

Revision - Units 3 _ 4

Revision - Units 3 & 4

#Chemistry

#Exam

#Revision

- [Chemical Equilibrium Systems](#)
 - [Dynamic Equilibrium](#)
 - [Measuring Equilibrium](#)
 - [Acids](#)
 - [Water Self-Ionisation and the pH Scale](#)
 - [The Brønsted-Lowry Model and Buffer Solutions](#)
 - [Dissociation Constants](#)
 - [Acid Base Indicators](#)
 - [Volumetric Analysis](#)
- [Oxidation and Reduction](#)
 - [Redox Reactions](#)
 - [Rules of Oxidation Numbers](#)
 - [Balancing Redox Reactions](#)
 - [Electrochemistry](#)
 - [Galvanic Cells](#)
 - [Standard Electrode Potential](#)
 - [Electrolytic Cells](#)
- [Organic Materials](#)
 - [Structure of Organic Compounds](#)
 - [Order of Priority for functional groups \(Higher priority should be the suffix\):](#)
 - [Physical Properties and Trends](#)
 - [Organic Reactions and Pathways](#)
 - [Markovnikov Rule](#)
 - [Haloalkane Reactions](#)
 - [Chemical Tests](#)
 - [Alkane and Alkene](#)
 - [Alcohols](#)
 - [Macromolecules - Structure and Function](#)
 - [Proteins](#)
 - [Primary](#)
 - [Secondary](#)
 - [Tertiary](#)

- [Quaternary](#)
 - [Enzymes](#)
 - [Carbohydrates](#)
- [Lipids](#)
- [Synthetic Polymers](#)
- [Analytical Techniques](#)
 - [Mass Spectrometry](#)
 - [How to Analyse Mass Spectrometry Graphs](#)
- [Chemical Synthesis](#)
 - [Haber Process](#)
 - [Contact Process](#)
 - [Biofuel Production](#)
 - [Base-catalysed Transesterification](#)
 - [Hydrogen Production](#)
 - [Hydrogen Fuel Cells](#)
 - [Acidic Conditions](#)
 - [Alkaline Conditions](#)
- [Green Chemistry](#)
 - [Renewable Feedstocks](#)
 - [Safer Solvents and Auxiliaries](#)
 - [Waste Prevention](#)
 - [Atom Economy](#)
- [Macromolecules - Synthesis](#)
 - [Addition Polymerisation](#)
 - [Condensation Polymerisation](#)
 - [Polymer Use](#)
 - [Strength](#)
 - [Density](#)
 - [Lack of Reactivity](#)
 - [Use of Natural Resources and Biodegradability](#)
- [Molecular Manufacturing](#)

Unit 3

[Unit 3](#)

Chemical Equilibrium Systems

Dynamic Equilibrium

[Chemical Equilibrium](#) is referred to as dynamic as a change to the conditions can alter the [equilibrium position](#).

Two factors which influence the [equilibrium position](#) of a reaction are **concentration** and **temperature**.

Changes in **concentration** can occur by:

- Diluting an aqueous solution
- Changing pressure and volume
- Adding or removing reactants or products.

A change in [concentration](#) will result in the system partially opposing this change by shifting the equilibrium away from the side which concentration was added to.

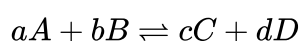
[In gaseous systems](#), if the **pressure** of the system is increased by decreasing volume, the system will oppose the change by moving towards the side with less molecules and vice versa.

[A change in temperature](#) will result in the system partially opposing the change by moving in either the endothermic or exothermic direction, whichever direction opposes the change.

A **catalyst** increases the rate of both the forward and reverse reactions equally, [therefore it does not change the equilibrium position by simply allows the reaction to reach equilibrium faster](#).

Measuring Equilibrium

A [chemical equilibrium](#) can be quantified by the use of the equilibrium constant (K_c). For the reaction:



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

If a system is not at equilibrium, Q_c is used to calculate its current position. A RICE table can be used to determine the changes necessary to return to equilibrium.

Acids

Acids are substances which donate H^+ ions when dissolved in water.

A **monoprotic** acid can donate [one proton](#).

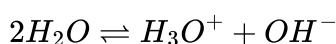
A **polyprotic** acid can donate multiple protons. In polyprotic acids, normally the acid becomes weaker as it donates protons so it tends not to fully donate all H^+ ions.

Strong acids and bases completely dissociate in water whereas weak acids do not completely dissociate.

Acids and bases are electrolytes as they consist of positive and negative ions. Strong acids and bases are **more conductive** than weak acids and bases.

Water Self-Ionisation and the pH Scale

Water is a weak electrolyte meaning that a small fraction of H_2O molecules react to form H_3O^+ and OH^- ions. This process is called the self-ionisation of water.



The equilibrium constant for water dissociation is:

$$K_w = [H^+] \times [OH^-]$$

In pure water, there is always an equal amount of H^+ and OH^- ions.

The self-ionisation of water is **endothermic** meaning with an increase of temperature, the reaction will favour the forward direction, creating more H^+ and OH^- ions.

pH is a scale which measures the **concentration** of H^+ ions in a solution.

$$pH = -\log[H^+]$$

pH values below 7 are considered acidic and above 7 are considered basic. A pH of 7 is neutral.

pOH represents the concentration of OH^- ions in a solution, meaning it measures a solution's **alkalinity**.

$$pH + pOH = 14 \text{ at standard conditions (SLC).}$$

pH and pOH

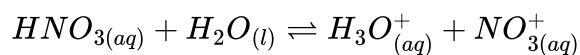
The Brønsted-Lowry Model and Buffer Solutions

Acids are defined as proton donors and bases are proton acceptors.

A **conjugate acid** is formed when a base **accepts** a H^+ ion.

A **conjugate base** is formed when an acid **loses** a H^+ ion.

In the dissociation of nitric acid (HNO_3), a conjugate pair is formed.

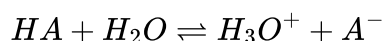


Amphiprotic substances can **either donate or accept** a proton and can therefore act as an acid or a base. Common examples are water, [Amino Acids](#) and HCO_3^- ions.

[A buffer solution](#) is a solution which resists changes in pH when small quantities of acids or alkalis are added.

It does so by being a weak amphiprotic solution meaning it holds an equilibrium which will oppose any change according to LCP.

The general equation for a [Buffer](#) is:



Where HA is a weak acid and A^- is the conjugate base.

For a weak acid, the conjugate base is strong and for a weak base, the conjugate acid is strong and vice versa.

Dissociation Constants

Weak acids partially dissociate in an aqueous solution, the degree to which they dissociate is represented by the K_a value.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak acids have a $K_a < 1$ and strong acids have a $K_a > 1$. It can be assumed that H_3O^+ and A^- concentration are equal for all intents and purposes.

Similar to acids, the general dissociation constant for bases is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$K_a \times K_b = K_w$$

Values of K_a and K_b that are similar to pH, are often very small or very large numbers. As a result, pK_a and pK_b are normally used.

Acid Base Indicators

An **indicator** is a chemical substance that changes colour at different pH values. Most indicators are weak acids in equilibrium with their conjugate base. The acid and the conjugate base are different colours.

Weak bases can also be used as indicators, and they work in the same way.

Generally, indicators are effective over a range of $pK_a \pm 1$. They change colour when $pK_a = pH$.

Volumetric Analysis

Titration is a method for determining the concentration of an unknown acid or base by neutralising it with a known base or acid.

The **equivalence point** of a titration is when just enough titrant has been added to **completely neutralise** the analyte. For a strong base - strong acid titration, the number of moles of base is equal to the number of moles of acid and the solution contains only salt and water. For a strong base and weak acid the equivalence point is above 7 and vice versa due to the production of a conjugate.

pH indicators are crucial for finding the **end point** of a titration which is as close as possible to the equivalence point but is where the solution actually **changes colour**.

To complete a titration a **standard solution** must be prepared to be used as the **titrant**. A standard solution is created from a **primary standard** solute dissolved in an aqueous solvent. Once the titrant is dispensed from the burette, it is called the **titre**.

Aliquot is the volume measured by a pipette.

The intercept with the pH axis on a titration graph is the pH of the analyte.

When titrating a weak acid or base, the **Buffer zone** is a flatter part of the curve that exists over a pH range of approximately ± 1 of the pK_a . The point when $pH = pK_a$ is called the half-equivalence point which is also when the concentration of the titre is equal to half the original concentration of the analyte.

Oxidation and Reduction

Redox Reactions

Redox reactions are any chemical reactions involving the transfer of electrons from one reactant to another.

An **oxidising agent** causes another reactant to be oxidised and is itself reduced.

A **reducing agent** causes another reactant to be reduced and is itself oxidised.

OIL RIG is an acronym to remember that **oxidation** involves the **loss** of electrons whereas **reduction** is a **gain** of electrons.

Oxidation Is Loss

Reduction Is Gained

Elements in group 1 and 2 of the periodic table readily lose their valence electrons in order to have a complete outer shell. This makes them **strongest reducing agents**. Elements in group 17 are the **strongest oxidising agents** because they have a high electronegativity and wish to gain an electron to complete their outer shell.

There are 3 main types of [Redox Reactions](#):

- Displacement reactions
- Combustion reactions
- Corrosion reactions

Displacement reactions occur when a stronger reducing agent replaces a weaker reducing agent in a molecule.

Combustion reactions occur when a substance reacts with oxygen.

Corrosion reactions occur when a metal reacts with chemicals in the atmosphere. Normally results in the production of a metal oxide (rust).

An **oxidation number** is the number of electrons lost or gained by an atom in a redox reaction.

Rules of Oxidation Numbers

Elements have an oxidation number of 0

Group 1 metals are +1

Group 2 metals are +2

Hydrogen is +1 (except in metal hydrides where it is -1)

Oxygen is -2 except in peroxide where it is -1

For monatomic ions, the charge of the ion is the oxidation number (H^+ is +1)

In polyatomic ions, the sum of the oxidation numbers is the charge (NH_4^+ is +1)

In a neutral compound, the sum of the oxidation numbers is equal to 0.

The most electronegative element has a negative oxidation number (Stronger Oxidising Agents)

Balancing Redox Reactions

Transition metals have multiple oxidation states. When there is no rule for oxidation state, oxidation numbers can be calculated by using the charge of the compound and the known oxidation state of the other element/s.

All redox chemical reactions can be written as two half-equations, the oxidation and the reduction half-reaction. [Steps for balancing a reaction using the half reaction method](#):

1. Work out oxidised and reduced species.
 2. Exclude spectator ions.
 3. Work out oxidation states.
 4. Create balanced skeleton half equations.
 5. Use water to balance oxygen.
 6. Use protons to balance.
 7. Use electrons to balance.
 8. Multiply half equations to balance electrons lost and gained.
 9. Combine half equations and cancel anything that is the same on both sides.
-

Electrochemistry

[Redox Reactions](#) can convert chemical potential energy to electrical energy or vice versa. For this reason, they are often used in batteries as they can store and release electrical energy. In galvanic and electrolytic cells, there are two simultaneous half-reactions occurring at the anode (oxidation) and cathode (reduction). The flow of electrons from one to another is either provided by an external source in the case of a non-spontaneous reaction (electrolytic cell) or utilised by a load (galvanic cell).

Galvanic Cells

Galvanic cells use spontaneous [Redox Reactions](#) to generate an electrical current.

A galvanic half-cell consists of a metallic ion solution and an electrode made out of the same metal or an inert electrode. Two half-cells connected by a salt bridge form a full galvanic cell. In a galvanic cell, the anode is negatively charged and the cathode is positively charged.

A salt-bridge is the internal circuit that connects the two half-cells. Its purpose is to allow the movement of ions between the half-cells to neutralise the charge.

Standard Electrode Potential

Some chemicals gain or lose electrons more readily than others. The electrochemical series is a table of the strength of oxidants and reductants that demonstrates using reversible half-reactions the reactivity of certain species in standard conditions.

[The standard electrode potentials of certain substances can be used to predict the electrical output of galvanic cells.](#)

In galvanic cells, the reduction half-equation is lower on the electrochemical series. Therefore, to calculate EMF subtract the top E° from the bottom E° . In electrolytic cells, the opposite is the case.

$$EMF = E_{reduction}^\circ - E_{oxidation}^\circ$$

Electrolytic Cells

Electrolytic cells use an external potential difference to provide the energy to allow a spontaneous reaction to occur. An electrolytic cell is similar to a backwards galvanic cell, except the half-cells are separated by just a porous membrane instead of a solid divider. In an electrolytic cell, the cathode is negative, and the anode is positive. The voltage required by an electrolytic cell must be greater than the EMF that the galvanic cell would normally generate on discharge.

Electrolytic cells can be used for practical application such as metal plating and purification. Copper can be purified by electrolysis by the use of a pure copper cathode and an impure anode. As copper is the strongest reductant and oxidant in this reaction, the copper from the anode is oxidised and falls into solution and then is reduced at the cathode to form pure copper. A very similar process is employed for metal plating.

The electrolysis of molten salt occurs at very high temperatures as the salt must be a liquid. The electrolysis of NaCl would form molten sodium and chlorine gas.

Unit 4

[Unit 4](#)

Organic Materials

Structure of Organic Compounds

Hydrocarbons are the simplest form of organic compound, consisting of the elements carbon and hydrogen.

The **main chain** is the longest chain of carbon atoms in a hydrocarbon molecule.

Alkane - Single Bonds

Alkene - Double Bond/s

Alkyne - Triple Bond/s

Chain Length	1	2	3	4	5	6	7	8	9	10
Prefix	Meth-	Eth-	Prop-	But-	Pent-	Hex-	Hept-	Oct-	Non-	Dec-

When there is **more than one** substituent in a molecule, then name the substituents in alphabetical order. If more than one of the same type, then use a prefix **multiplier**.

Number of Homogenous Substituents	2	3	4	5
Prefix	Di-	Tri-	Tetra-	Penta-

IUPAC Rules specify:

- Suffix must have the lowest possible locant (location of double and triple bonds in organic compound)
- When there are multiple substituents, number the positions from left to right or right to left so they have the lowest value
- When there are multiple branches and no points of difference, list the substituents in alphabetical order

The main chain can either be straight (**non-cyclic**) or **cyclic**. Cyclic hydrocarbons have the prefix cyclo-.

A **functional group** is an atom or group of atoms in an organic compound that determines the reactivity of the compound.

Alcohols are a class of organic compound that contains the hydroxyl functional group. The hydroxyl group can be located on any carbon atom in the main chain.

Primary alcohols are alcohols in which the carbon that is bonded to the hydroxyl group is only bonded to one other carbon atom.

Secondary is where the carbon atom is bonded to two others.

Tertiary is where it is bonded to three other carbon atoms.

Aldehydes and **ketones** are two classes of organic compound that contain the **carbonyl** functional group, but in different locations on the main chain. Aldehydes have the carbonyl group on the end of the main chain. Ketones have a carbonyl group within the main chain.

To name an aldehyde, identify the main chain and omit the final e and replace with al. Position does not need to be indicated.

To name a ketone, identify the main chain and omit the final e and replace with one. This should be preceded by the locant.

Carboxylic acids are a class of organic compound that have a carboxyl functional group. Carboxyl is a carbon atom double bonded to an oxygen atom and single bonded to a hydroxide group.

Naming:

- Count the carbons in the chain containing the carboxylic acid, omit the final e of the parent hydrocarbon name and add -oic acid. The carboxyl carbon is numbered 1 but do not include the locant for the COOH group in the name.

Esters are a class of organic compound that are derived from a carboxylic acid and an alcohol. The ester functional group contains a carbonyl attached to an oxygen linked to another carbon.

Naming:

- Assign the carbon in the carbonyl function as carbon 1
- Count the number of carbons in the chain attached to the carbonyl group, name the chain and add the suffix -oate.
- Count the number of carbons in the chain attached to the oxygen, name the chain and add the suffix "-yl"

Amine is a class of organic compound that contains a nitrogen atom bonded to three other groups, either hydrogen atoms or alkyl groups (an alkane missing one hydrogen).

Naming:

- Name each alkyl group
- Place in alphabetical order
- Add the suffix amin

Amide is a class of organic compound that contains amine and carbonyl functional groups adjacent to each other.

Naming:

- Name the main chain
- Number the carbonyl carbon as carbon 1
- Add the suffix amide
- Use N to represent bonds to the nitrogen atom in complex amide molecules

Nitrile is a nitrogen triple bonded to a carbon. The suffix nitrile is used.

Haloalkane contains a halogen substituent. The Halogen is always represented in the prefix component of a molecule's name. The name of the halogen is shortened and ends with -o.

Order of Priority for functional groups (Higher priority should be the suffix):

Class of Compound	Prefix	Suffix
Carboxylic Acid	Carboxy-	-oic acid
Ester	Alkoxycarbonyl-	-oate

Class of Compound	Prefix	Suffix
Amide	Carbamoyl-	-amide
Nitrile	Cyano-	-nitrile
Aldehyde	Formyl-	-al
Ketone	Oxo-	-one
Alcohol	Hydroxy-	-ol
Amine	Amino-	-amine
Alkene	Alkenyl-	-ene
Alkyne	Alkynyl-	-yne
Alkane	Alkyl-	-ane

Structural formulas demonstrate the arrangement of a molecule.

Extended structural formulas demonstrate the:

- Approximate bond angles
- Arrangement of all atoms
- Bond sizes

Condensed structural formulas show:

- Carbon arrangement

Line structural formulas show:

- Carbon arrangement
- Other atoms
- Hydrogen is not shown but assumed to be present

Structural isomers are compounds that have the same molecular formula but a different structural formula.

Stereoisomers are compounds that have the same molecular and structural formula but a different arrangement of atoms in space.

Geometrical isomers are stereoisomers that have different arrangements of atoms around a rigid double bond. They can be *cis* or *trans* depending on whether the substituent is on the same or different side across the double bond. *Cis* isomers have lower melting points but higher boiling points.

Physical Properties and Trends

Compounds	IMFs	Volatility	Solubility
Hydrocarbons	Weak dispersion forces	Lowest MP and BP of all organic compounds.	Soluble in non-polar solvents.
Tertiary Amines	Dispersion forces (N-C bonds) H bonds to water only	More volatile than other amines due to lack of hydrogen bonds.	Comparable solubility in water to aldehydes and ketones. C1-3 miscible in water.
Secondary Amines	Dispersion forces Hydrogen bonds	Can form less hydrogen bonds (than primary).	
Primary Amines	Dispersion forces More Hydrogen bonds	Primary amines have the highest melting and boiling points as they can form the most hydrogen bonds.	
Ketones and Aldehydes	Dispersion forces Dipole-dipole attraction	Cannot experience hydrogen bonds between each other, but they can experience dipole-dipole attractions which make them less volatile than their hydrocarbon counterparts.	Soluble in water and non-polar organic solvents. C1-3 completely soluble in water (miscible).
Esters	Dispersion forces Dipole-dipole attraction	Contain carbonyl and alkoxy functional groups which both contain polar carbon-oxygen bonds	C1-3 soluble in water. Soluble in organic solvents.
Alcohols	Dispersion forces Hydrogen bonds	Significantly HP and MP compared to hydrocarbons. Short chain alcohols are relatively volatile but as the chain length increases, volatility decreases. Diols and Triols are less volatile.	Soluble in non-polar solvents up to 3 carbon chains. Soluble in water due to hydrogen bonds.
Carboxylic acids	Dispersion forces Hydrogen bonding Dipole-dipole attraction	Carbonyl and hydroxyl groups which can both participate in hydrogen bonding. This gives carboxylic acids a very low volatility.	C1-4 miscible in water - decreasing solubility with chain length. Most soluble in organic solvents.
Amides	Dispersion forces Hydrogen bonds Very strong dipole-dipole attraction	Highest stability of all organic compounds. The non-bonding pair from the N atom interacts with the oxygen to create strong +ve and -ve charges in the molecule. Similar to amines, properties depend on if primary, secondary or tertiary.	Solubility slightly higher than carboxylic acids in water.

Organic Reactions and Pathways

[Reaction Pathways](#)

Markovnikov Rule

In addition reactions to unsymmetrical alkenes, the electron-rich component of the reagent will bond to the carbon atom with the fewer hydrogens, while the electron deficient component will bond to the carbon with the most hydrogen (rich get richer).

Haloalkane Reactions

Primary and secondary haloalkanes react more easily than tertiary. Primary haloalkanes generally undergo substitution reactions while secondary haloalkanes undergo both substitution and elimination reactions depending on the conditions and tertiary haloalkanes mostly undergo elimination. If water is the solvent, lower temperatures and lower concentrations of sodium hydroxide favour substitution. If ethanol is the solvent, higher temperatures and concentrations favour elimination.

Chemical Tests

Alkane and Alkene

The addition of bromine either dissolved in water or as a 1% solution in carbon tetrachloride is used to distinguish between alkanes and alkenes. Bromine is a bright orange colour, but when it is added across a double bond, the colour slowly disappears. No colour change occurs for alkanes, so this determines the class of hydrocarbon.

Alcohols

Oxidation reactions using colour-changing reactants are used to distinguish between primary, secondary and tertiary alcohol. Tertiary alcohols do not oxidise so there will be no colour change. Primary alcohols oxidise twice and secondary alcohols oxidise once. Oxidising reagents include:

- $KMnO_4$ (purple aqueous) reduces to MnO_2 (brown precipitate)
- $Kr_2Cr_2O_7$ (orange aqueous) reduces to Cr^{3+} (green aqueous)
- Benedict's solution - $CuSO_4$ (blue) reduces to CuO (red)

Macromolecules - Structure and Function

Proteins

Proteins consist of one or more polypeptides which are large peptide polymers made from amino acid monomers. Polypeptides with 50 or more AAs are referred to as simple proteins. [Amino Acids](#) are organic compounds which contain an amino and carboxyl functional group. [Amino acids differ in their side chain group](#) which can be non-polar neutral, polar neutral, polar acidic or polar basic. In solution, the hydrogen atom from the acidic carboxyl group is released and accepted by the basic amino group. This is called a **zwitterion**. **Isoelectric point** is the pH at which an amino acid has no net charge.

(insert image here)

The overall structure and function of a protein depends on its primary, secondary, tertiary and sometimes quaternary structures.

Primary

Primary structure refers to the sequence of [Amino Acids](#) within the peptides. The types of amino acids determine the shape of the protein which determines its function.

Secondary

The secondary structure refers to the localised folding of the polypeptide. The amino acids must maintain their bond lengths and angles, which limits the folding to either an α -helix or a β -pleated sheet.

α -helix is a coiled spring structure in which the side chains of the amino acids extend beyond the helix. The coil is stabilised by hydrogen bonding between each peptide bond's carbonyl oxygen atom and the hydrogen atom of the peptide bond four amino acids along the polypeptide.

β -pleated sheet is formed when adjacent polypeptides interact through hydrogen bonding similarly to α -helix.

Proteins fold into 3D structures to minimise repulsion and maximise attraction between [Amino Acids](#) and the surrounding environment.

- The hydrophobic effect refers to the folding of a protein to bury non-polar [Amino Acids](#) within the interior of a protein's structure in order to shield them from water at the surface of the protein. Polar [Amino Acids](#) tend to reside on the surface of proteins.
- Non-polar [Amino Acids](#) interact through hydrophobic interactions
- Polar neutral AAs interact through hydrogen bonding
- Polar acidic and basic AAs interact through ionic bonds, called a salt bridge
- Cysteine AAs interact through bonding of their sulphur atoms in a disulfide bridge.

Tertiary

Tertiary structure refers to the 3D interaction between the various AA side groups present in a polypeptide.

Quaternary

Quaternary structure refers to the interactions between polypeptides.

Tertiary and quaternary structure most act to shield hydrophobic AAs from an aqueous environment.

Enzymes

Enzymes are proteins that catalyse chemical reactions in living organisms. It is essential for their function as biological catalysts that they contain the correct active site for whatever substrate is reacting. Enzymes essentially act as a way of aligning biological reactants to

increase the success rate of collisions in a reaction. After the reaction is complete, products are expelled and the enzymes is unchanged and ready for the next reaction.

Carbohydrates

Carbohydrates

Monosaccharides are sugar monomers that have the empirical formula CH_2O . In aqueous solution, they exist in two forms in dynamic equilibrium - straight chain and α -ring. Glucose and fructose are common monosaccharides; glucose contains an aldehyde functional group so is an aldose and fructose contain a ketone so is a ketose.

Glucose exists in two ring configurations, α and β . The configurations differ by the position of the OH group of C1. α -glucose has a vertical bond down to the OH - opposite to C6 OH position - whereas β has an upward diagonal bond direction - similar to C6. The small difference means β glucose is slightly more stable.

Disaccharides are simple sugars made from two monosaccharides. Sucrose is a common example which consists of a glucose and fructose bonded through an α -1,4-glycosidic linkage.

A **glycosidic linkage** is simply a bond that connects monomers together; the formation of the bonds will be investigated later.

Polysaccharides are complex sugars made of multiple monosaccharides. Common examples include starch, cellulose, glycogen and chitin.

Starch is a polymer of glucose units found in plants. Starch is partially soluble and contains amylose and amylopectin polyglucose molecules the difference being the glycosidic linkage.

Cellulose is another common polysaccharide, also made of glucose units. Glucose monomers in cellulose are joined in β -1,4-glycosidic linkages along with hydrogen bonding between adjacent branches which gives it rigid structure and low solubility.

Lipids

Lipids are polymers with low melting points and which are insoluble in water (mostly hydrophobic). Common lipids include triglycerides (animal fats and plant oils), glycerophospholipids (detergents) and steroids and fat-soluble vitamins.

Lipids contain one or more **fatty acids** – carboxylic acids with long carbon chains – which can be saturated or unsaturated. Unsaturated fatty acids can be monounsaturated or polyunsaturated. Linoleic acid and linolenic acid are the only two essential fatty acids for animal diets and they are both polyunsaturated.

Fatty acids decrease in volatility as the length of the carbon chain and saturation increases. Also, trans isomers have stronger IMFs as they can pack closer together so isomerism has an impact.

Triglycerides are a type of lipid used by plants and animals to prevent water loss, store fat and provide a barrier against microorganisms. They consist of 3 fatty acids and a glycerol (propane-1,2,3-triol) and they are essentially very large esters. Each of fatty acids have a carbon chain 10-30 long and can be saturated or not.

Saponification of triglycerides involves boiling the animal fat or plant oil with excess aqueous NaOH to break the three ester linkages. The reaction creates a glycerol molecule and three fatty acid salts (soap).

Soap is **amphipathic** meaning it contains both hydrophobic and hydrophilic ends. The hydrophobic "tails" of the soap particles attract to other hydrophobic molecules such as dirt and grease. Soap particles break down and coat the dirt and grease while the hydrophilic "heads" of the soap particles allows the insoluble substance to dissolve in water.

Hard water is water containing high levels of dissolved metal ions. When using soap in hard water, the metal ions can bond to the polar, hydrophilic end meaning it can no longer dissolve. This means more soap must be used when cleaning in hard water.

Synthetic Polymers

Polyethylene (polyethene, PE) is a common plastic consisting of ethene monomers. It is not rigid, is chemically resistant, easy to clean and has a melting point of 80 degrees. Having a carbon chain of over 200 means PE has quite strong dispersion forces due to the number of electrons present. Dispersion forces are much stronger when in close proximity so HDPE is much stronger than LDPE due to less branching.

Substituted polymers of ethene are common and include PVC and PTFE. **PTFE** has strong polar bonds between carbon and fluorine yet the molecule itself is non-polar due to the polarity being opposed by the bonds on the other side of the polymer. As a result, PTFE is hydrophobic and nonreactive.

Polypropylene (polypropene, PP) is an asymmetrically substituted polymer containing many chiral centres which result in three stereoisomers: isotactic, syntactic and atactic. The tacticity of a polymer determines the volatility, solubility and strength.

The **isotactic** polymer has the methyl groups on the same side. It has a melting point of 165 degrees and is strong.

The **syntactic** has the methyl groups on alternating sides and has a melting point of 125 degrees (slightly lower).

The **atactic** polymer has randomly allocated methyl groups and is more flexible and rubbery.

Analytical Techniques

Common types of chromatography commonly used are paper and TLC chromatography. These test the solubility of proteins as more soluble proteins will remain in solution for

longer and travel further up the paper due to capillary action. The portion of the distance travelled by the dissolved substance compared to the mobile phase is called the retardation factor.

In electrophoresis, proteins are separated on the basis of their net charge, size and shape. Proteins are placed in a gel between two electrodes. Proteins will move towards the opposite electrode to their charge and at a speed relative to their net charge size.

Mass Spectrometry

Mass spectrometry is a technique used to determine the molecular mass of a compound. It works by first vaporising then ionising a compound using an electron gun or other method to remove an electron. It is then fired along a path and deflected by electromagnets. The time taken for the compound to reach the detector can be allocated to a certain mass-to-charge (m/z) which determines the molecular mass as the charge is 1. If the molecule is stable enough, it will remain intact and reach the detector but sometimes the electron beam causes molecules to break apart into lower fragments which will have a lower mass and reach the detector first.

How to Analyse Mass Spectrometry Graphs

The rule of 13 states that if you divide the m/z value by 13 (the molecular mass of carbon and hydrogen) you can get a ballpark figure for the number of carbons in the main chain. For carbon chains lower than 13, the remainder will be the number of hydrogens in the molecule.

Molecules that have an odd number of nitrogens have a molecular ion with an odd m/z as it forms 3 bonds.

Sometimes peaks can be observed 1 or 2 m/z above the molecular ion peaks. This is known as the isotope pattern and exists due to the existence of isotopes of atoms.

Infrared spectroscopy can be used to detect certain bonds in compounds. Atoms within molecules are always vibrating so their bonds stretch and bend. Using an infrared beam, the changes in bond length by stretching and bond angle by bending can be quantified due to a change in their absorbance. Bond angle spectroscopy is very difficult to quantify due to the number of variables present so normally bond stretching is used to determine functional groups. Each type of bond is given a wavenumber range for

when it will
absorb IR light.

X-ray crystallography gives information about the relative positions of the atom or ions in a compound. The substance must be a solid that forms crystals. X-rays are used because their wavelengths are similar to the sizes of atoms. The rays are directed into the crystal and the diffraction pattern is collected by a computer. X-ray crystallography data can be used to identify atoms based on their number of electrons as a greater number of electrons diffract more, distances between atoms and bond angles.

Chemical Synthesis & Design

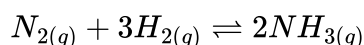
Chemical Synthesis

[Chemical Synthesis](#) is the production of a desired compound from selected reagents and conditions which are chosen to optimise yield and rate.

Haber Process

The [Haber Process](#) is the manufacturing of ammonia through industrial means and combines nitrogen from the air with hydrogen from natural gas in a 1:3 ratio.

In the process, the nitrogen and hydrogen are passed over catalysts (reagents) at high temperature and pressure and any unreacted gases are recycled and passed through the system again until the reaction is complete.

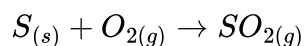


In line with Le Chatelier's Principle, the higher the pressure, the more the forward reaction is favoured so pressures of around 200 atm are usually used. The reaction is exothermic meaning at low temperatures the forward reaction is preferred. However, at low temperatures the reaction occurs very slowly meaning temperatures of around 450 degrees are normally used as this gives a good balance of reaction rate and yield.

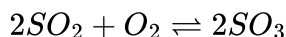
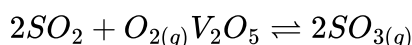
Contact Process

Sulphuric acid is formed naturally through the oxidation of sulphide mineral in rocks and the oxidation of SO_2 in burning fuels, precipitating as acid rain in the presence of water. The [Contact Process](#) for synthetic production of sulphuric acid involves three main steps:

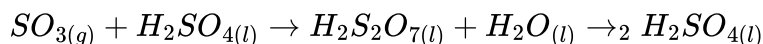
1. Sulphur is burnt to produce sulphur dioxide.



2. Sulphur dioxide is reacted with oxygen with a vanadium oxide catalyst to form sulphur trioxide.



3. Sulphur trioxide is dissolved into sulphuric acid which forms oleum ($H_2S_2O_7$) which then can be reacted with water to form concentrated H_2SO_4 .



The second stage is reversible so reaction conditions must be considered. The reaction is exothermic, so high temperatures lower the yield however a temperature of 450 degrees is normally used as the rate of reaction is quite high. As there are more molecules on the RHS of the reaction, higher pressures will favour the forward reaction however excessive pressure leads to corrosion of the reaction vessel. Hence pressures of around 1.5-1.7 atm are used.

Biofuel Production

Biofuels are liquid fuels obtained from natural materials such as plant and animal matter. The two most common ways of producing biofuels are by base catalysis and lipase catalysis.

Base-catalysed Transesterification

Transesterification exchanges an ester with an alcohol to form a new ester and new alcohol. This method involves combining and organic oil (e.g. vegetable oil) with an alcohol, catalysed by a proton-accepting base. The process can be performed at relatively low temperature and pressures (60-70 degrees and 1 atm) and has a yield of about 98%.

Normally a triglyceride is combined with methanol to form a mixture of fatty acids and glycerol, with the use of an NaOH or KOH base catalyst.

Hydrogen Production

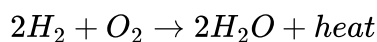
The majority of hydrogen is produced by steam reforming of methane. Steam at 700-1000°C reacts with methane in the presence of a metal catalyst (nickel) to produce hydrogen and carbon monoxide (CO). The carbon monoxide then reacts with water to CO_2 and more hydrogen.

Hydrogen Fuel Cells

Hydrogen fuel cells use hydrogen as a fuel to generate electricity and can have efficiencies of over 75%. They also lack the by-products of typical fuel cells as they only release water and heat. Hydrogen fuel cells can exist in acidic or alkaline conditions.

Acidic Conditions

A phosphoric acid fuel cell is an example of an acidic fuel cell. The cell consists of a porous anode and cathode sparsely coated with a platinum catalyst which are separated by a phosphoric acid electrolyte. The hydrogen atoms enter the fuel cell at the anode where they lose their electrons. They then travel through the electrolyte while the electrons travel through a wire, providing electricity. Oxygen enters the cell at the cathode and combines with the electrons and ionised hydrogen to form water which is then released as waste. The net chemical equation is:



Alkaline Conditions

Hydrogen and oxygen are combined in a redox reaction which produces the electricity. An alkaline solution such as NaOH or KOH is used as the electrolyte to separate the cathode and anode. On one other side of the cell, oxygen enters and is reduced by water and electrons at the cathode to form hydroxide. Hydrogen enters at the other side and is then oxidised at the anode by the hydroxide ions from the oxygen and water to form water and electrons which are carried out in a wire. The net equation is the same as acidic conditions, the difference is that the ions flow the opposite direction and water is exhausted at the anode instead of cathode.

Green Chemistry

Green chemistry aims to reduce waste and energy use, make reactions safer and reduce environmental impacts. There are 12 principles of green chemistry but only 3 are required.

1. Use of renewable raw materials (7)
2. Safer solvents and auxiliaries (5)
3. Waste Prevention (1)

Renewable Feedstocks

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

Safer Solvents and Auxiliaries

Solvents are used to extract and recrystallise products, dissociate reactants and to allow for required collisions for a reaction. When water can be used a solvent, it should be preferred as it is ideal for safety and minimising environmental harm. Sometimes however, reactants are not soluble in water or there are other conditions meaning water will not work. One work around for insolubility in water is the addition of surfactant molecules to form a micelle. This contains a non-polar interior where the desired reaction can take place. Another alternative to organic solvents is supercritical fluids which contain both liquids and gases at certain temperature and pressures. $scCO_2$ is an example of a good solvent that is non-toxic, non-flammable and readily available.

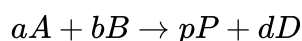
Waste Prevention

Minimise the production of harmful products - chose reactions which will synthesise the desired product with minimal by-products.

Atom Economy

Atom economy is a way of measuring the efficiency of a chemical reaction process at converting the mass of reactants into the desired products. It refers to the percentage of the reagent atoms that exist after the reaction as part of the desired product.

For the Reaction:



$$\% \text{ atom economy} = \frac{(p \times \text{molar mass of } P) \text{ g mol}^{-1}}{(a \times \text{molar mass of } A + b \times \text{molar mass of } B) \text{ g mol}^{-1}} \times 100\%$$

Where A and B are reactants, P is the desired product and D is a bi-product, and a, b, p, and d, are the stoichiometric coefficients for the respective reactants and products.

Macromolecules - Synthesis

Addition Polymerisation

[Addition polymers](#) are formed by linking polymers in an addition polymerisation reaction. By changing catalysts and additives, the degree of branching, crystallinity and cross-linking can be controlled.

LDPE is a recyclable thermoplastic, and it is produced under very high pressure (300-1000 atm) at temperatures of around 300 degrees by passing ethene molecules onto a reactor with an initiator such as a small amount of oxygen and/or an organic peroxide. HDPE is also produced from ethene monomers but at low temperature and pressure (2-3 atm and 60 degrees). Catalysts such as the Ziegler-Natta and metallocene and/or activated chromium/silica enable the formation of free radicals at the ends of the growing polyethylene chains. As there is less branching, HDPE is a much more crystalline, stronger material than LDPE. PP is produced by an addition reaction of propene. PTFE is produced by free-radical polymerisation of tetrafluoroethene.

Condensation Polymerisation

Condensation is an organic addition reaction where water or methanol is produced as a by-product.

Polypeptides are formed when [Amino Acids](#) are joined together by peptide bonds in a condensation reaction where one of the NH_2 from an amino acid bonds to a $COOH$ group of another producing water as a by-product.

[Polysaccharides](#) ([Carbohydrates](#)) are formed when monosaccharide monomers are joined by glycosidic linkages. Maltose is a disaccharide formed when two glucose monomers react and a glycosidic linkage is formed between the hydroxide substituents of carbon 1 and 4 of the respective monomers. Water is produced as a by-product.

Polyesters are plastics which contain an ester in their main chain. The most common type is polyethylene terephthalate which is made from an acid (benzene-1,4-dicarboxylic acid) and an alcohol (ethane-1,2-diol). Water is produced as a by-product.

Polymer Use

Strength

In general, increasing the chain length of a polymer increases its strength and toughness. Many materials that were once commonly used were replaced by stronger polymers.

Density

The density of polymers vary greatly depending on their structure. Polymers have a low density for their strength and even low-density polymers are still relatively strong. They are less dense than most metals and have a similar strength to wood and many metals but are not susceptible to weather damage and decomposition.

Lack of Reactivity

Polymers are the preferred material for many application due to their lack of reactivity. Unlike many metals, they do not rust.

Use of Natural Resources and Biodegradability

Some newer polymers are biodegradable and are made from renewable sources such as plant matter. They have similar structure to biological macromolecules which allows them to be broken down by biological methods.

Generally however, polymers have quite negative environmental impacts due to not being biodegradable or being somewhat biodegradable which forms microplastics which can carry toxins into ecosystems. Also the low-cost production and lack of reusability of many polymers means they are disposed of and when there is a lack of recycling infrastructure, they can end up in the environment threatening natural life. Furthermore, some of these polymers disposed into the environment can remain for thousands of years due to their physical properties.

Molecular Manufacturing

One of the goals of molecular manufacturing is to make new products by the precise placement of atoms. Organisms use enzymes to do exactly that, but scientists have tried to

employ a similar process to produce useful compounds and molecular machines. A molecular machine is a molecular system with defined energy input that can perform a useful function at the nanoscale (less than 100 nanometres).

The advancement of molecular machines accelerated recently with the development of methods to make mechanically interlocked molecular systems called catenanes and rotaxanes. The advantage of these was that the relative position of components can be controlled by outside stimuli such as changed in pH or reduction and oxidation. A catenane consists of two or more interlocked macrocycles. The interlocked rings cannot be separated without breaking covalent bonds. A rotaxane consists of a dumbbell shaped molecule that is threaded through a macrocycle. Chemists have also made rotaxanes in which the central axle is a single-walled carbon nanotube, and the macrocycle is made around the nanotube.

Although nano-robots are not currently used in medicine and other application, they have potential to be useful in the future. They would be very small (0.1-10 μ m) so they could perform very specific tasks with high precision. In order to function effectively they must be able to have:

- An onboard power supply
- Sensors to guide functions
- The ability to be directed or communicate
- Manipulators to grab onto molecules or cells
- The ability to move around the environment

Chemical sensors are widely used in medicine to do things such as measure glucose concentrations in blood. This is done by using oxidase which oxidises glucose to gluconic acid and hydrogen peroxide. The hydrogen peroxide is then detected electrochemically by oxidising to oxygen and water which produces an electric current proportional to the concentration of glucose.

Nanostructures can be constructed by either a top-down or bottom-up approach, referring to whether they are cut out from larger structures or constructed from smaller building blocks.