+H_2O_{(l)}$ (REDCAT)

Therefore, $Zn_{(s)} + 2MnO_{2(s)} + 2NH_4Cl_{(aq)} \rightarrow ZnCl_{2(aq)} + Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$

Oxidation Numbers:

- ➔ Zinc is initially a pure element, so its oxidation number is 0. It then is oxidized and loses two electrons, therefore making its oxidation number +2.
- ➔ Manganese is reduced from an oxidation state of +4 to +3.

Potential Difference Produced:

The EMF produced by a Lechlanche cell is 1.5 volts.

The Lead Acid Accumulator Battery:

Uses:

They are most commonly used in vehicles where a constant and uninterruptible source of energy is required.

- ➔ They are used for starting, lightning and ignition purposes in motor vehicles.

Description:

This cell has both a charging and discharging phase, however, the discharging one is the one that produces the electric energy via redox reaction.

At the Anode:

- ➔ Electrode is made of a metallic spongy lead (Pb) in a lead frame (porous lead plate).

- Oxidation occurs here.

Pb is oxidized at the anode.

Pb^{2+} reacts with SO_4^{2-} in sulfuric acid to produce $PbSO_4$ as a precipitate.

- $Pb^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} \rightarrow PbSO4_{(s)}$
- $PbSO_{4(s)}$ sticks to the lead frame of the anode.

Therefore, $Pb_{(s)} + SO_4{}^{2-}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

- Electrons are produced at the anode.
- The anode is negatively charged.
- Electrons migrate from the anode to the cathode along wires connecting the electrodes.

At the Cathode:

- ➔ Electrode: lead frame covered with lead dioxide (PbO_2)
  - Reduction occurs here.
- ➔ Pb in PbO_2 is reduced at the cathode by hydrogen ions (protons) from the sulfuric acid.
  - $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

Pb^{2+} reacts with SO_4^{2-} in sulfuric acid to produce Pb $SO_{4(s)}$ as a precipitate:

- $Pb^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)} \rightarrow PbSO4_{(s)}$
- $PbSO_{4(s)}$ sticks to the lead frame of the cathode.

Therefore, $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- + SO_4{}^{2-}_{(aq)} \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

- Electrons are consumed at the cathode.
- Cathode is positive.
- Protons, H^+, are consumed at the cathode.

Equations:

$Pb_{(s)} + SO_4{}^{2-}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ (ANNOX)

$PbO_{2(s)} + 4H^+_{(aq)} + 2e^- + SO_4{}^{2-}_{(aq)} \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$ (REDCAT)

Therefore, $Pb_{(s)} + PbO_{2(s)} + 2SO_4{}^{2-}_{(aq)} + 4H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Oxidation Numbers:

$Pb_{(s)}$ goes from 0 as a free element, to +2 at the anode.

The Pb in PbO_2 goes from +4 to +2 at the cathode.

Potential Difference Produced:

The potential difference for one lead-acid cell is 2.05V.

- ➔ Since there are 6 cells in a battery, the total EMF for the battery is roughly 12V.

Environmental Considerations:

- ➔ Concentrated Sulfuric acid can potentially harm the environment in the event of a battery leakage or if the battery is not disposed of correctly.

- ➔ Hydrogen gas pollutes the atmosphere.
- ➔ Overheats during charging
- ➔ Can sustain and deliver high current flows

The Proton Exchange Membrane (PEM):

Uses:

Used for transportation applications and some stationary applications.

- ➔ Due to their fast startup time and favourable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

Description:

The fuel for the PEM cell is hydrogen, and the charge carrier is the hydrogen ion (proton).

At the Anode:

- ➔ Hydrogen is oxidized.
- ➔ The hydrogen molecule is split into hydrogen ions (protons) and electrons.
  - The hydrogen ions permeate across the electrolyte to the cathode, whilst the electrons flow through an external circuit and produce electric power.

At the Cathode:

- ➔ Oxygen is reduced.
- ➔ Oxygen, in the form of air, is supplied to the cathode.
  - Oxygen combines with the electrons and the hydrogen ions to produce water.

Equations:

$2H_2 \rightarrow 4H^+ + 4e^-$ (ANNOX)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (REDCAT)

Therefore, $2H_2 + O_2 \rightarrow 2H_2O$ + heat (energy)

Oxidation Numbers:

- ➔ Hydrogen goes from a free element (0) to becoming an ion (+1) – oxidation.
- ➔ Oxygen goes from existing as a free element (0) to existing in water molecules (-2). Therefore, it is reduced.

Potential Difference Produced:

The theoretical exothermic potential is +1.23 V overall.

Environmental Considerations:

Relative to other car engines and thermal power stations, the PEM cells are more efficient.

- ➔ Modern fuel cells use the waste heat to make steam which can be used additionally, moving the overall efficiency up to around 70%. Also, hydrogen/oxygen fuel cells are safe for the environment, as they are not fossil fuels.

The Chloroalkali Process/ Electrolysis of Brine:

Uses:

The electrolysis of brine is an industrial process for the electrolysis of sodium chloride solutions.

- ➔ It is used to produce chloride and sodium hydroxide which are commodity chemicals required by industry.

Description:

The electrodes are typically made of an inert material like platinum/titanium which is not attacked by chlorine or alkali.

In the diaphragm cell process, there are two compartments separated by a permeable diaphragm, often made of asbestos fibers.

- ➔ Brine (NaCl) is introduced into the anode compartment and flows into the cathode compartment.

At the Anode:

- ➔ The chloride ions are attracted to the anode.
  - They lose electrons and are oxidized to chlorine gas.

At the Cathode:

- ➔ Water is attracted to the cathode.
  - It is reduced to produce hydrogen gas.
  - Caustic soda (NaOH) also forms.

The diaphragm prevents the reaction of the caustic soda with the chlorine.

- ➔ Na^+ ions pass through the diaphragm and react with OH^- ions to produce NaOH.
  - A diluted caustic brine leaves the cell.

The caustic soda must usually be concentrated to 50% and the salt removed.

- ➔ This is done using an evaporative process with about three tons of steam per ton of caustic soda.
  - The salt separated from the caustic brine can be used to saturate diluted brine.
  - The chlorine contains oxygen and must often be purified by liquefaction and evaporation.

Equations:

$2Cl^- \rightarrow Cl_2 + 2e^-$ (ANNOX)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (REDCAT)

Therefore, $2H_2O_{(l)} + 2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2OH^-_{(aq)}$

- ➔ The sodium ions are spectator ions.

Oxidation Numbers:

- The oxidation number of chlorine goes from -1 to 0 – oxidation.
- The oxidation number of hydrogen goes from +1 to 0 – reduction.

Environmental Considerations:

- This process uses a lot of electricity that is mainly produced by the burning of fossil fuels.
- During the actual process of electrolysis, metal must be in contact with the solution of brine. A metal commonly used is mercury which is toxic.
    - Some mercury escapes into the solution and into the environment.
- The chlorine will react with sodium hydroxide to form sodium chlorate(I) NaOCl, which is how a bleach is made.

Electroplating Metals:

Uses:

- Forming a protective barrier
- Enhancing appearance
- Reduces friction
- Makes something a conductor
- Resists heat
- Making something magnetic
- Increasing hardness

Description:

Electroplating involves the deposition of a layer of metal on top of another metal.

- The metal we wish to coat is placed on the negative terminal of the power source.
- wasqThis is then immersed in an electrolyte that contains ions of the metal we wish to coat with, in this case, silver ions.

Equations:

The equations for electroplating vary for different electroplating systems. The most common process is using copper to electroplate other objects.

- $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ (ANNOX)
- $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (REDCAT)

Oxidation Numbers:

- Copper goes from 0 to +2 at the anode.
- Copper goes from +2 to 0 at the cathode.

Electrorefining of Copper:

Uses:

Electrorefining refers to the process of using electrolysis to increase the purity of a metal extracted from its ore.

- The electrorefining of copper is used to produce pure copper that is then used for a variety of reasons:
    - Making wires for circuits
    - Making building materials.

Description:

- A series of impure copper anodes and thin starter sheet cathodes (such as thin copper foil) are suspended in a tank.
- The electrolyte containing the copper ions flows through the tank.
  - The electrolyte is often copper dissolved in sulfuric acid (acidified copper sulphate) → This makes an aqueous solution of copper ions.
- An external power supply is used to pull electrons out of the anode and push them to the cathode.

Equations:

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ (ANNOX)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (REDCAT)

Oxidation Numbers:

- Copper goes from 0 to +2 at the anode.
- Copper goes from +2 to 0 at the cathode.

Organic Chemistry

Intermolecular Forces:

Dispersion Forces:

Dispersion forces are demonstrated by all atoms and molecules.

- The electron distribution around an atom or molecule undergoes fluctuations in time.
  - These fluctuations create instantaneous electric fields which are felt by other nearby atoms and molecules → this adjusts the spatial distribution of their own electrons.

    - The net effect is that the fluctuations in electron positions in one atom induce a corresponding redistribution of electrons in other atoms, such that the electron motions become correlated.

This effect, without a physics background, is frequently described as the formation of instantaneous dipoles that attract each other.

- ➔ This is the weakest of all intermolecular forces.

Dipole-Dipole Interactions:

Dipole-dipole interactions are electrostatic interactions between molecules which have permanent dipoles.

- ➔ These interactions tend to align the molecules to increase attraction.
  - The positive end of a polar molecule will attract the negative end of another molecule and influence its position.
    - Polar molecules have a net attraction between them.

If there is symmetry within the molecule, then the dipoles exhibited by groups of atoms cancel out and there is no overall dipole moment.

- ➔ This is stronger than dispersion forces, but weaker than hydrogen bonding.

Hydrogen Bonding:

A hydrogen bond is an attraction between an electronegative atom's lone pairs and a hydrogen atom that is bonded to either N, O, F.

- ➔ Hydrogen bonds are described as a strong electrostatic dipole-dipole interaction.

Intermolecular hydrogen bonding is responsible for the high boiling point of water because a greater amount of energy is required between molecules to separate them.

- ➔ This is the second strongest intermolecular force; it is weaker than ion-dipole interactions.

Ion-Dipole Interactions:

Ion-dipole forces are involved in solutions where an ionic compound is dissolved into a polar solvent – these only occur in solutions and not pure substances.

- ➔ This occurs due to the Coulombic electrostatic attractions between an ion and the charged ends of a dipole.
  - This is the strongest intermolecular force.

Hydrocarbons:

Aliphatic hydrocarbons:

Aliphatic compounds are hydrocarbon compounds containing carbon and hydrogen joined together in straight chains, branched trains or non-aromatic rings.

- ➔ Aliphatic compounds can be saturated, joined by single bonds (alkanes), or unsaturated, with double bonds (alkenes) or triple bonds (alkynes).
  - Besides hydrogen, other elements can be bound to the carbon chain, the most common being oxygen, nitrogen, sulphur and chlorine.

Alicyclic hydrocarbons:

Alicyclic hydrocarbons are organic compounds that are both aliphatic and cyclic.

- ➔ They contain one or more all-carbon rings which may be either saturated or unsaturated.
  - Alicyclic compounds may have one or more aliphatic side chains attached.

Aromatic hydrocarbons:

Aromatic hydrocarbons are hydrocarbon compounds which contain a benzene ring (whilst benzene rings are the most common foundations for aromatic hydrocarbons, this isn’t always the case).

- ➔ They have cyclic, planar structures with a ring of resonance bonds that gives increased stability when compared other arrangements of atoms.
  - This gives rise to their high stability, the difficulty to break apart when attempting to react with other substances i.e low reactivity.

Homologous Series:

A group or class of compounds related to each other by a general molecular formula.

- ➔ Each member of a homologous series differs from each other by a CH_2 group.
  - Hence, homologues would have the same functional group(s) as others within the same series → there will be a regular trend in their physical properties.

An example of a trend that exists within homologous series is melting/ boiling points increase with molecular mass.

- ➔ This is because dispersion forces are proportional to the surface area, so as you increase the length of the chain, you also increase the surface area and hence the ability for individual molecule to attract each other.

If the molecular masses are too similar, then the symmetry of the molecule should be examined.

- ➔ The more rod-like the molecules are, the better they are able to line up and bond.
  - The more sphere-like the molecule, the lower its surface area will be and fewer dispersion forces will operate.

Nomenclature:

1. Count the longest continuous chain of carbon atoms that contains the main functional group – this gives the stem name.
2. The main functional group of the molecule provides the suffix.
3. Number the longest carbon chain so that it gives the functional group the lowest number.
4. Any alkyl groups or functional groups of lesser importance are included alphabetically as prefixes at the start of the name and given numbers corresponding to the carbon to which they are attached.
5. If there is more than one of the same side chains or functional groups, use di-, tri- etc, before their part of the name. This does not count towards the alphabetical order.

IUPAC PRIORITY OF FUNCTIONAL GROUPS (most important at the top)
Carboxylic acids
Esters
Amides
Aldehydes
Ketones
Alcohols
Amines
Alkenes
Alkynes
Alkanes

Isomers:

Structural isomers:

- ➔ Chain structural isomers = same molecular formula but different chain length.
  - Pentane → methyl butane → dimethylpropane.
    - They'll have similar chemical properties but differing physical properties due to their different molecular shape.
- ➔ Position structural isomers = same molecular formula but with functional groups attached at different parts of the chain with the same chain length.
  - Chloropent-1-ane → chloropent-2-ane → chloropent-3-ane.
    - they will all have different chemical and physical properties.
- ➔ Geometric isomers (cis-trans isomerism) = same molecular formula and the atoms are connected in the same way, but they are arranged differently in space.
  - They can only exist where there is a C-C double bond because of the restrictive nature of this bond → there must also be two different radicals attached to each of the double bond.
  - The physical properties differ because the shape is different between cis and trans isomers and hence, the intermolecular forces present are affected.
    - Cis isomers = on the same side of the double bond.
    - Trans isomers = diagonally opposite across the double bond.

Properties, Preparation and Reactions of Alkanes:

Alkanes (C_nH_{2n+2}):

Alkanes are organic compounds that consist of entirely single-bonded carbon and hydrogen atoms and lack any other functional groups.

- ➔ They are also saturated; the carbon is holding the maximum number of hydrogen atoms in single bonds without having any C-C bonds.
  - Alkanes can be further divided into the subgroups: straight-chain alkanes, branches alkanes and cycloalkanes.

Melting and boiling point:

The melting and boiling point of alkanes increases as molecular mass increases.

- ➔ This is because the dispersion forces become greater with increasing chain length.
  - Dispersion forces are the most prevalent intermolecular force because the there is not a significant electronegativity between carbon and hydrogen, and hence, there is no significant bond polarity.

The melting and boiling point of alkanes decreases as their chain becomes more branched.

- ➔ This is because there is less opportunity for dispersion forces to have an effect because the molecules aren't able to get close enough together.

Solubility:

Alkanes (including cycloalkanes) are virtually insoluble in water, but dissolve in organic solvents.

- ➔ However, liquid alkanes are good solvents for many other non-ionic organic compounds.

When a molecular substance dissolves in water, the following must occur:

- ➔ The intermolecular forces within the substance must be broken, in the case of the alkanes these are the dispersion forces.
- ➔ The intermolecular forces within the water must be broken so that the substance can fit between the water molecules. In water, the primary intermolecular attractions are hydrogen bonds.

If entropy is disregarded, then we can see that a substance will dissolve if there is enough energy released when new bonds are made between the substance and the water to compensate for what is used in breaking the original attractions.

Substances that predominantly have dispersion forces do not release sufficient amount of energy to compensate for the energy required to break the hydrogen bonds in water; alkanes do not dissolve in water. Contrastingly, in an organic solvent, the dispersion forces can be broken and replaced, essentially cancelling each other out and thus, there is no barrier to solubility.

Chemical properties:

PROPERTIES	**EXPLANATION**
Not very reactive	The backbone carbon atoms in alkanes have attained their octet of electrons through forming four covalent bonds. These four bonds formed by carbon in alkanes are sigma bonds, which are more stable than other types of bonds because of the greater overlap of carbon's atomic orbitals with neighbouring atom's atomic orbitals – the input of additional energy is needed; either through heat or radiation.
Less dense than water	One can observe, oil, an alkane, floats on water.
Non-polar solvents	Since only C and H atoms are present, alkanes are nonpolar. Alkanes are immiscible in water but freely miscible in other non-polar solvents. Alkanes consisting of weak dipole-dipole bonds can not break the strong hydrogen bond between water molecules hence it is not miscible in water.

Reactions:

- ➔ Combustion = usually occurs when a hydrocarbon reacts with oxygen to produce carbon dioxide and water.
  - It is an exothermic reaction.
  - If limited oxygen is present, then carbon monoxide is formed instead of oxygen.
- ➔ Halogenation = alkanes undergo substitution reactions with halogens in the presence of UV light.
  - Always forms 2 products, a hydrogen-halide and the resultant hydrocarbon.

Properties, Preparation and Reactions of Alkenes:

Alkenes (C_nH_{2n}):

Alkenes are a class of unsaturated organic compounds with at least one C-C double bond.

- ➔ This C-C double bond changes the physical properties of alkenes, to allow it to exist in all three phases.

Melting and boiling point:

The melting and boiling points of alkenes are similar to that of alkanes.

- ➔ Isomers of cis alkenes have lower melting points than that of trans isomers because the ‘U’ shape of the cis isomer doesn’t pack as well as the straighter shape of the trans isomer.
  - This means that the intermolecular forces aren’t as effective as they should be and so less energy is needed to melt the molecule.

The boiling point, however, works in the same way that alkanes do.

- ➔ Alkenes have slightly lower boiling points than alkanes, because dispersion forces are the prevalent intermolecular force.
  - Alkanes have 2 less electrons than an alkane with the same number of carbons, explaining the slightly lower boiling point.

Solubility:

Alkenes are virtually insoluble in water, but dissolve in organic solvents. The reasons for this are exactly the same as for the alkanes.

Chemical properties:

PROPERTIES	EXPLANATION
Differing physical state	4 carbons or less = colourless gas. 5 carbons or more = liquid. 15 carbons or more = solids.
Less dense than water	Alkenes are lighter than water and are insoluble in water due to their non-polar characteristics.
Polarity → boiling point	Alkenes possess an electron-attracting sp^2 carbon, which creates a weak dipole along the substituent alkenyl carbon bond, forming a net dipole. Trans-substituted alkenes = the dipoles cancel each other out. Cis-substituted alkenes = a net dipole does exist → higher boiling point

- ➔ Combustion = usually occurs when a hydrocarbon reacts with oxygen to produce carbon dioxide and water.
  - It is an exothermic reaction.

- If limited oxygen is present, then carbon monoxide is formed instead of oxygen.
- ➔ Addition = two new atoms are added across the double bond, converting unsaturated compounds into saturated compounds.
    - Halogenation
        - Bromine water is decolourized when shaken with an alkene (Br_2) is absorbed). This is a test for unsaturation.
    - Hydrogenation
        - Requires a catalyst such as Pt, Pd, Ni.
    - Hydrohalogenation
        - Requires a catalyst such as Pt, Pd, Ni.
    - Hydration
        - Heat and concentration H_2SO_4 are catalysts.
        - When hydrohalogens and water are added to asymmetrical alkenes, Markovnikov's rule is applied to predict the predominant product.
          → the hydrogen atom of the added molecule will attach to the carbon with the greater number of hydrogens.

Properties, Preparation and Reactions of Halogenoalkanes:

Halogenoalkanes:

Halogenoalkanes are hydrocarbons which contain one or more halogen atoms attached in place of hydrogen.

- ➔ The presence of halogen atoms can produce polar or non-polar molecules, depending upon their position and the molecule's shape.
    - Some halogenoalkanes can have dipole-dipole bonding in addition to dispersion forces.
        - These generally exhibit low melting and boiling points and make good solvents.

Properties, Preparation and Reactions of Alicyclic Hydrocarbons:

Alicyclic hydrocarbons:

Alicyclic hydrocarbons form closed rings with as few as 3 carbon atoms.

- ➔ They can be saturated cycloalkanes or unsaturated cycloalkenes.
    - Alicyclic hydrocarbons have similar physical properties to their corresponding straight chain and branched hydrocarbons.
    - They undergo similar chemical reactions to those of their corresponding straight chain and branched chain hydrocarbons.

Properties, Preparation and Reactions of Alcohols:

Alcohol ($C_nH_{2n+1}OH$):

Alcohols are alkanes containing a hydroxide group, -OH.

Alcohols can be classified as: primary, secondary or tertiary depending on how the number of alkyl groups (R) are attached to the carbon atom the hydroxide group -OH is bonded to.

- ➔ The more exposed the -OH group is, the more available it is for bonding.
  - It is most exposed in primary, and least exposed in tertiary.
    - Primary is the most reactive.

Unlike the alkyl halides, this group was two reactive covalent bonds, the C-O bond and the O-H bond.

Melting and boiling point:

The boiling point of alcohols are generally higher when compared to hydrocarbons of equal molecular mass.

- ➔ This is owing to the fact that hydrogen bonding is present between the hydroxide groups of alcohol molecules.
  - In addition to this, the boiling point of alcohols increases as the number of carbon atoms in the aliphatic carbon chain increase → same reasons as mentioned previously.

Boiling points decrease from primary to tertiary.

Solubility:

The solubility of the alcohol is dependent on the hydroxide group present. The hydroxide group is able to form hydrogen bonds with water molecules, which allows it to be soluble in water.

- ➔ However, if the length of the hydrocarbon chain increases, the solubility in water decreases as there is a greater, polar end of the chain than non-polar.
  - This means that the predominating intermolecular force is now dispersion forces, which results in the hydrocarbon being less miscible with water.

Properties

- ➔ The electronegativity of oxygen is substantially greater than that of carbon and hydrogen.
  - Consequently, the covalent bonds of this functional group are polarized so that the oxygen is electron rich and both carbon and hydrogen are electrophilic.
- ➔ The dipolar nature of the O-H bond is such that alcohols are much stronger acids than alkanes (10^{30} times stronger).
  - The most reactive site in an alcohol is the hydroxide group, despite the fact that the O-H bond strength is significantly greater than the other bonds present.

Reactions:

- ➔ Hydration of alkenes = the alkene reacts with water in the presence of concentrated H_2SO_4 and heat
  - This is how alcohols formed.
- ➔ Combustion = all alcohols can undergo complete combustion in excess oxygen to produce carbon dioxide and water.
- ➔ Oxidation = depending on whether the alcohol is primary, secondary or tertiary it can be oxidized.

  - Primary alcohols = readily oxidized with strong oxidizing agents like acidified solutions of MnO_4^- or $Cr_2O_7^{2-}$.
    - Primary alcohols → aldehydes → carboxylic acid (avoided by isolating on formation, through distillation typically).
  - Secondary alcohols = also oxidized with strong oxidizing agents like acidified solutions of MnO_4^- or $Cr_2O_7^{2-}$.
    - Secondary alcohol → ketone (they are not susceptible to further oxidation).
  - Tertiary alcohols = resistant to oxidation.
- Reaction with sodium = alcohols react to form alkoxide (sodium alkoxide) ions and hydrogen gas.
  - This reaction can be used to test for the presence of the hydroxide group in alcohols.
  - Less vigorous reaction to that of sodium and water.
    - Alcohol + 2Na → $2RO^-$ + $2Na^+$ + H_2 / 2RONA + H_2

Note*: chemical reactivity with Na and oxidation with MnO_4 = 1 > 2 > 3

Properties, Preparation and Reactions of Aldehydes:

Aldehydes and ketones are characterized by the presence of a carbonyl group C=O and their reactivity can generally be understood by recognized that the carbonyl carbon contains a partial positive charge and the carbonyl oxygen contains a partial negative charge.

- As a result, dipole-dipole interactions between molecules can occur.
- Molecules that have a hydrogen atom bonded directly to a N, O or F can form hydrogen bonds with the oxygen of the carbonyl group.

Aldehydes:

Aldehydes are the oxidized products of primary alcohols and have a carbonyl group (C=O) at their terminal carbon end atom. They have the general formula R-CHO.

Melting and boiling point:

Aldehydes are typically gases at room temperature, but larger ones are liquids due to increased dispersion forces from longer chains.

- This is, as mentioned previously, due to the fast as molecules get larger, they have more electrons, and this increases the size of the temporary dipoles that are set up.
  - This is an overshadowing idea for boiling point, irrespective of whether you are talking about aldehydes or ketones.
- Both aldehydes and ketones are polar molecules because of the presence of the carbonyl group. In conjunction with the dispersion forces, there is also attractions between the permanent dipoles on nearby molecules.
  - The boiling points will be higher than those of similarly sized hydrocarbons – which only have dispersion forces.
    - They may have similar lengths, but they have different numbers of electrons.

Solubility:

Smaller aldehydes are soluble in water, but as the chain gets longer, their miscibility decrease.

- Their carbonyl group enables them to hydrogen bond with water molecules.

- As the hydrocarbon portion of the molecule increases in length it can only form dispersion forces with water, which do not provide enough energy on formation to break the hydrogen bonds between water molecules.

Reactions:

Aldehydes are prepared in the laboratory by oxidation of primary alcohols, but they must be isolated once produced so that they do not oxidize further to carboxylic acids.

- ➔ Oxidation = aldehydes can be oxidized to form carboxylic acids.
- ➔ Combustion = aldehydes can burn completely in oxygen to produce carbon dioxide and water.

Note*: no numbering is required to place the aldehyde and carboxylic acid groups as they must be on the end.

Properties, Preparation and Reactions of Ketones:

Ketones:

Ketones are oxidation products of secondary alcohols which have a carbonyl group within their carbon chain. They have the general formula R-COR’

Melting, boiling point and solubility:

Ketones are liquids at room temperature with boiling points that increase with increasing chain length due to increased dispersion forces as the chains get longer.

See ‘Properties, Preparation and Reactions of Aldehydes’ because ketones and aldehydes overlap in their properties.

Reactions:

Ketones are prepared in the laboratory by the oxidation of secondary alcohols. Unlike aldehydes, they are very difficult to oxidize further.

- ➔ Combustion = ketones can burn completely in oxygen to produce carbon dioxide and water.

Properties, Preparation and Reactions of Carboxylic Acids:

Carboxylic acid:

The carboxyl functional group that characterizes the carboxylic acids is unusual in that is composed of two functional groups: the carboxyl group and a hydroxide group bonded to a carbonyl group. This is written as -COOH and the general formula is RCOOH.

Melting and boiling point:

The boiling points of carboxylic acids increases as the molecules get bigger. Carboxylic acids have even higher boiling points then alkanes and alcohols.

- ➔ This is due to the fact that carboxylic acids, similar to alcohols, can form hydrogen bonds with each other as well as dispersion forces and dipole-dipole interactions.

  - However, unique to carboxylic acids, hydrogen bonding can occur between two molecules to produce a dimer.
    - The presence of dimers increases the strength of dispersion forces, resulting in the high boiling points of carboxylic acid.

Solubility:

Carboxylic acids do not dimerize in water, but forms hydrogen bonds with water.

- ➔ Carboxylic acids are polar and due to the presence of the hydroxide in the carboxyl group, they are able to form hydrogen bonds with water molecules.
  - As the hydrocarbon chain increases, then its dispersion forces increase and if its dispersion forces are greater than the hydrogen bonds present in the water, the carboxylic acid will not dissolve.

Reactions:

Carboxylic acids can be prepared by the oxidation of primary alcohols or aldehydes.

- ➔ Carboxylic acids are weak acids and dissociate to a small extent into the H^+ ion and a carboxylate ion. They have the chemical properties of weak acids.
  - Neutralization = carboxylic acids undergo neutralization reactions with alkalis to produce a salt and water.
  - Acid + hydrogencarbonate/ carbonate = salt + water + carbon dioxide
  - Carboxylic acid + reactive metal = salt + hydrogen gas

Esterification:

Carboxylic acids react with alcohols to produce esters.

- ➔ Concentrated sulphuric acid is used to link the alcohol and the carboxylic acid together by removing a water molecule.
  - The H^+ comes from the alcohol and the OH^- from the carboxylic acid.

Properties, Preparation and Reactions of Esters:

Esters:

Esters are known for their distinctive odours and are commonly used for food aroma and fragrances. The general formula of an ester is RCOOR'.

Melting and boiling point:

Small esters have boiling points which are similar to those of aldehydes and ketones with the same number of carbon atoms.

- ➔ Esters, like aldehydes and ketones have dipole-dipole interactions and dispersion forces due to their polar nature.
  - However, they do not form ester-ester hydrogen bonds, so their boiling points are significantly lower than those of an acid with the same number of carbon atoms.

They tend to be liquids at room temperature but evaporate easily.

Solubility:

Small esters are fairly soluble in water, but solubility decreases with increasing chain length.

- ➔ This is because esters cannot hydrogen bond with each other; they can hydrogen bond with water molecules.
  - As the hydrocarbon chain increases in size however, their long chain forces itself between water molecules, breaking the relatively strong hydrogen bonds between these water molecules without offering an energetic compensation.
    - Furthermore, the water molecules are forced into an ordered alignment along the chain, decreasing the entropy in the system → this process is thermodynamically less favourable, and so solubility decreases.

Reactions:

Esters are produced in a laboratory through esterification of carboxylic acids and alcohols.

- ➔ Hydrolysis = esters can be hydrolyzed to form alcohols and carboxylic acids.
  - Acid hydrolysis splits the ester into an acid and an alcohol which is the reverse of the esterification reaction.
    - The ester is refluxed with a dilute acid like hydrochloric or sulphuric acid.
  - Alkaline hydrolysis splits the ester into an alcohol and a carboxylate ion.
    - The ester is refluxed with a dilute alkali like sodium hydroxide.

Fats and oils:

Fats and oils (triglycerides) are esters or glycerol and fatty acids. Triglycerides can be made into soaps.

Properties, Preparation and Reactions of Amines:

Amines:

Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. They have the general formula RNH_2

Amines are further divided into primary, secondary and tertiary groups:

- ➔ Primary amines = only one of the hydrogen atoms in the ammonia molecule has been replaced.
- ➔ Secondary amines = two of the hydrogens in the ammonia molecule have been replaced by hydrocarbon group.
- ➔ Tertiary amines = all of the hydrogens in the ammonia molecule have been replaced by hydrocarbon groups.

Note*: the simplest naming convention to name these compounds is to just have the ‘amino’ prefix before the hydrocarbon.

Note**: it is also noted that very small amines have a smell alike to ammonia, as the amine gets bigger, its smell mimics that of the early stages of decaying flesh.

Melting and boiling point:

Primary amines have high boiling points because they can form hydrogen bonds with each other as well as dispersion forces and dipole-dipole interactions.

- ➔ Hydrogen bonds can form between the lone pair on the very electronegative nitrogen atom and the slightly positive hydrogen atom in another molecule.
  - The hydrogen bonds are not as efficient as they could be because there is a shortage of lone pairs – there are twice as many suitable hydrogens as there are lone pairs.

Secondary amines have a slightly lower boiling point than that of its corresponding primary amine with the same number of carbons. It can still form hydrogen bonds however.

- ➔ But, having the nitrogen atom in the middle of the chain rather than at the end reduces the permanent dipole on the molecule.
  - The lower boiling point is due to the lower dipole-dipole attractions.

Tertiary amines do not contain any hydrogen atoms attached directly to the nitrogen.

- ➔ That means that hydrogen bonding between tertiary amine molecules is impossible.
  - Tertiary amines have the lowest boiling point of all classes of amines.

Solubility:

The small amines of all types are very soluble in water.

- ➔ All of the amines, apart from the tertiary ones, can form hydrogen bonds with water.
  - Even so, tertiary amines can form hydrogen bonds with water molecules just using the lone pair on the nitrogen.
- ➔ As the chain length increases, solubility decreases because the chain forces its way between the water molecules, breaking hydrogen bonds between water molecules.
  - These broken hydrogen bonds are not replaced with anything as strong, and so the process of forming a solution becomes less and less energetically feasible.

Reactions:

Amines that are able to dissolve act as weak bases. They form alkaline solutions by accepting a proton from water, leaving hydroxide ions.

- ➔ Neutralization = amines react with acids to produce a salt and water.

Properties, Preparation and Reactions of Amides:

Amides:

Amides are carboxylic acid derivatives, where the hydroxide group is replaced by an amine group. Hence, this functional group is in the form of $-CONH_2$ and have the general formula $RCONH_2$.

Amides are neutral compounds, unlike their seemingly close relatives the amines, which are basic.

Melting and boiling point:

With the singular exception of $HCONH_2$, which is a liquid, all simple amides are solids.

- ➔ Amides have high boiling points and melting points, this is a result of the polar nature of the amide group and hydrogen bonding.

Solubility:

The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms.

Polymers and Amino Acids

Polymers:

Polymers are covalent molecular substances composed of many small molecules joined together to form a long chain of atoms.

- ➔ Polymers are formed by joining together thousands of smaller molecules, called monomers through the process of polymerization.
  - Polymer chains are made up of identical segments that are repeated along the length of the molecule.
    - Each of these segments is called a repeating unit.

Structural Properties of Polymers

- ➔ Straight-chain polymers = polymers where the monomers form a simple, linear polymer chain like those shown below.
  - Plastics made from straight-chain polymers are known as thermoplastic polymers → they are recyclable.
    - These plastics can be melted to form a liquid and then injected into a mould. Once the polymer cools, it hardens and remains in the shape of the mould → this process is known as injection moulding.

    - In addition, thermoplastic polymers can be shaped by forcing the plastic through a hole of a particular shape, in a process called plastic extrusion.

- ➔ As the chain gets longer, the strength of the dispersion forces between neighbouring polymer chains increases, resulting in the polymer being harder and more rigid.

- ➔ Branched polymers = formed when some monomers react with sites on the side of the polymer chain instead of at the end of the polymer chain
  → these can also be classified as a thermoplastic polymer, as long as there are no covalent cross-linkes between polymer chains.
  - When a monomer joins to the side of a polymer chain, it begins a new polymer chain growing in a different direction.
    - Depending on the nature and extent of the branching, the properties of the polymer change significantly.

e.g. branches can cause the polymer molecules to be spaced further apart, resulting in a material that is less dense.

e.g. the branches can interfere with the intermolecular bonding between the polymer molecules because the polymer molecules are spaced further apart, resulting in a less dense material.

- ➔ With a greater distance between the polymer chains, the intermolecular attraction between neighbouring chains is weakened, increasing the flexibility of the material.
  - As a result, there are less crystalline regions.

Note*: 'plastic' describes a property of a material, rather than the material itself. A substance is described as plastic if it can be easily moulded. Thermoplastic polymers soften when heated, which means they can be remoulded or recycled.

- ➔ Polymers are only thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole-dipole bonds or weak dispersion forces, rather than covalent bonds.
  - When heated, the molecules in thermoplastic materials have enough energy to overcome the intermolecular forces and become free to move and slip past one another.

- ➔ Cross-linked polymers = the polymer branches in a cross-linked polymer are covalently bonded to neighbouring polymer chains. This bonding creates a polymer network.
  → these usually exist as thermosetting polymers.
  - Polymers of this type cannot be liquids because the polymer chains are held in place by the cross-linking and are unable to flow.
  - Thermosetting polymers decompose or burn when heated, rather than melting, and are hard and rigid.
    - They do not soften because the bonds between the chains are very strong. If the temperature is high enough to break the covalent bonds, the bonds may break at any point, causing the polymer to decompose.

- ➔ Elastomers = formed when only occasional cross-links are present. The chains in these polymers can still move past each other when stretched, but the cross-links return the chains to their original positions once the force causing the stretching is released.

- The cross-links stop elastomers from completely melting when heated and makes recycling difficult.
  - A notable example of this is the sulfur cross-links in the polymer used for car tyres.

- Crystalline regions = regularly arranged monomers, bringing the polymer chains closer together, the intermolecular forces between the closely packed chains are stronger and the presence of these regions strengthens the material overall.
  - Crystalline regions also prevent the transmission of light through the material, making it appear opaque (cloudy)

- Amorphous regions = polymer chains are randomly tangled and unable to pack very closely, typically less rigid and weaker and are often transparent.

Natural Polymers:

Natural polymers are those substances which are obtained naturally.

- They are mostly biodegradable, as they are precursor of food and fuel for natural species, which are products of biodegradation.

Examples of natural polymers include:

- Silk = a natural protein fiber produced by the mulberry silkworm, which is able to be woven into textiles.
  - Silk consists of two main proteins, with one of those proteins forming beta pleated sheets, with hydrogen bonds forming between chains, and side chains form above and below the plane of the hydrogen bond network.
    - The addition of the proteins alanine and serine makes the fibres strong and resistant to breaking.
      - This tensile strength is due to the many interceded hydrogen bonds, and when stretched the force is applied to these numerous bonds and they do not break.
- The shimmering appearance of silk is due to the triangular prism-like structure of the silk fibre, which allows silk cloth to refract incoming light at different angles, thus, producing different colours.
- Silk is resistant to most mineral acids, except for sulfuric acid, which dissolve it.
  - It is yellowed by perspiration.
    - Chlorine bleach will also destroy silk fabrics.

- Cotton = the seed hair of plants of the genus *Gossypium* and is primarily composed of the carbohydrate cellulose.
  - Cotton consists of 99% cellulose → These cellulose chains within cotton fibers tend to be held in place by hydrogen bonding; these hydrogen bonds occur between the hydroxide groups of adjacent molecules and are most prevalent between the parallel, closely packed molecules in the crystalline areas of the fiber.
    - The three hydroxide groups, one primary and two secondary, in each repeating cellobiose unit of cellulose are chemically reactive. These groups can undergo substitution reactions in procedures designed to modify the cellulose fibers as well as being the principle sorption sites for water molecules.

- ➔ The web of a Darwin's bark spider = possesses the strongest natural polymer ever studied, in the form of its web.
  - The web is composed of proteins and amino acids that polymerize upon contact with air. The average spider has a web of similar tensile strength to high-grade steel.
    - The Darwin's bark spider's web is twice as strong as the average spider's web and is 10 times stronger than Kevlar.

Synthetic Polymers:

Synthetic polymers are human-made polymers.

- ➔ They can have very different properties of those of materials found in nature; they can be tailored to meet specific applications.
  - They can be made stronger, harder, or more flexible than wood and are resistant to moisture and insects.
  - Furthermore, they can be strong, malleable and ductile like metals.
    - Their primary purpose however is the altering of molecular weight or chemistry to influence degradation or mechanical properties.

Examples of synthetic polymers include:

- ➔ Bakelite = a synthetic plastic that was revolutionary for its electrical nonconductivity and heat-resistant properties in electrical insulators, radio and telephone casings.
  - It is formed from a condensation reaction of phenol with formaldehyde.

Addition Polymerization:

Addition polymerization occurs when under some conditions, alkenes undergo an addition reaction with themselves to produce long chains, known as addition polymers.

- ➔ The reaction of the monomer ethene with itself to form polyethene is an example of this.

Large square brackets and the subscript *n* are used to simplify the drawing of long polymer molecules.

- ➔ The value of *n* may vary within each polymer molecule, but the average molecular chain formed might contain as many as 20,000 carbon atoms. i.e polymers are very large molecules.
  - Because all the atoms of the monomers are present in the addition polymer, the empirical formula of the monomer is the same as that of the polymer.

Ethene is an unsaturated molecule because it contains a carbon-carbon double bound.

- ➔ When ethene polymerizes, the double bond breaks and new covalent bonds are formed between carbon atoms on nearby monomers.
  - The polyethene formed does not contain any double bonds and is therefore a saturated molecule.

Note*: addition polymerization requires monomers that are unsaturated (Contain a double or triple bond carbon-carbon covalent bond). During the polymerization process, the double or triple bond is broken, and single C-C bonds are formed between monomers.

- ➔ The name of a polymer formed through addition polymerization often includes the monomer that was used to make it with the prefix of 'poly'.

Addition Polymers:

Polyethene is the simplest example of an addition polymer, consisting of a long C-C chain.

- ➔ It is essentially an extremely long alkane and as a result, it is non-polar and exhibits only dispersion forces between adjacent long polymer chains.
  - These dispersion forces are sufficiently strong to cause polyethene to be a solid at room temperature.

Polyethene can exist in two different structural forms, depending on its manufacture:

- ➔ Low-density polyethene (LDPE)
  - This polymer is produced under harsh conditions (high temp + high pressure) through the process of free-radical polymerization.
    - The free radicals break the double bonds in the ethane monomers to start the polymerization reaction.

However, the free radicals also attack the sides of the polymer chain, resulting in significant branching.

- ➔ The presence of these branches affects the properties because the molecules cannot pack closely together; dispersion forces become weaker when the molecules are further apart.
  - As a result, it is low-density material that is soft and flexible.
- ➔ The arrangement of the polymer molecules can be described as non-crystalline.

Note*: free radicals are highly reactive atoms, molecules or ions with an unpaired electron.

PROPERTIES (LDPE)
Low density
Relatively soft
Low melting point
Non-crystalline
Non-conductor of electricity

- ➔ High-density polyethene (HDPE)
  - Obtained using low-pressure and highly specialized transition metal catalysts are used to avoid the need for high pressures.
    - The polymer molecules are produced under much milder conditions and have very few branches.

The lack of branches allows the molecules to pack together tightly, increasing the density and the hardness of the polymer formed.

- ➔ The arrangement of the polymer molecules is more ordered, resulting in crystalline sections.

PROPERTIES (HDPE)
High density
Hard
Relatively high melting point
Crystalline sections

Non-conductor of electricity

- ➔ Polytetrafluoroethene (PTFE)
  - More commonly known as Teflon; it is used in non-stick cookware, plumber's tape, machinery parts that require lubrication amongst other applications.
    - It is also non-polar, meaning that it only has weak dispersion forces.

PROPERTY	APPLICATIONS
Non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water and aqueous solutions).
Heat resistance	The melting point of Teflon is 335 C and its upper operating temperature is 260 C.
Chemical resistance	Because of the strength of the C-F bond. Teflon is extremely resistant to all known chemicals. It is not attacked by strong acids and alkalis and is inert to all organic solvents.
Good mechanical properties	Teflon is strong and durable
Low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low due to its very strong C-F bond that renders its highly unreactive.
Flame resistance	Teflon is non-flammable

- ➔ Polyvinylchloride (PVC)
  - when a polymer is made from polar monomers, the chains will be held together by stronger polar attractions, such as dipole-dipole interactions or hydrogen bonds.
    - PVC is polar and comes from the polymerization of chloroethene.

The C-Cl bonds in a PVC molecule are polar and allow dipole-dipole attractions to form between polymer chains. Hence, PVC is harder and more rigid than polyethene and Teflon.

Condensation Polymerization:

Addition polymerization is limited to the use of unsaturated monomers. For this process to occur:

- ➔ The monomers must have two functional groups, one on each end of the monomer. –
  - These functional groups react chemically with the functional groups on neighbouring monomers.

Another feature of condensation reactions is that small molecules are also produced during the reaction.

- ➔ For the condensation polymerization of polyamides and polyesters, a molecule of water is produced.

The polymer backbone contains functional groups such as amides or esters as opposed to the C-C bond backbone that characterizes addition polymers.

Polyesters:

Polyesters are a class of polymers that are formed through the process of condensation polymerization.

- ➔ Polyesters are formed by combining monomers that contain carboxyl and hydroxide functional groups.
  - Typically formed by reacting a dicarboxylic acid monomer with a diol monomer.
  - They can also be formed between monomers that contain both a carboxyl and hydroxide function group within the same monomer.

Polyester Examples:

PET is synthesized by reacting 1,4-benzenedicarboxylic acid monomers with ethane-1,2-diol monomers.

- ➔ PET is a strong material because the ester groups are polar and therefore PET exhibits dipole-dipole attractions between polymer chains.
  - It is used in fibres for clothing, containers for liquids and food, thermoforming for manufacturing, and in combination with glass fibre for engineering resins.

PROPERTIES (PET)
Rigid
Lightweight
Good gas and moisture barrier
Colourless, semi-crystalline
Viscous (the longer the polymer chains, the more entanglements between chains and therefore the higher the viscosity)

Polyamides:

Polyamides typically form when dicarboxylic acid molecules react with diamine molecules.

- ➔ They can also form between monomers that contain both a carboxyl and amino functional group within the same molecule.

Note*: polyamides tend to be stronger than polyesters of similar structures due to the hydrogen bonds that can form between the amide groups on neighbouring polymer chains. In polyesters, ester groups can only form dipole-dipole interactions with each other.

Polyamides Examples:

- ➔ Nylon = refers to a group of polyamides in which the monomers contain linear carbon chains
  - Nylon-6,6 is a common example of this.
    - This polyamide is used most commonly in the textile and plastic industries.

Nylon-6,6 is named because the dicarboxylic acid monomer has a six-carbon chain and the diamine monomer has a chain of six carbon atoms.

PROPERTIES (Nylon 6,6)
Crystalline structure
Relatively high melting point
Exhibits greater mold shrinkage
Good chemical resistance to acids
Strong, yet lightweight
Stiff and rigid

Kevlar comes about when you replace the carbon chains in nylon with benzene rings.

- ➔ Kevlar is extremely strong and is very lightweight.
  - It has used in items such as bulletproof vests and anchor cables.

Kevlar's strength is a product of its molecular structure; the benzene rings make the polymer chains rigid and also allows them to align closely together.

- ➔ As a result, there is strong hydrogen bonding between the amide groups in these molecules.

Amino Acids:

Structure of a-amino acids:

Amino acids are naturally occurring and are molecules that contain both the basic amine group -NH_2 and the acidic carboxyl group -COOH.

- ➔ This makes them amphoteric; they can accept or donate protons.
  - If both the amino and the carboxyl groups are attached to the first or alpha carbon atom, they are called a-amino acids.
- ➔ The part of the molecule that distinguishes it from others is the R group.

Zwitterions:

When amino acids are solid and within a solution, they can exist as zwitterions.

- ➔ This is because the amino acids can form hydrogen bonds with water molecules are soluble in water.

- ➔ These are dipolar ions; they have separate positively and negatively charged groups.
  - This explains their high melting and boiling points as well as their solubility in water.
  - This is due to the zwitterion being present in the solid state, meaning that the amino acids are held together by ionic bonds in the solid state → these ionic bonds require a large amount of energy to break, resulting in their high melting point.
    - Whilst there are oppositely charged groups within this molecule, the net electrical charge is zero – maintaining electrical neutrality.

Solutions of amino acids are also buffers; this means that they resist changes in pH when an acid or base is added to the amino acid in solution.

i.e. different chemical forms of amino acid can be in equilibrium.

- ➔ When an acid is added, the $-NH_2$ group combines with H^+ ions to form $-NH_3^+$
- ➔ When a base is added, the -COOH group combines with OH^- ions by loss of H^+ to form $-COO^-$

At a low pH, due to the equilibrium, the cation forms.

At an intermediate pH, a zwitterion is formed.

At a high pH, the anion forms.

Dipeptides:

A dipeptide is an organic compound derived from two amino acids.

- ➔ The amino acids that make up the dipeptide can be the same or different.
  - When different, two isomers of the dipeptide are possible depending on the sequence.
- ➔ A peptide bond holds together these two amino acids.
  - This peptide bond or amide link is in the form of: -CONH-

Dipeptide Formation:

To form a dipeptide, two amino acids must undergo a condensation reaction.

- ➔ Peptide bonds can be broken down by hydrolysis.
  - Rotation about the carbon-nitrogen bond in the peptide link is restricted, thus, having an influence on the shape and structure of the proteins that are formed from dipeptides.
- ➔ In condensation reactions, water is alleviated in order to synthesize the dipeptide.
  - This H_2O contains an oxygen and hydrogen from the carboxyl group of one amino acid and a hydrogen from the amine group of the other amino acid.

Polypeptide Formation:

Polypeptides form when amino acids form peptide bonds to produce polymer chains.

- ➔ The amino acid monomers are joined by peptide bonds to form polypeptides.
  - A polypeptide is a long, continuous, and unbranched peptide chain.
    - Polypeptides are also said to contain amino acid residues.

Note*: when two or more amino acids combine to form a peptide, the elements of water are removed, and what remains of each amino acid is called an amino-acid residue.

By convention, the structure is drawn so that the free amino group is on the left and the free carboxyl group is on the right.

- ➔ The order of the amino acids is also given in this direction to name the polypeptide or protein.

Primary Structure of Proteins:

The primary structure of a protein refers to the sequence of amino acids in the polypeptide chain.

- ➔ The primary structure is held together by peptide bonds and consists of a polypeptide of more than 50 amino acids.

Note*: the primary structure may be represented by the three-letter abbreviations for the amino acids or by a structural formula of the protein.

Secondary Structure of Proteins:

Secondary structure refers to the highly regular local sub-structures on the actual polypeptide backbone chain.

- ➔ The two main types of secondary structure, the a-helix and b-pleated sheets are defined by patterns of hydrogen bonds between the main-chain peptide groups. → the hydrogen bonds cause the chain to cross-link, resulting in the above structures.
  - Hydrogen bonding between amide and carbonyl functional groups within a peptide chain = a-helix.
  - Hydrogen bonding between adjacent polypeptide chains = b-pleated sheets.

Tertiary Structure of Proteins:

Tertiary structure refers to the three-dimensional structure of monomeric and multimeric protein molecules.

- ➔ The a-helixes and b-pleated sheets are folded into a compact globular structure.

This structure arises as a result of:

- ➔ Disulphide bridges = covalent bonds between two sulphur-containing side groups. This forms a very strong bond.
- ➔ Hydrogen bonding = occurs between groups like OH^- and NH_2.
- ➔ Dipole-dipole interactions = occurs between polar side groups.
- ➔ Dispersion forces = weak interactions between non-polar side groups such as methyl and CH_3.
- ➔ Ionic interactions = occurs between charged side groups like CO_2^- and NH_3^+

Enzymes:

Enzymes are biological catalysts that accelerate chemical reactions.

- ➔ Most enzymes are proteins and from their 3D structure, they are specific to certain biological reactions.
  - They allow substrates to react and form products at the rate necessary for the cell to survive.
- ➔ Being catalysts, they aren't used up in the reaction and work by providing an alternative pathway to lower activation pathway.
  - Their activity is affected by inhibitors, activators, temperature and pH.

Examples of enzymes include:

- Protease = hydrolyzes peptide bonds of proteins and aids digestion.
- Lipase = hydrolyzes fat and lipids.
- Amylase = hydrolyzes dietary starch into disaccharides and trisaccharides, enabling them to be converted by other enzymes into glucose
- Catalase = catalyzes the decomposition of hydrogen peroxide into water and oxygen.

The Protein Data Bank (PDB):

The PDB houses an international repository of the structural data of known proteins.

- Most of the data has been determined by X-ray crystallography which provides the 3-D coordinates of the atoms within a protein. Other methods including nuclear magnetic resonance (NMR), vibrational spectroscopy and cryo-electron microscopy
  - This has enabled more structures and many of higher resolution to be recorded.
- When a new protein is discovered, comparison to other proteins through databases like PDB can help predict its function.

- The function of a protein is dependent on its 3-D structure.
  - This arises as a result of the various functional groups within the protein, which account for its function and shape.

Examples include:

- Structural proteins = proteins that are more rigid than others and can form structural parts of cells.
  - Collagen for example, which provides support for connective tissues such as tendons and ligaments.
- Contractile proteins = more flexible and their function is due to their ability to act as springs, levers or hinges.
  - Myosin which is involved in muscle contraction and movement.
- Hormonal proteins = messenger proteins which help coordinate certain bodily activities.
  - Insulin which controls blood-sugar concentration.
- Transport proteins = move molecules from one place to another around the body.
  - Haemoglobin transports oxygen through the blood via red blood cells.
- Storage proteins = store metal ions and amino acids.
  - Ferritin stores iron in the body.

Chemical Synthesis

Ethanol Production:

Industrial Production by Fermentation:

Grains and matter, usually sugar and sugar cane, are crushed and ground finely, before adding water and then heating to 85-105°C in the presence of the amylase and cellulase enzyme.

- ➔ This process breaks down the polysaccharides present in the raw materials into monosaccharides – these can undergo fermentation.

Following cooling, the processed raw materials undergo fermentation in fermentation tanks.

- ➔ The process stops when the ethanol content is between 15% and 18%; this is because otherwise the yeast cells and their enzymes can no longer function.

Yeast and its enzymes are annihilated by ethanol concentrations greater than 15%.

- ➔ Hence, the purity of the ethanol is significantly limited.
  - The ethanol is separated from the mixture by fractional distillation to give roughly 96% pure ethanol.
    - It is impossible to remove the last 4% of water by fractional distillation because of it being azeotropic – part of the mixture exhibits the same concentration in the vapour phase and the liquid phase which results in no part of the mixture being volatile, thus rendering it unextractable via boiling point.
      - ■ Minimum boiling point azeotrope.

The fermented mixture then undergoes repeated distillations to purify the ethanol.

- ➔ When cooled, the resulting liquid contains about 96% ethanol and 4% water.

Air is kept out of the mixture to prevent oxidation of the ethanol produced to ethanoic acid.

A biological catalyst used in this process is zymase.

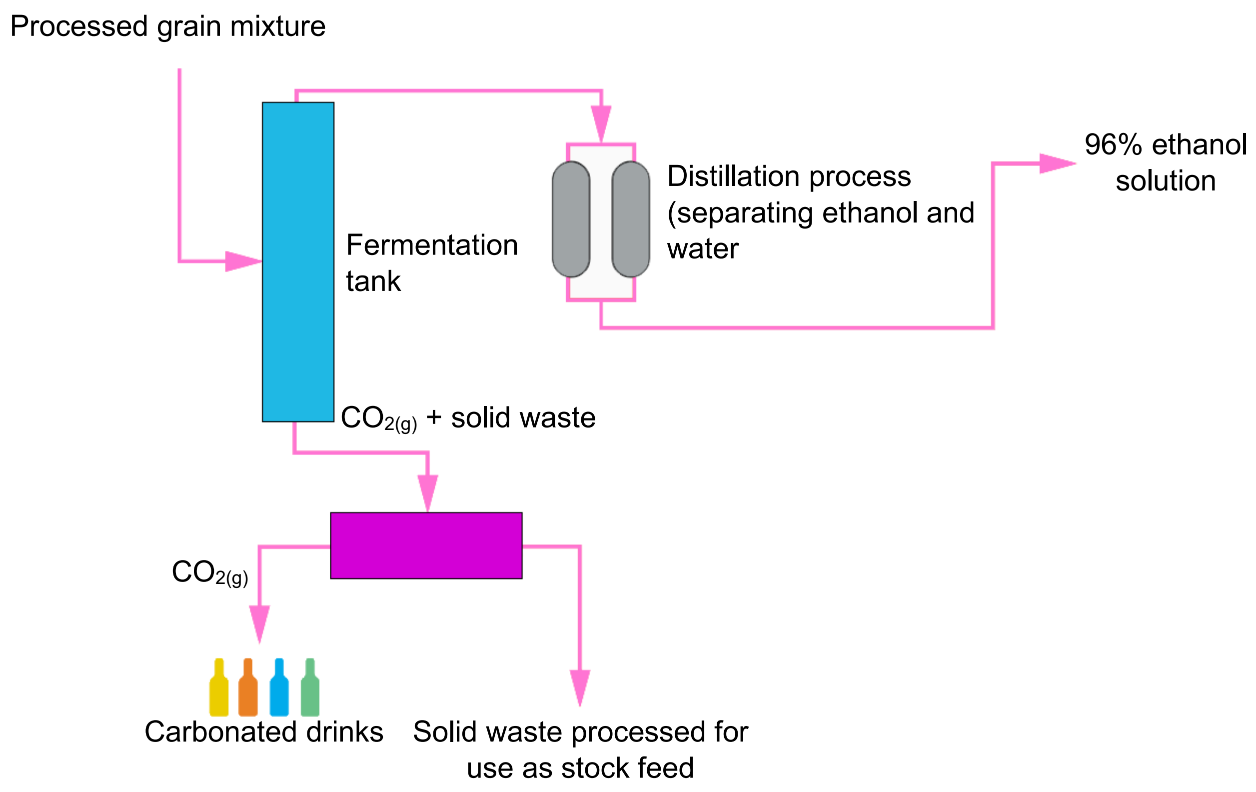
$$\boxed{C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2CH_3CH_2OH + 2CO_2}$$

Type of Process	Everything is placed in a container and then left until the fermenting process is complete. This is very inefficient
Rate of Reaction	Very slow.
Quality of Product	Produces extremely impure which requires further processing.
Reaction Conditions	Gentle temperatures and atmospheric pressure.
Materials	Uses renewable resources based on plant material; monosaccharides from grains etc.
Purification Method	Many distillations are needed.
Cost	Low.

Raw Materials:

Although starches and sugars are often used as the raw material for fermentation, another polysaccharide called cellulose – found in biomass such as woody plants – can function as a raw material for fermentation.

- ➔ The *E. coli* bacteria has been developed to convert polysaccharides in materials like forestry waste, corn stalks and sugarcane residue into ethanol, in conjunction with the cellulase enzyme.
    - This material simultaneously produces a valuable chemical and reduces the need to dispose of these waste materials in landfills or by burning.



Once the fermentation and distillation processes are complete, the 96% ethanol mixture is then dehydrated (the water is removed); this leaves a 99.7% pure ethanol mixture.

- ➔ If the production of ethanol isn't for the purpose of alcoholic beverages, then the final ethanol is poisoned by adding up to 5-10% of methanol or petrol typically.
    - This is to prevent its consumption as drinking alcohol.

Industrial Production by Hydration of Ethene:

Ethanol is produced via the reaction between steam and ethene.

- ➔ The catalyst used is solid silicon dioxide coated with phosphoric acid.
    - The reaction is reversible.

$$\mathbf{CH_2CH_{2(g)} + H_2O_{(g)} \xrightarrow{H_3PO_4} CH_3CH_2OH_{(l)}} \quad \Delta H = -45kJ/mol$$

- ➔ This reaction is carried out with the following conditions:
    - High temperature = 300°C

  - High pressure = 60-70 atm
  - Catalyst = phosphoric acid catalyst.
    - These compromise conditions come about for the same reasons as the Haber process and the Contact process.

The reaction mixture passes through a reactor several times, converting about 5% of the ethene to ethanol each time.

- ➔ The reaction mixture is then cooled to liquefy the ethanol, and hence, water that did not react also is liquefied.
  - A solution of ethanol and water combined is then collected.
    - Unreacted ethene is heated and cycled back into the reactor.

Note**: other alcohols can be made with similar reactions; the catalyst used, and reaction conditions will vary from alcohol to alcohol.

- ➔ However, problems arise when you attempt to replicate this process with other alcohols:

Consider the following:

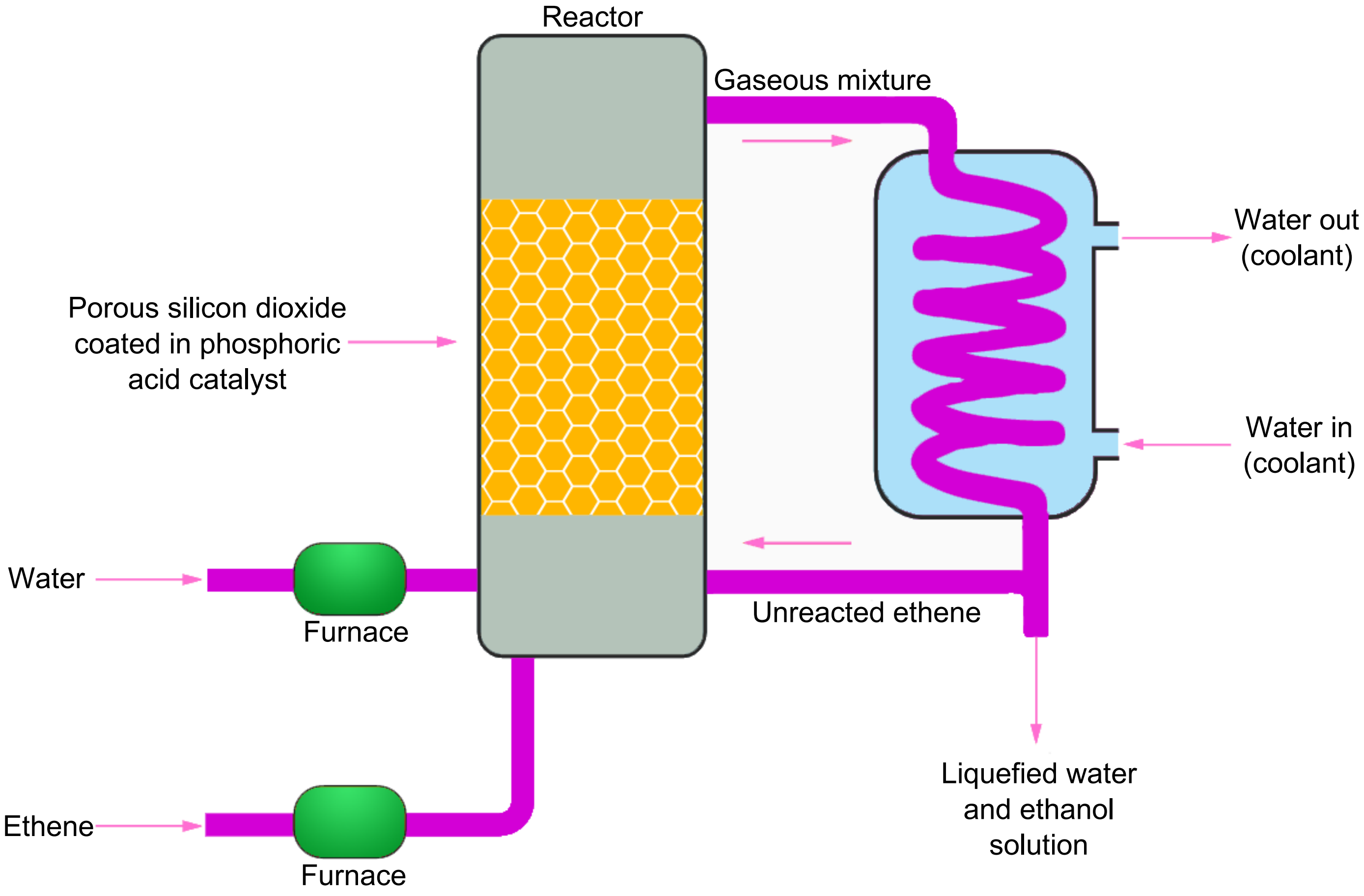
If you tried to make an alcohol from propene, two alcohols might be formed.

- ➔ Propan-1-ol.
- ➔ Propan-2-ol.
  - Theoretically, you should get propan-2-ol because the hydrogen most of the time is attached to the carbon with the most hydrogens on it (Markovnikov's rule).
    - The effect of this is that there are some alcohols which are impossible to make by reacting alkenes with steam because the addition would be the wrong way around.

Raw Materials:

Many small hydrocarbons are obtained through catalytic cracking.

- ➔ This is a process where large carbon-based molecules from crude oil are broken up into small molecules using a catalyst and a moderate temperature.



Type of Process	A continuous, flowing process. A stream of reactants is passed continuously over a catalyst – this is very efficient.
Rate of Reaction	Very rapid.
Quality of Product	Produces much more pure ethanol than fermentation.
Reaction Conditions	Uses high temperatures and pressures; this requires lots of energy input.
Materials	Uses finite resources based on crude oil.
Purification Method	Limited distillations required.
Cost	High.

Ethyl Ethanoate Production:

To produce ethyl ethanoate, a multi-step process is required.

- ➔ Put simply, to product ethyl ethanoate the following can be done:

1. Hydration of an ethene to produce ethanol.

$$CH_2CH_{2(g)} + H_2O_{(g)} \xrightarrow{H_3PO_4} CH_3CH_2OH_{(l)} \quad \Delta H = -45kJ/mol$$

2. Ethanol can be oxidised to ethanoic acid.

$$CH_3CH_2OH_{(l)} \xrightarrow{[O]} CH_3COOH_{(l)}$$

3. Ethanoic acid can then be used to react with more ethanol, production ethyl ethanoate.

$$CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \xrightarrow{H_2SO_4} CH_3COOCH_2CH_{3(l)} + H_2O_{(l)}$$

Biodiesel Production:

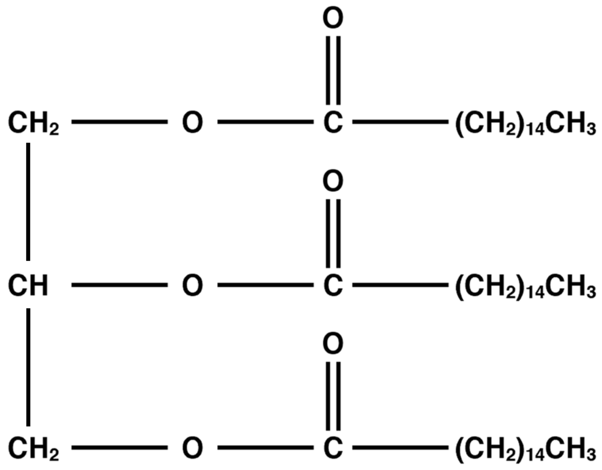
Biodiesel is a mix of esters when vegetable oil and an alcohol (usually methanol) react.

- ➔ The physical and chemical properties of biodiesel esters closely resemble those of diesel – a fossil fuel.

Raw Materials:

Vegetable oil is usually derived from soybeans, canola or palm oil.

- ➔ Vegetable oil previously made can be recycled and animal fats can also be used.

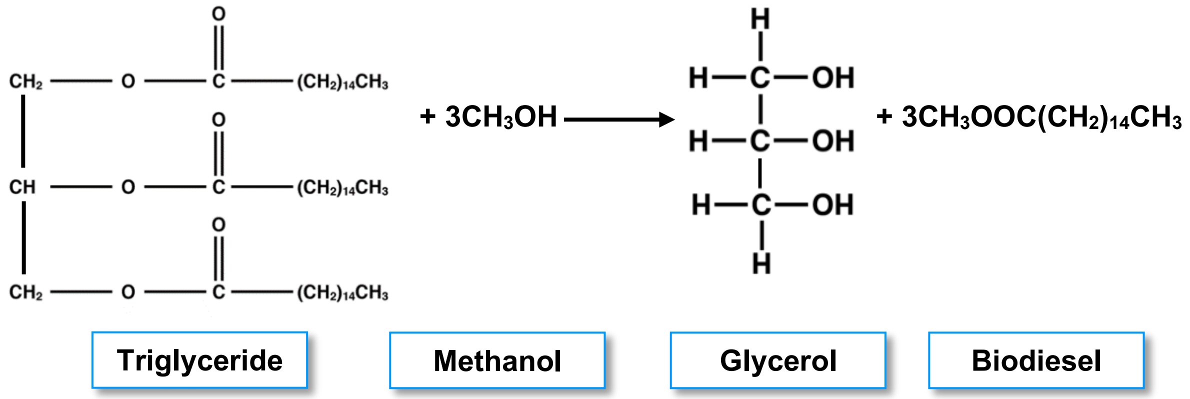


Triglyceride

Oils and fats are triglycerides with a molecular structure consisting of three hydrocarbon chains, attached by ester functional groups to a backbone of three carbon atoms.

- The triglyceride is converted into biodiesel by warming it with an alcohol (methanol)
  - This process is known as transesterification.

Transesterification = triglyceride is converted into three molecules of fatty acid ester, carboxylic acids with long carbon chains, and glycerol.



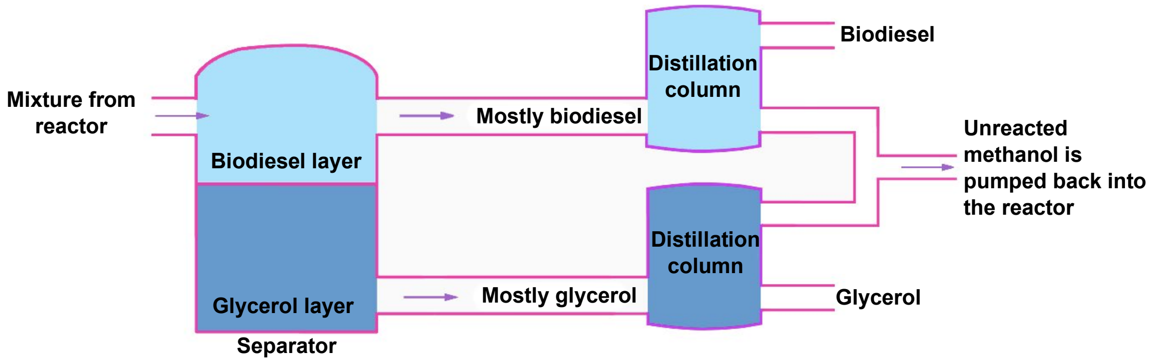
To produce biodiesel:

1. Triglycerides, methanol and a catalyst are added to a reactor in a batch process.
2. The initial mixture is heated gently and left for at least 30 minutes; the time depends on the catalyst used and conditions selected.
3. The reaction mixture is then pumped into a separator.

- Glycerol is a relatively small molecule with three hydroxyl functional groups; it is quite polar.
- However, the long hydrocarbon chain on the methyl ester makes the molecule non-polar.
  - Hence, inside the separator, the two products do not dissolve in one another and separate into two distinct layers.

The biodiesel and glycerol extracted from the separator then undergoes distillation to remove any unreacted methanol.

- This methanol is then recycled back into the reactor.
  - The biodiesel and glycerol can then be collected separately.



Biodiesel Catalysts:

For the production of biodiesel, there are two types of catalysts that can be used:

- ➔ Lipase = naturally occurring enzyme.
- ➔ Sodium Hydroxide = base catalyst.

Currently, the base-catalyzed process is the most used.

- ➔ This is because it can use methanol and allows for plant operation at high temperatures; this makes the conversion process quicker and more economical.
  - However, the base can only be used once in each batch.

Note**: the amount of base added must be carefully monitored.

- ➔ When a mole ratio of 3:1 between the base and triglyceride is reached, the formation of soaps occurs. This:
  - Reduces the conversion of triglycerides to biodiesel.
  - Causes issues with the separation process.

Conversely, lipase can be used for up to 100 days.

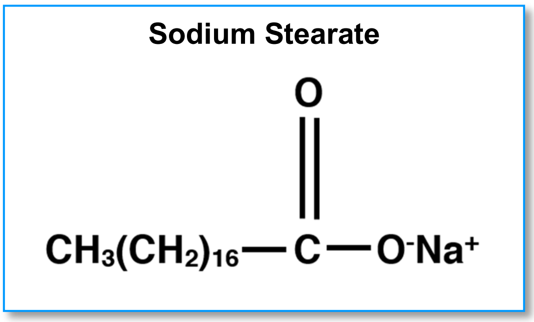
- ➔ It also requires less energy to produce and the transesterification process can be carried out at lower temperatures and pressures, reducing costs.
  - The slow reaction rate of lipase limits it use.

Condition	**Base-catalyzed production**	**Lipase-catalyzed production**
Temperature	60-70°C	20-37°C
Pressure	1.4-4 atm	1 atm
Time	30-60 min in the reactor	A minimum of 150 min in the reactor
Catalyst use	Only able to be used for one cycle of the production process	Can be used for up to 100 days
Yields	96-98%	Up to 92% but typically approximately 80%

Soap:

Soap particles contain a long hydrocarbon chain attached to a charged end.

- ➔ The structure of sodium stearate – a common soap – is shown below:



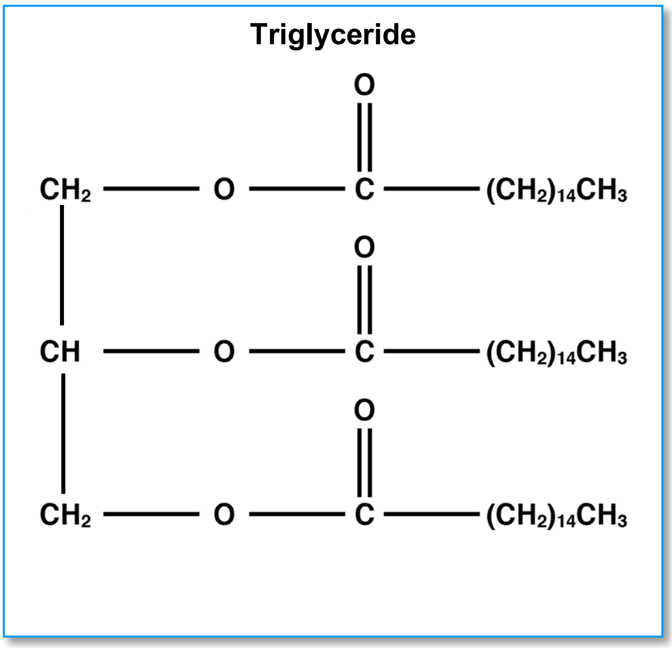
Sodium Stearate

$$CH_3(CH_2)_{16}-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+$$

The main ingredient required for the manufacture of soaps is a triglyceride.

- ➔ A triglyceride is a type of ester formed by the reaction of glycerol and three carboxylic acid molecules.

Fatty acids = carboxylic acids with long hydrocarbon chains.



Triglyceride

Note**: the formation of a triglyceride is an esterification reaction, and hence, water is a by-product in this reaction.

Triglycerides, commonly referred to as fats and oils, are produced naturally in plants and animals.

- ➔ Animal fats tend to be saturated – single bonds between carbon atoms.

Olive oil, canola oil and palm oil exist as liquids at room temperature and are unsaturated fats – contain one or more double or triple carbon-carbon bonds.

To make a soap from a triglyceride:

- ➔ The ester functional group must be broken.

- Although this can occur through the reaction of a triglyceride and water, the reaction rate is very slow and hence, a strong base like sodium hydroxide or potassium hydroxide is used.
  - This is known as base hydrolysis.
    - Specifically, for esters, this is called saponification.

Base hydrolysis breaks the three ester bonds into:

1. **$CH_3(CH_2)_{16}COO^-$**

2. **$CH_2(OH)CH(OH)CH_2(OH)$**

Soap particle = metal ion from the base used for hydrolysis + fatty acid ion.

- ➔ Soaps consist of:
  - A long hydrocarbon chain – this is an alkyl group as the hydrocarbon is saturated.
  - A carboxylate ion attached to the hydrocarbon tail – it is often referred to as the 'head' of the soap.
    - These are the conjugate bases of carboxylic acids.
  - A metal ion.

Even if a pure source of oil is used, the fatty acids in the triglyceride can vary.

- ➔ Hence, **R, R'** and **R''** are used for the fatty acid and their ions.

A by-product of soap manufacture is glycerol.

- ➔ It is sometimes retained because it improves moisturizing properties, however, usually it is separated for other purposes.

Laboratory Production of Soaps:

Soap can be prepared by heating a mixture of a suitable fat or oil with a concentrated sodium hydroxide solution.

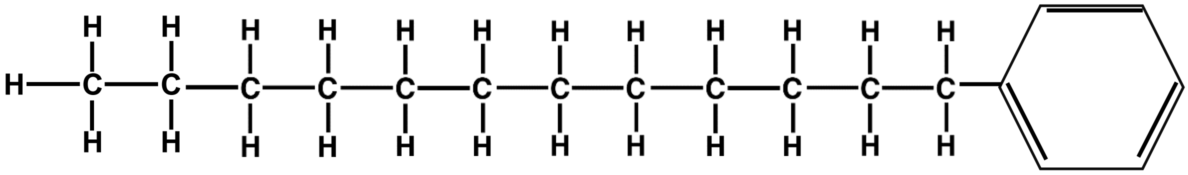
- ➔ The product is then rinsed and pressed into a mould.

Detergent:

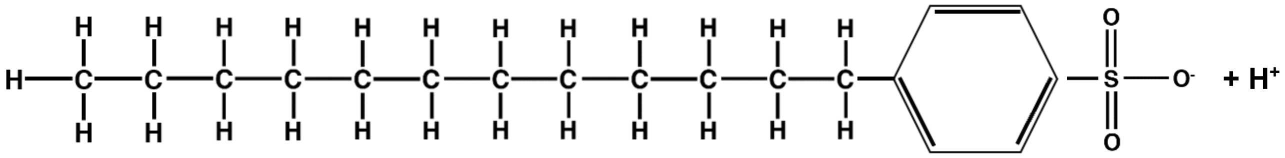
Detergents are typically alkylbenzenes sulfonates:

They are produced in a three-step process:

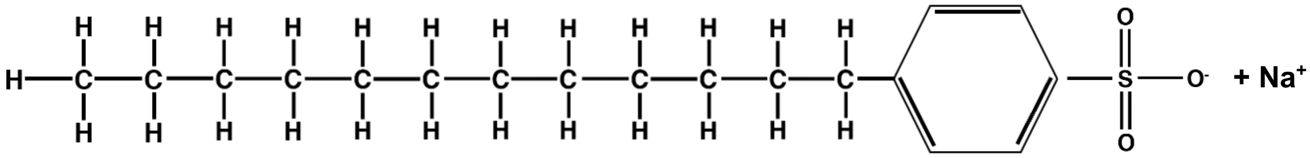
1. Alkylbenzenes are produced from the reaction between benzene and a halogenoalkane.



2. The alkylbenzene is reacted with concentrated sulphuric acid to produce an alkylbenzene sulphonic acid.



3. The alkylbenzene sulphonic acid is neutralized with sodium hydroxide to produce a detergent – sodium alkylbenzene sulphonate.



How do Soaps and Detergents Work?

Soaps and detergents are surfactants/ wetting agents.

- ➔ They enable water to wash away oils and grease.
  - Oil and grease are non-polar and do not dissolve in water.

Once soaps and detergents dissolve, they have:

- ➔ A hydrophobic, non-polar hydrocarbon ends which will bond with oil and grease.
- ➔ A hydrophilic, polar, charged end which will bond with water.

With soaps, the non-polar end is the hydrocarbon chain and the polar end is the carboxylate group.

With anionic detergents, the non-polar end is a hydrocarbon chain containing a benzene ring (often dodecylbenzene) and the polar end is the sulfonate group.

- ➔ On agitation in water, the surfactant molecules can surround small droplets of oil and grease; a micelle then forms.
  - The hydrophobic end dissolves in the oil and the hydrophilic end in water.
    - These small droplets can now be washed away as they are effectively dissolved in water.

Soaps are not effective in hard water as it contains calcium and magnesium ions and these form a precipitate – scum – with the soap ions, removing them from solution.

$$2CH_3(CH_2)_{16}COO^-Na^+ + Ca^{2+} \longrightarrow (CH_3(CH_2)_{16}COO^-)_2Ca^{2+} + 2Na^+$$

Contrastingly, detergents do not form scum with calcium or magnesium ions and so can be used in hard water.