

OCR Chemistry A

By Logan Filipovich

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Part I

Foundations In Chemistry

Chapter 1

Atoms and Reactions

1.1 Particles

1.1.1 Protons, Neutrons and Electrons

Particles such as protons and neutrons have a number of properties that allow them to behave the way they do

- Atoms and their subatomic particles all have **mass**. Due to the masses of particles being very small, chemists will always use relative mass.
- Charge** is a property that some particles have and others don't such as neutrons that are electrically neutral. Charge always follows electrostatic repulsion and attraction.

The values of relative charge and mass of the proton, neutron and electron that build the atom are shown below

Particle	Abbreviation	Relative charge	Relative mass
proton	p^+	$1+$	1
neutron	n	0	1
electron	e^-	$1-$	$\frac{1}{1836}$

the total positive charge of the protons is cancelled out by the charge of the electrons so the atom is neutral. It is also common that atoms have equal amounts of protons and neutrons.

1.1.2 Atomic Number

- every atom of the same element has the same number of protons which identifies it. Different elements have different numbers of protons.
- the periodic table lists elements based on their **atomic number** - the number of protons in their atoms. Every atom of an element contains the same number of protons as neutrons.
- When an atom doesn't have the same number of protons as neutrons it is called an isotope. Different isotopes of the same element have the same number of electrons and hence has no effect on the reactions of that element

Isotope	Protons, p^+	Neutrons, n	Electrons, e^-
${}_{8}^{16}\text{O}$	8	8	8
${}_{8}^{17}\text{O}$	8	9	8
${}_{8}^{18}\text{O}$	8	10	8

1.1.3 Ions

An ion is a charged atom. The overall charge is due to the number of electrons not equalling the number of protons

- Cations** are positive ions and have atoms with fewer electrons than protons
- Anions** are negative ions and have atoms with more electrons than protons

Ion	Protons	Neutrons	Electrons	Overall relative charge
${}_{12}^{24}\text{Mg}^{2+}$	12	12	10	$(12+) + (10-) = 2+$
${}_{17}^{35}\text{Cl}^{-}$	17	18	18	$(17+) + (18-) = 1-$

1.1.4 Relative Mass

Because the mass of an atom will depend on the energy holding the nucleus together and is also very small, mass is relative to the carbon-12 isotope in chemistry which is given to have a relative mass of 12u. The standard definitions are as followed:

- Relative atomic mass** is the weighted mean mass of an atom relative to 1/12 th the mass of an atom of carbon-12.

- **Relative isotopic mass** is the mass of an isotope relative to $1/12$ th the mass of an atom of carbon 12.
- **Relative molecular mass** is the mass of a molecule relative to an atom of carbon-12 and is easily calculated by adding the relative atomic masses of all the atoms in a molecule. This is similar to **relative formula mass**.

The relative atomic mass also takes into account the abundance of each isotope and the relative isotopic mass of each isotope. The percentage abundances are measured by a **mass spectrometer**:

- I A sample is placed in the mass spectrometer where it is vaporised and ionised into positive ions.
- II The ions are accelerated. Heavier ions move slower and take longer to reach the detector whereas smaller ones get there faster.
- III A mass to charge ratio m/z is read from the detector for each ion at a given time giving the abundance of that ion over the relative charge on the ion.

1.1.5 Ionic Charges

- Ions on the left of the periodic table lose electrons to become positive metal ions.
- Ions on the right are non-metals and gain electrons to become negative non-metal ions.
- **Binary Compounds**

Binary compounds contain only two elements. They are named together with the name of the second element changed to have a suffix -ide. For ionic compounds, the metal always comes first. For example sodium and oxygen form sodium oxide.

- **Polyatomic Ions**

Often, ions contain more than one atom which are called **polyatomic**. the table below shows the molecular formula and charge of some common polyatomic ions.

1+	1-	2-	3-
ammonium NH_4^+	hydroxide OH^-	carbonate CO_3^{2-}	phosphate PO_4^{3-}
	nitrate NO_3^-	sulfate SO_4^{2-}	
	nitrite NO_2^-	sulfite SO_3^{2-}	
	hydrogencarbonate HCO_3^-	dichromate(VI) $\text{Cr}_2\text{O}_7^{2-}$	
	manganate(VII) (permanganate) MnO_4^-		

When writing equations and molecular formulae, charge and atoms must always be balanced in a completed formula. Brackets are used to balance polyatomic ions. Molecules in equations can also be assigned state symbols, namely gas (g), liquid, (l), solid (s) and aqueous (aq).

1.1.6 Formulae

- **Molecular formula** - Some compounds are made up of molecules - two or more atoms held together by covalent bonds. the molecular formula is the number of atoms of each element in a molecule
- **Empirical formula** - The empirical formula is the smallest whole number of atoms in each element of a given compound. empirical formula is important when molecules have giant structures such as metals and some non-metals like sodium chloride NaCl. Empirical formula can be calculated by finding the number of moles of each atom present in a molecule.

1.2 Molarity

1.2.1 Amount of Substance

A quantity called the amount of substance is used to count the particles in a substance. The unit of the amount of substance is called the **mole mol**. The Avogadro constant 6.02×10^{23} is the number of particles present in 1 mol of Carbon-12.

the amount of substance present in a same of mass m with a relative atomic mass M_r is defined as,

$$n = \frac{m}{M_r}$$

1.2.2 Hydrated Salts

Coloured crystals are **hydrated** meaning water molecules are part of its crystalline structure. this called the **water of crystallisation**. when hydrated crystals such as hydrated copper (II) sulphate are heated, the water bonds are broken and water is driven off leaving an anhydrous salt.



Without water the crystalline structure is lost and a white powder remains although it is very difficult to remove the last traces of water.

- **Calculating Water of Crystallisation**

By measuring the mass of a chosen amount of hydrated salt, we can heat the salt in a crucible to break the water bonds. By measuring the mass of the anhydrous salt, we can calculate the mass of water that was part of the salts crystalline structure and hence work out the moles of water. By also calculating the moles of anhydrous salt formed you can work out the water of crystallisation.

Assumptions:

- When carrying out the calculations, you assume that there are no traces of water left in the anhydrous salt.
- Salts can decompose further when heated strongly; for example, copper (II) sulphate decomposes to black copper (II). We assume this does not occur

1.2.3 Moles and solutions

The **concentration** of a solution is defined as moles per unit volume. For a given volume and molarity the concentration can be calculated and vice versa - the moles can be calculated from volume and concentration.

$$c = \frac{n}{V}$$

Concentration is given the units mol dm^{-3} where 1dm^3 is equal to 1000cm^3 which is also equal to 1000ml. Volumes will usually be measured in cm^3 so the measurement will have to be divided by 1000.

- **Standard Solution**

A **Standard solution** is a solution of a known concentration and is created by dissolving a known mass of the solute in a solvent and making up an exact volume.

1.2.4 Molar Volume

The **molar gas volume** is the volume per mole of gas molecules at a stated temperature and pressure. Although it is dependant on temperature and pressure, experiments are usually carried out at room temperature and pressure;

- Temperature of 20 degrees celcius or 293K at 101kPa (1 atm).
- At RTP, 1 mol of gas occupies 24dm^3

- **Ideal Gas Equation**

In the event that the approximate values given by RTP do not match the conditions, Ideal gas equation is used:

$$pV = nRT$$

Where p and V are the pressures and volume of the gas in Pa and m^3 respectively. n is the number of moles, T is the temperature in kelvin and finally R is the ideal gas constant $R = 8.314\text{Jmol}^{-1}\text{K}^{-1}$. The ideal equations has numerous assumptions such as not taking into account random motion, elastic collisions, negligible size and intermolecular forces.

1.2.5 Percentage Yield

In an ideal world, all of our reactants will react to produce our product, however this isn't the case. The ideal situation where the maximum product is produced is called the **theoretical yield**. Reasons why a product isn't at its theoretical yield includes

- The reaction may not have gone to completion
- Side reactions might have taken place using up reactants or even the product itself
- The purification of the product may result in a loss of product

The amount of product made from a reaction or process is called the **actual yield**. Using the actual yield, the **percentage yield** can be calculated

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} * 100$$

The **limiting reagent** is the name given to the reactant that is not in excess - it is the reactant that will be fully used up first in a reaction. Calculations must be done based on the limiting reagent.

1.2.6 Atom Economy

The atom economy of a chemical reaction is a measure of how much of a desired product is produced in a single reaction. The higher the atom economy the more desirable the reaction. It is calculated by:

$$\text{atom economy} = \frac{\text{desired product}}{\text{all products}} * 100$$

- **Sustainability**

Atom economy doesn't always decide whether a reaction is desirable. A process may have a lower atom economy but may have readily available reactants such as carbon and water. Also, reactions may have a higher atom economy but the process required to complete the reaction may have a low percentage yield.

1.3 Acids

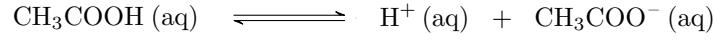
1.3.1 Strong and Weak Acids

All acids contain hydrogen. When dissolved in water an acid releases its hydrogen ions H^+ as a proton to undergo reactions. Different acids have different strengths based on their ability to dissolve protons in water.

- **Strong acids** such as hydrochloric acid HCl completely dissociate in an aqueous solution. The ionic equation for the dissociation of HCl is shown.

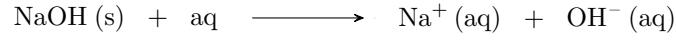


- **Weak acids** such as ethanoic acid CH_3COOH do not dissolve all their hydrogen atoms when dissolved in water. In an aqueous solution, they partially dissociates. Below shows the partial dissociation of CH_3COOH



1.3.2 Bases and alkalis

Metal oxides, hydroxides, carbonates and ammonia are classified as **bases**. A base is the ability to neutralise an acid to form a salt. An **alkali** is a base that dissolves in water and subsequently releases hydroxide ions

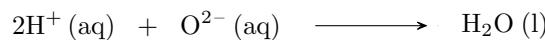


Metal oxides	Metal carbonates	Alkalies
MgO	Na_2CO_3	NaOH
CaO	CaCO_3	KOH
CuO	CuCO_3	NH_3

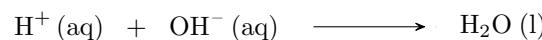
1.3.3 Neutralisation

A neutralisation reaction occurs between an acid and a base to produce water by bonding the hydrogen ion from the acid and the hydroxide ion from the base to form water as well as a salt. There are three main neutralisation reactions that are common with the bases shown above.

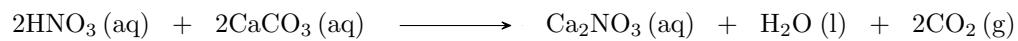
- When a metal oxide or hydroxide reacts with an acid, a salt is formed with water.



- When a metal hydroxide undergoes neutralisation a similar reaction to oxides occurs with the exception of the ionic equation.



- When a metal carbonate reacts with acid, a salt and water is formed as well as carbon dioxide gas



1.3.4 Titrations

An acid is a technique used to accurately measure the amount of one solution that will react with another. They can be used for:

- Finding the concentration of a known solution.
- Identification of unknown chemicals.
- Finding the purity of a substance.

A titration can be used in numerous circumstances but the steps taken are essentially identical.

I A standard solution is prepared in a volumetric flask to be as accurate as possible. A typical volumetric flask is very precise and will measure $250\text{cm}^3 \pm 0.3\text{cm}^3$ or $100\text{cm}^3 \pm 0.2\text{cm}^3$.

II The apparatus is set up consisting of a burette which will hold the base and a flask underneath which will hold the acid. The acid is measured out with a pipette usually $25\text{cm}^3 \pm 0.06\text{cm}^3$. The burette is tolerant to $50\text{cm}^3 \pm 0.1\text{cm}^3$.

III An **indicator** is added such as phenolphthalein so that when the acid is neutralised, there is a visible colour change and a reading can be taken. When carrying out the titration a trial must run first so that as you reach the **end point**, base can be added drop-wise.

IV After the trial titre, the titration must be repeated three more times taking readings within 0.05cm^3 (i.e. to 2 decimal places). The results must be concordant, so any reading outside 0.1cm^3 must be ignored when calculating the **mean titre**.

Trial	1	2	3
final burette reading / cm^3			
initial burette reading / cm^3			
titre / cm^3			
mean titre / cm^3			

- **Titration Calculations**

The calculations done in titration are also always very similar.

I Work out the amount in moles of the solute in solution as you know the concentration and the volume.

II Use the stoichiometry of the reaction equation to determine the moles of solute of the other solute.

III Work out the unknown information with the now known molarity of the solute.

1.4 Redox

1.4.1 Oxidation Numbers

The **oxidation number** is a number given to an atom in a compound based on its bonding to check that the electrons in the compounds formula is are balanced. the rules are as followed.

- in a pure element, any bond is to other atoms of that element hence the oxidation number of each atom is 0. Examples include FeH_2 and S_8 .
- Each atom has an oxidation number which usually follows a set of standard oxidation numbers shown below. Other atom's can work out their oxidation number by considering the total charge on that ion or molecule.
- Oxidation numbers are written as a number with the sign *before* the number. They can also be written in Roman numerals without the sign such as iron (III) representing Fe^{3+} with oxidation number +3.
- For polyatomic ions, names with prefixes such as -ite and -ate are given. However a more modern form of naming show oxidation numbers as roman numerals such as NO_3^- given the name nitrate(V) and NO_2^- given the name nitrate(III).

Combined element	Oxidation number	Examples
O	-2	H_2O , CaO .
H	+1	NH_3 , H_2S .
F	-1	HF
Na^+ , K^+	+1	NaCl , K_2O
Mg^{2+} , Ca^{2+}	+2	MgCl_2 , CaO
Cl^- , Br^- , I^-	-1	HCl , KBr , CaI_2
<i>Special cases:</i>		
H in metal hydrides	-1	NaH , CaH_2
O in peroxides	-1	H_2O_2
O bonded to F	+2	F_2O

1.4.2 Redox Reactions

Redox reactions involve the reduction and oxidation of two different atoms - if one atom is oxidised another is reduced.

- **Oxidation** is the addition of oxygen. In terms of electrons it is the loss of electrons. It is the increase in oxidation number.
- **Reduction** is the removal of oxygen or again in terms of electrons, it is the gain of electrons. It is the decrease on oxidation number.

A redox reaction may not involve oxygen but it will involve the transfer of electrons.

Chapter 2

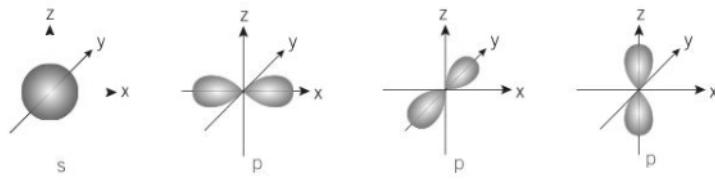
Electrons and Bonding

2.1 Electronic Configuration

2.1.1 Shells

Inside an atom, electrons make up shells that model the way they behave in bonds.

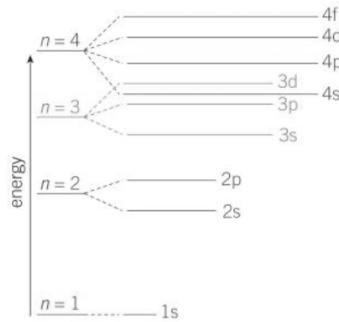
- Shells are regarded as energy levels. As the shell number increases, the energy increases. The shell or energy level is given a **principle quantum number n**.
- Shells are made up of sub-shells called **atomic orbitals** -modelled as a negatively charged cloud around the nucleus. An orbital can hold a maximum of two electrons of opposite spin state.
- There are different types of orbitals such as s, p, d and f in order of increasing energy levels. Each orbital has a different shape. An s orbital is a sphere, each energy level has one s-orbital. A p orbital has the shape of a dumb-bell and has 3 p-orbitals for every energy level - one in each direction.



- For each sub-shell, a new additional orbital is added. the number of orbitals increases for each new type of orbital (s-1, p-3, d-5 and f-7). Two electrons can fit into each sub-shell so the number of electrons increases.

Shell	Number of orbitals				Sub-shells present	Number of electrons in sub-shells	Number of electrons in shell
	s	p	d	f			
1	1				1s	2	2
2	1	3			2s + 2p	2 + 6	8
3	1	3	5		3s + 3p + 3d	2 + 6 + 10	18
4	1	3	5	7	4s + 4p + 4d + 4f	2 + 6 + 10 + 14	32

- Electrons fill up shells based on a set of rules. The electrons will always fill up the lowest energy shell and sub-shell. In n=1 that is 1s, in n=2 its 2s, 2p and n=3 its 3s, 3p, 3d. There is one exception, the 4s orbital is of a lower energy level than 3d so electrons will always fill 4s first.



- Electrons will pair in orbitals if they have opposite spin. The spin state of an electron is either up or down and is represented using an arrow. Within orbitals, one electron occupies each orbital before pairing in order to minimise repulsion as shown below.



- In the configuration on the right, the electrons will not pair in such a way as the electrostatic repulsion between electrons is greater than on the left as they do not occupy the same sub-shell.

2.1.2 Electron configuration

At A-level you must know the electron configuration of atoms up to $Z = 36$. The electron configuration is written in terms of how many electrons occupy each sub-shell in order of energy levels. For example, for $Z = 36$, Krypton, the electronic configuration is written as $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4s^6$

Li	Be	B	C	N	O	F	Ne
$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$

- **Shorthand Electron Configuration**

Electron configuration can be expressed in a simpler terms using the previous noble gas plus the electrons in the outer shells as a shorthand. The shorthand for some group 1 elements is shown below.

	Electron configuration	Shorthand notation
Li	$1s^2 2s^1$	$[\text{He}] 2s^1$
Na	$1s^2 2s^2 2p^6 3s^1$	$[\text{Ne}] 3s^1$
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$[\text{Ar}] 4s^1$

- **Electron Configuration of Ions**

Ions form by losing or gaining electrons from the highest energy orbitals. The table below shows how oxygen gains electrons in the 2p sub-shell and how calcium loses two electrons from the 4s orbital.

	Number of electrons	Electron configuration	
Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	\downarrow
Ca^{2+}	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	2 electrons lost from 4s sub-shell
O	8	$1s^2 2s^2 2p^4$	\downarrow
O^{2-}	10	$1s^2 2s^2 2p^6$	2 electrons gained by 3p sub-shell

We have seen how the 4s orbital will fill before the 3p orbital. When losing electrons, the 4s will also empty before the 3p orbitals. This is because once the orbitals are filled, 3p falls below the energy level of 4s making 4s the highest energy level.

- **Periodic Table Blocks**

The periodic table is divided into blocks depending on what the highest energy sub-shell is. For example, groups 1 and 2 are s-block as it is their highest orbital. The central block is the d-block and the right block, groups 3-8 are p-block.

2.2 Ionic Bonding

Ionic Bonding is the electrostatic attraction between positive and negative ions - holding anions and cations together. The anions commonly being Cl^- , or NO_3^- and the cation being Na^+ , or NH_4^+ as examples.

2.2.1 Dot and Cross Diagrams

Dot and cross diagrams show the transfer of electrons between metal and non-metal ions. The examples below shows how ionic bonding in MgCl_2 forms. The magnesium atom gives one of two electrons to each chlorine atom forming a $2+$ magnesium atom attracted to two -1 chlorine ions.

	transfer of 2 electrons					
	Cl atom	Mg atom	Cl atom	\rightarrow	$[\text{Cl}^- \text{ ion}]$	$[\text{Mg}^{2+} \text{ ion}]$
	$17 \text{ p}^+, 17 \text{ e}^-$	$12 \text{ p}^+, 12 \text{ e}^-$	$17 \text{ p}^+, 17 \text{ e}^-$		$17 \text{ p}^+, 18 \text{ e}^-$	$12 \text{ p}^+, 10 \text{ e}^-$
electron structure	2,8,7	2,8,2	2,8,7		2,8,8 (argon)	2,8 (argon)
charge	neutral	neutral	neutral		1-	2+

2.2.2 Ionic Structure

In an ionic bond, ions attract oppositely charged ions in all directions forming a **giant ionic lattice** structure. Such a structure contains billions of ions. The most common example is the salt sodium chloride NaCl where every chloride ion is surrounded by 6 sodium ions, and every sodium ion is surrounded by 6 chloride ions.

2.2.3 Properties of Ionic compounds

The properties of ionic compounds can be explained in terms of their structure on bonding.

- **Melting and Boiling Points** - Almost all ionic compounds are solid at room temperature and have very high melting and boiling points due to the large amount of energy required to overcome the strong ionic bonds between every ion. Ions with higher charges will have stronger electrostatic attractions and hence have higher melting points to overcome the stronger bonds.

Ionic compound	Ions	Melting point / °C
NaF	Na ⁺ and F ⁻	993
CaF ₂	Ca ²⁺ and F ⁻	1423
Na ₂ O	Na ⁺ and O ²⁻	1275
CaO	Ca ²⁺ and O ²⁻	2614

- **Solubility** - Ionic compounds dissolve in **polar** solvents such as water as the polar water molecules surround and break down the giant ionic lattice. In a compound made of ions with large charges, the solvent may not be polar enough to break the ionic bonds hence the compound has low solubility. *Note:* Solubility always occurs in two steps; first the lattice must be broken, then the molecules must attract and surround the ions.

Ionic compound	Ions	Solubility at 20 °C / mol dm ⁻³
NaCl	Na ⁺ and Cl ⁻	6.1
CaCl ₂	Ca ²⁺ and Cl ⁻	0.67
Na ₂ CO ₃	Na ⁺ and CO ₃ ²⁻	2.0
CaCO ₃	Ca ²⁺ and CO ₃ ²⁻	1.3 × 10 ⁻⁴

- **Electrical Conductivity** - In a solid state, the ions are in a fixed position in the lattice and there are no mobile charge carriers. However as a liquid or dissolved in water, the lattice has been broken down and the ions are free to move as mobile charge carriers.

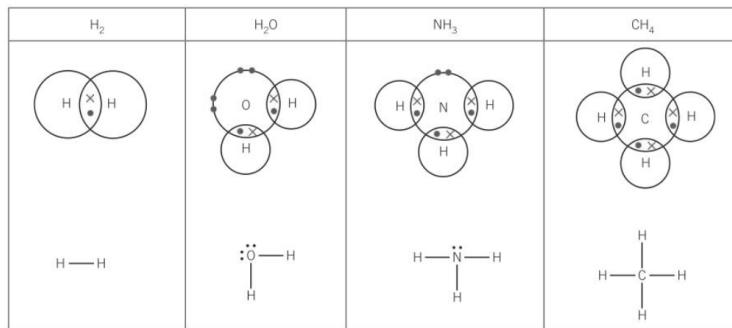
2.3 Covalent Bonding

Covalent bonding is the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms. Covalent bonding only occurs in non-metal elements. It is modelled as the overlap of orbitals each containing one electron. In ionic bonds, the ion attracts in all direction forming a giant structure whereas covalent bonds are **localised** forming a molecule consisting of two or more atoms such as H₂ or H₂O.

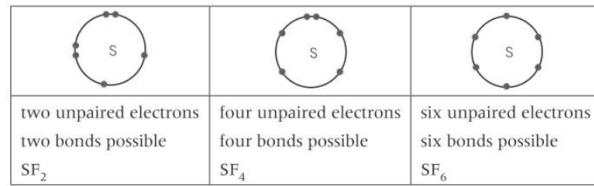
2.3.1 Dot-and-Cross Diagrams

Like with ionic bonding, dot and cross diagrams can be drawn to show the electron configuration of atoms in covalent bonds

- unlike dot-and-cross a **displayed formula** shows the relative positioning of atoms and the bonds between them as lines as shown below.
- Paired electrons that are not shared are called **lone pairs**. They can also be added to displayed formula.



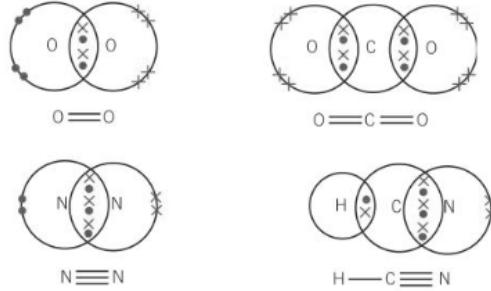
the number of bonds depends on the number of unpaired electrons available whilst the remaining electrons always exist in a pair. For example, carbon always forms four bonds as it has four lone pairs available, oxygen will form two bonds as its remaining 4 electrons form two lone pairs. Other elements like sulfur and phosphorus can form a varied number of bonds as it has more energy levels available and more electrons.



Boron is an exception to the rules of covalent bonding. It can form boron trifluoride BF_3 such that its outer shell only has six electrons which shows that prediction of covalent bonding cannot be based solely on the noble gas electron structure.

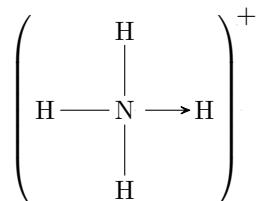
2.3.2 Multiple Covalent Bonds

- In a double covalent bond, the electrostatic attraction is between two shared pairs of electrons and the nuclei of the bonded atoms. Examples include oxygen gas O_2 and carbon dioxide CO_2 which have double covalent bonds whilst having completed outer shells.
- In a triple bond the electrostatic attraction is between three lone pairs of electrons and the bonded nuclei. Examples include nitrogen gas N_2 and hydrogen cyanide HCN .



2.3.3 Dative Covalent Bonds

A **dative covalent** or **coordinate** covalent bond is a covalent bond in which the shared pair of electrons comes from a single bonded atom. For example, in the ion NH_4^+ an ammonia molecule has donated a lone pair of electrons to a hydrogen ion. The covalent bond is shown as an arrow.



2.4 Shapes of Molecules and Ions

An electron has a negative charge, so electrons repel one another. Around a central atom electrons are arranged such that they are as far away from each other as possible given the atom a definite shape. Different numbers of electron pairs results in different shapes.

2.4.1 Bonded-pair and Lone-pair Repulsion

A lone pair of electrons is closer to the central atom and occupies more space which results in a greater repulsion than a bonding pair. This results in numerous different shapes and **bond angles**.

Name of Shape	Shape	Bond Angle	Bonded Pairs	Lone Pairs
Tetrahedral		109.5°	4	0
Pyramidal		107°	3	1
Non-linear		104.5°	2	2
Linear	$O=C=O$	180°	4	0
Trigonal Planar		120°	3	0
Octahedral		90°	6	0

- Electrons repel each other around the central atom as far as possible. However as lone pairs are more repulsive, the bond angle decreases by 2.5° for every bonded pair replaced by a lone pair in a tetrahedral molecule.

2.4.2 Shapes of Ions

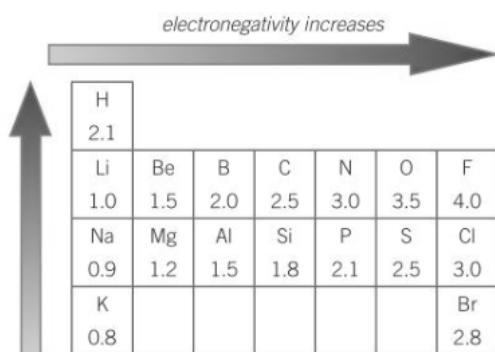
- An ammonium ion has a central atom with 4 bonds to four hydrogen atoms with no lone pairs of electrons. The dative covalent bond to one of the hydrogen atoms has no effect. It is equivalent to a normal covalent bond hence it has tetrahedral shape with bond angles of 109.5°. The charge of the ion has no effect on ion shape.
- Carbonate and nitrate ions both contain four bonds however two bonds form a double bond so there are only three electron densities around the central atom, so the shape is trigonal planar with a bond angle of 120°. Again coordinate bonds and charge do not affect bond angle.

2.5 Electronegativity

2.5.1 Pauling electronegativity

In a covalent bond where the atoms are the same such as H₂ and O₂, the pair of electrons is shared evenly. This changes when the nuclear charges are different, the atoms may be different sizes, and the shared pair of electrons is closer to one of the bonded atoms.

- The attraction between a bonded atom and its shared pair of electrons is called **electronegativity**. Electronegativity is compared by **Pauling electronegativity values**. The higher up the group, the more electronegative and the higher the nuclear charge across a period, the higher the electronegativity.
- The non-metals, oxygen, nitrogen, fluorine and chlorine have the highest electronegativities whereas group 1 elements have the least electronegative atoms. Because of this the Pauling electronegativity value is based on fluorine with the highest electronegativity of 4.0.



- If the electronegativity difference is larger than 1.8, one of the bonded atoms will have gained enough control of the electrons and bond will be ionic rather than covalent. When the electronegativity difference is less than 1.8 a polar covalent bond is formed, and for a 0 electronegativity difference the bond is non-polar.
- In a **non-polar** bond, the atoms are the same such as in H₂ or very similar such as in a carbon-hydrogen bond. In molecules including the same atom, the bonded electron pair is shared equally and called a **pure covalent bond**.
- In a molecule with atoms of different electronegativities such as HCl, a **polar covalent bond** is formed. Because chlorine is more electronegative than hydrogen the chlorine has a greater attraction to the shared pair of electrons making HCl **polarised** - chlorine becomes slightly negative and hydrogen slightly positive.

2.5.2 Polar Molecules

In a molecule of water, the O-H bonds are polar; because two of these bonds exist in water, and because the dipoles act in different directions due to a 104° bond angle, the overall molecule is polar. The oxygen is slightly negative and the hydrogens slightly positive.

Carbon dioxide is non-polar as although it contains two polar C=O covalent bonds, the dipoles act in opposite directions and hence cancel out making the molecule non-polar.

2.5.3 Polar Solvents

NaCl dissolves in water as the ionic bonds are broken. This is done by the water molecules attacking the sodium and chloride ions. We have seen that water is a polar molecule this means that it can break down an ionic lattice by attracting Na⁺ ions to the δ- oxygen and the Cl⁻ to the δ+ hydrogen atoms allowing the water molecules to surround the ions.

2.6 Intermolecular Forces

Intermolecular forces are weak interactions between dipoles of different molecules. There are three main types of intermolecular forces.

I **Induced dipole-dipole interactions** with a bond strength of 1-10 kJmol⁻¹

II **Permanent dipole-dipole interactions** with a bond strength of 3-25 kJmol⁻¹

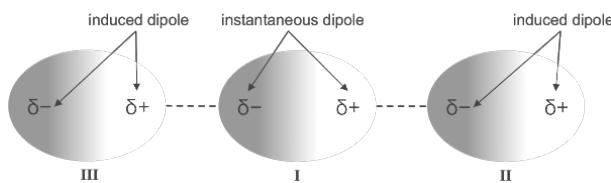
III **Hydrogen bonds** with a bond strength of 10-40 kJmol⁻¹

2.6.1 Induced Dipole-Dipole Interactions

Induced dipole-dipole interactions, also called London forces, are weak intermolecular forces that exist between all polar and non-polar molecules. They act between induced dipoles.

- I The movement of electrons produces a changing dipole in a molecule.
- II At any instant, an instantaneous dipole will exist but its position is constantly shift.
- III the instantaneous dipole induces a dipole on a neighbouring molecule.
- IV the Induced dipole induces further dipoles on neighbouring molecules which will attract one another.
- V Induced dipoles only exist at one instant and will disappear at the next instant of time, only for the process to start all over again.

London forces occur due to electrons in the molecules. As the number of electrons increases the larger the instantaneous dipoles so the larger the London forces between molecules. the larger number of electrons also means more energy is required to overcome the intermolecular forces and hence the higher the boiling point.



2.6.2 Permanent Dipole-Dipole Forces

permanent dipole interactions occurs between the the dipoles in different polar molecules such as hydrogen chloride HCl and fluorine F₂.

- Fluorine and hydrogen chloride have the same number of electrons but HCl has a boiling point of -85°C whilst F₂ has a boiling point of -220°C. This is because fluorine does not interact with permanent dipoles where as hydrogen chloride does as well as having London forces. Meaning more energy is required to overcome the intermolecular bonds.



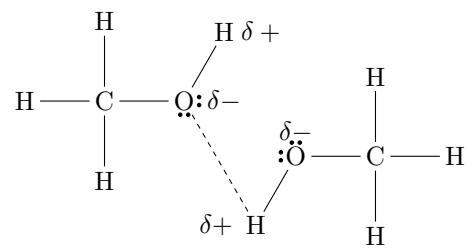
2.6.3 Simple Molecular substances

A **simple molecular substance** is made up of simple molecules such as hydrogen, water and carbon dioxide. In a solid state, these molecules are held together in a **simple molecular lattice** by weak intermolecular forces. They have numerous properties:

- **Melting and boiling points** - A simple molecular substance has relatively low melting and boiling points as the weak intermolecular forces are broken at very low energies meaning they are usually a liquid or gas at room temperature. When heating only the intermolecular forces break, not the covalent bonds.
- **Solubility of non-polar molecules** - Non-polar simple molecular substances tend to be soluble in non-polar solvents. When a non-polar solvent is added the intermolecular forces with the solvent weaken the intermolecular forces in the lattice so the lattice dissolves. However for polar solvents, there is little interaction with the lattice; the intermolecular forces between solvent molecules is too strong to be broken.
- **Solubility of polar molecules** - Polar simple molecular substances will dissolve in polar substances as the molecules are attracted to the solvent molecules by permanent dipole forces. However solubility depends on the strength of the dipole. For example, for alcohols as the chain increases the dipole strength decreases making them less soluble.
- **Electrical conductivity** - There are no mobile charge carriers in simple molecular structures as they are held by intermolecular forces so simple molecules do not conduct electricity.

2.6.4 Hydrogen Bonding

A hydrogen bond is a special type of permanent dipole between a lone pair of electrons such as on oxygen or nitrogen to a hydrogen atom. They are the strongest form of intermolecular forces.



- Hydrogen bonds hold water molecules apart in a lattice structure so the water molecules in ice are further apart than in water as the bonds extend outwards making ice less dense than water. Less dense objects float, so ice floats. Each water molecule has four hydrogen bonds - 2 hydrogens, 2 lone pairs.
- Simple molecular structures are usually gaseous at RTP yet water is a liquid as hydrogen bonds need to be overcome. When ice melts, the rigid arrangement of hydrogen bonds break and then break completely when water boils.
- Other unusual properties of water that are a result of hydrogen bonds include its high surface tension allowing insects to walk across a pond and low viscosity compared to other liquids.

Part II

Physical Chemistry

Chapter 3

Periodicity

3.1 Periodic Table

3.1.1 Structure of the Periodic Table

The periodic table displays elements from hydrogen (H) to oganesson (Og). The main table has groups 13-18 and groups 3-12. A 'Key' box defines atomic number (top), symbol (middle), and relative atomic mass (bottom). Below the main table are two additional tables: one for lanthanides (Ce-Lu) and one for actinides (Ac-Lr).

1	2
H	Be
3	4
Li	Mg
5	6
Sc	Ti
7	8
V	Cr
9	10
Mn	Fe
11	12
Co	Ni
13	14
Cu	Zn
15	16
Ga	Ge
17	18
As	Se
19	20
Br	Kr
21	22
Ca	Sc
23	24
25	26
27	28
29	30
31	32
33	34
Al	Si
35	36
P	S
37	38
Cl	Ar
39	40
41	42
Rb	Sr
43	44
Y	Nb
45	46
Tc	Mo
47	48
Ru	Rh
49	50
Pd	Ag
51	52
Ir	Pt
53	54
Re	Os
55	56
Ba	Hf
57	58
Cs	Ta
59	60
Fr	Rf
61	62
La	Ce
63	64
Pr	Nd
65	66
Pm	Sm
67	68
Eu	Gd
69	70
Tb	Dy
71	72
Ho	Er
73	74
Tm	Yb
75	76
V	Lu
77	78
Cr	Lu
79	80
Ru	Lu
81	82
Pt	Lu
83	84
Os	Lu
85	86
Hg	Lu
87	88
Tl	Lu
89	90
Pb	Lu
91	92
Bi	Lu
93	94
Fm	Lu
95	96
Md	Lu
97	98
No	Lu
99	100
101	102
103	104
105	106
Bh	Hs
107	108
109	110
111	112
Mt	Ds
113	114
Rg	Cn
115	116
Fl	Lv

The first periodic table was organised by a chemist named Mendeleev who organised just over 60 elements in order of atomic mass, leaving gaps for undiscovered elements and even swapping elements assuming the measurements were wrong. Today, the periodic table consists of 114 elements arranged in seven vertical periods and 18 horizontal groups.

- Reading from left to right, the elements are arranged in order of increasing atomic number, H-1, He-2 etc.
- Elements are arranged in vertical columns called **groups**. Each element in a group has atoms with the same number of electrons in its outer shells giving them similar chemical properties
- Elements are arranged in horizontal rows called **periods**. The period number is the number of the highest energy electron shell of the element's atom. Across a period there are a number of trends such as boiling point, electron configuration structure and ionisation energy called its **periodicity**.

3.2 Trends in Electron Configuration

3.2.1 Trend across a period

Each period starts with a single electron in its highest energy shell.

- Across period 2, the 2s shell will fill first adding one new electron for every next element, followed by the 2p shell.
- Across period 3, the same pattern is repeated as period 2.
- Across period 4, although 3d is involved, the highest energy level is n=4 so only 4s and 4d are occupied.

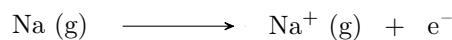
3.2.2 Trend down a group

- The group number is defined by the number of electrons in an atom's outer shell (with an extra fully filled shell going down the group) giving atoms in the same group similar properties
- Elements in the periodic table can be divided into groups based on their subshells. Groups 1 and 2 are the s-block, groups 3-12 are d-block etc.
- Some groups are given names and a number from one to 18. They are also assigned an 'old' number based on an older numbering scheme that excluded groups 3-12 - the transition metals

Group number		Name	Elements
Old	New		
1	1	alkali metals	Li, Na, K, Rb, Cs, Fr
2	2	alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
	3–12	transition elements	
5	15	pniotogens	N, P, As, Sb, Bi
6	16	chalcogens	O, S, Se, Te, Po
7	17	halogens	F, Cl, Br, I, At
0	18	noble gases	He, Ne, Ar, Kr, Xe, Rn

3.3 Ionisation energy

The **First Ionisation Energy** is defined as the energy required to remove a single electron from one mole of gaseous atoms to form one mole of gaseous ions. Below shows the first ionisation energy for sodium.



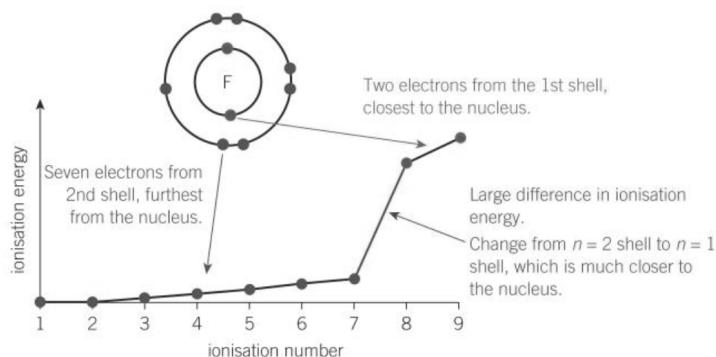
The electron removed from the first ionisation energy will always be removed from the highest energy level with the lowest electrostatic attraction with the nucleus. There are three factors that affect this:

- **Atomic Radius** - The greater the distance between the nucleus and the outer most electron, the lower the electrostatic attraction. Attraction decreases drastically with distance so it has a large effect
- **Nuclear Charge** - The higher the atomic number, the greater the charge in the nucleus (more protons) hence a greater force of attraction
- **Electron Shielding** - Negatively charged electrons in inner-shells repel electrons in outer shells. This is called the shielding effect and reduces the attraction between the nucleus and the outer electron.

The **Second Ionisation Energy** is the energy required to remove one electron from one mole of gaseous 1+ ions forming one mole of gaseous 2+ ions. The second ionisation of sodium is shown below



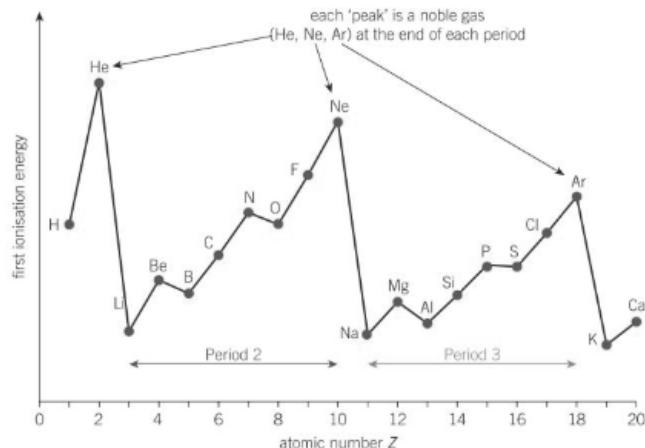
Successive ionisation energies can provide evidence for different energy levels in an atom by identifying: the number of electrons in the outer shell the group of the element and the identity of the element. the successive ionisation energies for Fluorine are shown below.



The group can be identified by the number of electrons in the outer shell which is 7 identifying the group to be the Halogens with 2 periods hence the element has to be fluorine.

3.3.1 Trends down a Group

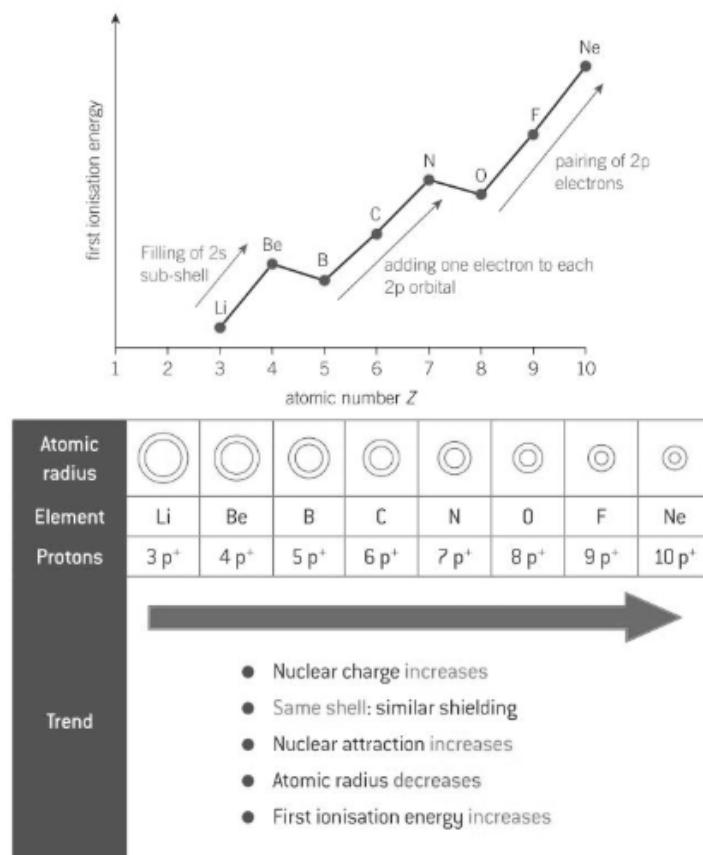
The first ionisation energy increases down a group decreases due to the factors previously mentioned. The atomic radius increases, the shielding effect increases due to more inner shells, the nuclear attraction decreases with the outer electron and the first ionisation energy decreases.



Noble gas	Atomic radius	Number of inner shells	Trend
helium, He	○	0	
neon, Ne	○○	1	
argon, Ar	○○○	2	<ul style="list-style-type: none"> ● atomic radius increases ● more inner shells so shielding increases ● nuclear attraction on outer electrons decreases ● first ionisation energy decreases

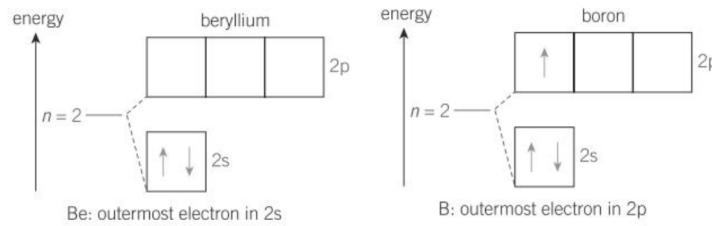
3.3.2 Trends down a Period

The first ionisation energy increases across a period as the nuclear charge increases, shielding remains similar as the number of shells is unchanged, the nuclear attraction increases, atomic radius decreases and hence the first ionisation energy increases.

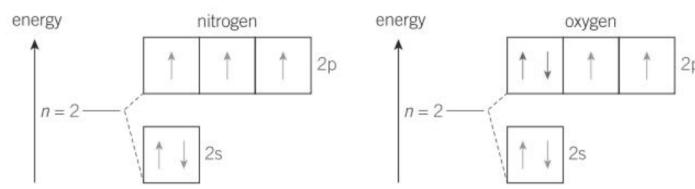


There are some visible exceptions in the trends across a period namely a decrease in ionisation energy from beryllium to boron and a decrease from nitrogen to oxygen.

- The fall in ionisation energy from beryllium to boron marks the start of the filling of the 2p sub-shell. The 2p-subshell in boron is a higher energy sub-shell than the 2s hence it requires less energy to remove a 2p electron than a 2s, this is due to repulsion between subshells. Therefore the ionisatio energy decreases.



- the fall in ionisatio energy from nitrogen to oxuge marks the pairing of electrons in the 2p sub-shell. In both atoms, the highest energy orbital is 2p however in oxygen one of the 2p electrons is paired. These electrons repel each other making it easier to remove than non-paired electrons in nitrogen, so less energy is required and the ionisation energy is lower.



3.4 Structure and Bonding

3.4.1 Giant Metallic Lattices

One of the key trends in the periodic table is the transition from metals to non-metals which takes place in a diagonal lad from the top of group 13 to the bottom of group 17. Elements on the right of this line such as boron, silicon and arsenic are non-metals and aluminium, germanium and antimony being metals. In the periodic table there are far more metals than non-metals.

Properties can be explained by the structure of metals which is kept together by a special type of bonding for metals. Metallic bonding is the attraction of fixed positive metal ions with delocalised electrons:

- All metal atoms donates its outer shell electrons creating a sea of **delocalised** electrons. These electrons are mobile and are able to move throughout the structure.
- The positive ions (cations) are left behind in a fixed position, maintaining the structure called a **giant metallic structure**.

Metals are known to have a number of key properties:

- Electrical Conductivity** - The only constant property of metals is their ability to conduct electricity. This is again due to the mobile electrons that are free to conduct through the metal. This is unlike ionic compounds that do not have this ability at room temperature.
- Melting and Boiling points** -All metals are solid at room temperature with the exception of mercury which is a liquid. This high melting and boiling point is due to the strong electrostatic attractions between the cations and electrons which require a large amount of energy to overcome.
- Solubility** -Metals are not soluble and do not dissolve. Although it may be thought that the delocalised electrons may interact with polar solvents however this is more likely to result in a reaction.

3.4.2 Giant Metallic Lattices

Many non-metal structures exist as simple molecular substances and exist as simple molecular lattices in a solid state. However, the non-metals, boron, carbon and silicon are kept together by a very strong network of covalent bonds instead of weak intermolecular bonds. These structures are called **giant covalent lattices**

Carbon and silicon can both form four covalent bonds with neighbouring atoms and hence form a tetrahedral lattice with bond angles of 109.5° by electron repulsion.

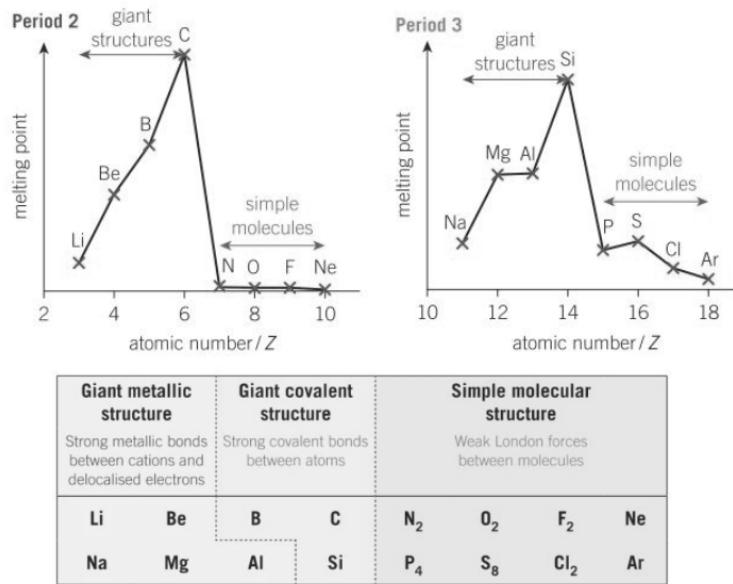
The properties of giant covalent structures are shown below, they are mainly dominated by the strong covalent bonds within the structure.

- **Electrical Conductivity** - Giant covalent structures are not conductors of electricity. The only exceptions are graphite and graphene, both special types of carbon structures where one of the electrons is free per carbon.
- **Melting and Boiling points** - The strong covalent bonds between atoms require a large amount of energy to break hence they have a high melting and boiling point
- **Solubility** - Like metals, giant covalent have far too strong bonds to be broken by polar solvents - they are insoluble.

3.5 Period Trends in Melting Points

- Across periods 2 and 3 the melting point increases from group 1 to group 14
- There is a sharp decrease in melting points between groups 14 and 15.

This large decrease is the transition from giant metallic and covalent structures to simple molecular structures where only weak intermolecular bonds need to be overcome.



3.6 Alkaline Earth Metals

Group 2 elements are known as the alkali earth metals, the name coming from the alkali properties of their metal hydroxides. They have numerous properties and reactions.

3.6.1 Reactions

Each group 2 element has two electrons in its outer shell which is typically lost by a redox reaction. Redox reactions are the most common type of reaction for group 2 elements where they are usually oxidised as shown below.

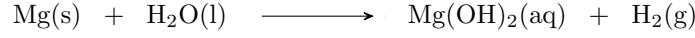


Another species will gain these electrons to be reduced. This makes group 2 elements good **reducing agents**

I The most common redox reaction is with oxygen to form a metal oxide. For example, magnesium will burn a brilliant white light to form a white magnesium oxide in air.



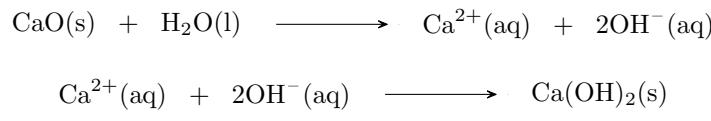
II Group 2 elements also react with water to form alkaline hydroxides and hydrogen gas. Magnesium reacts slowly with water but increases down the group.



III Like most metals, group 2 elements undergo redox reactions with acids to form a salt and hydrogen gas. The reaction of magnesium with hydrochloric acid is shown. In this reaction the hydrogen is reduced.



IV Group 2 oxides can also react with water to form the metal ion with hydroxide ions. When the solution becomes saturated the aqueous group 2 metal ions will bond with the hydroxide ions to form a metal hydroxide precipitate.

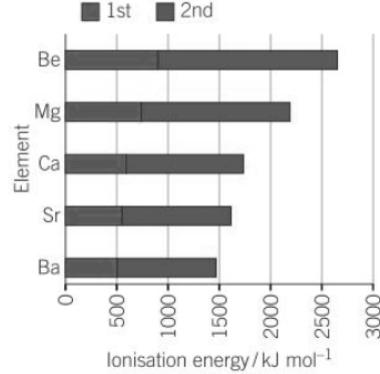


V Group 2 hydroxides such as calcium hydroxide are used as bases to neutralise acids. In agriculture, it is used as lime in fields to increase the pH of acidic soils. The typical reaction is as follows:



3.6.2 Reactivity and Solubility

As previously known, the ionisation energy decreases down the group due to the increase in atomic radius and shielding. This means the first ionisation energy and the second ionisation energy decreases down group 2 making reactivity increase down the group as the energy required for a reaction decreases.



The solubility of group 2 metal hydroxides increase down the group.

- $\text{Mg(OH)}_2\text{(s)}$ is only very slightly soluble in water. The solution has a low hydroxide ion concentration and a pH of about 10
- $\text{Ba(OH)}_2\text{(s)}$ is much more soluble in water. The solution has a greater concentration of hydroxide ions and hence a higher pH of 13
- The trend can be shown by adding each group 2 element to water in separate test tubes and shaking. By measuring the pH of each solution, the alkalinity will decrease down the group.

3.6.3 Uses of Group 2 Metals

Group 2 bases are often used as antacids to treat indigestion. Many indigestion tablets use calcium or magnesium carbonates to neutralise the acids. Examples of such medicines are Gaviscon and Rennie

3.7 The Halogens

The Halogens are group 7 elements that have 7 electrons in their outer shell. They exist as simple diatomic molecules and take part in various organic and inorganic reactions.

3.7.1 Trends in boiling points and reactivity

At RTP the halogens exist in all states. Fluorine and chlorine are gaseous, bromine is a liquid and iodine is a solid. In other words the boiling point of the halogens increases down the group as the London forces increase in strength.

Halogen molecule	Number of electrons	Boiling point / °C	Appearance and state at RTP	Trend
F ₂	18	-188	pale yellow gas	
Cl ₂	34	-34	pale green gas	
Br ₂	70	59	red-brown liquid	
I ₂	106	184	shiny grey-black solid	
At ₂	120	230	never been seen	<ul style="list-style-type: none"> • more electrons • stronger London forces • more energy required to break the intermolecular forces • boiling point increases

As you descend the halogens, the reactivity decreases as the first ionisation energy decreases. In redox reactions, a halogen's tendency to gain an electron decreases making fluorine the most reactive halogen.

3.7.2 Reactions

Chlorine mainly react by redox reactions where they are reduced by gaining electrons making them **oxidising agents**:



I A common reaction of the halogens is the displacement reaction, if a halogen reacts with a halogen halide or halide metal it will displace it only if it is more reactive. For example bromine is less reactive than chlorine so chlorine will displace bromine in sodium bromide. This causes a colour change from pale green to orange.



The colours of the halogens can be difficult to tell apart in solution so an organic non-polar solvent is used such as cyclohexane to give the following colours:

Cl ₂	Br ₂	I ₂	Cl ₂	Br ₂	I ₂
solution in water			solution in cyclohexane (top layer)		
pale green	orange	brown	pale green	orange	violet

II Chlorine will react with water to produce chloric (I) acid and hydrochloric acid. It is a **disproportionation** reaction where an element (chlorine) is simultaneously oxidised and reduced. The reaction is widely used for killing bacteria in water.



III The problem with the reaction of chlorine and water is that chlorine is not very soluble. If the water contains dissolved sodium hydroxide then much more chlorine dissolves.



3.7.3 Benefits and Risks of Chlorine

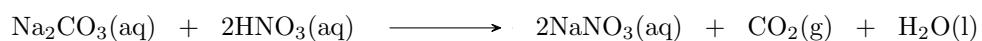
- Chlorine is beneficial ensuring that our drinking water doesn't contain bacteria so it is fit to drink. This use of chlorine revolutionised public health over 100 years ago.
- Chlorine is an extremely toxic gas and a respiratory irritant in small concentrations - large concentrations can be fatal.
- In drinking water chlorine can react with hydrocarbons to form chlorinated hydrocarbons which are suspected to be a cause of cancer, however this risk is outweighed by the benefit of having disinfected water.

3.8 Qualitative Analysis

Qualitative analysis tests are experiments to determine information simply based on observation, in comparison, titrations are a quantitative analysis technique. There are three main tests for identifying anions:

3.8.1 Test for Carbonates

- Carbonates react with acids to form carbon dioxide gas which will produce bubbles in a test tube - this is called effervescence. The reaction is shown below



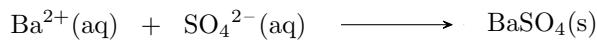
- To show that the gas is carbon dioxide, the gas is bubbled through lime water. Carbon dioxide will turn lime water milky as a fine white precipitate, calcium carbonate, forms in the following reaction:



- The carbonate test is always the first test when testing for anions as sulfate and halide test produce no bubbles.
- It is important to use nitric acid in this test as hydrochloric acid contains halides and sulfuric acid contains sulfate ions.
- When analysing a mixture of chemicals, add nitric acid until there is no more effervescence, at this point all the carbonate will have reacted.

3.8.2 Test for Sulfates

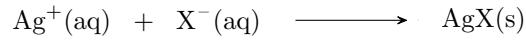
- Almost all sulfates are insoluble in water with the exception of barium nitrate BaSO_4 . When barium, provided by barium nitrate, is added to a solution containing sulfate, a dense white precipitate forms in the following reaction.



- The test must be carried out after the carbonate test as barium carbonate BaCO_3 is also insoluble and a white precipitate.
- It is important to use barium nitrate and not barium chloride as the chloride will produce a positive halide test.
- When analysing a mixture of chemicals, add excess barium nitrate so the remainder of the sulfate will form the precipitate which can be filtered out.

3.8.3 Test for Halides

- Most halides are soluble in water with the exception of silver halides which are insoluble. Aqueous silver ions from silver nitrate are added to an aqueous halide to form a silver halide precipitate.



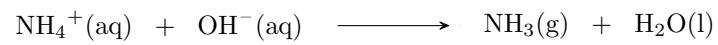
- The silver halide precipitates are different colours which helps identify which halide is present. When the colours are difficult to tell apart, aqueous ammonia is added as silver chloride will dissolve in dilute ammonia and iodide will not dissolve in concentrated ammonia. The results are shown below.

Halide	Ionic equation	Colour of precipitate	Solubility in $\text{NH}_3(\text{aq})$
chloride, Cl^-	$\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$	white	soluble in dilute $\text{NH}_3(\text{aq})$
bromide, Br^-	$\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$	cream	soluble in conc. $\text{NH}_3(\text{aq})$
iodide, I^-	$\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$	yellow	insoluble in conc. $\text{NH}_3(\text{aq})$

- This test must be conducted after the sulfate and carbonate test as silver carbonate AgCO_3 and silver sulfate Ag_2SO_4 will also form white precipitates.

3.8.4 Test for Ammonium

- When ammonium ions react with hydroxide ions, ammonia gas is produced. The reaction when sodium hydroxide is added to a solution of ammonia and warmed is shown below.



- The gas has a very distinct smell, although it can be tested. Ammonia is alkaline and will turn a moist pH indicator paper blue.

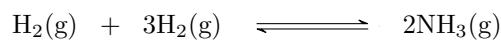
Chapter 4

Equilibrium

4.1 Dynamic Equilibrium

4.1.1 Reversible Reactions

When a reaction occurs, the reactants turn into products and this cannot be undone, however this isn't true of all reactions. A **reversible reaction** are reactions that take place the 'forward' and 'reverse' directions. For example, the Haber process is a reversible reaction.



- At Equilibrium, the rate of the forward reaction is always equal to the rate of the backwards reaction. Equilibrium systems are **dynamic** - the forward and backwards reactions are always taking place.
- For a reaction to remain in equilibrium, it must be a **closed system** - isolated from its surroundings so the temperature, pressure and concentrations are affected by external factors.
- The concentrations of products and reactants in dynamic equilibrium are constant and do not change.

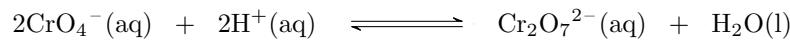
The position of equilibrium indicates the extent of a reaction. A change in temperature, pressure or concentration will shift the position of equilibrium.

4.1.2 Le Chatelier's Principle

Le Chatelier's Principle states that when a system in equilibrium is subjected to an external change, the system readjusts to minimise the effect of that change.

I Concentration: Changing the concentration of a reactant or product in an equilibrium system will change the rate of the forward or backwards reaction.

- If there are *more products* formed, the position of equilibrium will shift to the *right*.
 - If there are *more reactants* formed, the position of equilibrium will shift to the *left*.
- For example, the equilibrium between chromate and dichromate ions is sensitive to change in acid concentration.



- Increasing the concentration of H^+ ions will shift equilibrium to the right producing dichromate ions. This will turn the solution orange as dichromate ions are orange.
- Decreasing the concentration of H^+ ions will shift equilibrium to the left producing chromate ions. This will turn the solution yellow as chromate ions are yellow.

II Temperature: Changing the temperature of a solution or mixture in an equilibrium system will change the rate of the forward or backwards.

- Forward and reverse reactions have the same value of enthalpy change with opposite sign - one is endothermic (positive ΔH) and the other exothermic (negative ΔH).
- An *increase* in temperature will shift position of equilibrium in the *endothermic* direction.
- A *decrease* in temperature will shift the position of equilibrium in the *exothermic* direction.

For, example consider the reaction between blue cobalt chloride and pink cobalt in water:



- Increasing the temperature will favour the forward, endothermic, reaction so the solution will turn blue.
- decreasing the temperature will favour the backwards, exothermic, reaction so the solution will turn pink.

III Catalyst: A catalyst does not change the position of equilibrium. However it does increase the rates of reaction and the rate that the equilibrium is established.

IV Pressure: Changing the pressure of a reaction mixture in an equilibrium system will change the rate of the forward or backwards.

- *Increasing* the pressure of a system in equilibrium will favour the side of the reaction with *fewer* gas moles.
- *Decreasing* the pressure of a system in equilibrium will favour the side of the reaction with the *most* gas moles.

Consider the brown gas nitrogen dioxide set up in a reversible reaction with the colourless dinitrogen tetroxide.



- An Increase in pressure will favour the dinitrogen tetroxide N_2O_4 as it has fewer moles turning the gas colourless.
- A decrease in pressure will favour the nitrogen dioxide NO_2 as it has more moles turning the gas brown.

4.2 Equilibrium Constant K_c

4.2.1 Expressions for K_c

The exact position of equilibrium can be calculated using the equilibrium law. For any reaction at equilibrium it is possible to write an equilibrium constant K_c for a general reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D} \quad K_c = \frac{[\text{A}]^a[\text{B}]^b}{[\text{C}]^c[\text{D}]^d} = \frac{[\text{products}]}{[\text{reactants}]}$$

For example, the K_c expression for the Haber process is written as:

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3 \quad K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

The units for K_c depends on the number of concentration terms on the top and bottom of the fraction. To work out the units, units for concentration must be substituted and then cancelled to show the units on a single line.

4.2.2 Homogeneous and Heterogeneous equilibria

Equilibria are separated into two main types:

- **Homogeneous equilibrium** contains equilibrium species that are all the same states or phases. The equilibrium in the Haber process is an example of a homogeneous equilibrium as all species are gaseous.
- **Heterogeneous equilibrium** contains equilibrium species that are not of the same state or phase. The most common example is the neutralisation reaction between an base and a weak acid. In heterogeneous equilibria, the concentrations of solids and liquids are essentially constant and are therefore omitted from the K_c expression.

4.3 Equilibrium Constant K_p

Equilibria involving gases are usually expressed in terms of K_p , the equilibrium constant in terms of partial pressures. Concentration and pressure are proportional so K_c and K_p are closely related. Some terms are used when expressing K_p .

- **Partial pressure** p in a gas mixture is the contribution that the gas makes towards the total pressure P such that the sum of the partial pressures equal the total pressure P . The partial pressure is calculated based on the mole fraction $x(A)$ of P .

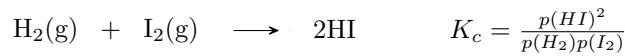
$$p(A) = x(A) \times P$$

- **Mole fraction** is the number of moles of a gas A as a fraction of the total number of moles. The mole fraction is the same under any temperature and pressure as the same volume of different gases contains the same amount of gas molecules.

$$x(A) = \frac{n(A)}{\Sigma n}$$

4.3.1 Expressions for K_p

K_p is written in a very similar way to K_c with partial pressures instead of concentrations and the exclusion of non-gaseous molecules. For the equilibrium:



The units of K_p are derived in a similar way done to find the units of K_c . Appropriate units for partial pressure include the pascal (Pa), the kilo-pascal (KPa) or atmospheres (atm).

4.4 Controlling the Position of Equilibrium

The magnitude of the value of the equilibrium constant indicates the extent of the chemical equilibrium.

- When $K=1$, the position of equilibrium is exactly halfway between the reactants and the products
- When $K=100$ indicates an equilibrium in favour of the products (position of equilibrium is to the right)
- When $K=0.01$ indicates an equilibrium in favour of the reactants (position of equilibrium is to the left)

4.4.1 Effect of Temperature on K

Temperature is the only factor that will affect the value of the equilibrium constant. If pressure, concentration and the presence of a catalyst change it will have no effect on K. How K changes based on temperature depends on whether a reaction endothermic or exothermic.

If the forward reaction is exothermic

- Increasing the temperature will shift the position of equilibrium to the left, so the equilibrium constant decreases.
- For K_p , the partial pressure of the products must decrease and the partial pressure of the reactants must increase.

If the forward reaction is endothermic

- Increasing the temperature will shift the position of equilibrium to the right, so the equilibrium constant increases.
- For K_p , the partial pressure of the products must increase and the partial pressure of the reactants must decrease.

4.4.2 Effect of Concentration and Pressure on K

The value of the equilibrium constant is unaffected by changes in concentration. As the value of K_c does not change a change in concentration of the products will be counteracted by change in the product concentrations

- An increase in the concentration of the reactants will result in an increase in the concentration of the products as the ratio must remain the same. For example, consider the equilibrium:

$$K_c = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]}$$

- If the concentration of NO_2 increases by a factor of 4, then the concentration of N_2O_4 must times by a factor of 16 to ensure K_c remains unchanged.

Similarly, pressure does not affect the equilibrium constant and the reason is the same as for concentration, the partial pressures must change such that K_p is unchanged.

- If the total pressure increases, then the partial pressures of the products and the reactants increase by the same factor. For example, consider the K_p expression:

$$K_p = \frac{p(\text{NO}_2(\text{g}))^2}{p(\text{N}_2\text{O}_4(\text{g}))}$$

- If the total pressure doubles, then the partial pressure of NO_2 will double and the partial pressure of N_2O_4 will also double. Hence K_p does not change.

Chapter 5

Rates of Reaction

5.1 Reaction Rates

The **rate of a chemical reaction** is a measure of how fast a chemical reaction is being used up or how fast a product is being formed. It can be defined as the change in concentration per unit time.

- The rate of reaction is the fastest at the start of the reaction as the concentrations are the greatest.
- As the reactants are used up, their concentration decreases and the rate of reaction decreases.
- Once the reactants are used up, its concentration is zero, and the rate of reaction is zero.

5.1.1 Effective Collisions

An effective collision is one that leads to a chemical reaction. A collision will be effective if two conditions are met:

- Particles involved in the reaction must have the correct orientation when colliding.
- Particles need to have sufficient energy to overcome the activation energy of the reaction.

5.2 Factors affecting Rates of Reaction

There are four main factors that affect the rate of reaction:

I **Concentration:** An increase in concentration increases the rate of reaction as the number of reactant particles in the same volume increases. the particles are closer together and will collide together more frequently. in a given period of time there will be more effective collisions.

II **Pressure:** When pressure increase, the rate of reaction increases. As the gas is compressed into a small volume, the concentration of the gas molecules increases. The gas molecules are closer together and collide more frequently leading to more effective collisions.

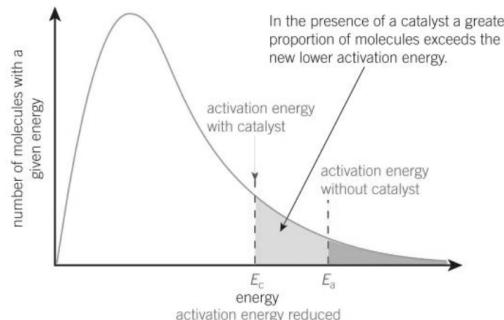
III **Temperature**

IV **Presence of a Catalyst**

5.2.1 Catalysts

A catalyst is a substance that changes the rate of reaction without being used up in a reaction. The catalyst does this by reacting with a reactant to form an intermediate or providing a surface for a reaction to take place. However the catalyst must always be reformed.

- A catalyst increases the rate of reaction by finding a alternate pathway to a reaction decreasing the activation energy
- By reducing the activation energy a greater proportion of particles have enough energy to overcome the activation energy, hence effective collisions are more frequent. the increase in proportion of particles that have $E < E_c$ is greater than $E < E_a$.



- A **homogeneous** catalyst has the same physical state as the reactants and will reactant to form an intermediate. Examples of a homogenous catalyst is sulfuric acid H_2SO_4 in esterification or chlorine radicals $Cl\cdot$ in ozone depletion.
- A **heterogeneous** catalyst has a different physical state to its reactants. It usually a solid in contact with gaseous or aqueous reactant. Reactants are **absorbed** onto the surface where the reaction takes place and then leave by **desorption**. An example of this the Iron catalyst in the Haber process.

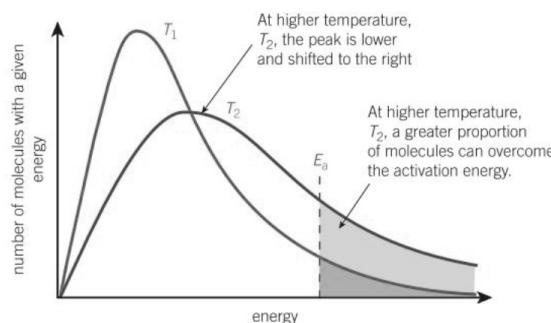
5.2.2 Sustainability and Economic Importance of Catalysts

- Over 90% of industrial processes use a catalyst as they significantly reduce the activation energy of reactions which reduces the temperature needed for a reaction and hence the energy requirements are lowered.
- If a chemical process requires less energy then less fossil fuels will need to be burned so less carbon dioxide gas or other greenhouses gases linked to global warming need to be burned
- The costs of developing a catalyst are lower than the costs of energy saved in using one, it is more economical.

5.2.3 Effect of Temperature on Rate

A higher temperature increases the rate of reaction:

- As temperature increases, the average energy of the molecules also increases
- Although, a small fraction of particles will still have low energy, more molecules will have energy greater than the activation energy as shown by the following Boltzmann distribution.



- Therefore a greater proportion of collisions will be effective and lead to a reaction, increasing the rate of reaction.
- Collisions will also be more frequent as the molecules are moving faster, although the increased energy is a much bigger factor than the frequency of collisions.

5.3 Order of a Reaction

Changing the concentration often changes the rate of reaction. The rate is always proportional to the concentration of a reactant A to the power of n.

$$R \propto [A]^n$$

- **Zero order** is when $R \propto [A]^0$. The concentration of a zero order reactant has no effect on the rate of reaction as anything raised to the zeroth power is 1.
- **First order** is when $R \propto [A]^1$. When the concentration of a first order increases by a factor k, the rate will also increase by that same factor as they are directly proportional.
- **Second order** is when $R \propto [A]^2$. When the concentration of a second order increases by a factor k, the rate increases by a factor k^2 as the rate is proportional to the square of the concentration.

5.3.1 Rate equation

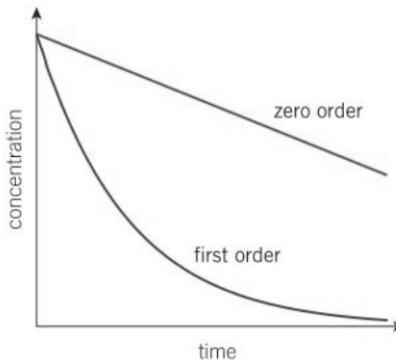
the **rate equations** gives the mathematical treatment between the concentration of the reactants and the reaction rate. The general form for the rate equation of two reactants A and B is shown below.

$$R = k[A]^n[B]^m$$

- the overall order of the reaction is the overall effect of the concentrations on the rate. In this example the overall order is $n+m$.
- the **rate constant** k is the proportionality constant. It is the number that mathematically converts the concentrations and the rate. The units of the rate constant depend on the overall order and can be worked out by substituting units for concentration and rate.

5.4 Rate Graphs

5.4.1 Concentration-Time Graphs



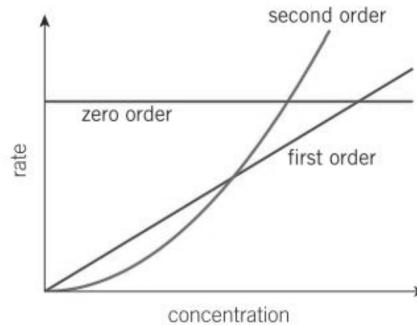
the gradient of a concentration-time graph is the rate of reaction. The order of a reactant can also be determined from this graph - this is assuming the concentrations of the other reactants remain constant.

- A *zero* order reactant will not change the rate of reactions hence the concentration-time graph will be a straight line. the value of the gradient is equal to the rate constant
- A *first* order reactant will produce a downwards curve with a decreasing gradient over time - this type of decreases is called **exponential decay**. for a first order reactant, the time taken for the concentration to half, the **half-life**, is constant.
- A *second* order reactant will produce a similar graph to a first order reactant with a steeper start and a greater decrease in the gradient.

The half life can be calculated from a concentration-time graph for a first order reactant by finding the time taken for any concentration to reach half its original value. This value of the half life $t_{\frac{1}{2}}$ can be used to calculate the rate constant using the following equation

$$k = \frac{\ln 2}{t_{\frac{1}{2}}}$$

5.4.2 Rate-Concentration Graphs



Rate-concentration graphs can be plotted from measurements of the rate of reaction at different concentrations. They are important as they allow for graphically solutions to the rate equation.

- A *zero* order reactant will produce a straight horizontal line on a rate-concentration graph as the rate doesn't change with concentration. the rate constant k is equal to the rate which can be worked out from the y-intercept.
- A *first* order reactant will also produce a straight line but through the origin and a constant gradient as the relationship is directly proportional. the rate constant can be determined by the gradient of this line.
- A *second* order reactant will produce a parabolic graph going through the origin. the rate constant cannot be obtained from this graph; a second graph must be plotted of rate and against concentration² which will produce a straight line with the rate constant as its gradient.

5.5 Rate-Determining Step

An overall chemical equation compares the reactants and products by balancing them to give their stoichiometry. For reactions to occur, particles need to collide, the collisions of multiple reactants simultaneously is very unlikely; a much more likely mechanism involves the reaction occurring in multiple steps. These series of steps is called the **reaction mechanism**.

5.5.1 Reaction Mechanisms

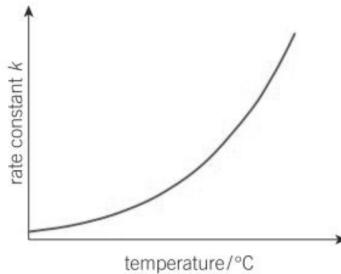
The **rate-determining step** is the slowest step in the reaction mechanism and affects the rate of reaction the most.

- The rate-determining step includes only the species included in the rate equation.
- The orders in the rate equation match the number of moles of a species involved in the rate-determining step.

5.6 The Arrhenius Equation

5.6.1 Effect of Temperature on the Rate Constant

As temperature increases, the rate of reaction increases and so does the rate constant. For a typical reaction, the rate constant will double for every 10K increase in temperature the rate of reaction and rate constant doubles. Below shows a typical graph of rate constant against temperature.



5.6.2 Arrhenius equation

The relationship between the rate and temperature is exponential and is modelled by the Arrhenius equation:

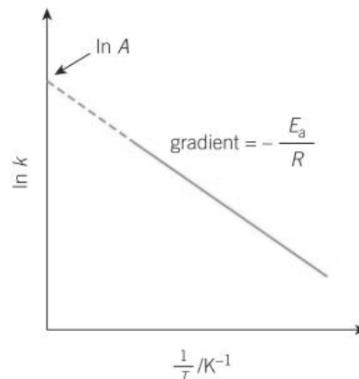
$$k = Ae^{-E_a/RT}$$

- R is the molar gas constant and has a constant value of $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$.
- T is the temperature measured in kelvin.
- E_a is the activation energy of the reaction in Joules.
- A is the pre-exponential factor or frequency factor. A takes into account the frequency of effective collisions and can be thought of as the rate if the activation energy was zero.

A more useful form of the Arrhenius equation is in logarithmic form:

$$\ln k = -\frac{E_a}{R}(\frac{1}{T}) + \ln A$$

In this form, a graph of $\ln k$ against $1/T$ to form a straight line with gradient $-E_a/R$. This makes the Arrhenius equation very useful in finding the activation energy of the reaction as well as the pre-exponential factor A which is simply the y-intercept of the graph.



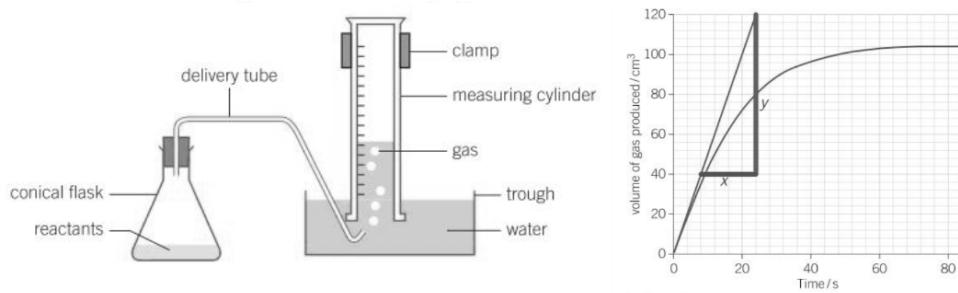
5.7 Rates from Experiments

5.7.1 Continuous Monitoring

concentration-time graphs can be plotted from continuous measurements taken over the course of a reaction. this is called **continuous monitoring**.

If a reaction produces gas two methods can be used to calculate the initial rate.

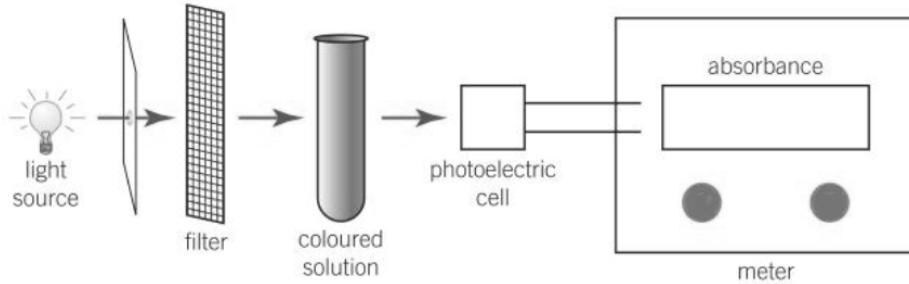
- By monitoring the volume of gas produced using a gas syringe or inverted conical flask, the volume of water can be recorded at regular time intervals. By plotting the volume of the gas produced against time, the rate of reaction at any time can be calculated by drawing tangents to the curve.



- An alternative method places the flask on a balance and monitoring the loss of mass lost as gas during the reaction. the reaction is complete when the mass stays at a constant value. A graph of mass against time can be plotted.

Not all reactions produce gas so methods shown above cannot be used. Instead a **colorimeter** can be used.

- In a colorimeter, the wavelengths of light passing through a solution is controlled using a filter. The apparatus transmits the light through a coloured solution and onto a photoelectric cell where the absorbance is measured. the absorbance of light through the reaction solution is measured at regular intervals.



- However the absorbance readings need to be converted into concentrations, to do this an absorbance-concentration graph is drawn for known concentrations of the solution to obtain a calibration curve. this provides a mean to convert and hence produce a concentration-time graph.

5.7.2 Initial Rates Method

the initial rate is the instantaneous rate at the start of the reaction when $t=0$ and typically found by drawing a tangent at this point. However this is not the most efficient way

A **clock reaction** is a more convenient way of obtaining the initial rate by measuring the time t from the start of reaction until a visual change is observed. Assuming there is no significant change in rate, the initial rate is proportional to $1/t$. The experiment is repeated for different concentrations which can be used to determine the order.

Chapter 6

Acids and Bases

6.1 Bronsted-Lowry Acids and Bases

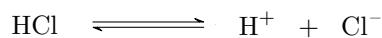
We have already seen how acids and bases dissociate to release H^+ and OH^- ions in a solution. The Bronsted-Lowry model extends this definition to emphasise the transfer of protons.

I A **Bronsted-Lowry acid** is a proton donor.

II A **Bronsted-Lowry base** is a proton acceptor.

6.1.1 Conjugate Acid-Base Pairs

The equation below shows the dissociation of hydrochloric acid into a hydrogen ion and a chloride ion.

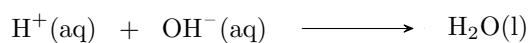


HCl and Cl^- are called **acid-base conjugate pairs**, two species that can be inter-converted by the exchange of a proton.

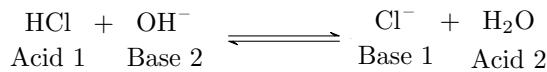
- In the forward reaction, HCl *releases* a proton to form its conjugate base, Cl^-
- In the backwards reaction, Cl^- *accepts* a proton to form its conjugate acid, HCl

Note: although the equilibrium sign is shown, HCl is a strong acid, so equilibrium position is well to the right.

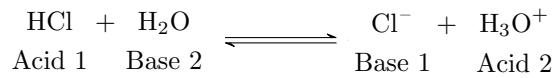
In the neutralisation of hydrochloric acid, the neutralisation using hydrogen ions can be shown simply by the following equation:



We can combine the two equations to give the acid-base equilibrium. In this reaction, there are two acid-base conjugate pairs.



in an aqueous solution, dissociation requires a proton to be transferred from an acid to a base. The dissociation does not take place without water as the water acts as a base to form a hydronium ion H_3O^+ which accepts a proton in the acid-base equilibrium shown.



6.1.2 Monobasic, Dibasic and Tribasic

The terms, **monobasic**, **dibasic** and **tribasic** refer to the total number of protons (hydrogen atoms) that can be replaced per molecule in an acid-base reaction. Some examples of the types of acids are shown:

Acid	Name	Type
HCl	hydrochloric acid	monobasic
CH_3COOH	ethanoic acid	monobasic
H_2CO_3	carbonic acid	dibasic
H_3BO_3	boric acid	tribasic

6.1.3 Acids, Bases and Metals

In a reaction between an acid and a base or metal, ionic equations can be written. Ionic equations are written by cancelling out spectator ions - ions that do not change during a reaction. For example consider the redox reaction between magnesium and sulfuric acid:



Ionic:



In this reaction, the SO_4^{2-} ions are the spectator ions and are excluded from the ionic equation.

6.1.4 The pH scale

The concentration of hydrogen ions in solution have a very large range of values with negative powers of 10 ranging from 0 to 14. It is this range of concentrations that is used to measure acidity of solutions using a pH scale from 0 to 14.

- A pH greater than 7 shows increasing alkalinity.
- A pH of 7 is a neutral solution.
- A pH less than 7 shows increasing acidity.

The mathematical relationship between $[H^+(aq)]$ and pH is logarithmic and can be calculated by the equation:

$$[H^+(aq)] = 10^{-pH} \quad pH = -\log [H^+(aq)]$$

- A *low* value of hydrogen ion concentration will match with a *higher* pH.
- A *high* value of hydrogen ion concentration will match with a *smaller* pH.

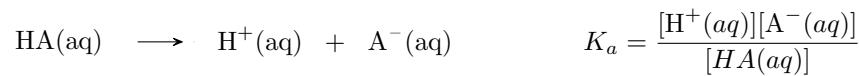
6.1.5 pH of a Strong Acid

The pH of a strong acid HA can be calculated directly from the concentration of that acid such that

$$[H^+(aq)] = [HA(aq)] \quad pH = -\log [HA(aq)]$$

6.2 Acid Dissociation Constant K_a

The acid dissociation constant K_a is one of the special equilibrium constants used for acid-base equilibria. All equilibrium constants are simply versions of K_c . For the partial dissociation of the acid HA, K_a is written as



As with other equilibrium constants, K_a only changes with temperature and a larger K_a , the further the equilibrium to the right.

The only problem with using K_a to determine the strength of an acid, is it can be hard comparing the values of negative indices. So like the pH scale, the pK_a value is calculated by finding the negative log of K_a .

$$K_a = 10^{-pK_a} \quad pK_a = -\log K_a$$

- The *weaker* the acid, the *smaller* the value of K_a and the *larger* the value of pK_a .
- The *stronger* the acid, the *greater* the value of K_a and the *smaller* the value of pK_a .

Acid	$K_a / \text{mol dm}^{-3}$	pK_a	Relative acid strength
nitrous acid	HNO_2	4.10×10^{-4}	3.39
methanoic acid	HCOOH	1.77×10^{-4}	3.75
ethanoic acid	CH_3COOH	1.76×10^{-5}	4.75
chloric(I) acid	HClO	3.00×10^{-8}	7.53



6.2.1 pH of Weak Acids

For a monobasic acid, HA, in an aqueous solution:

- A strong acid HA completely dissociates so $[H^+(\text{aq})] = [\text{HA(aq)}]$.
- A weak acid HA partially dissociates so $[H^+(\text{aq})] \neq [\text{HA(aq)}]$

The concentration of hydrogen ions depends on the concentration of the acid and the acid dissociation constant.

	HA(aq)	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{A}^-(\text{aq})$
start	$[\text{HA(aq)}]_{\text{start}}$		0		0
equilibrium (eqm)	$\begin{cases} [\text{HA(aq)}]_{\text{eqm}} \\ [\text{HA(aq)}]_{\text{start}} - [\text{H}^+(\text{aq})]_{\text{eqm}} \end{cases}$		$[\text{H}^+(\text{aq})]_{\text{eqm}}$		$[\text{A}^-(\text{aq})]_{\text{eqm}}$

K_a can be calculated using the equilibrium concentrations.

$$K_a = \frac{[\text{H}^+(\text{aq})]_{\text{eqm}}[\text{A}^-(\text{aq})]_{\text{eqm}}}{[\text{HA(aq)}]_{\text{eqm}}} = \frac{[\text{H}^+(\text{aq})]_{\text{eqm}}[\text{A}^-(\text{aq})]_{\text{eqm}}}{[\text{HA(aq)}]_{\text{start}} - [\text{H}^+(\text{aq})]_{\text{eqm}}}$$

6.2.2 Approximations

For weak acids, approximations can be made to simplify the K_a expression:

- **Approximation 1:** $[\text{H}^+(\text{aq})] = [\text{A}^-(\text{aq})]$. Ha will dissociate to form equal amounts of H^+ and A^- however a very small concentration of hydrogen ions will be present from the dissociation of water, however this can be neglected.
- **Approximation 2:** $[\text{HA(aq)}]_{\text{eqm}} = [\text{HA(aq)}]_{\text{start}} - [\text{H}^+(\text{aq})]_{\text{eqm}}$. this approximation assumes that the concentration of acid is much larger than the concentration of hydrogen. this approximations only works for weak acids as for stronger acids H^+ concentrations get much larger.

Hence the expression for K_a becomes

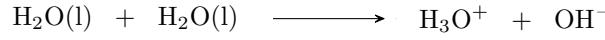
$$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{HA(aq)}]}$$

Using this expression for K_a , the acid-dissociation constant can be determined experimentally.

- Preparing a standard solution of the weak acid of known concentration.
- Measuring the pH of the standard solution using a pH meter to determine the concentration of hydrogen ions.

6.3 Ionic Product of Water K_w

Water ionises very slightly acting as an acid and a base, setting up the acid base equilibrium:



This special type of acid-base equilibrium is described by the **Ionic product of Water** constant K_w the concentration of hydrogen ions multiplied by the concentration of hydroxide ions:

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

The significance of K_w is huge as it has a value $1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 25°C . This value sets up the neutral point in the pH scale. The value of K_w is essentially an equilibrium constant that controls the concentration of H^+ and OH^- ions:

- A solution is acidic when $[\text{H}^+(\text{aq})] > [\text{OH}^-(\text{aq})]$
- A solution is neutral when $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$
- A solution is alkaline when $[\text{H}^+(\text{aq})] < [\text{OH}^-(\text{aq})]$

6.3.1 pH of Strong Bases

An alkali is a soluble base that releases OH^- ions in an aqueous solution. For example, sodium hydroxide completely dissociates in water releasing OH^- :



Sodium hydroxide is a monobasic base as each mole of NaOH releases one mole of hydroxide ions. The pH of a strong base can be calculated from the concentration of the base and the ionic product of water.

Weak Bases are also an alkali and dissolve in water to release hydroxide ions such as ammonia:

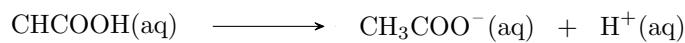


For one mole of ammonia, far less than one mole of hydroxide is produced.

6.4 Buffer Solutions

A **Buffer Solution** is a system that minimises pH changes when small amounts of acid or base are added. A buffer system contains an acid and a conjugate base. A buffer solution of a weak acid can be prepared from adding a weak acid to one of its salts

- The weak acid, HA will remove alkali. When ethanoic acid is added to water, the acid partially dissociates into hydrogen ions and ethanoate ions.



- Salts of weak acids are ionic compounds and provide a source for the conjugate base. When a salt is added to water, it completely dissolves. For a buffer solution of ethanoic acid, sodium ethanoate can be used.



the conjugate acid and base provide two reservoirs that are able to act independently to remove acid or alkali from the solution. However when the base is used up the solution loses its buffering ability. The buffer works as follows

- When the acidity increases, the concentration of H^+ increases and the ions react with the base. Equilibrium shifts to the left removing the H^+ ions and the pH returns to normal.
- When the alkalinity increases, the concentration of OH^- increases. The small concentration of H^+ ions react with the hydroxide to form water. The acid dissociates to shift equilibrium to the right and restore the H^+ ions which decreases the pH to its original value.

6.4.1 Choosing Components for a Buffer Solution

A buffer solution is more effective when there are equal concentrations of acid and base such that $[\text{HA}(aq)] = [\text{A}^-(aq)]$.

- the pH of the buffer solution becomes the same as $\text{p}K_a$
- The pH value is typically over 2 pH units, centered at the pH of the $\text{p}K_a$ value.

the table below shows some examples of some weak acids together with their base and typical pH range.

Acid	Name	$\text{p}K_a$	Typical operating pH range
CH_3COOH	ethanoic acid	4.76	3.76–5.76
HOCH_2COOH	glycolic acid	3.83	2.83–4.83
HCOOH	methanoic acid	3.75	2.75–4.75
$\text{CH}_3\text{CHOHCOOH}$	lactic acid	3.08	2.08–4.08

6.4.2 Calculating the pH of a buffer Solution

When calculating the pH of a weak acid, the approximation that the concentration of H^+ is equal to the concentration of A^- . this is not true for buffer solutions. The K_a expression can be rearranged to find the pH of a buffer solution.

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

$$\text{pH} = -\log \left(K_a \times \frac{[\text{HA}(\text{aq})]}{[\text{A}^-(\text{aq})]} \right)$$

Provided the concentrations of the acid and the base are known as well as K_a , the pH can be found. In the event that $[\text{HA}(\text{aq})] = [\text{A}^-(\text{aq})]$, then $K_a = [\text{H}^+(\text{aq})]$ and $\text{pH} = \text{p}K_a$

6.4.3 controlling the pH in our blood

Blood plasma needs to be maintained at a pH of 7.35 and 7.45. This is done using a buffer of carbonic-acid H_2CO_3 and hydrogencarbonate HCO_3^- which maintains blood at a pH of 7.4.



If blood pH falls below 7.35, people can develop acidosis which can cause fatigue, shortness of breath, shock or death. If the pH rises above 7.45, people can develop alkalosis, which is linked to muscle spasms and nausea.

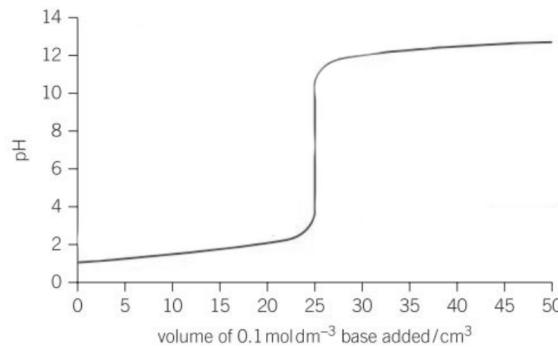
- When blood becomes too acidic, the H^+ ion concentration increases and reacts with the base HCO_3^- . This shifts equilibrium to the left, removing the H^+ ions and reducing the pH
- When the blood becomes too alkaline, OH^- ion concentration increases and reacts with the small concentration of H^+ ions. the acid dissociates to reform the hydrogen by shifting equilibrium to the right to decrease the pH.

6.5 Neutralisation

When carrying out acid-base titrations, indicators are used to monitor neutralisation reactions accurately. The pH changes of neutralisation reactions are done experimentally using a **pH meter** to determine the pH and certain concentrations.

6.5.1 Titration Curves

A **pH titration curve** shows the variation of pH with volume of base added during a titration, a typical titration curve is shown below.



- At the start of the titration, the pH increases slowly as the acid is in much greater excess.
- The vertical section shows a rapid increase in pH on addition of a small amount of base as the acid and base concentrations are similar.
- The **equivalent** point of the titration is where the volume of one solution exactly reacts with the volume of the other solution and is the center of the vertical section on the pH curve.
- The pH then goes back to increasing slowly as the base is in much greater excess than the acid.

A pH curve can also be plotted for acid added to base. In this case, the pH of the solution will decrease as the volume of acid added increases.

6.5.2 Indicators

An acid-base indicator is a weak acid that has a different colour to its conjugate base e.g. methyl orange is red but its conjugate base is yellow. At the **end point** of a titration the acid and base will be in equal concentrations and the colour will be a midpoint of the two - for methyl orange the colour is yellow.

The colour change can be explained by an equilibrium. For a titration with methyl orange indicator where a strong base is added to a strong acid

- OH^- ions are added to the acid and react with H^+ in the indicator to form water. The indicator acid dissociates to reform the hydrogen ions shifting equilibrium to the right

- The colour changes, first to orange at the endpoint and then yellow as the equilibrium position is shifted to the right.

When acid is added to a base:

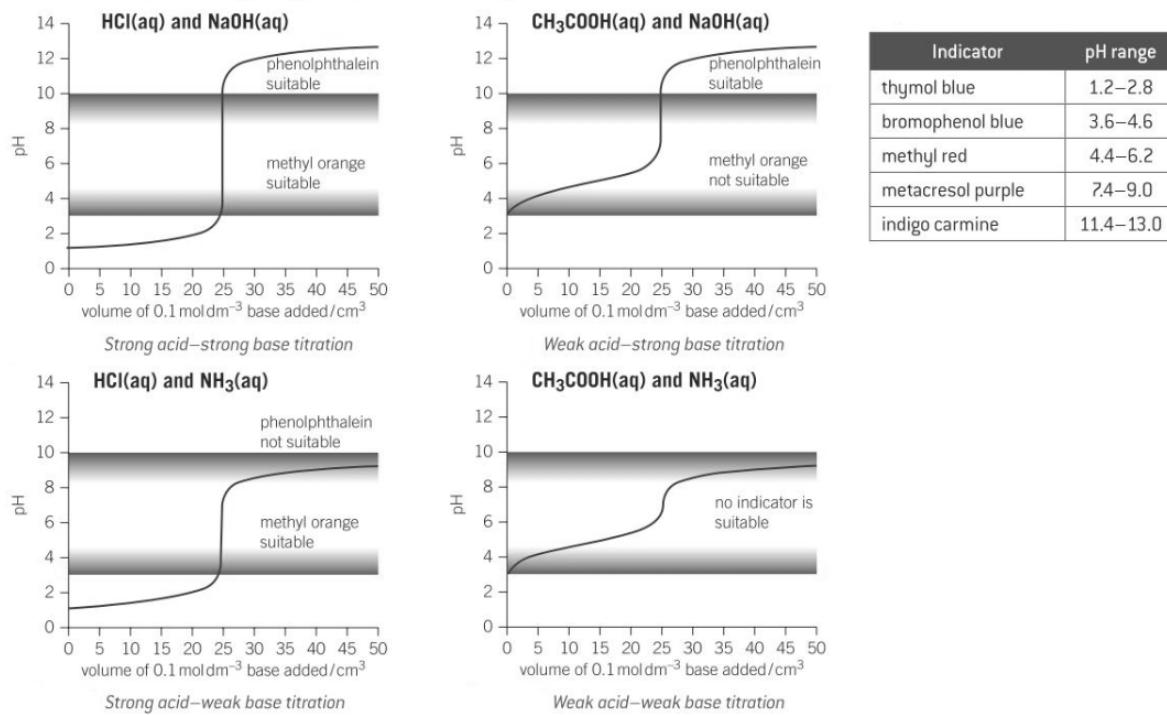
- H^+ ions react with the conjugate base shifting equilibrium to the left reforming the acid.
- The colour changes, first to orange at the end point and finally to red when equilibrium is shifted to the left.

Remember the pH at the endpoint is equal to the $\text{p}K_a$ value of the indicator as the acid and base are in equal concentrations.

6.5.3 Choosing an Indicator

In a titration, you must use an indicator that has a colour change which coincides with the vertical section of the titration curve.

The following curves show the suitable indicators that can be used for titrations between different combinations and strong and weak acids and bases. For example, methyl orange is suitable indicator for strong acid-weak base as it coincides with the vertical second unlike phenolphthalein.



Note: The titration curve between a weak acid and a weak-base has no vertical section so no indicators can be used to determine the equivalence point.

Chapter 7

Energy, Enthalpy and Entropy

7.1 Enthalpy

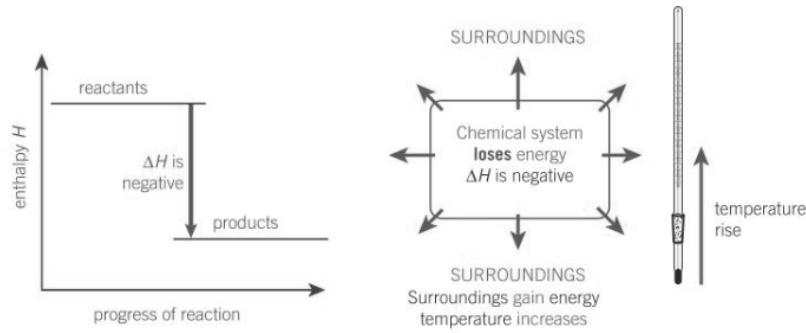
Enthalpy H is a measure of the heat energy in a chemical system and can be thought of the energy stored within the bonds. the enthalpy cannot be calculated but enthalpy change can and is defined as:

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

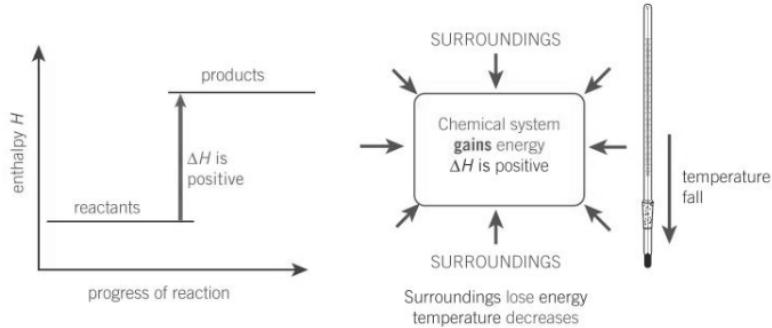
7.1.1 Exothermic and Endothermic

the law of **conservation of energy** is one of the fundamental laws stating that the total energy and matter in a system cannot be created or destroyed. When a chemical reaction takes place energy is transferred to the surroundings which include: the chemicals, the apparatus and the universe.

- Energy transfer from the system to the surroundings is **exothermic**. The chemical system releases energy which is gained in the surroundings so ΔH is negative.

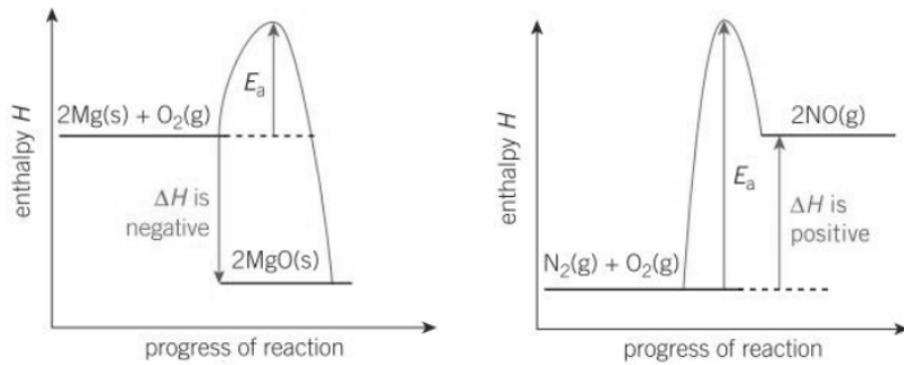


- Energy transferred from the surroundings to the system is **endothermic**. The chemical system gains energy and is balanced by a decrease in energy in the surroundings so ΔH is positive.



7.1.2 Activation Energy

Atoms and ions are held together by chemical bonds which need to be broken during reactions. This requires energy known as the **activation energy** E_a . In general, reactions with a lower activation energy occur more rapidly and have a higher rate of reaction. The activation energy can be represented on an energy change diagram as shown:



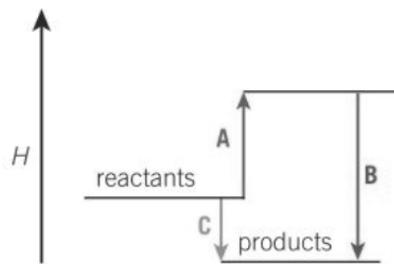
7.1.3 Standard Conditions

A standard physical value such as enthalpy is shown in data tables using a special sign \ominus . The standard state conditions for energy changes are set as the following:

- **Standard pressure** is 100kPa. this is very close to atmospheric pressure which is 101KPa
- **Standard temperature** is 298K or 25°C however for calculations 298K must be used.
- **Standard concentration** is 1 moldm⁻³. this value is relevant for solutions only.
- **Standard state** is the physical state of a substance under standard conditions.

7.1.4 Hess' Law

Enthalpy changes can be difficult to determine directly but they can be measured indirectly by **Hess' law**. Hess' law states that if a reaction can take place by two routes and the starting and finishing conditions are the same, the enthalpy change is the same. For example:



- following the reactants to the products there are two routes A+B and C.
- By Hess' law, the enthalpy change is the same so C=A+B

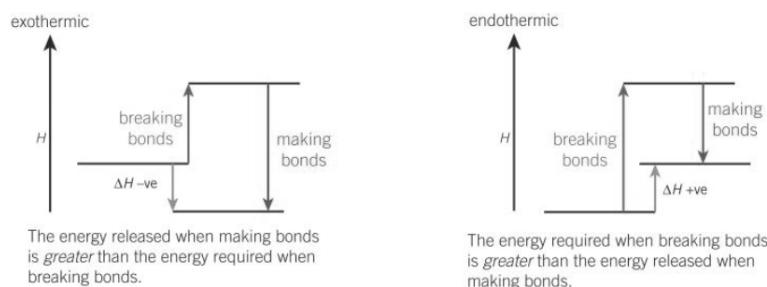
7.1.5 Bond Enthalpy

the **Average bond enthalpy** is the energy required to break 1 mole of a specific type of bond in a gaseous molecule.

- Energy is required to break bonds
- Bond enthalpies are always endothermic and hence have positive values of ΔH

The main problem with calculating bond enthalpies is that it varies depending on a bond's chemical environment. An average bond enthalpy is calculated from a variation of different chemical environments. In calculations average bond enthalpies or actual bond enthalpies can be given.

- Energy is required to break bonds so bond breaking is endothermic $\Delta H = +$
- Energy is released to make bonds so bond breaking is exothermic $\Delta H = -$



7.2 Enthalpy Changes

7.2.1 Enthalpy Change of Reaction

The **standard enthalpy change of reaction** $\Delta_r H^\ominus$ is the enthalpy change that accompanies a reaction in the *molar quantities* shown in a chemical equation under standard conditions.

- For example, $\Delta_r H^\ominus$ can be calculated for the equation between magnesium and oxygen gas using a fraction to balance the oxygen.



- If the equation was balanced using whole numbers, if the moles of each species was doubled, the enthalpy change of reaction would also double.



- Using the bond enthalpies for the reactants and products we can deduce by Hess' law the enthalpy change of reaction is the sum of breaking the bonds subtracting the energy lost to surroundings from forming the bonds.

$$\Delta_r H^\ominus = \Sigma(\text{bond enthalpy of reactants}) - \Sigma(\text{bond enthalpies in products})$$

7.2.2 Enthalpy Change of Formation

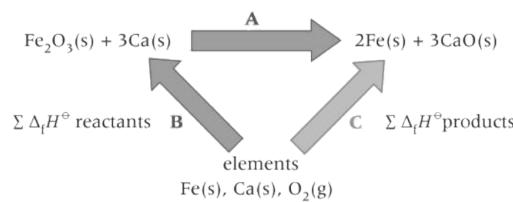
The **standard enthalpy change of formation** $\Delta_f H^\ominus$ is the enthalpy change that takes place when one mole of a compound is formed from its elements under standard conditions.

- For example, the fractional chemical equation for the formation of one mole magnesium from its base elements is shown below. Hence by definition, the enthalpy change associated is $\Delta_f H^\ominus$.



- The enthalpy change of formation can be calculated from the enthalpy changes of formation of the individual products and reactants from its base elements as a second route. Hence $\Delta_f H^\ominus$ can be calculated.

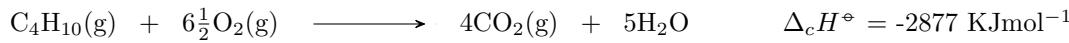
$$\Delta_r H^\ominus = \Sigma \Delta_f H^\ominus(\text{products}) - \Sigma \Delta_f H^\ominus(\text{reactants})$$



7.2.3 Enthalpy Change of Combustion

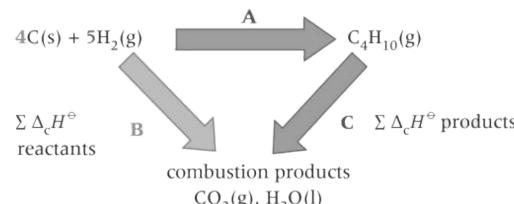
The **standard enthalpy change of combustion** $\Delta_c H^\ominus$ is the enthalpy change that takes place when one mole of a substance reacts completely with oxygen under standard conditions.

- When a substance reacts with oxygen, the products are the oxides of the elements in a substance. The combustion and its associated enthalpy change of butane is shown below.



- The enthalpy change of combustion for a reaction can be calculated by Hess' law. The energy required to go from the elements to substance is equal to the enthalpy of combustion of those elements subtracted from the enthalpy change of the substance.

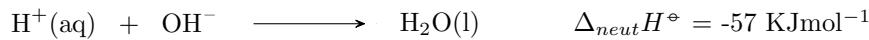
$$\Delta_r H^\ominus = \Sigma \Delta_c H^\ominus(\text{reactants}) - \Sigma \Delta_c H^\ominus(\text{products})$$



7.2.4 Enthalpy Change of Neutralisation

The **standard enthalpy change of neutralisation** $\Delta_{neut}H^\circ$ is the energy change that accompanies the reaction of an acid by a base to form one mole of H_2O under standard conditions.

- The enthalpy change of neutralisation can be generalised for all neutralisation reactions as the reaction between hydrogen ions and hydroxide such that:



7.2.5 Enthalpy Change of Atomisation

The **standard enthalpy change of atomisation** $\Delta_{at}H^\circ$ is the enthalpy change that takes place when one mole of gaseous ions are formed from the element in standard state under standard conditions.

- For example, half a mole of chlorine gas will undergo atomisation to form one mole of chlorine gaseous atoms.

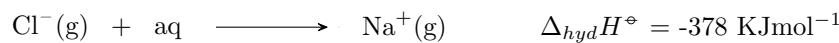
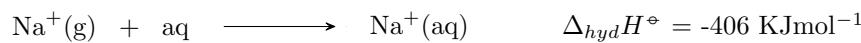


- Atomisation is an endothermic enthalpy change as bonds are being broken which requires energy. When the element is already in gaseous state, the $\Delta_{at}H^\circ$ is closely related to the bond enthalpy.

7.2.6 Enthalpy Change of Hydration

The **standard enthalpy change of hydration** $\Delta_{hyd}H^\circ$ is the enthalpy that accompanies the dissolving of gaseous ions in water to form one mole of aqueous ions under standard conditions.

- The equations below show the enthalpy changes of hydration involved when dissolving sodium chloride in water. the enthalpy changes occur:

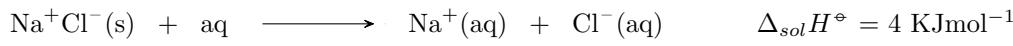


- The enthalpy change of hydration is exothermic as the ions lose energy.

7.2.7 Enthalpy Change of Solution

The **standard enthalpy change of solution** $\Delta_{sol}H^\circ$ is the enthalpy change that takes place when one mole of a solute dissolves in a solvent.

- When the solvent is water, the ionic lattice ends up surrounded with water molecules as aqueous ions. The standard enthalpy change of sodium chloride is shown below:



- the enthalpy change of solution can be exothermic or endothermic.
- In an ionic structure, the sodium and chloride ions are attracted to one another. In an aqueous solution ions are separate, but now surrounded by water molecules
 - The $\delta+$ partial charges on the water are attracted to the negative chloride ions.
 - The $\delta-$ partial charges on the water are attracted to the positive sodium ions.

7.2.8 Lattice Enthalpy

The **lattice** $\Delta_{LE}H^\circ$ is the enthalpy change that accompanies the formation of one mole of an ionic compound from its gaseous ions under standard conditions.

- For 1 mole of an ionic lattice of potassium chloride formed from gaseous potassium ad chloride ions, the lattice enthalpy can be written as:



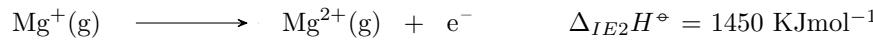
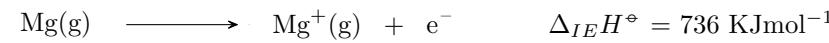
- Lattice enthalpy is always an exothermic energy change and the value will always be negative as energy is released forming the ionic bonds.

7.2.9 Ionisation Energy and Electron Affinity

The **first ionisation energy** $\Delta_{IE}H^\circ$ is the enthalpy change required to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous $1+$ ions.

The **second ionisation energy** $\Delta_{IE2}H^\circ$ is the enthalpy change required to remove one electron from each atom in one mole of gaseous $1+$ ions to form one mole of gaseous $2+$ ions.

- For example, the first and second ionisation energies of magnesium are shown:

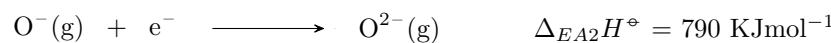
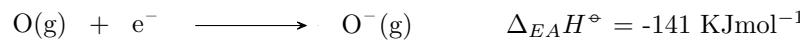


- Ionisation energies are always endothermic as energy is required to remove electrons from atoms to overcome the nuclear attraction between the electrons and the nucleus.

The **first electron affinity energy** $\Delta_{EA}H^\circ$ is the enthalpy change that takes places when one electron is added is added to each atom of one mole of gaseous atoms to form one mole of $1-$ gaseous ions.

The **first electron affinity energy** $\Delta_{EA2}H^\circ$ is the enthalpy change that takes places when one electron is added is added to each ion of one mole of $1-$ ions to form one mole of $2-$ gaseous ions.

- The first two electron affinities for oxygen are shown below:

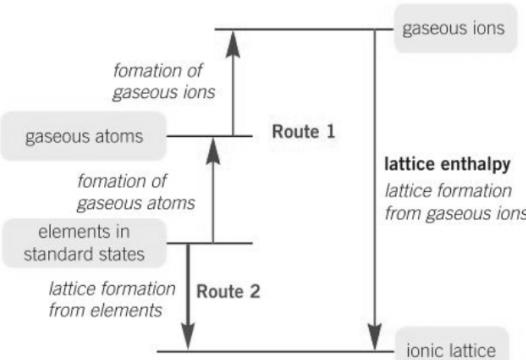


- Electron affinity can essentially be thought of as the inverse of ionisation energy as it gains electrons rather than losing them.
- First electron affinities are always exothermic however second electron affinities are endothermic.

7.3 Born-Haber Cycles

7.3.1 Forming a Solid Ionic Compound

Lattice enthalpy cannot be measured directly and must be measured indirectly using known energy changes, this requires a type of energy cycle called a **Born-Haber** cycle. The Born-Haber cycle for the formation of an ionic lattice is shown below:



There are two possible routes to go from elements in a standard state to an ionic lattice. The first route requires 3 different processes:

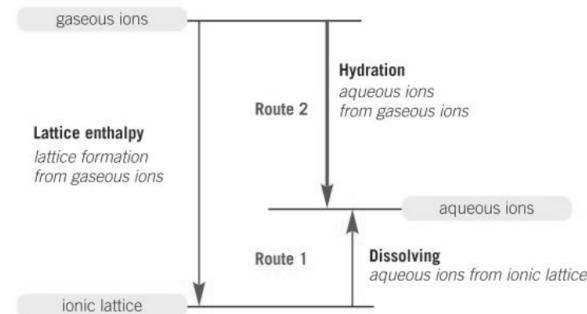
- Atomisation:** the formation of gaseous atoms from the elements in their standard state, endothermic change.
- ionisation energy and electron affinity:** the gaseous atoms must form positive and negative gaseous ions. the overall enthalpy change is endothermic.
- Lattice enthalpy:** changing the gaseous ions to form a solid ionic lattice. This change is exothermic.

The second route only requires a single energy change:

- Formation:** converts the elements in standard state to the ionic lattice in an exothermic enthalpy change.

7.3.2 Dissolving an Ionic Lattice

Like lattice enthalpy, the energy change of solution cannot be directly measured but can be indirectly. A Born-Haber cycle shows the energy changes associated when an ionic lattice (solute) is dissolved in a solvent. the Born-Haber cycle is shown below:



There are two possible routes to go from elements in a standard state to an ionic lattice. The first route requires 2 different processes:

- *Lattice enthalpy:* from gaseous ions, an ionic lattice is formed in an exothermic energy change.
- *Solution:* aqueous ions are formed from the lattice in an endothermic change.

The second route requires a single type of energy change:

- *Hydration:* the aqueous ions are formed from gaseous ions in an exothermic enthalpy change.

7.4 Factors Affecting Lattice Enthalpy

7.4.1 Ionic Size

Ionic size can affect the value of lattice enthalpy. As the atomic radius increases, the attraction between the ions will decrease as there will be a greater distance between them, this will make lattice enthalpy less negative and decrease the melting and boiling point.

Cation size	Compound	Lattice enthalpy / kJ mol ⁻¹	Melting point / °C	Effect of ionic size
Na ⁺	NaCl	-786	801	<ul style="list-style-type: none"> • ionic radius increases • attraction between ions decreases • lattice energy less negative • melting point decreases
K ⁺	KCl	-715	771	
Rb ⁺	RbCl	-689	718	

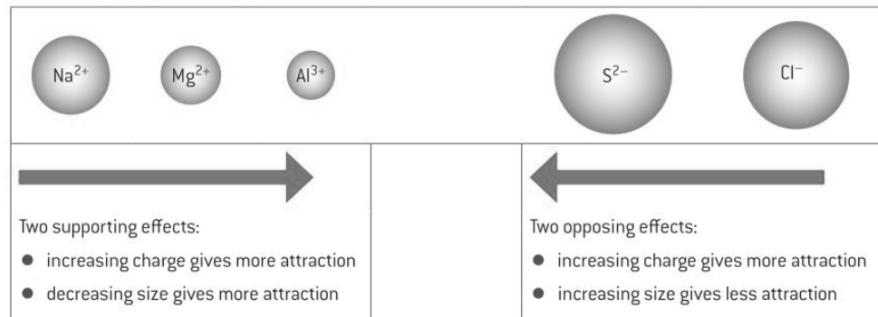
7.4.2 Ionic Charge

The lattice enthalpy can change drastically based on the charges on the ion. the greater the ionic charge, the greater the force of attraction between ions and hence the more negative the lattice enthalpy ad the higher the melting and boiling points.

Compound	Na ₂ O	CaO
	Na ⁺	Ca ²⁺
Lattice enthalpy / kJ mol ⁻¹	-2455	-3414
Melting point / °C	1132	2900
<ul style="list-style-type: none"> • Ionic charge increases • Attraction between ions increases • Lattice energy becomes more negative • Melting point increases 		

Across period 3, there are two major factors affecting lattice enthalpy

- For cations, a greater charge means more attraction and a smaller atomic radius gives more attraction
- For anions, a greater charge means more attraction and a larger atomic radius gives less attraction - the effects oppose one another.



The lattice enthalpy gives a good indication of what the melting point will be. In general the greater the lattice enthalpy the higher the melting point

7.5 Factors Affecting hydration

7.5.1 Ionic Charge

Like lattice enthalpy, hydration is affected by atomic radius and ionic charge

- As ionic radius increases, the attraction between ions and water molecules decrease as they are further apart so the hydration energy decreases.
- As ionic charge increases, the attraction between ions and water molecules increase and the hydration energy increases.

Cation size	Hydration enthalpy / kJ mol ⁻¹	Effect of ionic size	Ionic charge	Hydration enthalpy / kJ mol ⁻¹	Effect of ionic charge
Na ⁺	-406	● ionic radius increases ● attraction between ion and water molecules decreases ● hydration energy less negative	Na ⁺	-406	● ionic charge increases ● attraction with water molecules increases ● hydration energy becomes more negative
K ⁺	-320				
Rb ⁺	-296				

Hydration and lattice enthalpy are partially involved in the solubility of an ionic compound.

- The energy required to break down a lattice is equal to the lattice enthalpy.
- The energy produced when forming bonds of attraction between ions and water molecules is the hydration energy.
- When the sum of the hydration energies is greater than the lattice enthalpy, the ionic compound is soluble.

7.6 Entropy

Entropy is a measure used to describe and explain the dispersion and tendency of energy in nature. the greater the entropy the greater the dispersal of energy; the units of entropy are JK⁻¹mol⁻¹.

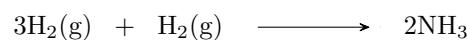
- Solids have the smallest entropy.
- Liquids have a greater entropy than solids (but less than gases).
- Gases have the greatest entropy.

The change of entropy of a reaction can hence be predicted based on a few factors

- If a system changes to become more random, energy becomes more spread out so ΔS is positive.
- If a system changes to become less random, energy becomes more ordered ad concentrated - ΔS is negative.

Examples of entropy changes include:

- When changing state from a solid to a liquid to gas, the temperature of the substance increases and becomes more disordered and random as particles and energy is free to move randomly hence ΔS is positive.
- If a chemical reaction produces molecules with a greater entropy the system becomes more random. Consider the Haber process:



There are a greater number of gas moles on the left than on the right so the system becomes less random and more ordered, hence entropy decreases and ΔS is negative.

7.6.1 Standard Entropy Changes

Every substance has a standard entropy that can be found in data books. the **standard entropy** S° is the entropy of one mole of a substance under standard conditions - these values are always positive.

The standard enthalpies can be used to determine the standard entropy change of a reaction ΔS°

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

7.6.2 Free Energy

The **feasibility** of a reaction is used to describe whether or not a reaction is able to happen and is energetically feasible. The overall change in energy during a reaction ΔG and is calculated using the Gibb's free energy equation:

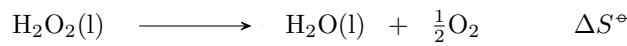
$$\Delta G = \Delta H - T\Delta S$$

- The enthalpy change ΔH is the heat transfer between the chemical system and the surroundings.
- The entropy change at the temperature of the reaction $T\Delta S$ is the dispersal of energy within the chemical system itself.

A reaction is feasible if ΔG is *less than* zero. This means that the feasibility of a reaction depends on the balance between ΔH and $T\Delta S$. The table below summarises the different possibilities.

ΔH	ΔS	T	$\Delta G = \Delta H - T\Delta S$	Feasible?
negative	positive	low or high	negative	yes
positive	negative	low or high	positive	no
negative	negative	low	negative	yes
		high	positive	no
positive	positive	low	positive	no
		high	negative	yes

The greatest limitation with predicting the feasibility of reactions using ΔG is that some reaction may have a negative ΔG but have a very large activation energy such as the decomposition of hydrogen peroxide:



This reaction does not take place at 25°C as the activation energy is very large despite the negative ΔG .

Chapter 8

Redox and Electrode Potentials

8.1 Redox Reactions

We have already seen that oxidation and reduction can be described by the transfer of electrons.

- *Oxidation:* the loss of electrons, the increase in oxidation number.
- *Reduction:* the gain of electrons, the decrease in oxidation number.

We can update these definitions in terms of oxidising and reducing agents:

- The oxidising agent takes electrons from the species being oxidised. The oxidising agent is always reduced.
- The reducing agent adds electrons to the species being reduced. The reducing agent is always oxidised.
- Consider the redox reaction below:



- The Ag^+ is the oxidising agent as it has oxidised Cu.
- The Cu is the reducing agent as it has reduced Ag^+

8.1.1 Redox Equations

There are a number steps that are taken to work out redox equations from half equations.

- Half equations are equations that show the oxidation or the reduction of a single species. They can be determined from oxidation numbers of a reaction or they can be given.
- The first step requires balancing hydrogens and oxygens. Oxygens are balanced using water molecules H_2O and hydrogen balanced using hydrogen ions H^+ .
- The atoms have not been balanced but there may be a charge imbalance, charge is balanced using electrons. The oxidation reaction will lose electrons and the reduction equation will gain electrons.
- To find the full redox reaction, ensure there are an equal amount of electrons in each half equation by multiplying all the species and add the equations, cancelling out common molecules.

Redox reactions can also be written based on oxidation numbers:

- For a given equation, assign each atom an oxidation number. For the oxidised and reduced elements write the change in oxidation number. The element being oxidised will have a positive change and the element being reduced will have a negative change.
- For the electron transfer to be conserved, the change in oxidation numbers must be the same (with opposite signs), hence multiply all species containing that element such that this is true.

8.1.2 Manganate (VII) Redox Titrations

Redox titrations are very similar to acid-base titrations. There are two important redox titrations to know:

- Potassium Manganate (VII) $\text{KMnO}_4(\text{aq})$ under acid conditions.
- Sodium Thiosulfate $\text{NaS}_2\text{O}_3(\text{aq})$ for determination of iodine

Consider the redox titration of potassium manganate (VII) to determine the purity of iron in an iron tablet.

- A standard solution of potassium manganate is prepared and added to the burette.
- Using a pipette, measure a known volume (usually 25cm^3) from a standard solution of iron. Sulfuric acid is also added in excess to provide the acidic conditions.
- During the reaction, the manganate (VII) reacts and is decolourised as it turns into the colourless Mn_2^+ hence no indicator is needed.
- The titration is repeated until concordant titres are obtained with $\pm 0.1 \text{ cm}^3$
- The mean titre is recorded and used in calculations. Also recorded is the mass of impure iron tablets calculated from the weighing bottle.

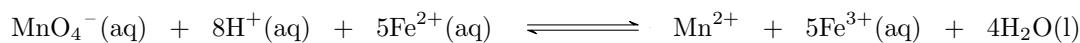
Mass measurements

Mass of weighing bottle + impure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /g	18.34
Mass of weighing bottle/g	11.37
Mass of impure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /g	6.97

Titration readings

	Trial	1	2	3
Final burette reading/cm ³	24.10	23.70	23.15	23.35
Initial burette reading/cm ³	1.00	0.00	23.70	0.00
Titre / cm ³	23.10	23.70	23.45	23.35
Mean titre / cm ³	23.40			

- Using the recorded measurements, the number of moles of manganate required to fully react with iron can be calculated to work out the mass of iron present. However the stoichiometry of the reaction must be taken into account. The reaction below shows that 5 moles of Fe^{2+} will react with one mole of MO_4^- .

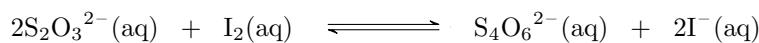


- Now that the number of moles of iron reacted is known, the mass can be found and hence the percentage purity of the tablets.

Manganate redox titrations are always used to analyse reducing agents hence potassium manganate (VII) can be replaced with other oxidising agents such as acidified potassium dichromate $\text{Cr}_2\text{O}_7^{2-}$.

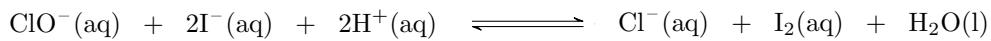
8.1.3 Iodine-Thiosulfate Redox titrations

Where Manganate (VII) titrations are used to analyse reducing agents, iodine-thiosulfate reactions are used to analyse oxidising agents. The typical redox for this reaction shows the reduction of iodine and the oxidation of iodine.



Examples of oxidising agents used in thiosulfate-iodine titrations include chlorate (I) ions ClO^- that are analysed in solutions of bleach or copper (II) ions Cu^{2+} . The outline of the procedure of the titration is shown below.

- A standard solution of sodium thiosulfate is added to the burette.
- Prepare a standard solution of oxidising agent to be analysed and add to the conical flask using a pipette with potassium iodide in excess.
- The iodide ions will react with the oxidising agent forming iodine which turns the solution brown.
- As the solution is titrated the thiosulfate reduces the iodine back to iodide I^- and the solution loses its brown colour. All the iodide will have reacted when the solution is colourless.



- From the equation above, 1 mole of ClO^- produces 1 mole of I_2 which reacts with 2 moles of $\text{S}_2\text{O}_3^{2-}$. Since the number of moles can be calculated from the mean titre, the number of moles of chlorate can be calculated and analysed.

Iodine/thiosulfate reactions can be used to determine copper content in salts or alloys. The procedure is very similar to chlorate however the copper ions are formed from dissolving in nitric acid HNO_3 and neutralising the acid.



When copper (II) ions are added potassium iodide, the redox reaction is:



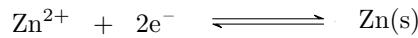
2 moles of copper Cu^{2+} ions react with iodide to produce 1 mole of iodine I_2 which reacts with 2 moles of thiosulfate. Hence 1 mole of copper ions reacts with 1 mole of thiosulfate.

8.2 Electrode Potentials

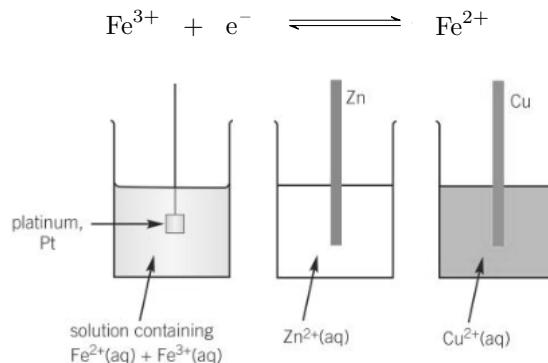
8.2.1 Half-Cells

A **voltaic cell** is an electrochemical cell which converts chemical energy into electrical energy. This is done by setting up redox reactions that transfer electrons from one species to another. A **half-cell** contains the chemical species in a redox reaction. Two half cells can be connected by a salt bridge to produce a voltage.

- The simplest half cell consists of a metal rod dipped into a solution of its aqueous metal ion. This is represented using a vertical line showing the phase boundary where the solid is in contact with the ions and an equilibrium is set up. By convention the equilibrium is always shown as the forward reaction as reduction. For example,



- The direction of electron flow depends on the tendency of the relative tendency of each electrode to release electrons.
- In an ion-ion half cell the equilibrium is set up between two different aqueous ions. In this case a platinum electrode is used. An example of an ion-ion half-cell occurs between iron 2+ and 3+ ions:

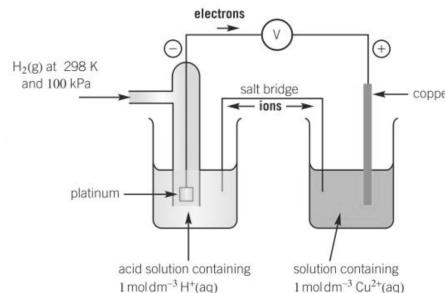


- The electrode with the more reactive metal loses electrons and is oxidised (negative electrode). The electrode with the less reactive metal will gain electrons and will be reduced (positive electrode).

8.2.2 Standard Electrode Potentials

The tendency to be reduced is measured as the **standard electrode potential** E^\ominus . The standard half-cell contains hydrogen gas into a solution containing hydrogen ions and an inert platinum half cell under standard conditions. The standard hydrogen electrode has an electrode potential of 0V.

- To measure the standard electrode potential, the half-cell is connected to a standard hydrogen electrode connected by a wire and a voltmeter. The voltmeter will measure the standard electrode potential of that half-cell.
- A **salt bridge** is used between the two solutions that let ions flow. The salt bridge is usually soaked in an electrolyte such as potassium nitrate $\text{KNO}_3(\text{aq})$



- The more negative E^\ominus , the greater the tendency to lose electrons and undergo oxidation, the lower the tendency to gain electrons and undergo reduction.
- The more positive E^\ominus , the lower the tendency to lose electrons and undergo oxidation, the greater the tendency to gain electrons and undergo reduction.

The standard electrode potentials of common ions and atoms are shown below:

Redox system	E^\ominus / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

A standard cell potential can be calculated directly from the standard electrode potential of each half cell by looking at the difference between the half-cell potentials:

$$E^\ominus = E^\ominus(\text{positive electrode}) - E^\ominus(\text{negative electrode})$$

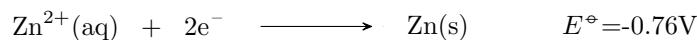
8.2.3 Predicting Redox Reactions

The feasibility of a redox reaction can be determined from E^\ominus values. A redox reaction will take place if the E^\ominus of the cell is positive, the reaction will take place.

- The strongest oxidising agent has the most negative E^\ominus .
- The strongest reducing agent has the most positive E^\ominus .

The main problem associated with predicting feasibility based on electrode potentials, like ΔG is that a reaction may seem feasible based on E values but the reaction may have a very high activation energy, resulting in a slow rate.

Standard electrode potentials are measured using concentrations of 1 mol dm^{-3} . If these concentrations change, so does the electrode potential. For example, consider the redox system:



- If the concentration of zinc ions Zn^{2+} increases from standard conditions, equilibrium will shift to the right, removing electrons from the system making the cell potential less negative.
- If the concentration of zinc ions Zn^{2+} decreases from standard conditions, equilibrium will shift to the left, electrons will be added to the system making the potential more negative.

The actual conditions for a reaction may differ from standard conditions which will affect the value of the cell potential.

8.2.4 Storage cells

Modern day cells and batteries use the chemistry of electrode potentials to store electrical energy. There are three types of cells used today, primary, secondary and fuel cells:

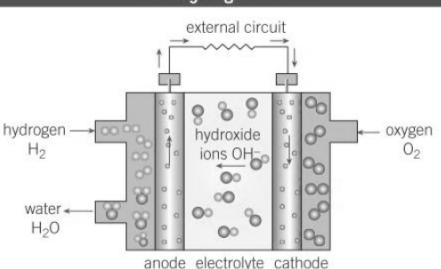
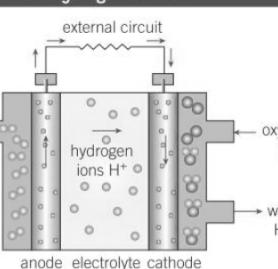
- *Primary cells* are non-rechargeable. They produce electrical energy by oxidation and reduction at the electrodes, but eventually the chemicals used at the electrodes will be used up. The most common cells are alkaline based on zinc and manganese dioxide.



- *Secondary cells* are rechargeable unlike primary cells. The cell reaction in secondary cells can be reversed to remake the chemicals that can of course be used again. Examples include lead-acid batteries and lithium-ion cells.

Fuel cells use energy from a reaction of a fuel with oxygen to create a voltage. Fuel and oxygen flows into the fuel cell and the products flow out, the electrolyte remains in the cell. They do not need to be recharged provided a continuous supply of fuel and oxygen.

- A hydrogen fuel uses either an acid or alkali electrolyte to produce a constant E^\ominus value of 1.43 V . In these cells, hydrogen is always oxidised and oxygen is always reduced.

Alkali hydrogen fuel cell	Acid hydrogen fuel cell
 <p>hydrogen H_2 water H_2O</p> <p>anode electrolyte cathode</p>	 <p>hydrogen H_2 oxygen O_2</p> <p>anode electrolyte cathode</p>
Redox systems $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^\ominus = -0.83\text{ V}$ $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq) \quad E^\ominus = +0.40\text{ V}$	Redox systems $2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^\ominus = 0.00\text{ V}$ $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l) \quad E^\ominus = +1.23\text{ V}$
Oxidation: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ Reduction: $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$ Overall: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad E^\ominus_{\text{cell}} = 1.23\text{ V}$	Oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ Reduction: $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$ Overall: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad E^\ominus_{\text{cell}} = 1.23\text{ V}$

Chapter 9

Transition Metals

9.1 d-block elements

the **d-block elements** are located between group 2 and group 13 on the periodic table. Across the periodic table, from scandium to zinc, the highest energy orbital is 3d, hence the name. The d-block elements are all metals and have metal-like properties.

Because electrons occupy orbitals in order of increasing energy, the 4s orbital is filled first as we have previously seen to have a lower energy than the 3d subshell. Hence all d-block elements have 4s filled, with two exceptions: chromium and copper.

Element	Number of electrons	Electron configuration
scandium	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
titanium	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
vanadium	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
chromium	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
manganese	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
iron	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
cobalt	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
nickel	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
copper	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
zinc	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

- The exceptions of electron configuration for chromium and copper can be explained by stability. A partially filled 3d⁵ and 3d¹⁰ orbital gives additional stability their atoms.
- When forming an atom, the 4s orbital fills before 3d
- When forming an ion, the 4s orbital empties before 3d

9.1.1 Transition Elements

Transition elements are defined as d-block elements that form at least one ion with a partially filled d-orbital.

- Scandium has one electron its 3d orbital and only forms 3+ ions hence - it does not form a ion with a partially filled d-orbital hence scandium is no a transition element.
- Zinc has has a full 3d orbital and 4s orbital. Zinc only forms 2+ ions with a fully filled 3d orbital ad hence is not a transition metal.

Transition metals can form variable oxidation states. For example, Iron can form ionic compounds with chlorine as FeCl_2 or FeCl_3 . Each transition element form ions with a 2+ oxidation state resulting in a loss of two electrons. The oxidation states are shown below:

Element		Common oxidation states and their colours				
Sc		+3	By definition not a transition element			
Ti	+2	+3	+4	+5		
V	+2	+3	+4	+5		
Cr	+2	+3	+4	+5	+6	
Mn	+2	+3	+4	+5	+6	+7
Fe	+2	+3	+4	+5	+6	
Co	+2	+3	+4	+5		
Ni	+2	+3	+4			
Cu	+1	+2	+3			
Zn	+2	By definition not a transition element				

I Common oxidation states include iron that forms 2+ and 3+ ions. Iron (II) is pale green and iron (III) is yellow.

II Chromium forms two common oxidation states +3 and +6. Chromium (III) is green and chromium (VI) orange.

9.1.2 Transition Metals as Catalysts

A catalyst is a substance that increases the rate of reaction without itself being used. Transition metals are commonly used for heterogenous and homogeneous catalysis.

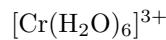
- The Haber process for the manufacture of ammonia is catalysed by an iron catalyst.
- The contact process in the production of sulfur trioxide is catalysed by vanadium.
- The hydrogenation of alkenes in vegetable fats also uses a Nickel catalyst.
- the redox reaction between zinc metal with acids is catalyst by aqueous copper ions (this is the only example on this list of a homogeneous catalyst.)

9.2 Complex Ions

One of the most important properties of d-block elements is their ability to form a **complex ions**. A complex ion is formed when one or more molecules or negatively charged ions bond to a central metal ion. These molecules or ions are called **ligands**.

- A ligand is defined as a molecule or ion that donates a pair of electrons to a central metal ion to form a coordinate bond (also called a dative covalent bond.)
- A dative covalent bond or coordinate bond is a special type of covalent bond where one of the bonded atoms provides both electrons for the shared pair.
- The **coordinate number** indicates the number of coordinate bonds attached to a central metal ion

The chemical formula for complex ions uses square brackets with a charge, for example, the complex ion formed when chromium is dissolved in water is shown.



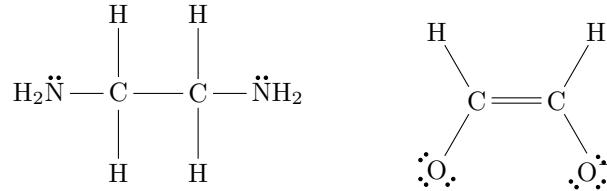
9.2.1 Ligands

There are two main types of ligands used in transition element chemistry monodentate and bidentate.

- A **monodentate** ligand donates one pair of electrons to a central metal ion to form a coordinate bond. Common monodentate ligands are shown below:

Monodentate ligands		
Name	Formula	Charge on ligand
water	$\text{H}_2\text{O}:$	neutral
ammonia	$:\text{NH}_3$	neutral
chloride	$:\text{Cl}^-$	-1
cyanide	$:\text{CN}^-$	-1
hydroxide	$:\text{OH}^-$	-1

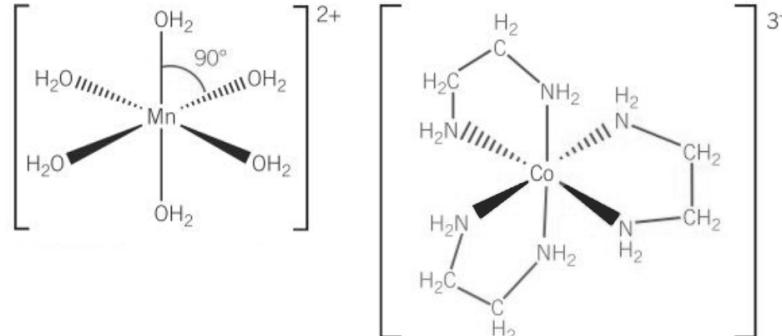
- A **bidentate** ligand donates two pairs of electrons to a central metal ion to form two coordinates. Common bidentate ligands are shown below.



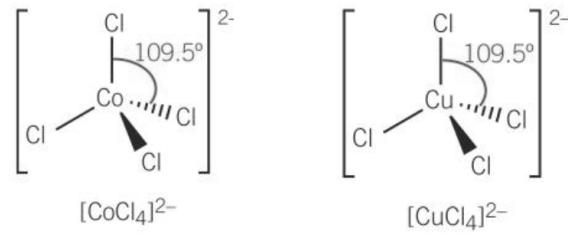
9.2.2 Shapes of Complex Ions

The shape of a complex ion depends upon its coordination number. the most common coordination numbers are six and four

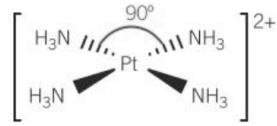
- Many complex ions have a coordination of six giving them a octahedral shape with a bond angle of 90° . The octahedral shape is common for almost all ligands including bidentate. The complex ions $[\text{Co}(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_3]^{3+}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ are shown.



- Complex ions with a coordination number of four can form two shapes, the first is tetrahedral. A tetrahedral shape is common for chloride ions as they take up too much space around the central metal ion to form octahedral. The complex ion $[\text{CuCl}_4]^{2-}$ is shown.



- A square planar shape occurs in complex ions of transition elements with electron configuration $3d^8$, this includes Platinum (II), Palladium (II) and gold (III). The complex ion $[\text{Pt}(\text{NH}_3)_4]^{2+}$ is shown.

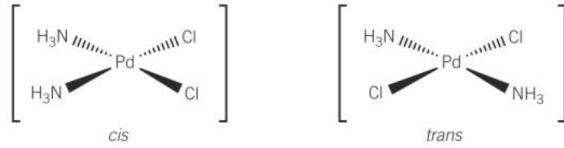


9.3 Stereoisomerism in Complex ions

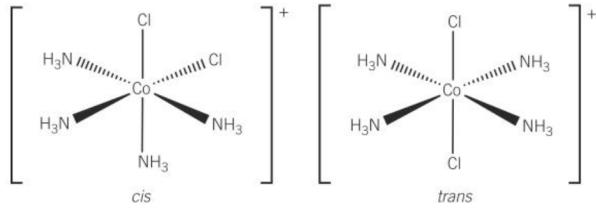
9.3.1 Isomers with Monodentate Ligands

Stereoisomers have the same structural formula but a different arrangement of atoms in space. Complex ions can display both cis-trans isomerism as well as optical isomerism.

- The simplest form of cis-trans isomerism occurs in planar complexes. In the cis-isomer the two identical groups are adjacent to each other and in the trans-isomer the two identical groups are opposite each other. The cis-trans isomers for $[\text{Pd}(\text{HH}_3)_2\text{Cl}_2]$ are shown.

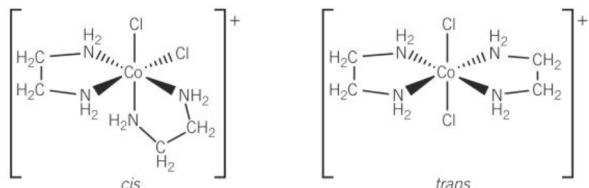


- Cis-trans isomerism is also displayed by octahedral complexes with four of one ligand and two of another type of ligand. In the cis-isomer, identical ligands are adjacent to one another (at 90°), for the trans-isomer identical ligands are opposite to each other (180°). Below shows the cis-trans isomers for $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

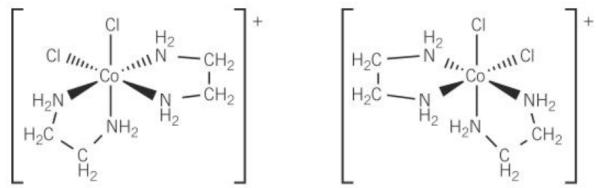


9.3.2 Isomers with Bidentate Ligands

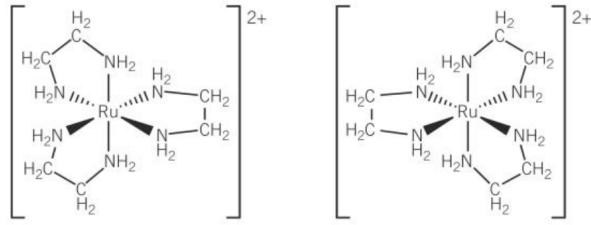
- Octahedral complexes containing two bidentate ligands can show cis-trans isomers. In the cis-isomer the bidentate ligands are adjacent to one another and opposite for the cis-isomer. The isomers of $[\text{Co}(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{Cl}_2]^+$ are shown.



- Unlike monodentate ligands, the cis-isomer of an octahedral complex containing two bidentate ligands can show optical isomerism. The optical isomers of $[\text{Co}(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{Cl}_2]^+$ are shown.



- Optical isomers can also be seen in octahedral complexes containing three bidentate ligands. The mirror images of $[\text{Ru}(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_3]^{2+}$ are displayed.



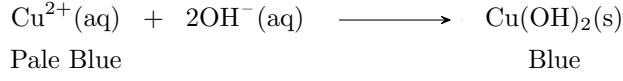
9.4 Reactions of Complex Ions

Two types of reactions take place that involve complex ions:

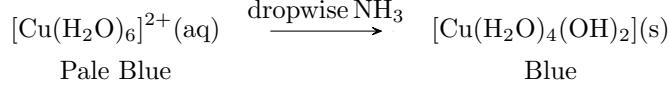
- A **ligand substitution** is a reaction where one ligand in a complex ion is replaced by another.
 - A **precipitation reaction** occurs when two aqueous solution containing ions react together to form a solid called a precipitate.

9.4.1 Reactions of Copper (II) Cu^{2+}

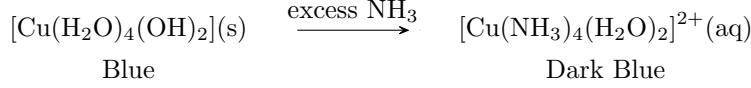
- When aqueous copper (II) reacts with hydroxide ions from sodium hydroxide, copper hydroxide precipitate $\text{Cu}(\text{OH})_2$ forms in a precipitation reaction.



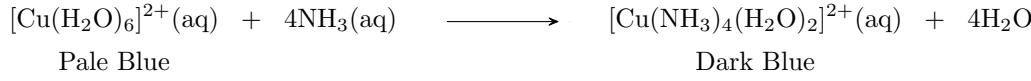
- When ammonia is added *dropwise* to hexaaqua copper (II), the copper hydroxide precipitate $\text{Cu}(\text{OH})_2$ forms.



- The copper hydroxide precipitate $\text{Cu}(\text{OH})_2$ will dissolve in excess ammonia by a ligand substitution reaction forming a complex with four ammonia ligands.



- When excess ammonia is added directly to hexaaqua copper (II), four ammonia ligands replace four water ligands in a ligand substitution reaction.

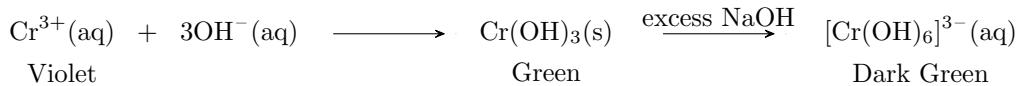


- Hexaaqua copper (II) can also undergo ligand substitution reactions with four chloride ions forming a tetrahedral yellow complex

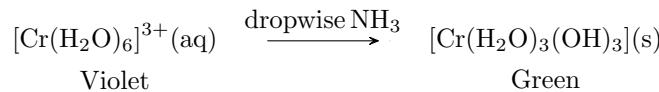


9.4.2 Reactions of Chromium (III) Cr^{3+}

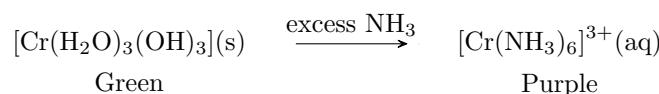
- When chromium (II) reacts with hydroxide ions from sodium hydroxide, a chromium hydroxide precipitate will form $\text{Cr}(\text{OH})_3$ by a precipitation reaction. Unlike other transition elements this precipitate is soluble in excess hydroxide and will form a hydroxide complex.



- When ammonia is added *dropwise* to hexaaqua chromium (III), the chromium hydroxide precipitate $\text{Cr}(\text{OH})_3$ forms.



- Like copper (II) hydroxide, the chromium hydroxide precipitate $\text{Cr}(\text{OH})_3$ will dissolve in excess ammonia by a ligand substitution reaction forming a complex with six ammonia ligands.

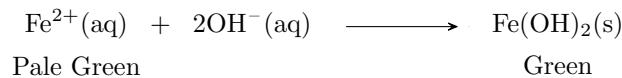


- When excess ammonia is added directly to hexaaqua chromium (III), six ammonia ligands replace the six water ligands in a ligand substitution reaction.

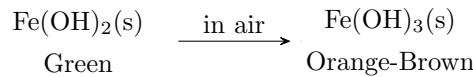


9.4.3 Reactions of Iron (II) Fe^{2+}

- Iron (II) will undergo precipitation reactions with sodium hydroxide to form the green precipitate $\text{Fe}(\text{OH})_2$.

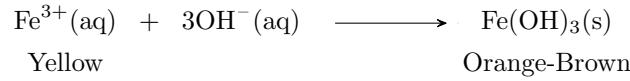


- The precipitate is insoluble in sodium hydroxide but is oxidised by oxygen in air to form iron (II) hydroxide. An orange-brown precipitate will form at the surface.



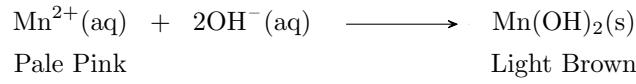
9.4.4 Reactions of Iron (III) Fe^{3+}

- Iron (III) will undergo precipitation reactions with sodium hydroxide to form the orange-brown precipitate $\text{Fe}(\text{OH})_3$.



9.4.5 Reactions of Manganese (II) Mn^{2+}

- Manganate (II) will undergo precipitation reactions with sodium hydroxide to form the light brown precipitate $\text{Mn}(\text{OH})_2$.



9.4.6 Ligand Substitution in Blood

Blood carries oxygen around our body due to the presence of haemoglobin. Haemoglobin contains the transition metal Fe_2^{2+} which can bind to oxygen gas to transport it around the body as well as carbon dioxide. Carbon monoxide can form strong dative bonds with haemoglobin also which are irreversible bonds, if too much CO bonds, then not enough oxygen will get around the body.

Part III

Organic Chemistry

Chapter 10

Theory

10.1 Basic Organic Chemistry

10.1.1 Introduction

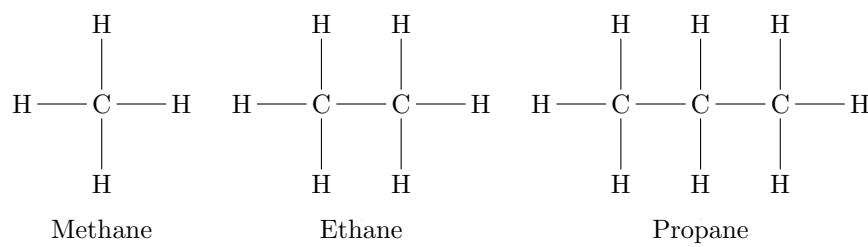
Carbon is group 14 on the periodic table with four electrons in its outer shell allowing it to form four covalent bonds. These bonds can be single, double or triple.

The simplest organic compounds are hydrocarbons. **Hydrocarbons** are compounds containing only carbon and hydrogen.

Hydrocarbons can be saturated or unsaturated.

- **Saturated** hydrocarbons contains only single bonds. An example of this would be methane CH_4 .
- **Unsaturated** hydrocarbons contain multiple carbon-carbon bonds - namely double or triple such as in ethene.

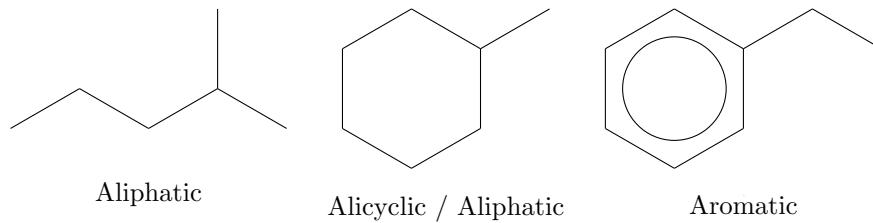
A homologous series is a family of compounds with similar chemical properties whose successive members differ by an additional CH_2 . The simplest example of a homologous series is the alkanes.



A **functional group** is the part of the compound responsible for its chemical properties. These are groups that can be non-carbon atoms, such as oxygen and nitrogen.

Organic compounds can be classified as

- **Aliphatic** - carbon atoms are bonded together in straight, branched or non-aromatic rings.
- **Alicyclic** - carbon atoms are joined together in a ring structure.
- **Aromatic** - Some or all of the carbon atoms are found in a benzene ring.



There are three homologous series of aliphatic hydrocarbons

- **Alkanes** - Containing single carbon-carbon bonds.
- **Alkenes** - Containing at least one double carbon-carbon bonds.
- **Alkynes** - Containing at least one triple carbon-carbon bonds.

10.1.2 Representing formulae

- **Molecular Formula**

The molecular formula shows the number and types of atoms present in the molecule. It does not show the structure of the molecule and multiple molecules can have the same molecular formula. Ethanol has the molecular formula $\text{C}_2\text{H}_6\text{O}$.

- **Empirical Formula**

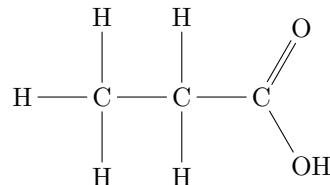
The empirical formula is the simplest whole number ratio of the atoms present in the molecule. for example, all alkenes have the same empirical formula to be CH_2 .

- **General Formula**

The general formula is the simplest algebraic form of a member of the homologous series. It can be used to generate the molecular formula for any member of the homologous series. For example alcohols have general formula $C_nH_{2n+1}OH$.

- **Displayed Formula**

A displayed formula shows the relative positioning of atoms in a molecule and the bonds between them. For example, propanoic acid with molecular formula $C_3H_6O_2$ has the display formula

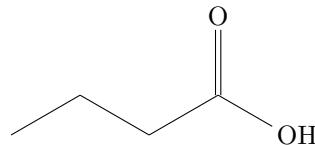


- **Structural formula**

The structural formula uses the smallest amount of detail possible to show the arrangement of atoms in a molecule. For example, propanol is represented as $CH_3CH_2CH_2OH$ and 2,2-dimethylpropane is $CH_3C(CH_3)_2CH_3$.

- **Skeletal formula**

A skeletal formula is a simplified organic formula where all carbons and hydrogens are removed as well as the bonds to any hydrogen atoms. A single line represents a bond and two lines would represent a double bond. For example, propanoic acid is represented in skeletal formula as:



10.1.3 Reaction Mechanisms

An equation tells you about the reactants, products and stoichiometry of a reaction, however *how* the reaction takes place is known as the **reaction mechanism**

A covalent bond is defined as a shared pair of electrons between two atoms. When reactions take place, these bonds must be broken either by **homolytic fission** or **heterolytic fission**

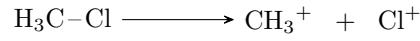
- **Homolytic Fission**

In homolytic fission, each bonded atom takes one of the shared pair of electrons from the covalent bond. Each atom now has a single unpaired electron - the name for such an atom is a **radical**. The homolytic fission of the carbon-carbon bond in ethane is shown.



- **Heterolytic Fission**

When a covalent bond breaks by heterolytic fission, one of the bonded atoms takes both pairs of electrons - this atom becomes a negative ion. The atom that does not receive any electrons becomes a positive ion. The heterolytic fission of the carbon-chlorine bond in chloromethane is shown



In a reaction mechanism, the movement of a pair of electrons is shown by a curly arrow.

- **Types of Reactions**

Numerous reactions occur with organic compounds, they are:

- **Addition** - two reactants join together to make a single product. It is common in reactions with alkenes and carbonyl compounds
- **Substitution** - an atom or group is replaced or substituted by another. Substitutions commonly occur with haloalkanes and reactions with benzene.
- **Elimination** - involves the removal of an atom or group from a larger molecule (usually by an acid catalyst) to form multiple products.
- **Hydrolysis** - the chemical breakdown of a compound by water or an aqueous solution - occurs in esters and polymers formed by condensation polymerisation.

10.1.4 Nomenclature

There are so many organic compounds, chemists have designed a set of rules that are followed in naming them known as the IUPAC standard names.

The *stem* of the name indicates the number of carbon atoms. the *prefix* can be added to indicate the presence of side chains. Finally the *suffix* indicates any functional groups.

- **Naming aliphatic hydrocarbons**

I If the compound is an alkane it is given the suffix -ane. If it is an alkene it is given -ene.

II Identify the longest carbon chain as the parent chain - if there are multiple chains of the same length, the parent chain is that which has the most branching.

III Identify any side chains known as **alkyl groups** as the prefix.

IV Label the position of the alkyl group based on which carbon of the parent chain it is bonded to.

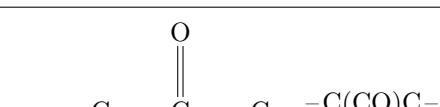
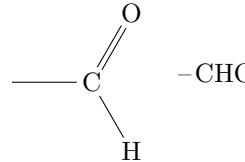
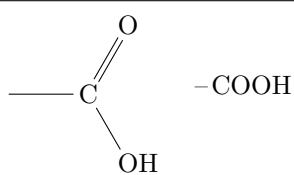
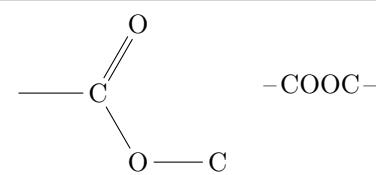
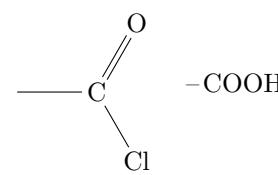
When naming alicyclic compounds, the prefix cyclo is given to indicate the presence of a ring structure.

- **Naming functional groups**

I Identify the longest unbranched carbon chain. the stem is now the name of the corresponding alkane.

II Recognise the presence of any functional groups and select the appropriate suffix.

III Number any alkyl group or any other functional groups present such as NH₂ (amino), or OH (hydroxy).

Compound	Functional Group	Prefix	Suffix
Alkene	C=C		-ene
Alcohol	-OH	hydroxy-	-ol
Haloalkane	-Cl -Br -I	chloro- bromo- iodo-	
Ketone		-C(CO)C-	-one
Aldehyde		-CHO	-al
Carboxylic Acid		-COOH	-oic acid
Ester		-COOC-	-oate
Acyl Chloride		-COOH	-oyl chloride
Amine	-NH ₂	amino-	amine
Nitrile	-CN		-nitrile

• Naming Aromatic Compounds

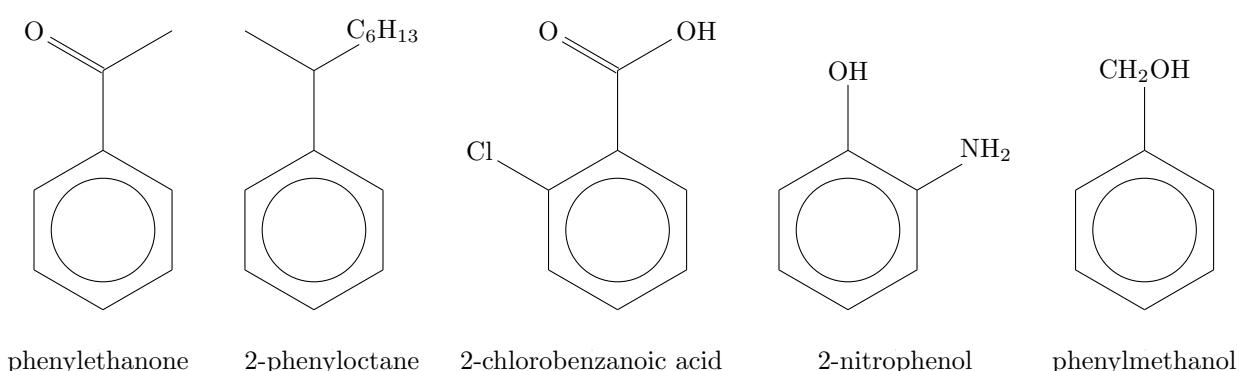
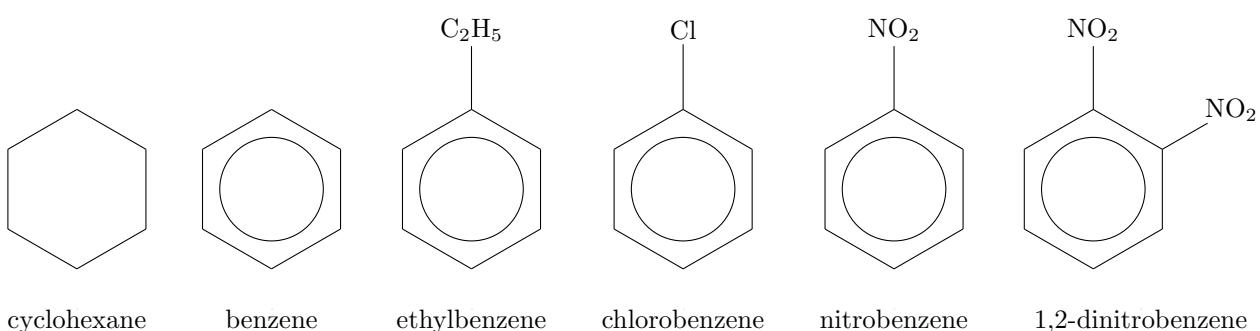
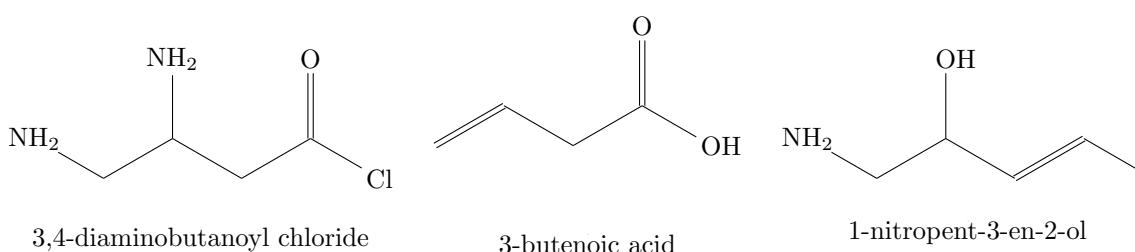
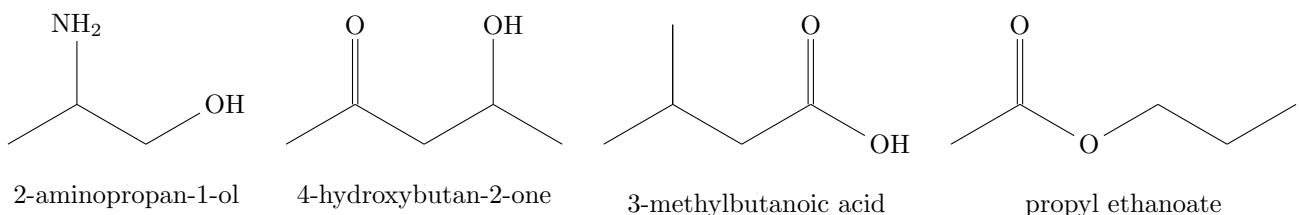
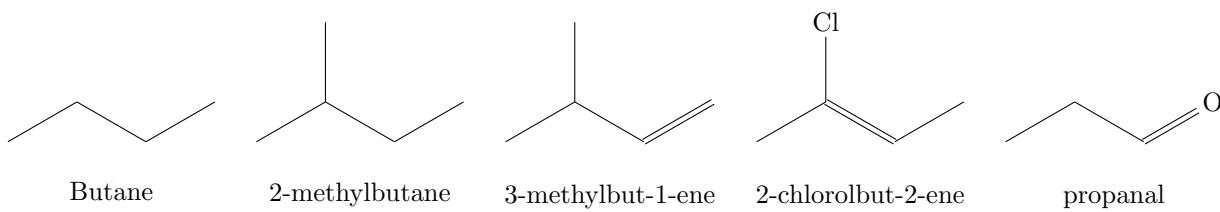
In their names some groups bonded to benzene rings are shown as prefixes to benzene such as short alkyl chains, halogens and nitro groups as the benzene ring is considered to be the parent chain.

When a benzene ring is attached to an alkyl chain with a functional group or alkyl chain with seven or more carbons, benzene is considered the substituent and given the prefix phenyl-.

• Naming Phenols

Phenols are a type of organic chemical with an -OH bonded to an aromatic ring. They are named as a functional group with the suffix -phenol. Some compounds such as $C_5H_5CH_2OH$, contain an -OH but it is considered an alcohol as it is bonded to a side chain.

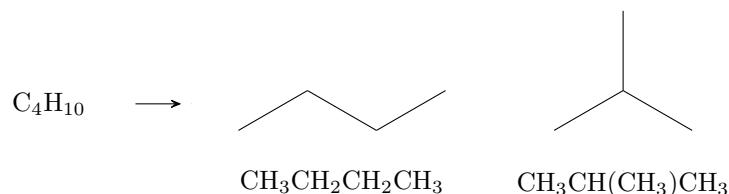
• Examples:



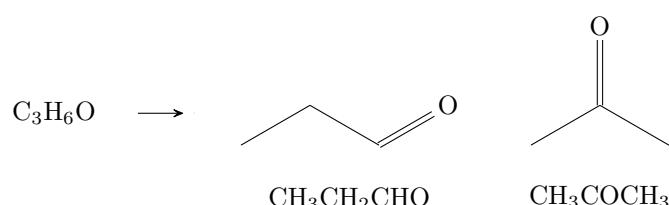
10.2 Isomerism

10.2.1 Structural Isomers

Structural isomers are compounds with the same molecular formula but have a different structural formula. The simplest type in structural isomerism is in alkanes. The compound with molecular formula C₄H₁₀ can produce butane and 2-methylpropane.



Sometimes two molecules containing different functional groups can have the same molecular formula. for example C₃H₆O can be an aldehyde but it can also be a ketone.



10.2.2 E/Z Isomerism

Stereo-isomers have the same molecular formula but a different arrangement in space. There are two types, E/Z isomerism and optical isomers. E/Z isomers only occurs in alkenes.

Due to the position of the π -bond above and below the plane in the double bond, rotation around the bond is restricted and the groups bonded to the carbons are fixed relative to each other.

E/Z Isomerism occurs when:

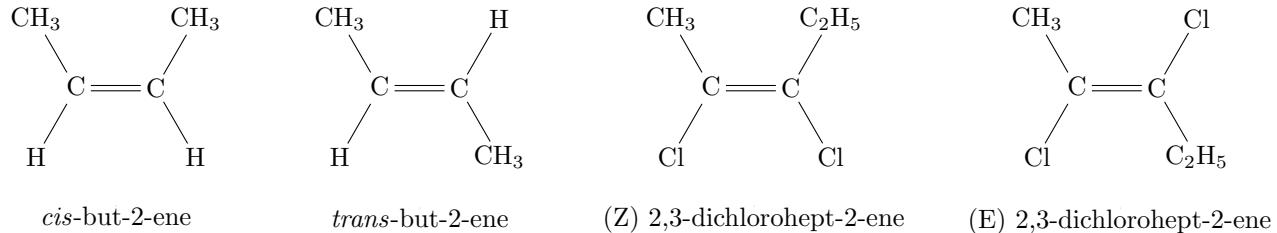
- A carbon-carbon double bond (C=C) is present.
- Different groups are attached to each carbon of the double bond.
- **Cis-Trans Isomers**

Cis-trans isomerism is a special case of E/Z isomerism where both carbon is bonded to a single carbon. When the hydrogen is on the same side of the double bond, it is called the *cis* isomer labelled Z. When the hydrogens are on opposite sides it is the *trans* isomer, labelled E. But-2-ene has cis and trans isomerism.

- **Cahn-Ingold-Prelog Rules**

When the groups attached to the carbon are different, but not hydrogen, the Cahn-Ingold-Prelog rules apply. In this system of atoms bonded to each carbon are given a priority based on their atomic mass.

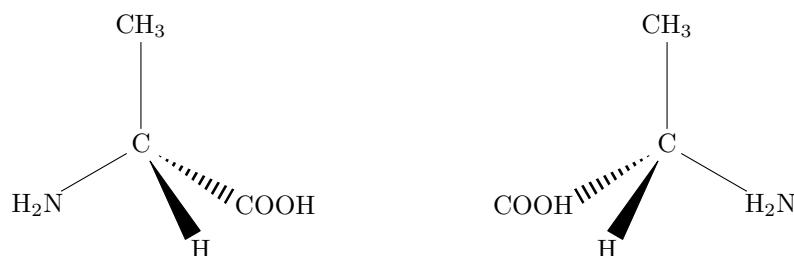
- If the groups of higher priority are on the same side, the compound is the Z isomer.
- If the higher priority groups are on opposite sides of the double bond, the compound is the E isomer.



10.2.3 Optical Isomers

Optical Isomerism is found in molecules that contain a **chiral centre** that is an atom in a molecule that is bonded to four different atoms or groups of atoms. The presence of a chiral centre leads to the existence of two non-super imposable mirror images called **enantiomers** or optical isomers.

An example of optical isomerism occurs in some α -amino acids (with the exception of glycine $\text{H}_2\text{NCH}_2\text{COOH}$). For example, the enantiomers of $\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$ is shown below.



10.3 Functional groups

10.3.1 Alkanes

Alkanes with general formula $\text{C}_n\text{H}_{2n+2}$ are the main components of natural gas and crude oil and are amongst the simplest and most stable organic compounds and are widely used as fuel due to their reactions with oxygen that create heat.

The saturated hydrocarbon only has carbon single covalent bonds - a type of covalent bond called a sigma σ -bond. A σ -bond is the result of the overlap of orbitals from each atom, allowing both atoms to share electrons.

Each carbon is surrounded by 4 electron pairs in σ -bonds creating a 3D tetrahedral shape with bond angles of 109.5° .

- **Variations in boiling points**

Crude oil contains hundreds of different alkanes. Oil refineries separate them by **fractional distillation** in a distillation tower. This is possible as different alkanes have different boiling points - namely the boiling point increases the longer the carbon chain.

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
-164°C	-99°C	-42°C	-1°C	36°C	69°C

The boiling point increases as the intermolecular forces, specifically the London forces become stronger as the chain grows in length

I Alkane chain length increases.

II Molecules have a greater surface and surface contact with neighbouring molecules

III The London forces between molecules is stronger and more energy is required to break them

However for some alkanes, their isomers will have a different boiling point compared to its straight chain isomer. This is because as branching increases in an alkane, the boiling point decreases

I An alkane increase its number of branching

II There are fewer points of contact with neighbouring molecules and branches get in the way and prevent molecules from getting close to one another

III Fewer and weaker London forces so less energy is required to break the bonds

- **Reactivity**

Alkanes are very unreactive. the lack of reactivity is because the C-H and C-C bonds are very strong σ -bonds. The C-C bonds are unpolar as they have the same electronegativity; the C-H bond is also considered non-polar as the electronegativity is so similar.

10.3.2 Alkenes

Alkenes are unsaturated hydrocarbons that contain at least one carbon-carbon double bond

In a double bond, electrons are shared in a covalent σ -bond in the same way a single bond is. the difference lies in a second covalent bond called a π -bond that exists above and below the plane of the double bond. The π -bond arises as each carbon atom donates one electron in overlapping p-orbitals so the electron density is concentrated above and below the plane.

- There are three regions of electron density around each carbon atom
- The three regions repel as far as possible at an angle of 120°
- All the atoms hence lie in the same plane creating a trigonal planar shape
- **Reactivity**

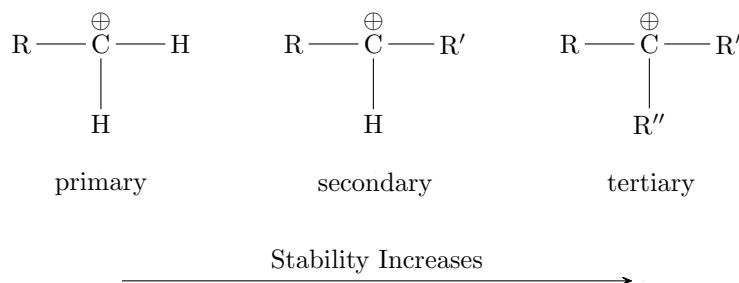
The carbon-carbon double bond is much more reactive than a single σ -bond in alkanes.

- The C-C single bond (σ) is known to have a bond enthalpy of 347 kJmol^{-1} and a C=C bond ($\pi + \sigma$) has a bond enthalpy of 612 kJmol^{-1}
- By subtracting the two amounts, we find that the bond enthalpy of the π -bond is 265 kJmol^{-1}
- The π bond is weaker than the σ bond hence it can be broken more readily
- **Markownikoff's Rule**

In reactions with alkenes, often multiple products will form but sometimes some in larger quantities than others. Markownikoff's rule states:

- The more stable the carbocation, the product with that carbocation as the intermediate will form in greater amounts

the stability of a carbocation depends on how many carbons that carbocation is bonded to. The more R groups attached, the more stable the carbocation.

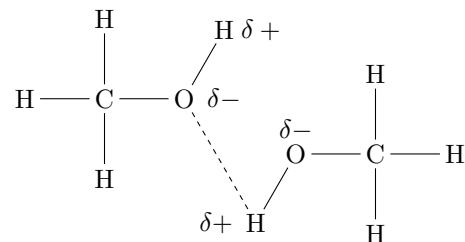


10.3.3 Alcohols

Alcohols contain the -OH functional group or the hydroxyl group that is responsible for its chemical properties. The simplest alcohol methanol, is used as a high performance fuel and feedstock and methanol is used in alcoholic drinks.

Compared to alkanes, alcohols are less volatile and have higher melting points and higher water solubility. Although as carbon chain length increases, the differences become smaller. the reason for the differences can be explained by the following:

- Alcohols, unlike alkanes have a polar O-H bond, due to the difference in electronegativity.
- The intermolecular forces in alcohols also consist of weak London forces like alkanes, but also have hydrogen bonds between the O-H groups.



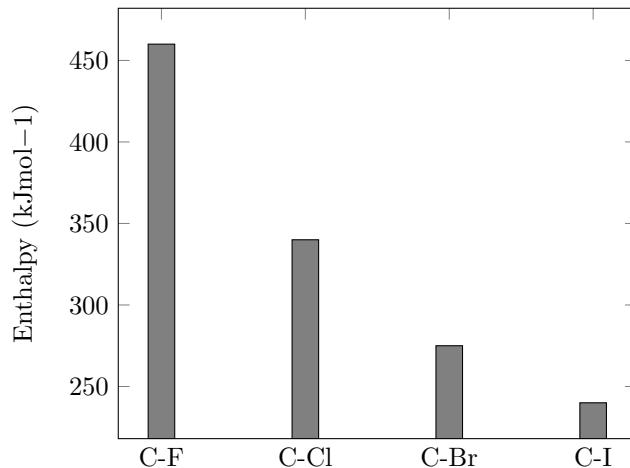
Because of these strong London forces, alcohols have a much higher boiling point to alkanes and it also makes them much more soluble in water as they can form hydrogen bonds with water molecules.

10.3.4 Haloalkanes

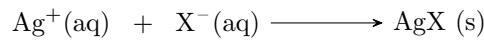
Haloalkanes are organic compounds with a halogen functional group. The halogen in the carbon-halogen bond is much more electronegative meaning the bond is polar. In haloalkanes the carbon has a slightly positive charge allowing it to be attacked by nucleophiles.

- **Variations in bond strength**

In reactions such as hydrolysis, the rate of reaction depends on the strength of the carbon-halogen bond as it breaks by heterolytic fission.



From the graph, we can see that C-F is the strongest bond, and C-I is the weakest, hence iodoalkanes will undergo hydrolysis reactions faster than other haloalkanes, with the rate of reaction increasing up the group. We can measure the rate of reaction by adding silver nitrate to the reaction. The following ionic equation occurs.



A silver halide precipitate forms allowing us to identify the haloalkane. The observations are shown:

- Chloroalkane: A white precipitate will slowly form
- Bromoalkane: A cream precipitate will form slower than iodine but faster than chlorine
- Iodoalkane: A yellow precipitate will form rapidly
- **Organohalogen Compounds**

Organohalogen compounds are molecules with at least one halogen atom joined to carbon chain. They have various uses such as dry cleaning solvents, making polymers, flame retardants and refrigerants.

- **Ozone**

Ozone is a layer at the outer edge of the stratosphere at a height of about 40km. It is responsible for adsorbing various types of UV-radiation from the sun that is biologically damaging. Organohalogen compounds break down ozone allowing UV-B radiation through the atmosphere - this type of radiation can lead to skin cancer and genetic damage.

10.3.5 Benzene

Benzene is a colourless, sweet smelling highly flammable liquid; naturally found in crude oil and cigarettes. It is classified as a carcinogen - it can cause cancer.

- **Kekule Model**

For many years a model of benzene called the kekule model was recognised to understand benzene. This model stated that the benzene structure contained three double carbon-carbon bonds and three single C-C bonds. However it was found that there are three significant problems with this model.

- If benzene contained C=C, it would be able to undergo electrophilic addition reactions like alkenes. Where an alkene will decolourise bromine water, benzene will not. So benzene cannot have a C=C bond.

- Using X-ray diffraction, it was found that the bond length of all bonds in benzene was 0.139nm, which differed from the 0.153nm length of C-C and the 0.134nm length of C=C.
- In a hydrogenation reaction with a single C=C bond, the bond enthalpy is measured as -120 kJmol⁻¹. Since the kekule structure has three C=C, it was expected to have a hydrogenation bond enthalpy of -360 kJmol⁻¹. This greatly differed from the actual value of -208 kJmol⁻¹.

• Delocalised Model

The following describes the delocalised model of benzene as it is understood today:

- Benzene is a planar, cyclic, hexagonal hydrocarbon containing six carbon and 6 hydrogen atoms.
- Each carbon uses three out of its available four electron to bond with a hydrogen and two carbon atoms.
- the fourth electron exists in a p-orbital, perpendicular to the plane of carbon bonds.
- adjacent p-orbitals overlap with neighbouring carbons, creating an electron density above and below the plane.
- this electron density creates a π -bond above and below the plane occupied by six delocalised electrons .

• Reactivity

Alkenes can undergo electrophilic addition reactions to de-colourise bromine whereas benzene cannot without a halogen carrier catalyst. This is because the π -bond in alkenes contains *localised* electrons above and below the plane, unlike benzene which has *delocalised* electrons - the electron density in benzene is lower than in a C=C bond. The π electron density between any two carbons is not high enough to attract non-polar molecules.

• Directing groups

Some groups that are bonded to benzene can **activate** the benzene ring by donating a lone of electrons it reacts more readily with electrophiles. Other groups **deactivates** the benzene ring, so it rates less readily with electrophiles and reduces the rate of reaction. This also affects where the substituent bonds:

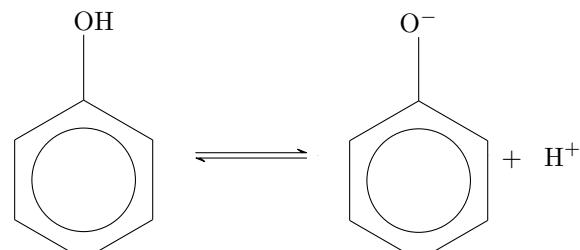
- When the benzene ring is activated, a second substitution directs the substituent to the 2nd or 4th carbon (ortho-para-directing).
- When the benzene ring is deactivated, a second substitution directs the group to the 3rd carbon (meta-directing).

Different groups, activate or deactivate the aromatic ring:

Activates (ortho-para-directing)	Deactivates (meta-directing)
-NH ₂ or NHR	RCOR
-OH	COOR
-OR	SO ₃ H
-R or C ₆ H ₅	-CHO
-F -Cl -Br -I	-COOH
	-CN
	-NO ₂
	NR ₃ ⁺

10.3.6 Phenol

Phenol is less soluble in water than alcohols due to the presence of the non-polar benzene ring. When dissolved in water, phenol has the ability to partially dissociate making it a weak acid unlike alcohols.



- **Reactivity**

Ethanol does not react with any bases whereas phenol can react with strong bases such as sodium hydroxide. Only carboxylic acids are strong enough to react with weak bases such as sodium carbonate.

phenols are more reactive than benzene and can undergo electrophilic substitutions more readily. This is because a lone pair of electrons from the oxygen p-orbital of the -OH is donated into the π system of benzene, increasing the electron density and increasing the ability to attract electrophiles.

10.3.7 Carbonyls

carbonyls are compounds that both contain C=O bonds. An aldehyde has the C=O bond bonded to the end of a carbon chain whereas ketones have the bond in the middle of a carbon chain.

- **Reactivity**

carbonyls react in nucleophilic addition reactions. It might be believed that carbonyls react in a similar way to alkenes as they both contain a π -bond above and below the plane, however there is a significant difference between the bonds that leads to different reactions.

- The C=O bond in carbonyls is a polar bond
- The C=C bond in alkenes is non-polar due to the same electronegativity of carbon.

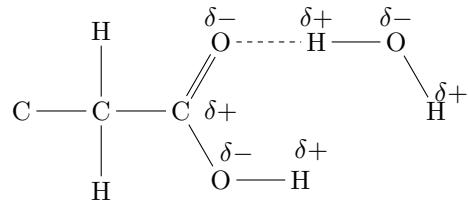
Due to the slightly positive carbon in the C=O bond, nucleophiles with a lone pair of electrons or negative ions can be attracted

10.3.8 Carboxylic acids

A carboxylic acid contains a **carboxyl** group that contains a carbonyl group and a hydroxyl group bonded to the same carbon. They are mainly used as intermediates for the formation of their derivatives.

- **Solubility**

Like alcohols, carboxylic acids form hydrogen bonds with water molecules.

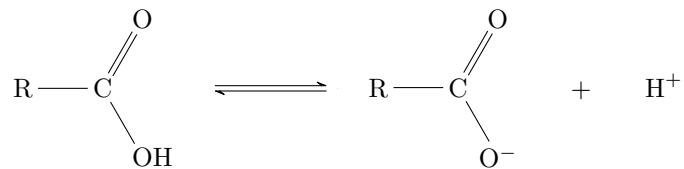


- carboxylic acids with up to four carbons are soluble in water
- As the number increases, solubility decreases as the non-polar carbon chain has greater effect on the overall polarity of the molecule.

Dicarboxylic acids have two polar carbonyl groups to form hydrogen bonds so they are much more soluble and dissolve readily in water. They are solids at room temperature.

- **Carboxylic acids as a weak acid**

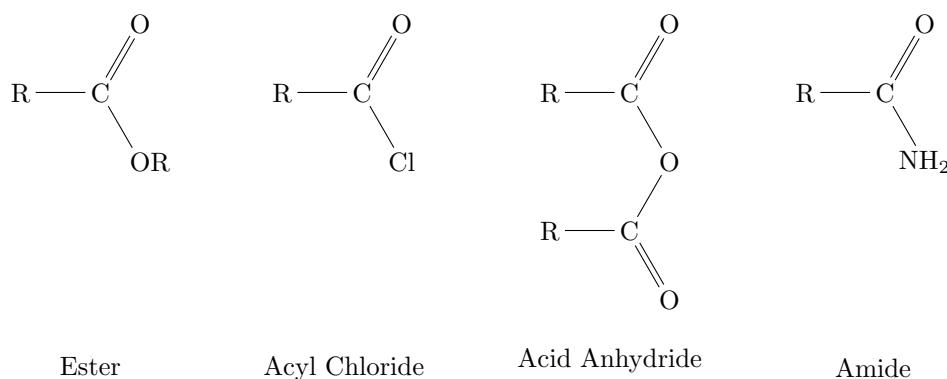
Carboxylic acids are classified as weak acids due to its ability to partially dissociate its hydrogen ion from the hydroxyl group. This forms a carboxylate ion.



Carboxylic acids can react as a weak acid in two ways:

- Redox reactions with metals.
- Neutralisation reactions with bases - alkalis, metal oxides and carbonates.

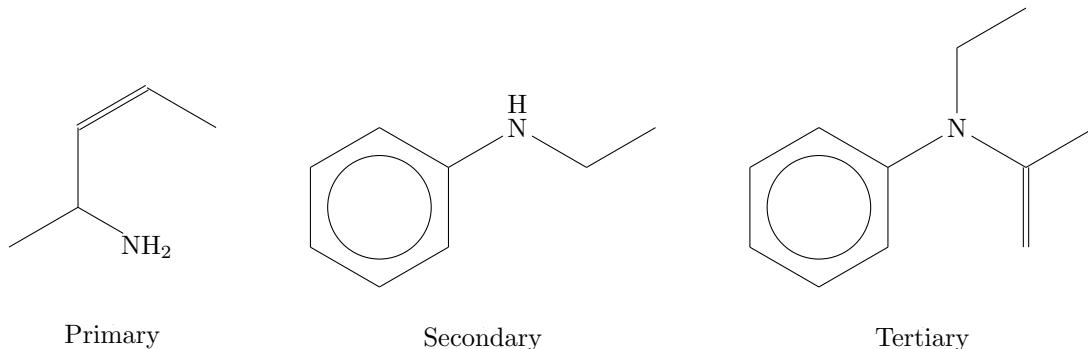
carboxylic acids have four derivatives: esters, acid anhydrides, amides and acyl chlorides.



10.3.9 Amines

Amines are an organic compound derived from ammonia in which at least one of the hydrogens is replaced by a carbon chain. In this case it is an aliphatic amine. An aromatic amine would mean the hydrogen is replaced by a benzene ring.

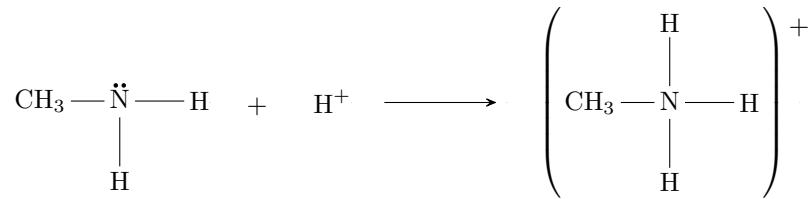
Amine can be classified as primary, secondary an tertiary - determined by the number of carbon chains or benzene rings are bonded directly to the nitrogen



Common uses involve serotonin which acts as a neurotransmitter responsible for the control of appetite, sleep etc. as well as pseudoephedrine which is used in decongestion medications such as nose drops.

- **Reactivity**

Amines act as bases as the lone pair of electrons on the nitrogen atom can accept a proton. When an amine accepts a proton a dative covalent bond is formed between the nitrogen and the proton.



10.3.10 Amino Acids

An amino acid is an organic compound that contains an amine functional group and a carboxylic acid group. The body has 20 amino acids that are used to make proteins. These amino acids are all α amino acids - the amine group is bonded to the second carbon; although β and γ amino acids also exist. Amino Acids behave similarly to amines and carboxylic acids.

10.3.11 Amides

Amides are a derivative of carboxylic acids and are produced by a reaction of acyl chlorides with ammonia. When amino acids bond together they produce an amide group.

10.3.12 Nitriles

Nitriles are organic compounds containing the -CN functional group where the carbon-nitrile bond is a triple bond. They are usually formed from a reaction between a haloalkane and potassium cyanide in a nucleophilic substitution reaction - this reaction increases the carbon chain length.

10.3.13 Polymers

Polymers are extremely large molecules formed of many thousand repeated units, they are formed by molecules called **monomers** in a process called polymerisation - in industry this process is carried out at very high pressures using catalysts. There are multiple types of polymerisation.

- **Addition Polymerisation**

Addition polymerisation uses unsaturated alkene molecules to produce long saturated chains containing no double bonds. Many different polymers can be formed depending on the monomer.

- Addition polymers have a high molecular mass. —item synthetic polymers are usually named after the monomer that reacts to form their giant molecule such as polyethene.

There are many types of polymers. For example, polychloroethene or PVC is a flexible or rigid polymer used to make bottles, pipes, film, and fabrics. Others include polypropene that is used in toys and packing crates as well as polystyrene used for packaging and insulating cups and trays due to its thermal properties.

- **Condensation Polymerisation**

Another type of polymerisation is condensation polymerisation which forms polyamides and polyesters. It is the joining of a small molecule such as water or hydrogen chloride. When polyesters are made, an alcohol must be part of the monomer; for polyamides the same is true for the amine function group.

- **Environmental Concern**

Polymers are widely available and are often chosen over alternative materials like glass and metal. However their lack of reactivity, while makes them useful, means they are non-biodegradable which is true for most alkene-based polymers. This can have serious environmental effects such as killing marine life. There are ways of dealing with this problem.

- **Recycling** polymers reduces environmental impact by decreasing waste to landfill sites and conserves finite fossil fuels. However, a polymer cannot be recycled if it is mixed. Once sorted, the polymers must be washed, dried, melted and cut into flakes.
- **PVC recycling** is hazardous due to the high chlorine content; dumping it in landfill is not sustainable, and burning it produces hydrogen chloride toxic gas. PVC can be ground to manufacture new products and new technology uses solvents to dissolve the polymer which is recovered by precipitation.
- **Waste polymer fuel** - some polymers are difficult to recycle and have a high energy store value waste polymers can be incinerated to produce heat.
- **Feedstock recycling** is a chemical and thermal process used to reclaim monomers, gases or oils from the waste polymers - they can hence be used as raw materials to make new polymers. The major advantage of this method is it works with unsorted and unwashed polymers.

Bioplastics are plastics produced from sustainable and renewable resources such as starch, cellulose, plant oils and proteins. They offer an alternative to oil-based products and hence conserve our oil reserves.

- **Biodegradable** polymers are broken down by micro-organisms into water, carbon dioxide and biological compounds. Such polymers contain additives to alter the structure for this to be possible. Compostable polymers are a type of biodegradable polymer that degrades leaving no visual or toxic residue (e.g. polylactic acid). Biodegradable polymers as the waste can decompose with the bag. Compostable bioplastics from sugar cane are replacing polystyrene.
- **Photodegradable** oil-based polymers can be used when plant-based polymers cannot. They contain bonds that are weakened by the absorption of light. Alternatively, light-absorbing additives can be used.

Chapter 11

Reactions

11.1 Alkanes

11.1.1 Combustion of Alkanes

- Complete Combustion

Despite their low reactivity alcohols will undergo combustion with oxygen to produce carbon dioxide and water. These reactions are very exothermic and hence why they are used as fuel. Below shows the complete combustion methane, ethane and propane.

Methane:



Ethane:



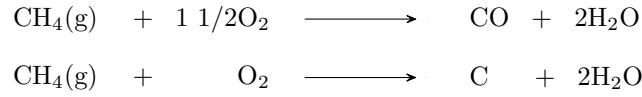
Propane:



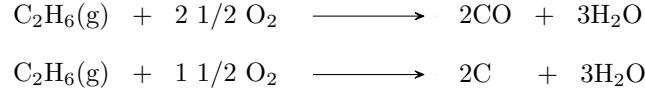
- Incomplete Combustion

In a limited supply of oxygen, there is not enough oxygen for complete combustion. In this case the hydrogen atoms are oxidised to water but combustion of the carbon is incomplete forming carbon monoxide gas CO or carbon soot particles. Below shows the incomplete combustion methane, ethane and propane.

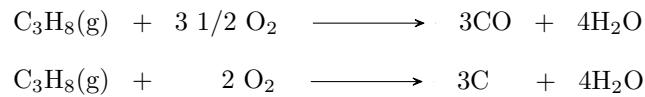
Methane:



Ethane:



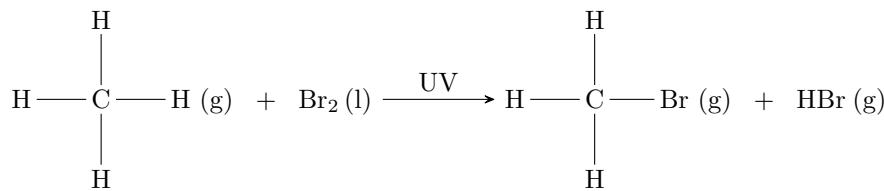
Propane:



We can see by the ratio of alkane to oxygen which reaction requires the highest supply of oxygen and least however all reactions react *some* oxygen.

11.1.2 Halogenation of Alkanes

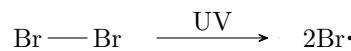
In the presence of high energy ultraviolet (UV) radiation, alkanes will react with halogens to form a haloalkane and a hydrogen halide. The following reaction shows the bromination of methane into bromomethane and hydrogen bromide.



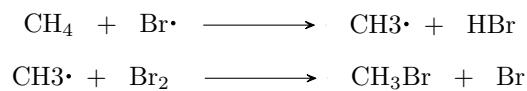
The reaction occurs by **free radical substitution**, the mechanism shown below

The free radical substitution mechanism occurs in three main steps:

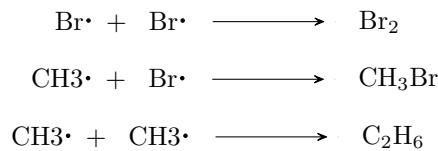
I The first step is known as the **initiation** reaction. A Bromine molecule is broken down by UV in homolytic fission forming two bromine radicals.



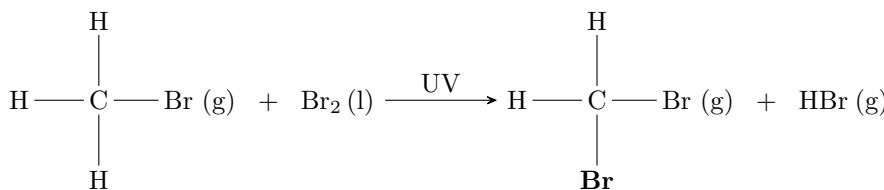
II The second step is **propagation**. In this step the reaction propagates in two propagation steps in a chain reaction.



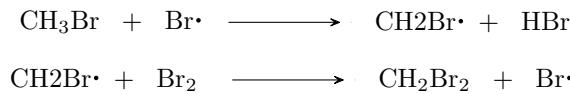
III In the final **termination** step any two combination of radicals will collide to form a molecule with paired electrons)



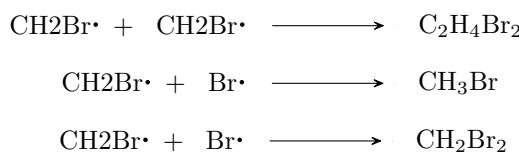
In the propagation step, CH_3Br was formed. A second bromine radical can also collide with a bromomethane molecule to create further substitutions of hydrogens with a bromine. For example:



A multisubstituted product is produced in the propagation step of the mechanism which is highlighted below.



With new radicals produced comes new termination reactions

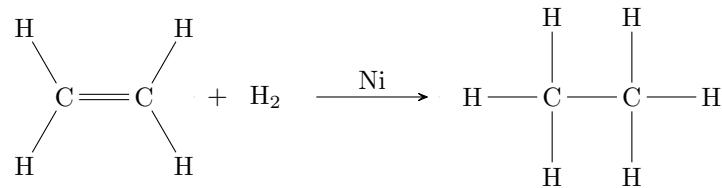


Many more substitutions can occur - specifically the number of the hydrogens in the alkane. Also note that longer carbon chains can form multiple monosubstituted isomers with the radical substitution occurring on different carbons.

11.2 Alkenes

11.2.1 Hydrogenation of Alkenes

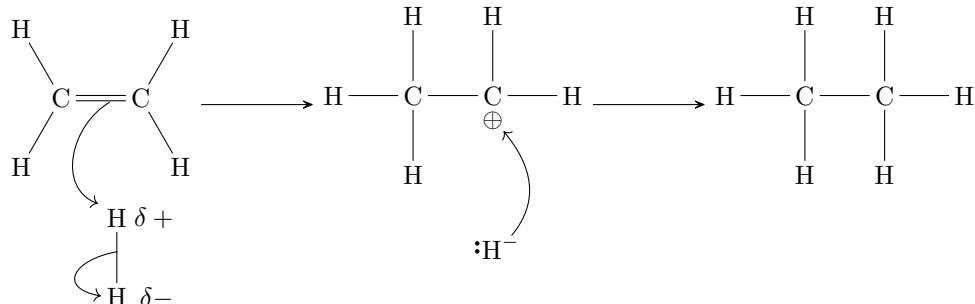
An alkene will undergo halogenation when mixed with hydrogen and passed over a nickel catalyst at 423K. An addition reaction takes place to form an alkane, removing the double carbon bond. For example, ethene will bond with hydrogen forming ethane.



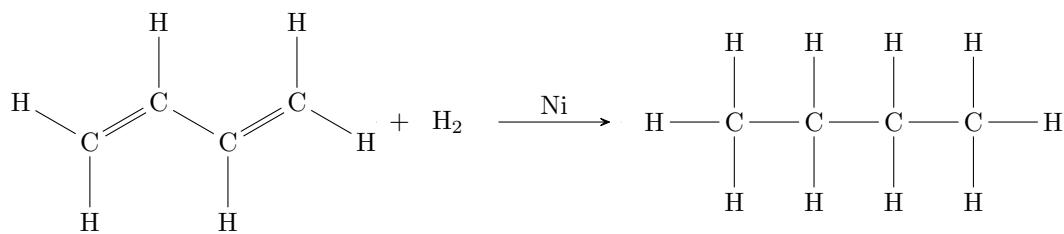
The reaction occurs by **electrophilic addition**. The mechanism is shown below

The addition reaction occurs in multiple main steps.

- I Hydrogen is a non polar molecule however its electrons interact with the π bond inducing polarisation and giving the each hydrogen a $\delta+$ and $\delta-$ charge respectively - this is an example of induced dipole.
- II The π bond is broken and bonds to a bromine atom causing the H-H bond to break by heterolytic fission. An intermediate carbocation is formed with a hydride ion containing a lone pair of electrons.
- III Finally, the hydride ion reacts with the carbocation to form the addition product.

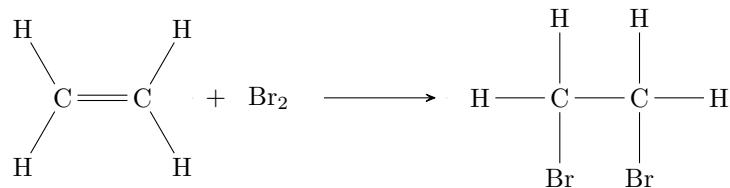


If an organic reaction with multiple C=C double bonds reacts in excess hydrogen, it will undergo multiple addition reactions - two hydrogens will bond for every double bond. Below shows the reaction of buta-1,3-diene into butane



11.2.2 Halogenation of Alkenes

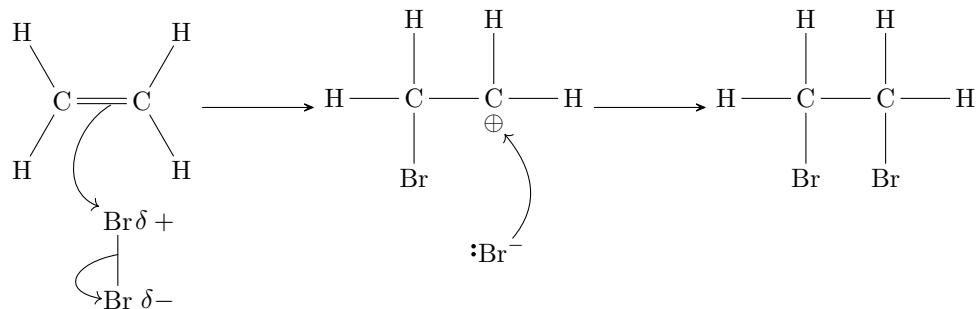
Alkenes undergo rapid addition reaction with the halogens at room temperature forming haloalkanes. The example below shows ethene and bromine water into 1,2-dibromoethane - the reaction will decolourise bromine water (orange to colourless)



The reaction occurs by **electrophilic addition**. The mechanism is shown below

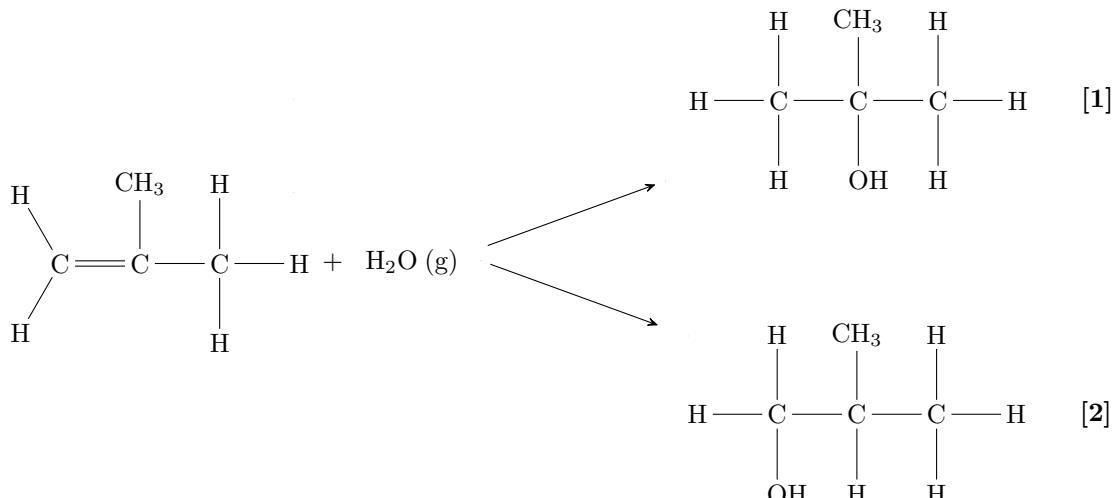
The addition reaction occurs in multiple main steps.

- I Bromine is a non polar molecule however its electrons interact with the π bond inducing polarisation and giving the each bromine a $\delta+$ and $\delta-$ charge respectively - this is an example of induced dipole.
- II The π bond is broken and bonds to a bromine atom causing the Br-Br bond to break by heterolytic fission. An intermediate carbocation is formed with a bromide ion containing a lone pair of electrons.
- III Finally, the bromide ion reacts with the carbocation to form the addition product.



11.2.3 Hydration of Alkenes

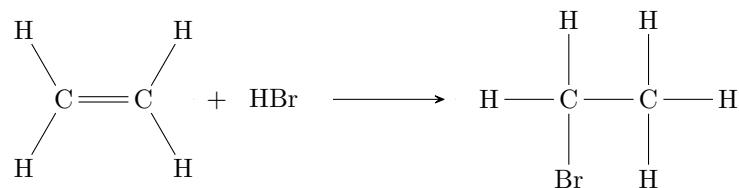
Alcohols are formed when gaseous water (steam) reacts with an alkene in the presence of a phosphoric acid catalyst. This is an addition reaction and often two isomers are formed as the position of the OH group can vary and produce different structural isomers.



Note that product [1] will be the major product and will be produced in greater amounts as it will produce the more stable carbocation compared to product [2] by Markownikoff's rule.

11.2.4 Halogeneration of Alkenes with Hydrogen Halides

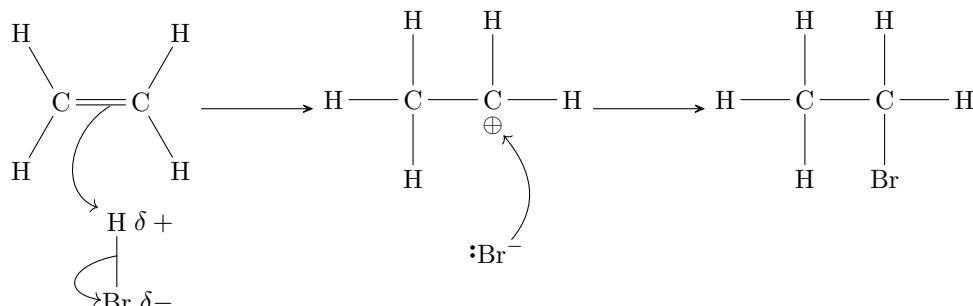
Alkenes undergo addition reaction with polar molecules that contain the halogens such as hydrogen halides to form haloalkanes. The following example shows the reaction of ethene with hydrogen bromide into bromoethane



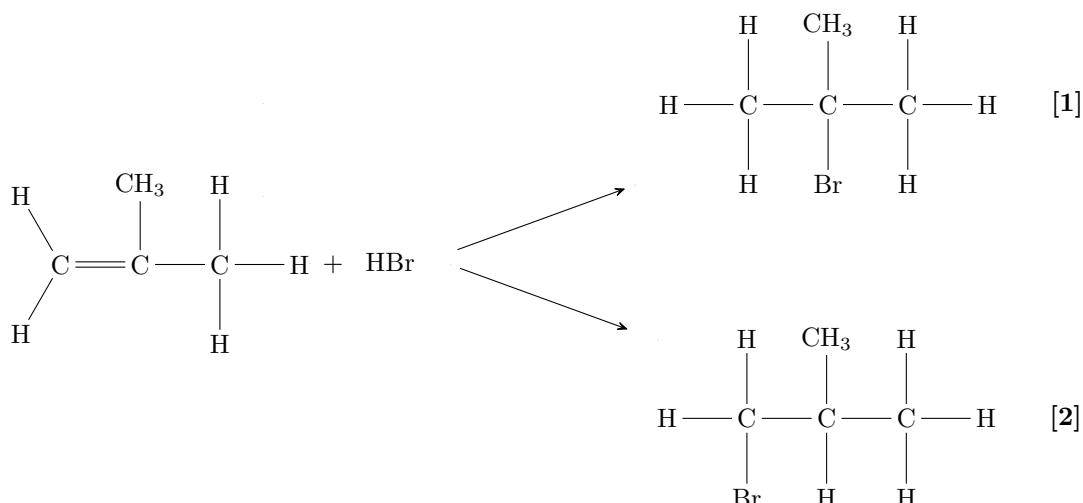
The reaction occurs by **electrophilic addition**. The mechanism is shown below

The addition reaction occurs in multiple main steps.

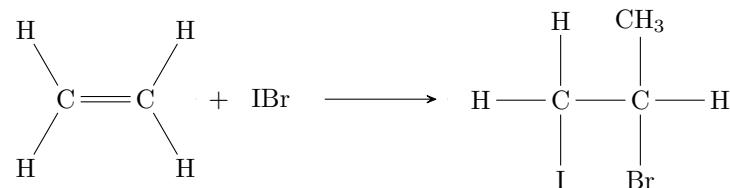
- I Unlike bromine and hydrogen, hydrogen bromide is a polar molecule and has permanent dipole-dipole forces, specifically a $\delta+$ charge on the hydrogen which is attracted to the π bond and a $\delta-$ on the bromine.
- II The π bond is broken and bonds to a bromine atom causing the H-Br bond to break by heterolytic fission. An intermediate carbocation is formed with a bromide ion containing a lone pair of electrons.
- III Finally, the bromide ion reacts with the carbocation to form the addition product.



For longer carbon chains, structural isomers of the addition product can form when alkenes react with asymmetrical molecules such as hydrogen bromide



Note that product [1] will be the major product and will be produced in greater amounts as it will produce the more stable carbocation compared to product [2] by Markownikoff's rule. Alkenes can also react with other polar molecules such as BrI .

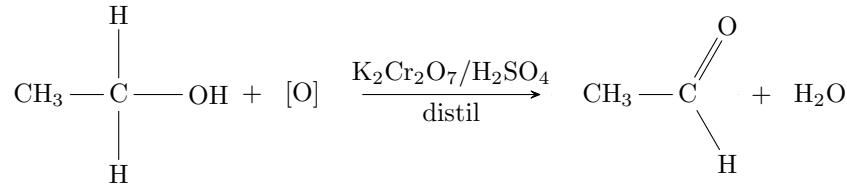


This will be the major product as bromine is more electronegative and will bond with the more stable carbocation.

11.3 Alcohols

11.3.1 Alcohols to form Aldehydes

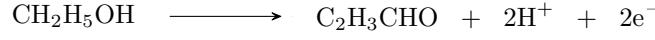
Primary and secondary alcohols can undergo **oxidation** reactions usually by potassium dichromate $K_2Cr_2O_7$ acidified in dilute sulfuric acid H_2SO_4 . When primary alcohols are oxidised by **distillation**, an aldehyde is produced. Below shows the oxidation of ethanol into ethanal



As the alcohol is oxidised, the dichromate(VII) ions are reduced to chromium (III) ions which has an associated colour change of orange to green. Below shows the redox system

The oxidation of the alcohol is accompanied by the reduction of the chromium present in the dichromate ions. The half equations in an acidic environment are shown below:

Oxidation of Alcohol:



Reduction of Dichromate Ion:

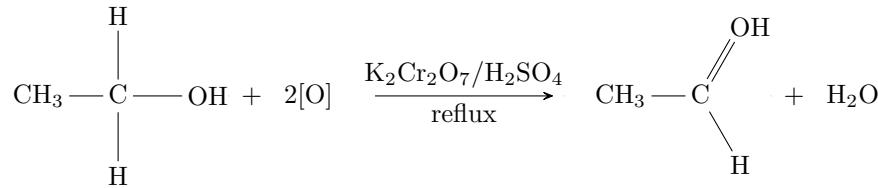


By multiplying the oxidation equation by 3 and adding both equations we reach the overall redox equation:



11.3.2 Alcohols to form Carboxylic Acids

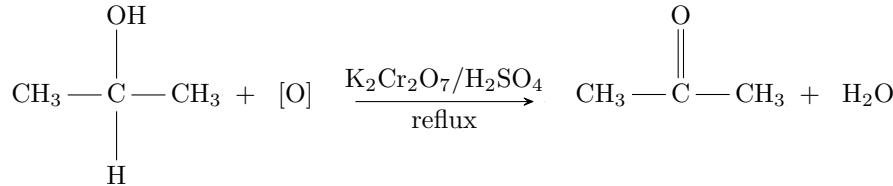
Primary Alcohols can also be **oxidised** to carboxylic acids if heated under **reflux** instead of distillation for an aldehyde. Below shows the reaction of ethanol into ethanoic acid with potassium dichromate and dilute sulphuric acid.



This reaction involves the same colour change from orange to green and has a similar associated redox system for the reduction of the dichromate ions.

11.3.3 Alcohols to form Ketones

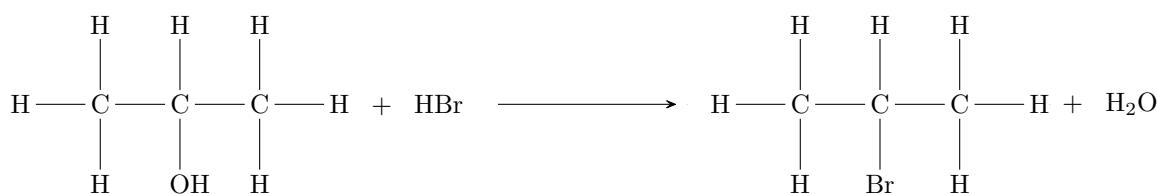
Secondary alcohols can also be **oxidised** to ketones if heated under **reflux**. Below shows the reaction of propan-2-ol into propanone with potassium dichromate and dilute sulphuric acid.



This reaction involves the same colour change from orange to green and has a similar associated redox system for the reduction of the dichromate ions.

11.3.4 Alcohols to form Haloalkanes

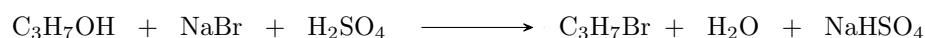
Alcohols react with hydrogen halides to form haloalkanes by a **substitution** reaction - the halogen replaces the OH functional group. The reaction of propanol with hydrogen bromide is shown below:



When preparing a haloalkane, the alcohol is heated under reflux with sulfuric acid and a sodium halide salt which forms the hydrogen halide

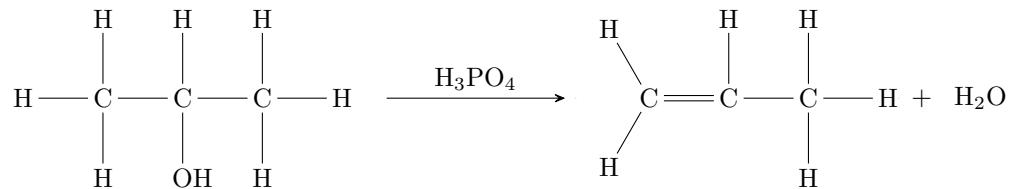


This means the overall equation for the reaction of propan-2-ol with NaBr and H₂SO₄ is:



11.3.5 Dehydration of the Alcohols

In a similar way alkenes can undergo hydration reactions with steam and phosphoric acid to make alcohols, alcohols can undergo dehydration reactions with concentrated phosphoric acid to form an alkene. Below shows the dehydration of propanol to make the propene



11.3.6 Combustion of Alcohols

Like alkanes, alcohols also undergo combustion reactions. In a plentiful supply of oxygen alcohols burn to produce carbon dioxide and water as well as in oxygen deficient conditions producing carbon monoxide or carbon particulates. Below shows the combustion of ethanol.

Complete:



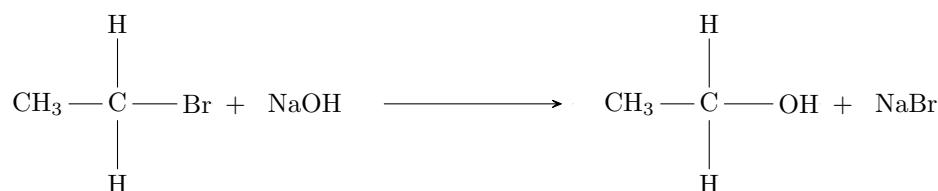
Incomplete:



11.4 Haloalkanes

11.4.1 Hydrolysis of Haloalkanes

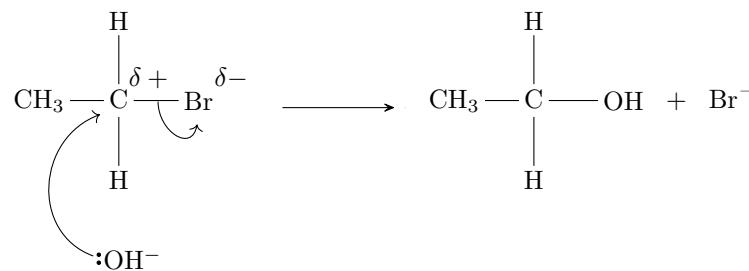
Haloalkanes undergo **hydrolysis** reactions to form an alcohol. Hydrolysis is a reaction involving water or an aqueous solution of hydroxide ion. Below shows the reaction of bromoethane with aqueous sodium hydroxide to form ethanol and sodium bromide



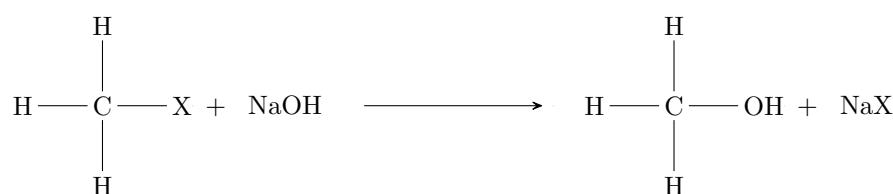
The reaction is very slow at room temperature so it is heated under reflux to obtain a high yield. The reaction occurs by a **nucleophilic substitution**, the mechanism is shown below

The nucleophilic substitution occurs in multiple main steps.

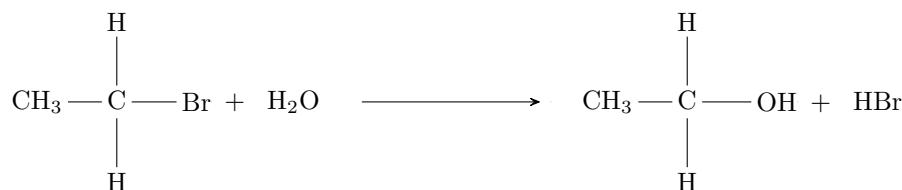
- I The nucleophile, OH^- approaches the carbon atom attached to the halogen by the opposite side of the halogen to minimise repulsion between the $\delta-$ OH^- and halogen.
- II The lone pair of electrons is attracted to the $\delta+$ carbon. A new bond forms between the carbon and hydroxide ion.
- III The carbon-halogen bond breaks by heterolytic fission forming the final substituted product



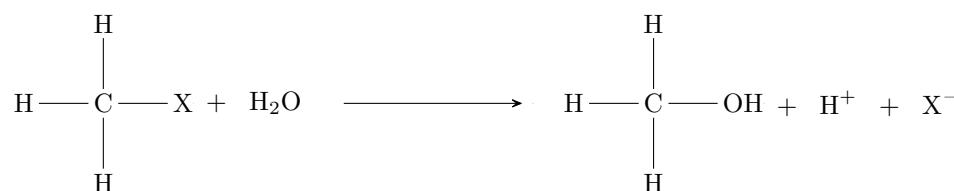
The general form for this reaction can be written as the following, where X is a halogen (usually chlorine, bromine or iodine).



Haloalkanes can also undergo hydrolysis with water forming a halogen halide. This is the reaction used to measure the rate of reaction for the haloalkanes. Below shows the hydrolysis of bromoethane into ethanol.



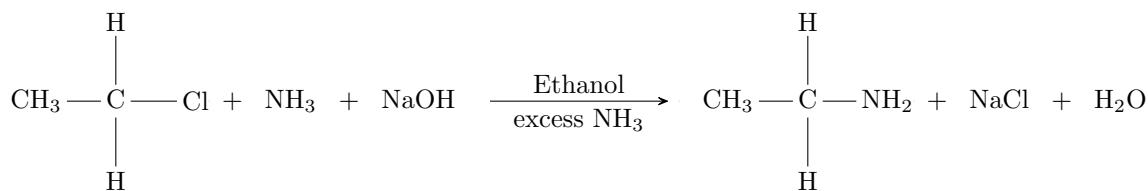
The hydrolysis with water is usually done in a water bath at 60°C to have a sufficiently high rate of reaction. The general form of this reaction is shown below.



11.4.2 Haloalkanes to form Aliphatic Amines

- **Formation of Primary Amines**

Haloalkanes can form amines by reactions with ammonia and an aqueous alkali. Ammonia has a lone pair of electrons on the nitrogen allowing it to act as a nucleophile in substitution reactions. the reaction below shows the formation of ethylamine from chloroethane with ammonia and aqueous sodium hydroxide as our alkali.



The conditions required for this reaction play an important role in the formation of the amine.

- I *Ethanol* is used as a solvent - it prevents substitutions from the water to form alcohols.
- II *Excess ammonia* is used to prevent further substitutions of the amine group to form secondary and tertiary amines.

The formation of primary amines from haloalkanes occurs in two steps:

- I Ammonia reacts with chloroethane by substitution forming an ammonium salt (namely ethylammonium chloride):

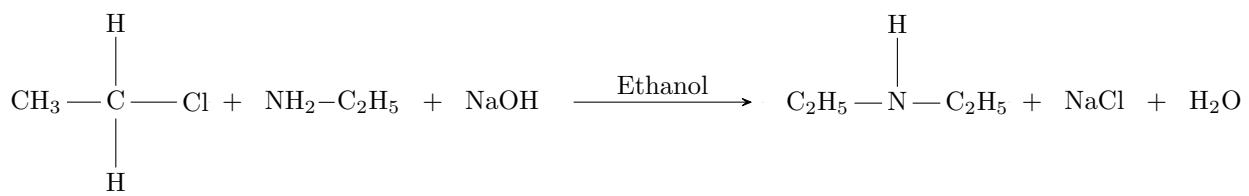


- II The aqueous alkali (usually sodium hydroxide) is added to the salt to make a primary amine



- **Formation of Secondary/Tertiary Amines**

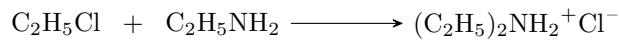
Because primary amines still have a lone pair of electrons on the nitrogen, they are prone to react further with the haloalkane to produce secondary and tertiary amines. This makes the reaction very unsuitable for producing pure primary amines. The reaction between chloroethane and ethylamine is shown below.



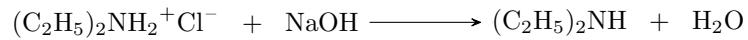
To prevent further substitutions into tertiary amines, we must add excess amine. Ethanol has the same purpose as for primary amines.

The formation of secondary amines from haloalkanes also occurs in two similar steps:

- I Ethylamine reacts with chloroethane by substitution forming an ammonium salt (namely diethylammonium chloride):



- II The aqueous alkali (usually sodium hydroxide) is added to the salt to make the secondary amine



An identical process occurs for secondary into tertiary amines.

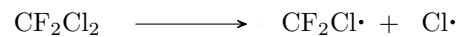
11.4.3 Organohalogen Compounds with Ozone

In the stratosphere UV radiation from the sun is constantly breaking down oxygen O_2 into oxygen radicals. A steady state is then set up involving oxygen gas and the oxygen radicals producing and breaking down ozone - the reaction is in equilibrium.

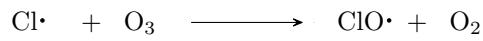


This was a very delicate equilibrium that humans upset as a result of chlorofluorocarbons (CFCs). Due to the mass production of CFCs in the early 20th century, CFCs caused **ozone depletion**. They remained very stable as the strength of the carbon-halogen bond means they have a long residence.

However after many years in the stratosphere, UV provides enough energy to break the C-Cl bond as it has the lowest bond enthalpy producing **free radicals** - the process is called photodissociation. The photodissociation of CF_2Cl_2 is shown below.



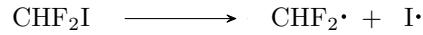
The mechanism for the depletion of ozone by a chlorine radical $Cl\cdot$ occurs by a two-step process.



By adding both steps, we arrive at the overall equation for ozone depletion to be



For the photodissociation of any organohalogen compound, the halogen of the lowest carbon bond enthalpy will form the radical. For example, in CHF_2I the iodine will form the radical



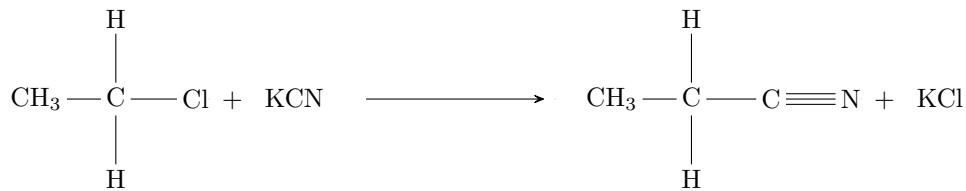
Despite CFCs playing a major role in the breakdown of ozone in the atmosphere, it is not the only cause of ozone depletion. Other radicals also catalyse the breakdown of ozone. Nitrogen oxide radicals are naturally formed from nitrogen and oxygen in the atmosphere. The mechanism is shown below

The mechanism for the depletion of ozone by a nitrogen oxide radical $NO\cdot$ occurs by a two-step process very similar to chlorine.



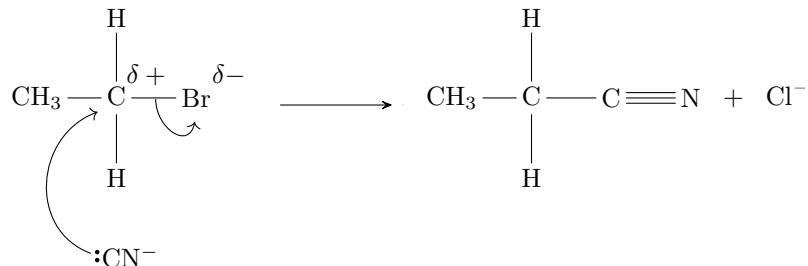
11.4.4 Haloalkanes to form Nitriles

Nitriles can be formed in a reaction of haloalkanes with potassium cyanide. The reaction is used to increase the carbon chain length. The reaction below shows the formation of propanenitrile.



The nucleophilic substitution occurs in multiple main steps.

- I The nucleophile, CN^- approaches the carbon atom attached to the halogen by the opposite side of the halogen to minimise repulsion between the $\delta-$ CN^- and halogen.
- II The lone pair of electrons is attracted to the $\delta+$ carbon. A new bond forms between the carbon and nitrile ion.
- III The carbon-halogen bond breaks by heterolytic fission forming the final substituted product

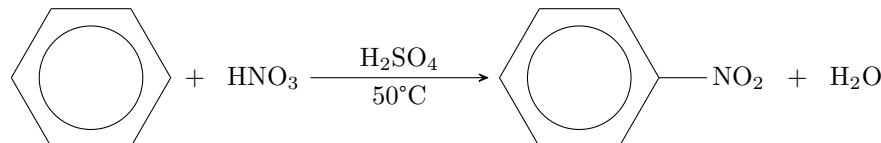


Note how in the haloalkane, chloroethane, there are only two carbons yet in the nitrile product, propanenitrile, there are three carbons - the carbon chain length has increased.

11.5 Benzene

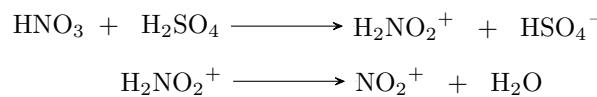
11.5.1 Nitration of Benzene

Benzene will react slowly with nitric acid to form nitrobenzene catalysed with sulphuric acid at 50°C by **electrophilic substitution**. A water bath can be used to maintain this temperature and conditions

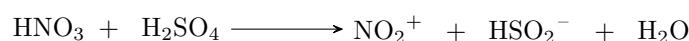


The nitration of benzene is an electrophilic substitution reaction however, nitric acid is not an electrophile, hence it must be produced in the mechanism. The reaction mechanism takes place in 3 steps shown below:

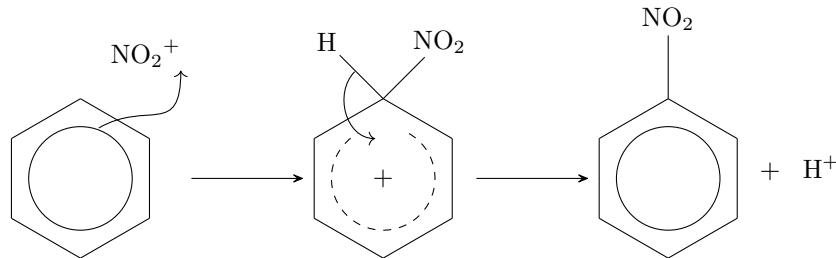
In **Step 1** of the nitration of benzene, the electrophile NO_2^+ (nitronium ion) must form from nitric acid and the sulphuric acid catalyst.



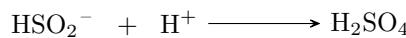
Overall:



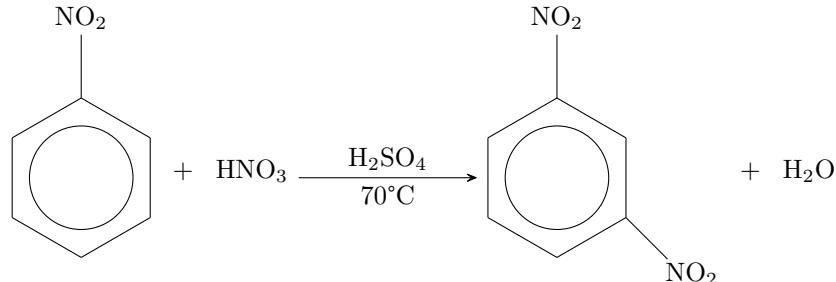
In **Step 2** the electrophile NO_2^+ bonds with the negative π -bond in benzene. The intermediate is unstable as the benzene ring has an overall positive charge; to overcome this the C–H bond is broken



Finally, **Step 3** reforms the acid catalyst H_2SO_4 using the HSO_4^- ion produced in step 1 and the hydrogen ion produced in the second step.



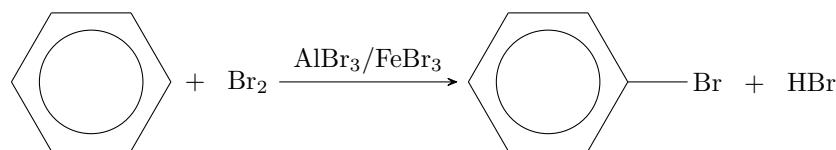
As mentioned, the substitution reaction occurs at around 50°C, however at higher temperatures, further substitutions occur such as the production of 1,3-dinitrobenzene at 70°C. The second nitro group bonds to the third carbon as NO_2 deactivates the benzene ring and hence is a meta (3) directing group.



the biggest use of nitrobenzene is the synthesis of paracetamol as well as making TNT (trinitrotoluene) from 2-nitromethylbenzene.

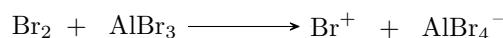
11.5.2 Halogenation of Benzene

At standard room temperature and pressure, benzene will react with the halogens such as bromine by **electrophilic substitution** in the presence of a halogen carrier catalyst e.g. FeBr_3 or AlBr_3 - or any metal bromide with a 3+ oxidation state - to form bromobenzene

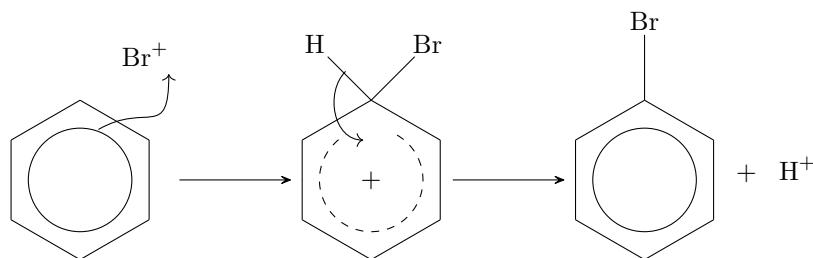


Benzene reacts with the halogens through an electrophilic substitution reaction. A polar bromine molecule cannot react with benzene as it is too stable, hence the electrophile Br^+ must be produced using the halogen carrier in the mechanism below

In **Step 1** of the bromination of benzene, the electrophile Br^+ (bromonium ion) must form from bromine and the halogen catalyst - we will use AlCl_3 in this example



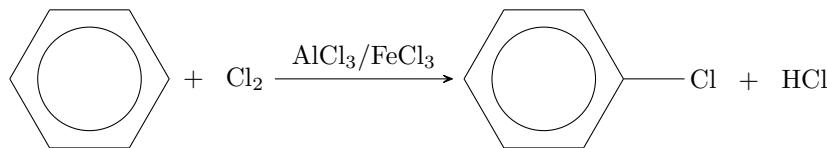
In **Step 2** the electrophile Br^+ bonds with the negative π -bond in benzene. The intermediate is unstable as the benzene ring has an overall positive charge; to overcome this the C–H bond is broken



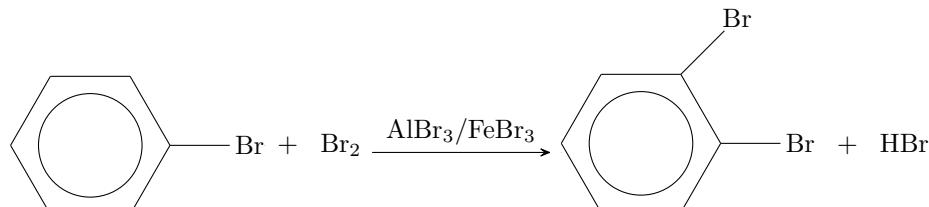
Finally, **Step 3** reforms the halogen carrier catalyst AlBr_3 using the AlBr_4^- ion produced in step 1 and the hydrogen ion produced in the second step as well as producing hydrogen bromide.



The chlorination of benzene is identical to the reaction and mechanism above with the use of Cl_2 and a chloride halogen carrier - AlCl_3 or FeCl_3

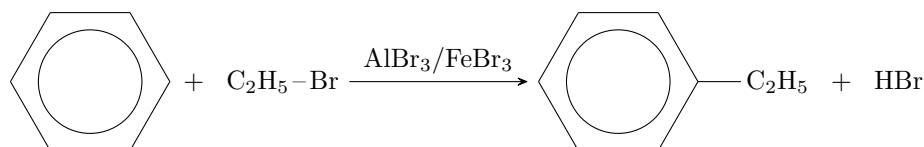


At higher temperatures and pressure, further substitutions of the Br^+ electrophiles occur. Since the halogens are ortho and para (2 and 4) directing groups, new bromine atoms will bond to adjacent or opposite carbon atoms



11.5.3 Alkylation of Benzene

The alkylation of Benzene is the substitution of a hydrogen for an alkyl group such as $\text{C}_2\text{H}_5\text{Br}$ by **electrophilic substitution**. The reaction occurs between benzene and a haloalkane namely $\text{C}_2\text{H}_5\text{Br}$ and a halogen carrier catalyst. It is sometimes referred to the Friedel-Crafts reaction and is shown below.

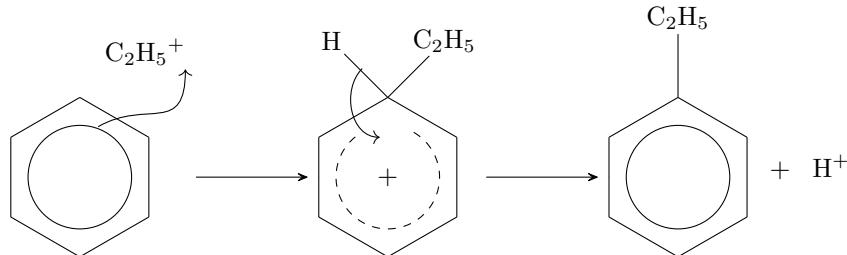


The reaction increases the number of C–C bonds in benzene. The halogen carrier is used to produce the electrophile as the haloalkane is unreactive on its own. Below is the reaction mechanism:

In **Step 1** of the alkylation of benzene, the electrophile C_2H_5^+ must form from the haloalkane and the halogen catalyst - we will use AlCl_3 in this example



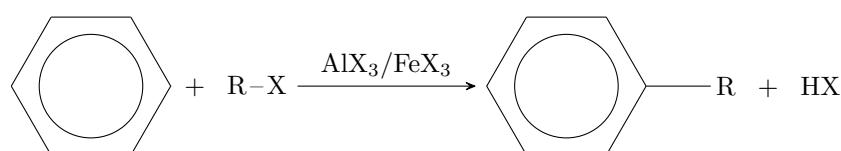
In **Step 2** the electrophile C_2H_5^+ bonds with the negative π -bond in benzene. The intermediate is unstable as the benzene ring has an overall positive charge; to overcome this the C–H bond is broken



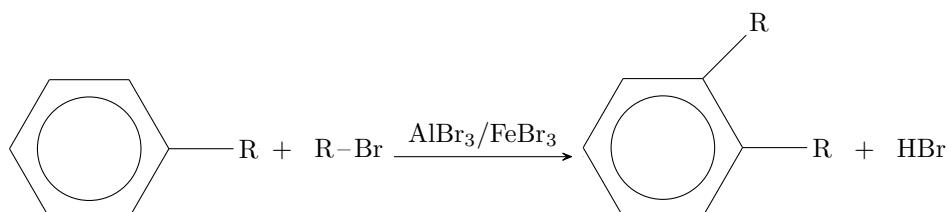
Finally, **Step 3** reforms the halogen carrier catalyst AlBr_3 using the AlBr_4^- ion produced in step 1 and the hydrogen ion produced in the second step as well as producing hydrogen bromide.



We can generalise this reaction to include an alkyl group of any length R or any halogen X such that the reaction is between benzene and a haloalkane R–X with a halogen carrier $\text{AlX}_3/\text{FeX}_3$

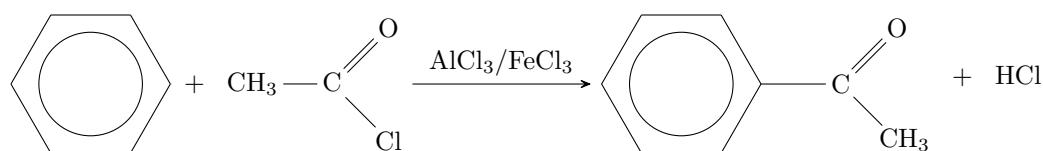


At higher temperatures and pressure, further substitutions of the alkyl R^+ electrophiles occur. Similar to the halogens, all carbon chains R are ortho and para (2 and 4) directing groups, new carbon chains will bond to adjacent or opposite carbon atoms

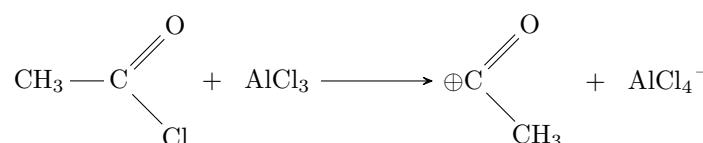


11.5.4 Acylation of Benzene

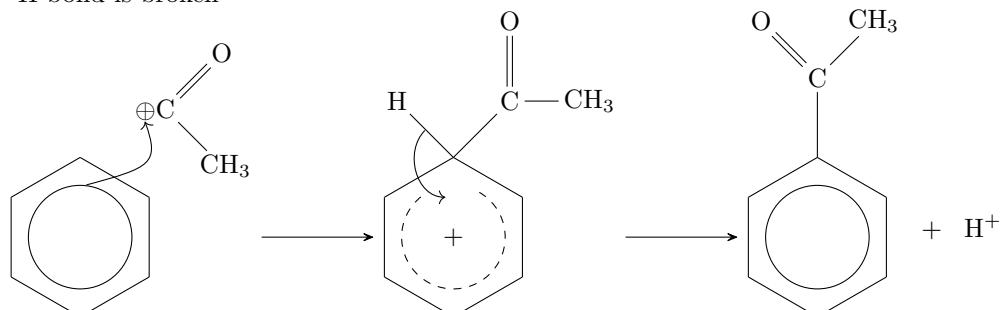
The acylation of benzene is the reaction between benzene and an acyl chloride such as ethanoyl chloride C_2HCOCl by **electrophilic substitution** in the presence of a halogen carrier to form an aromatic ketone, namely phenylethanone.



In **Step 1** of the acylation of benzene, the electrophile CH_3CO^+ must form from the acyl chloride and the halogen catalyst - we will use AlCl_3 in this example



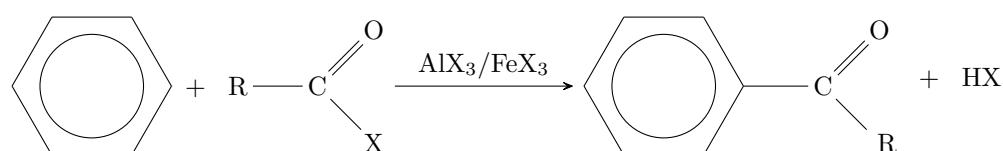
In **Step 2** the electrophile CH_3CO^+ bonds with the negative π -bond in benzene. The intermediate is unstable as the benzene ring has an overall positive charge; to overcome this the C–H bond is broken



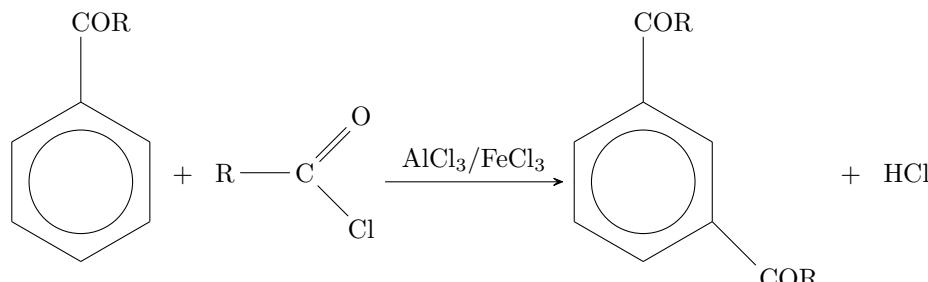
Finally, **Step 3** reforms the halogen carrier catalyst AlCl_3 using the AlCl_4^- ion produced in step 1 and the hydrogen ion produced in the second step as well as producing hydrogen bromide.



We can generalise this reaction to include a ketone group of any length R or any halogen X such that the reaction is between benzene and the acyl chloride with a halogen carrier $\text{AlX}_3/\text{FeX}_3$.

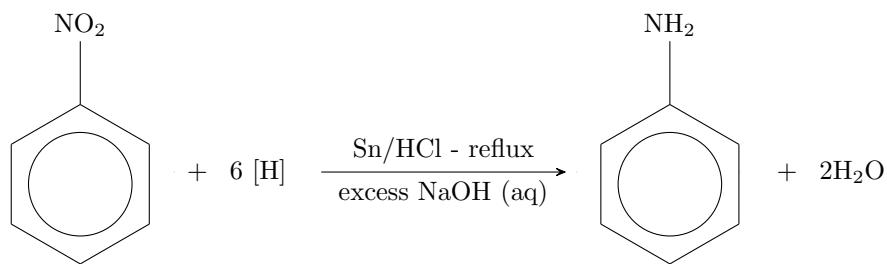


If temperatures are sufficiently high, further substitutions of the ketone will occur. Since ketones are meta (3) directing group, further substitutions will occur on the third carbon.

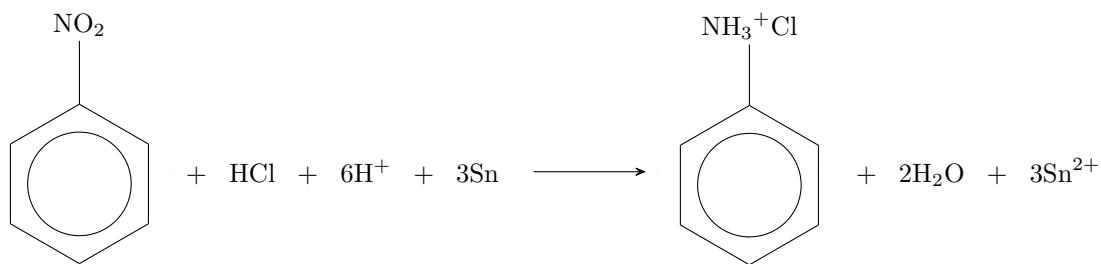


11.5.5 Nitrobenzene to form Aromatic Amines

Nitrobenzene, $C_6H_5NO_2$, can be reduced by heating under reflux with hydrochloric acid and tin (Sn) to produce the ammonium salt phenylammonium chloride. It is then reacted with excess sodium hydroxide to produce the aromatic amine, phenylamine. Tin and hydrochloric acid are the reducing agents.

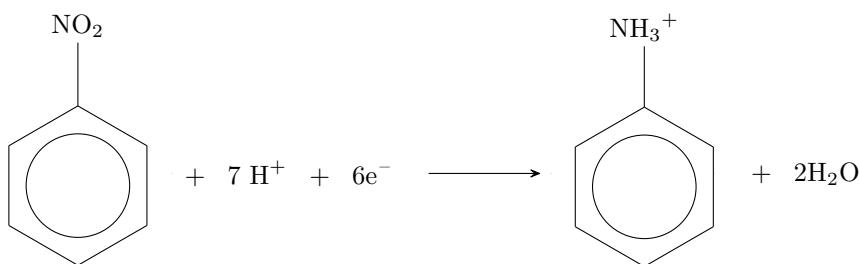


In the **first step**, nitrobenzene is reduced by HCl (or under acidic conditions) and tin to make the phenylammonium ion.

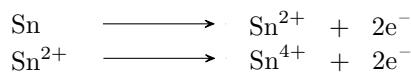


The redox system is shown below. The electrons that the nitrobenzene gains comes from the oxidation of tin which forms tin(II) and tin (IV).

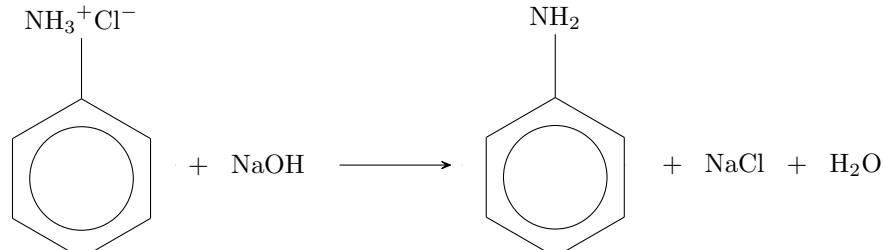
Reduction of Nitrobenzene:



Oxidation of Tin:



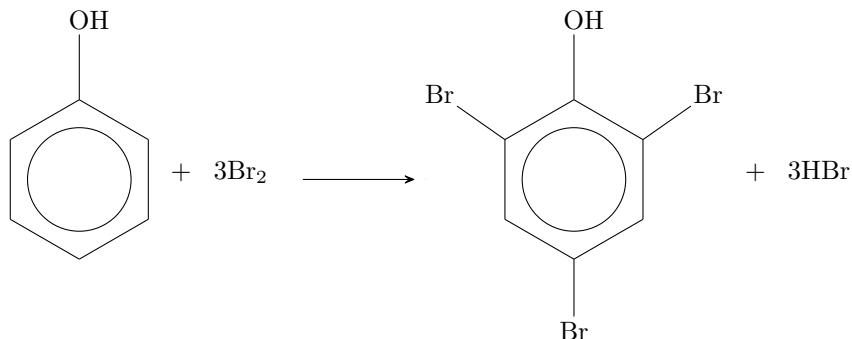
In the **second step** The phenylammonium ion loses a hydrogen to a hydroxide ion to form water. The hydroxide is supplied by sodium hydroxide - the sodium bonds with the chloride ion making sodium chloride.



11.6 Phenol

11.6.1 Bromination of Phenol

Phenol reacts with aqueous bromine (bromine water) by **electrophilic substitution** at room temperature to produce 2,4,6-tribromophenol *without* a halogen carrier catalyst as shown. The reaction will decolourise the orange bromine water to become a colourless solution.

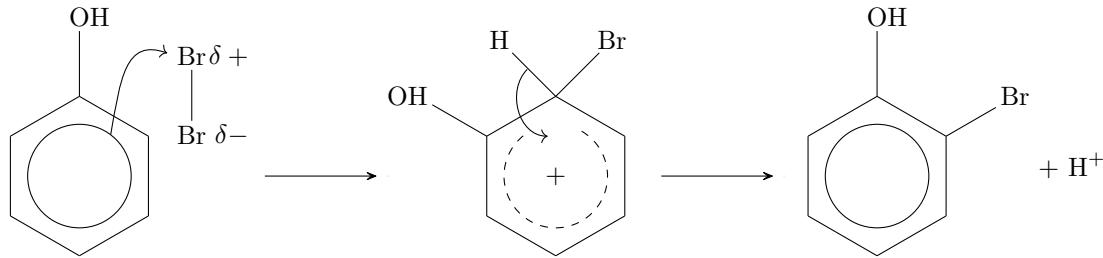


The reaction occurs more readily with phenol than benzene due to increased reactivity in phenol.

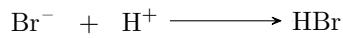
- I A pair of electrons from the p-orbitals of the OH is donated into the π system of phenol.
- II The electron density is higher in phenol and can attract electrophiles more readily such as polar molecules unlike benzene.

The mechanism for a single substitution is shown below.

In **Step 1** the polar bromine molecule is attracted to the benzene ring and one of the bromines bonds with the negative π -bond in benzene. The intermediate is unstable as the benzene ring has an overall positive charge; to overcome this the C–H bond is broken which bonds to the other bromine atom.

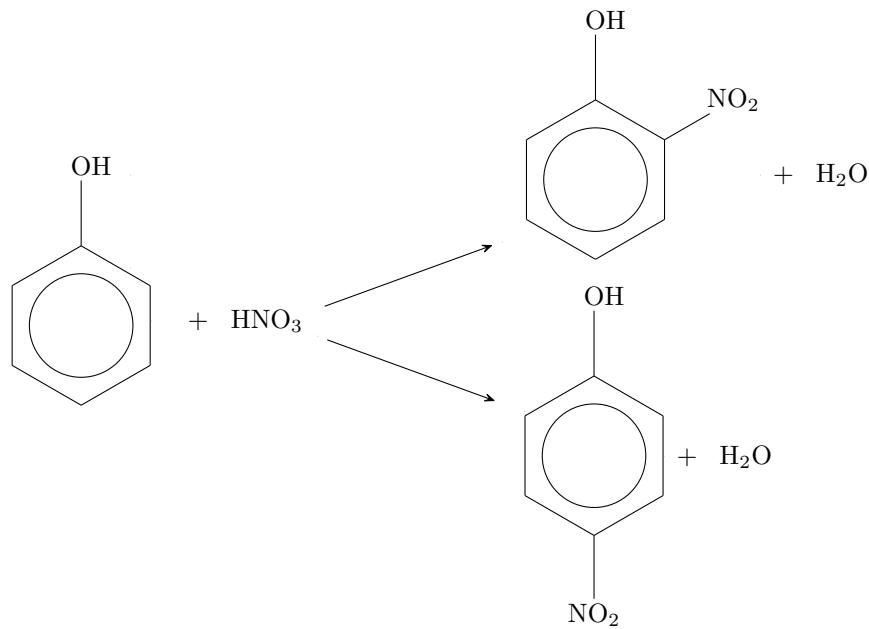


In **Step 2** the hydrogen ion H^+ forms a bond with the remaining Bromine ion forming hydrogen bromide HBr



11.6.2 Nitration of Phenol

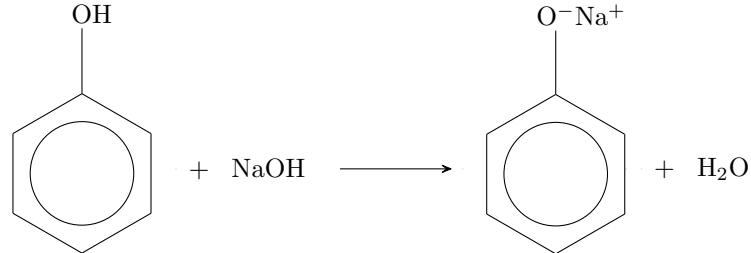
Phenol reacts readily with dilute nitric acid by **electrophilic substitution** at room temperature to form the major product 2-nitrophenol and minor product 4-nitrophenol.



Like in the bromination of phenol, the reaction happens very readily as the electron density in the benzene ring is high enough to attract the HNO₃ polar molecule. Hence no acid catalyst is needed and the reaction doesn't need concentrated nitric acid like with benzene.

11.6.3 Neutralisation of Phenol

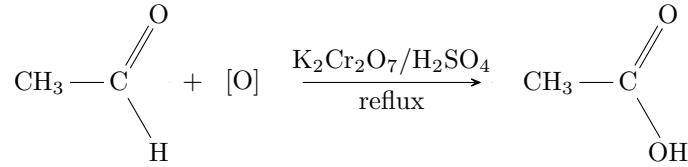
Because of its ability to partially dissociate, phenol is classified as a weak acid, hence it can undergo neutralisation reactions. However, phenol is only strong enough to neutralise hydroxides, not carbonates. The reaction of phenol with sodium hydroxide to produce the salt sodium phenoxide is shown below.



11.7 Carbonyls

11.7.1 Oxidation of Aldehydes

Aldehydes can be oxidised to carboxylic acids when heated under **reflux** with acidified dichromate (VI) ions, $\text{Cr}_2\text{O}_7^{2-}$ (and H^+), usually as a mixture of potassium or sodium dichromate and dilute sulfuric acid. The following example shows the oxidation of ethanal into ethanoic acid - the oxidising agent is shown as [O]

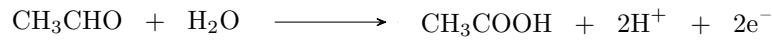


Much like the oxidation of alcohols, which also requires potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$, dichromate (VI) ions are reduced to chromium (III) ions. With this comes a colour change from orange to green which provides a mean for identifying this reaction. The Reduction is shown below.



The oxidation of the aldehyde is accompanied by the reduction of the chromium present in the dichromate ions. The half equations in an acidic environment are shown below:

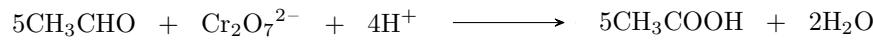
Oxidation of Aldehyde:



Reduction of Dichromate Ion:



By multiplying the oxidation equation by 5 and adding both equations we reach the overall redox equation:



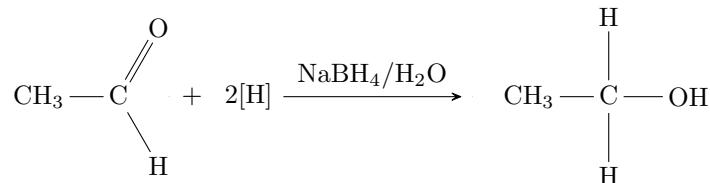
Ketones, unlike aldehydes, **do not** undergo oxidation reactions. This provides a means of distinguishing between aldehydes and ketones for a known carbonyl functional group

11.7.2 Reduction of Aldehydes

Aldehydes can be reduced by **nucleophilic addition** in two ways:

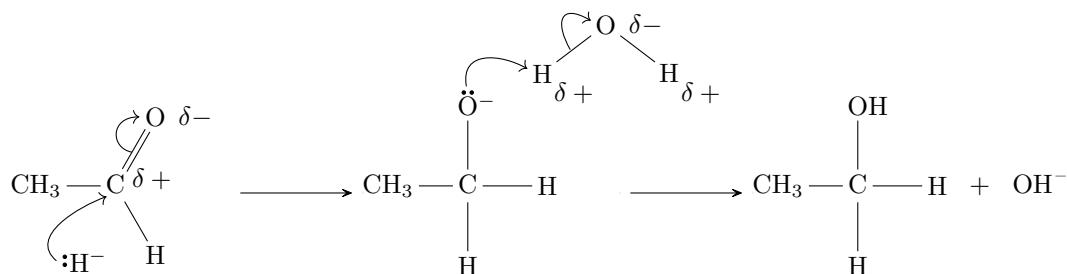
- **Reduction with NaBH₄**

Aldehydes can be reduced to primary alcohols with sodium tetrahydroborate (III) (NaBH_4) as a reducing agent in an aqueous or acidic solution. The following example shows the reaction of propanone into ethanal with the reducing agent [H] shown in an aqueous solution.



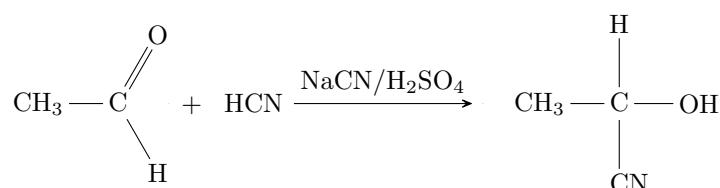
The nucleophilic addition mechanism in **aqueous solution** includes the following steps:

- I A negative hydride ion with a lone pair of electrons acts as our nucleophile. It is attracted to the $\delta+$ carbon and donates its electrons forming a dative bond.
- II The π bond is broken in the C=O by heterolytic fission forming a negative intermediate.
- III The intermediate is protonated as the oxygen donates a lone pair of electrons to a hydrogen atom in H_2O (In acidic environment, the lone pair can be donated to a hydrogen ion)



- **Reduction with HCN**

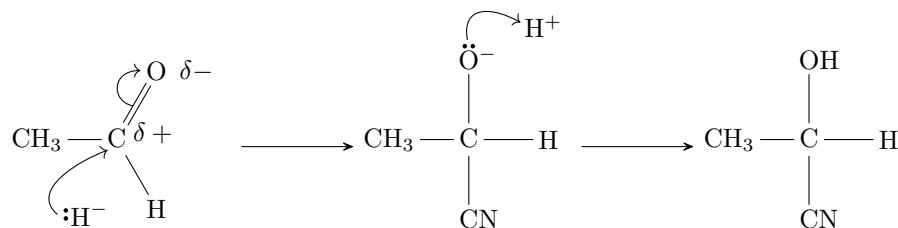
Aldehydes can be reduced by hydrogen cyanide to primary hydroxynitriles in acidic or aqueous solution. The example below shows the reduction of ethanal into hydroxyethanitrile in acidic solution.



HCN is very unsafe as it is colourless and extremely poisonous so sodium cyanide and sulfuric acid are used instead - the reaction must be carried out in a *fume cupboard* as the fumes are still potentially hazardous.

The nucleophilic addition mechanism in **acidic environment** includes the following steps:

- I A negative cyanide ion with a lone pair of electrons acts as our nucleophile. It is attracted to the $\delta+$ carbon and donates its electrons forming a dative bond.
- II The π bond is broken in the C=O by heterolytic fission forming a negative intermediate.
- III The intermediate is protonated as the oxygen donates a lone pair of electrons to a hydrogen ion or water such as in the example above.

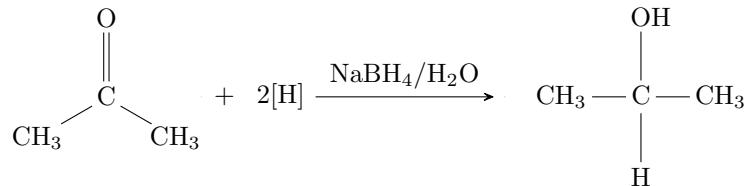


11.7.3 Reduction of Ketones

Ketones can be reduced by **nucleophilic addition** in two ways:

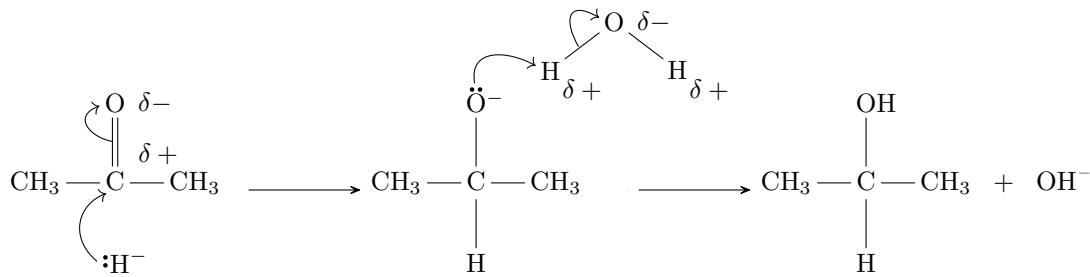
- **Reduction with NaBH₄**

Ketones can be reduced to secondary alcohols with sodium tetrahydroborate (III) (NaBH_4) as a reducing agent in an aqueous or acidic solution. the following example shows the reaction of propanone into propan-2-ol with the reducing agent [H] shown in an aqueous environment.



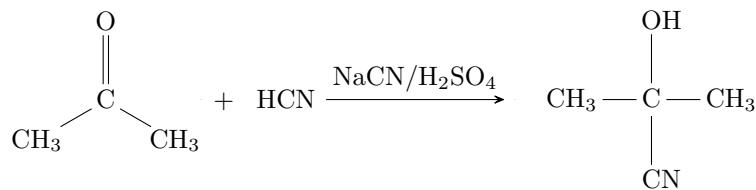
The nucleophilic addition mechanism in **aqueous solution** includes the following steps:

- I A negative hydride ion with a lone pair of electrons acts as our nucleophile. It is attracted to the $\delta+$ carbon and donates its electrons forming a dative bond.
- II The π bond is broken in the $\text{C}=\text{O}$ by heterolytic fission forming a negative intermediate.
- III The intermediate is protonated as the oxygen donates a lone pair of electrons to a hydrogen atom in H_2O (In acidic environment, the lone pair can be donated to a hydrogen ion)



- **Reduction with HCN**

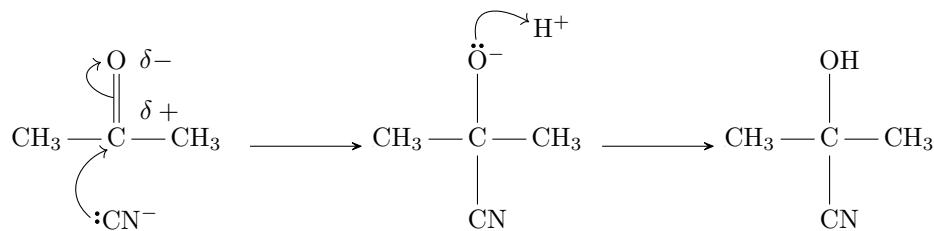
Ketones can also be reduced to secondary hydroxynitriles by hydrogen cyanide in an acidic or aqueous solution. Below shows the reaction between propanone into 2-hydroxypropan-2-nitrile in an acidic solution.



HCN is very unsafe as it is colourless and extremely poisonous so sodium cyanide and sulfuric acid are used instead - the reaction must be carried out in a *fume cupboard* as the fumes are still potentially hazardous.

The nucleophilic addition mechanism in **acidic environment** includes the following steps:

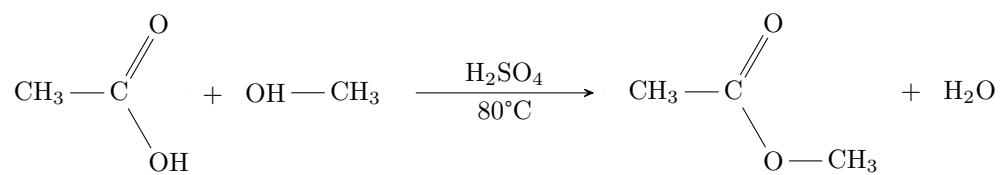
- I A negative cyanide ion with a lone pair of electrons acts as our nucleophile. It is attracted to the $\delta+$ carbon and donates its electrons forming a dative bond.
- II The π bond is broken in the $\text{C}=\text{O}$ by heterolytic fission forming a negative intermediate.
- III The intermediate is protonated as the oxygen donates a lone pair of electrons to a hydrogen ion or water such as in the example above.



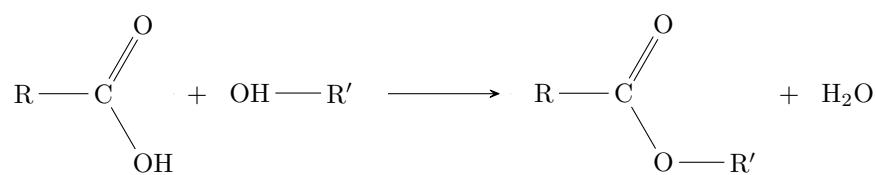
11.8 Carboxylic Acids

11.8.1 Carboxylic Acids to form Esters

The reaction for turning carboxylic acids into esters is known as **Esterification**. It is the reaction of a carboxylic acid with an alcohol in the presence of a small amount of concentrated sulfuric acid. Below shows the reaction of methanol with ethanoic acid to make methyl ethanoate and water.

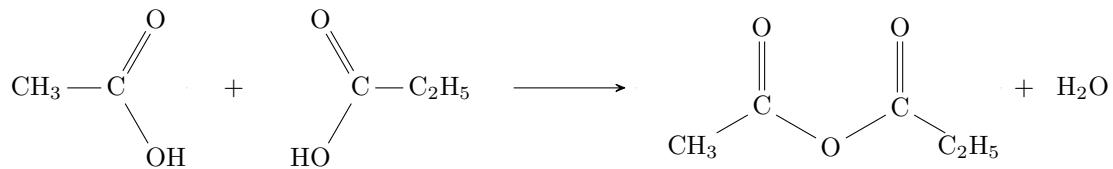


The alcohol needs a temperature of 80°C for a reaction to occur, hence the reaction must take place in a flask in a water bath. We can write the general form for esterification as follows:



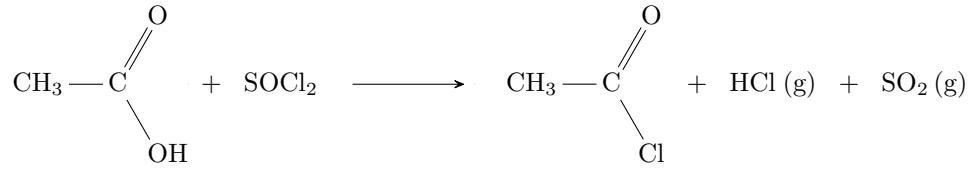
11.8.2 Carboxylic Acids to form Acid Anhydrides

Two carboxylic acids can undergo dehydration, the removal of water, to form an acid anhydride. A molecule of ethanoic acid and a one of propanoic acid can dehydrate to form the acid anhydride ethanoic methanoic anhydride.



11.8.3 Carboxylic Acids to form Acyl Chlorides

The only way to prepare an acyl chloride is in reaction with its parent carboxylic acid and thionyl chloride SOCl_2 . The products include the acyl chloride, sulfur dioxide gas and hydrogen chloride gas. the reaction to form ethanoyl chloride from ethanoic acid is shown below.



This reaction must be carried out in a fume cuboard as sulfur dioxide and hydrogen chloride are both toxic and corrosive in gaseous states.

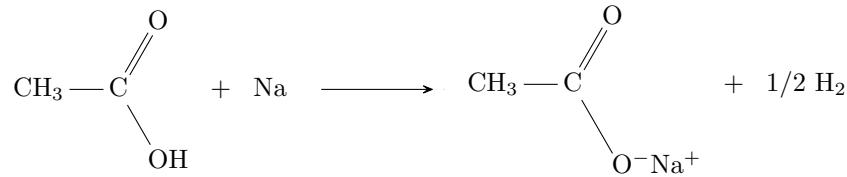
11.8.4 Neutralisation and Redox of Carboxylic Acids

Carboxylic acids undergoes various reactions due its property of being a weak acid as a result of its partial dissociation into a carboxylate ion:

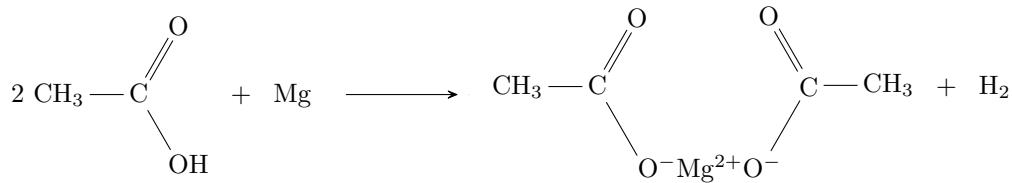


- **Carboxylic Acids with Metals**

Aqueous carboxylic acids react with metals (*s*) in a redox reaction producing hydrogen gas and a carboxylate salt (*aq*) - experimentally the metal will disappear and the H₂ will effervesce. Below shows the reaction of ethanoic acid with sodium metal.

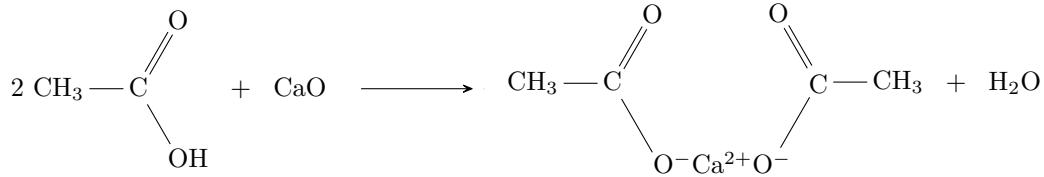


In cases such as magnesium multiple carboxylate ions will form ionic bonds as magnesium forms 2+ ions.



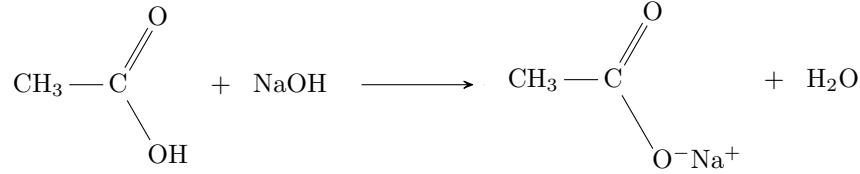
- **Carboxylic Acids with Metal Oxides**

Aqueous carboxylic acids will react with metal oxides (*s*) to form a salt (*aq*) and water (*l*). The following reaction shows the formation of the salt Calcium Ethanoate



- **Carboxylic Acids with Alkalies**

Aqueous carboxylic acids react with an alkali in solution in form a salt (*aq*) and water (*l*). The following shows the reaction between ethanoic acid and sodium hydroxide.

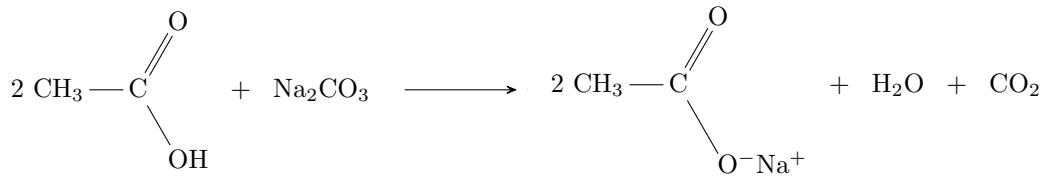


Ionic:



- **Carboxylic Acids with Carbonates**

Aqueous carboxylic acids will react with metal carbonates in solution producing a salt (*aq*), water (*l*) and carbon dioxide gas. This example uses sodium carbonate as the carbonate for the reaction.



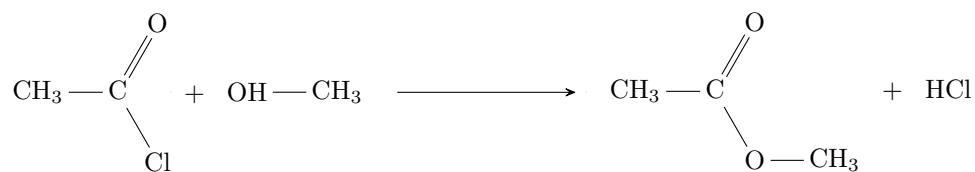
Carboxylic acids are the only organic compounds to undergo this reaction hence it provides a test for COOH groups - the CO₂ effervesces and turns lime water cloudy.

11.9 Acyl Chlorides

11.9.1 Acyl Chlorides to form Esters

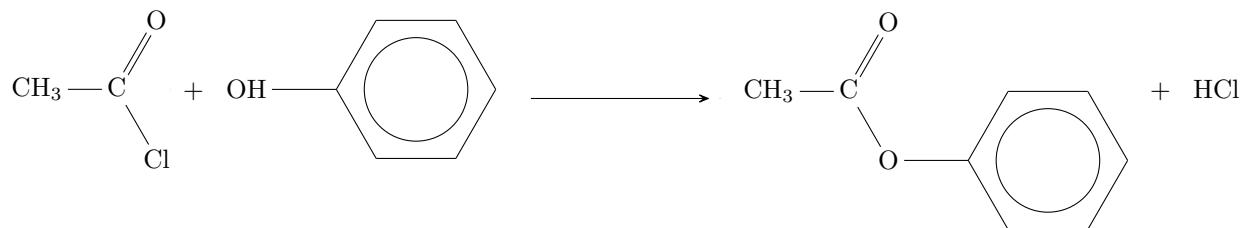
- Reaction with alcohols

Acyl chlorides react with alcohols to form an ester and hydrogen chloride. Below shows the reaction of ethanoyl chloride and methanol into methyl ethanoate.



- Reaction with Phenol

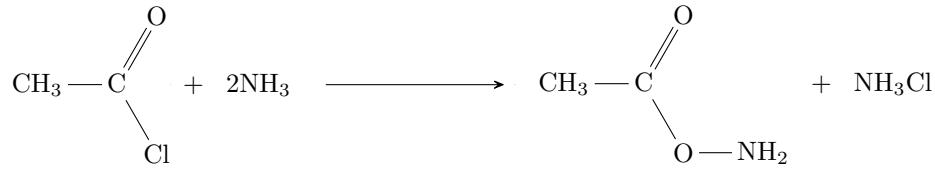
Carboxylic acids are not reactive enough to form esters from phenols but acyl chlorides are. The equation shows the reaction of ethanoyl chloride and phenol.



11.9.2 Acyl Chlorides to form Amides

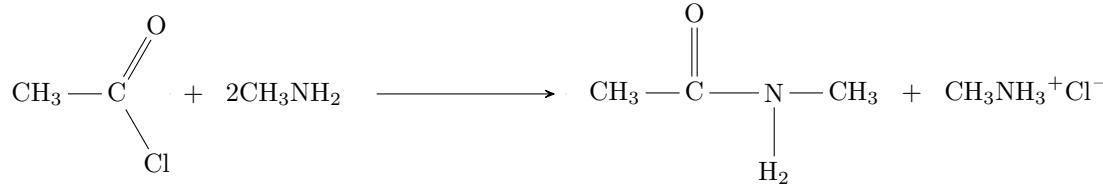
- Reaction with Ammonia to form Primary Amides

Acyl chlorides can react with ammonia and amines to form amides. They act as nucleophiles as the lone pair of electrons on the nitrogen is donated to the electron-deficient species. The reaction with ammonia forms primary amides. Below shows the production of ethanamide and ammonium chloride from ethanoyl chloride and ammonia.



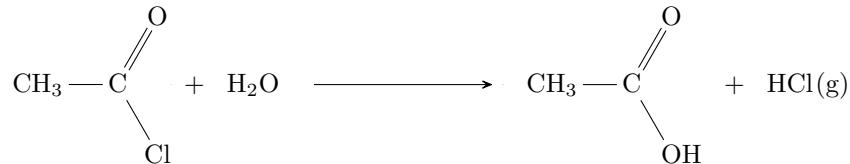
- Reaction with Amines to form Secondary Amides

Acyl chlorides react with primary amines to form secondary amides. For example, ethanoyl chloride and ethylamine react to form methylethanamide and methylammonium chloride.



11.9.3 Acyl Chlorides to form Carboxylic Acids

Acyl chlorides vigorously react with water to form a carboxylic acid and hydrogen chloride gas (hence reaction must take place in a fume cupboard). Below shows the reaction of ethanoyl chloride and water into ethanoic acid and hydrogen chloride gas.

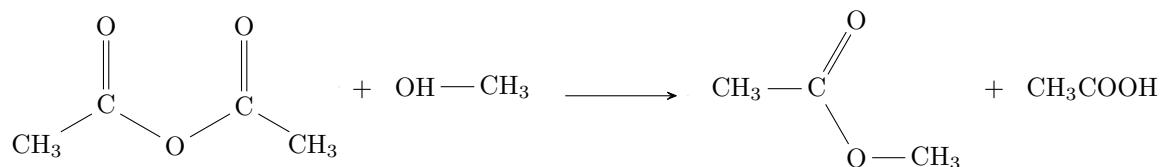


11.10 Acid Anhydrides

11.10.1 Acid Anhydrides to form Esters

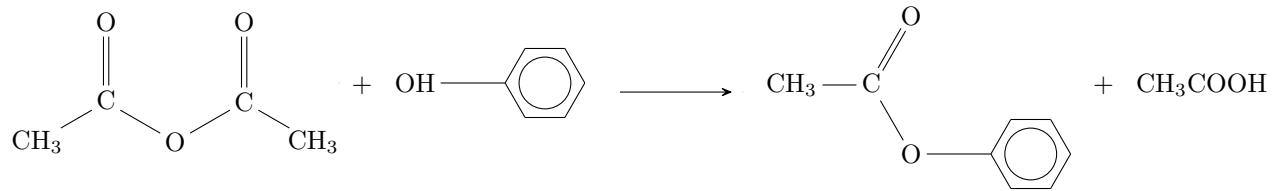
- Reaction with alcohols

Acid Anhydrides react with alcohols to form an ester and a carboxylic acid. Below shows the reaction of ethanoic anhydride and methanol into methyl ethanoate and ethanoic acid.



- Reaction with Phenol

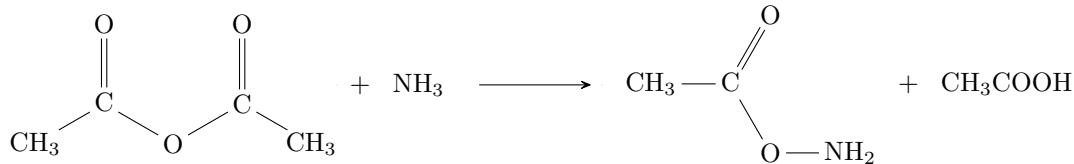
Carboxylic acids are not reactive enough to form esters from phenols but acid anhydrides and acyl chlorides are. The equation shows the reaction of ethanoic anhydride and phenol.



11.10.2 Acid Anhydrides to form Amides

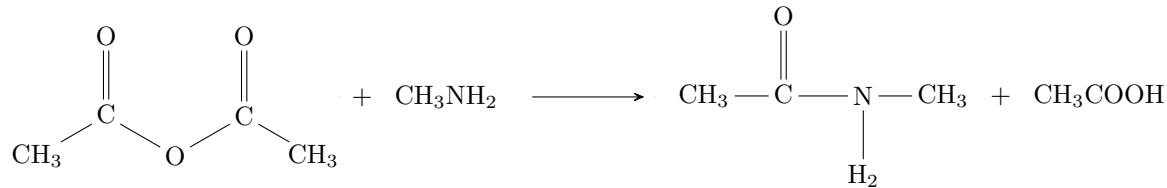
- Reaction with Ammonia to form Primary Amides

Acid anhydrides can react with ammonia and amines to form amides. They act as nucleophiles as the lone pair of electrons on the nitrogen is donated to the electron-deficient species. The reaction with ammonia forms primary amides. Below shows the production of ethanamide and ethanoic acid from ethanoic anhydride and ammonia.



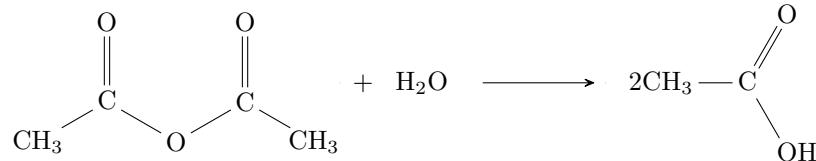
- Reaction with Amines to form Secondary Amides

Acid anhydrides react with primary amines to form secondary amides. For example, ethanoic anhydride and methylamine react to form methylethanamide and methanoic acid.



11.10.3 Acid Anhydrides to form Carboxylic Acids

Acid anhydrides react with water in a hydrolysis reaction to form two carboxylic acids. Below shows the reaction of ethanoic anhydride and water into two ethanoic acid molecules.



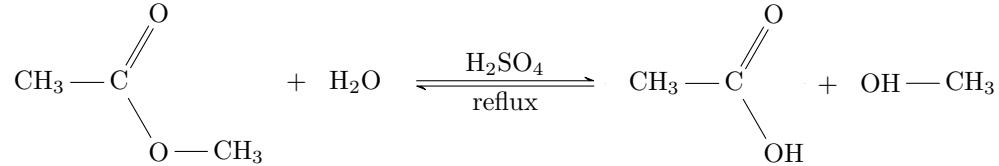
11.11 Esters

11.11.1 Hydrolysis of Esters

Esters can undergo **hydrolysis** (the chemical breakdown of a compound in the presence of water) as the reverse of esterification in two ways:

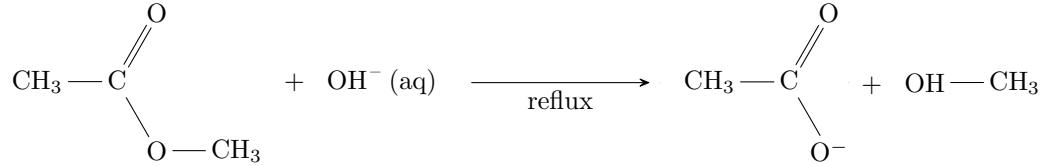
- **Acid Hydrolysis**

In acid hydrolysis the ester is heated under reflux with dilute aqueous acid. The ester is broken down by water with the ester acting as a catalyst producing a carboxylic acid and an alcohol. Below shows the acid hydrolysis of methyl ethanoate into ethanoic acid and methanol. The reaction is reversible.

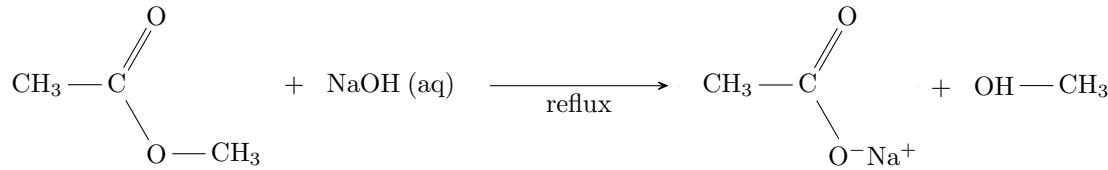


- **Alkali Hydrolysis**

Alkaline hydrolysis is also known as saponification and unlike acid hydrolysis is irreversible. The reaction occurs under reflux with aqueous hydroxide ions. This example shows the ester methyl ethanoate broken down into an ethanoate ion and methanol.



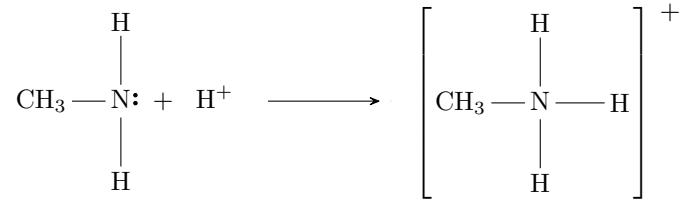
In the presence of a hydroxide molecule, the ethanoate ion will form a salt with the metal ion. For example, methyl ethanoate will undergo alkali hydrolysis with sodium ethanoate to form sodium ethanoate and methanol.



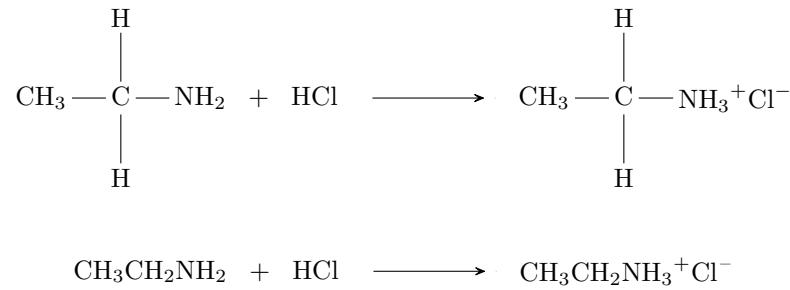
11.12 Amines

11.12.1 Neutralisation of Amines

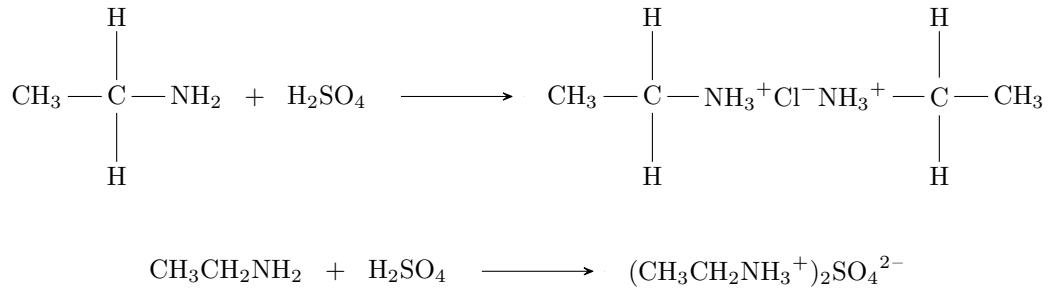
Amines act as bases as the lone pair of electrons on the nitrogen can accept a proton. When this occurs a dative bond forms between the lone pair of electrons on the hydrogen and the proton.



This means they can neutralise acids to form salts in a **neutralisation** reaction. The reaction of ethylamine and hydrochloric acid to form ethylammonium chloride is shown.



Two ethylamine molecules can also react with sulfuric acid to form ethyl ammonium sulfate

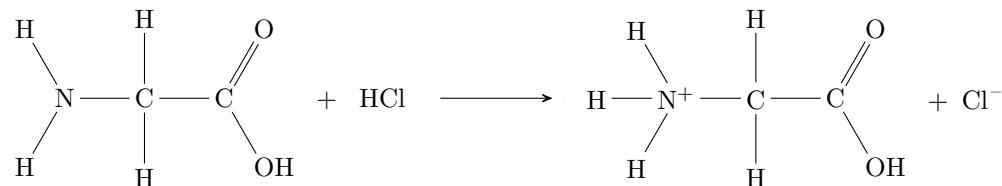


11.13 Amino Acids

11.13.1 Neutralisation of Amino Acids

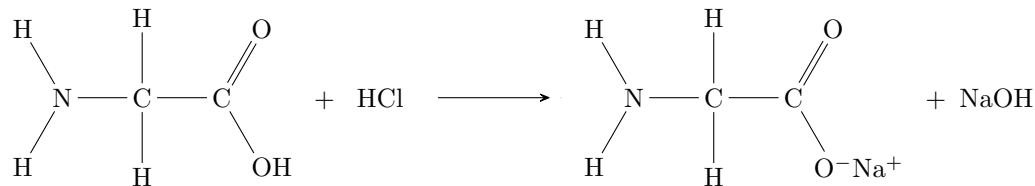
- Amino Acids as a Base

When reacted with an acid, amino acids undergo neutralisation as the amine functional group acts as a group in a similar way to amines. the reaction of aminoethanoic acid is shown below.



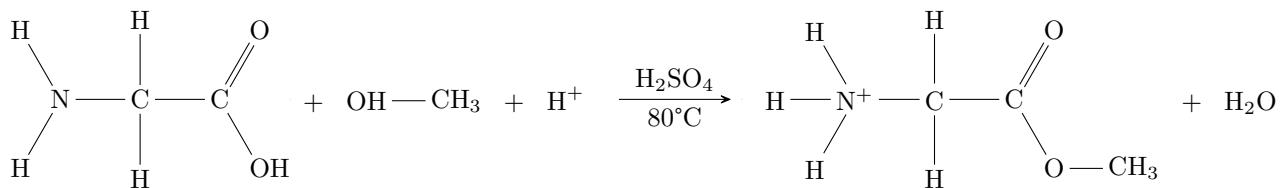
- Amino Acids as an acid

As suggested by the name, amino acids can also act as an acid as well as a base (meaning it can neutralise an acidic or an alkaline substance). The carboxylic functional group in the amino acid provides the proton for the neutralisation reaction. The reaction of sodium hydroxide and aminoethanoic acid is shown.



11.13.2 Amino Acids to form Esters

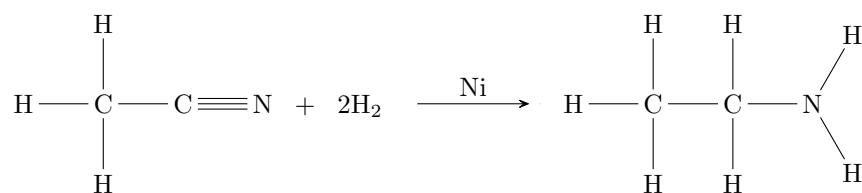
Similar to esterification of carboxylic acids and alcohols, amino acids will also undergo **esterification** with alcohols to form an ester. As we know from the carboxylic acids, this reaction requires concentrated sulfuric acid; the primary difference in this reaction is that the acidic conditions protonate the amine group. The reaction of aminoethanoic acid and methanol is shown below.



11.14 Nitriles

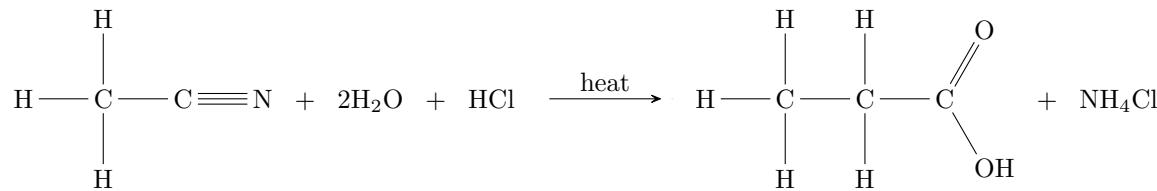
11.14.1 Reduction of Nitriles

Nitriles can be reduced by hydrogen in the presence of a nickel catalyst to form an amine. The reaction of ethanenitrile with hydrogen to form ethylamine is shown.

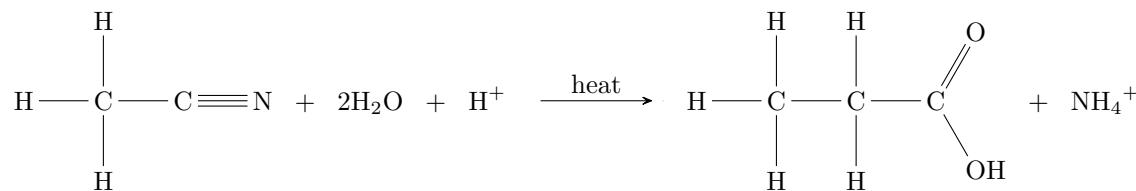


11.14.2 Hydrolysis of Nitriles

Nitriles can undergo hydrolysis to form carbocyclic acids and an ammonium salt with dilute acid such as aqueous HCl. Heat is required for the reaction. The hydrolysis (adding of water) of ethanenitrile and hydrochloric acid into ethanoic acid and ammonium chloride is shown below.



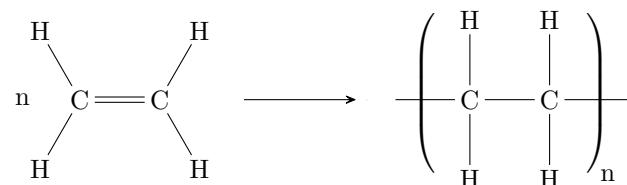
We can generalise this for any acid, H^+ such that an ammonium ion is produced.



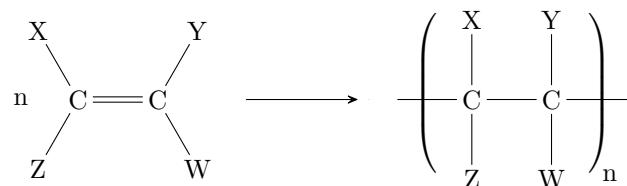
11.15 Polyalkenes

11.15.1 Polyalkenes by Polymerisation

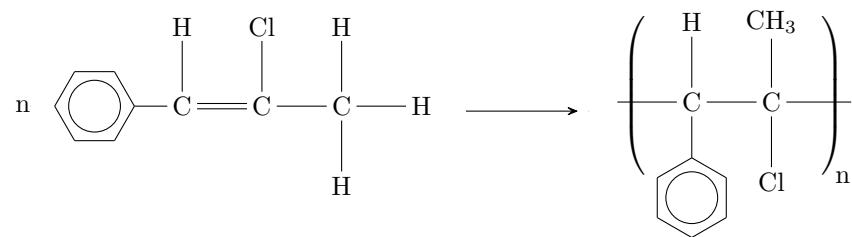
Polyethenes are produced from alkenes as the monomer unit, a reaction that requires a large amount of heat and pressure. Alkenes can undergo **addition polymerisation** to produce large unsaturated chains containing no double bonds. The addition polymerisation for ethene into polyethene is shown below.



The addition polymerisation of any alkene can hence be generalised into the form:



For example, the alkene *Z*-2-chlorophenylpropene will form the polymer poly-2-chlorophenylpropene

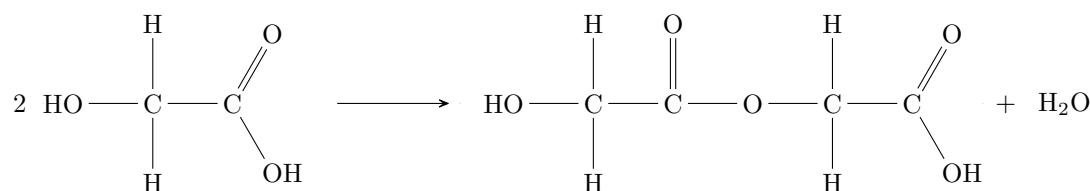


11.16 Polyesters

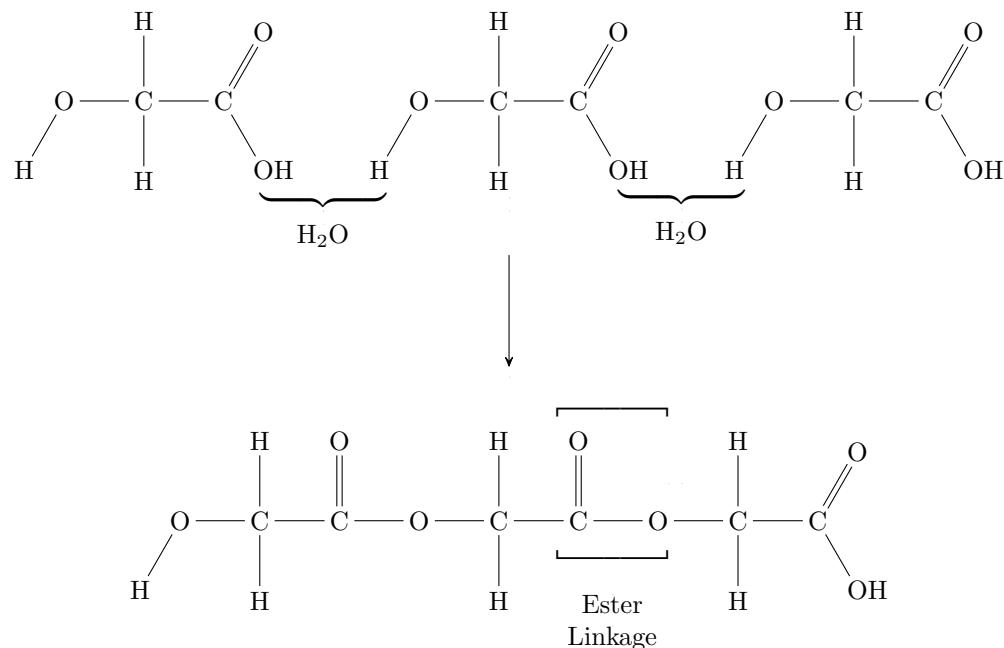
11.16.1 Polyesters by Polymerisation

- Polyesters from an alcohol and a carboxylic acid

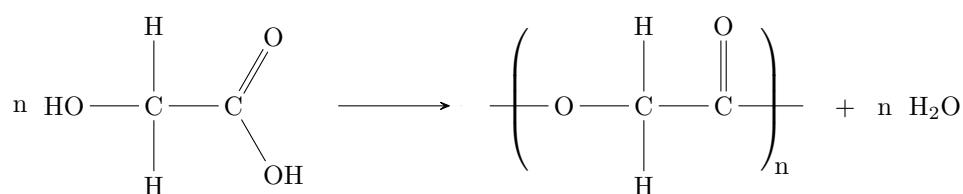
Polyesters are bonded together by **ester linkage** in a type of polymerisation called **condensation polymerisation**. A monomer with a carboxylic and alcohol functional group can hence bond by ester linkage making a polyester. The following example shows the condensation reaction of two glycolic acid molecules.



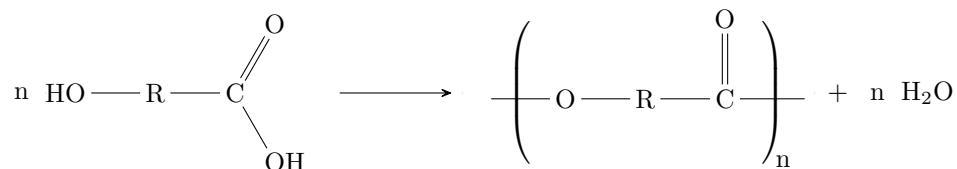
Ester linkage can form by removing an OH and a H from a carboxylic acid and an alcohol respectively creating a C-O bond. It can be thought of as a dehydration reaction.



Incidentally, for a large amount of glycolic molecules n , the polymer poly(glycolic acid) forms.

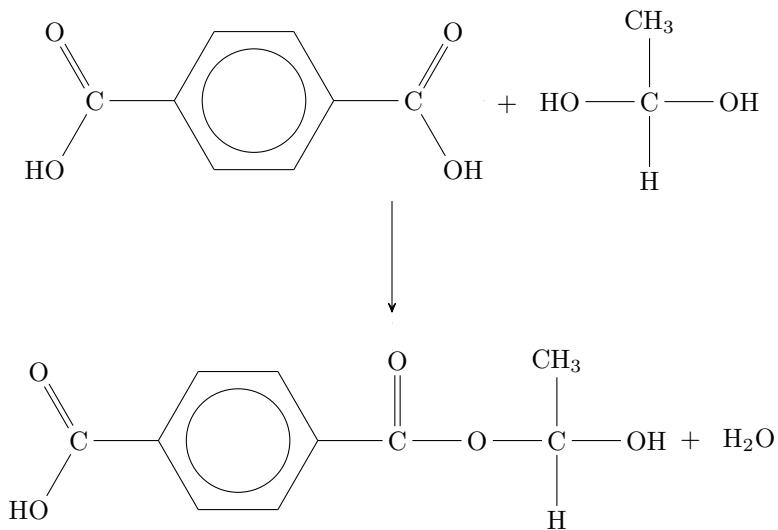


For a general organic structure R:

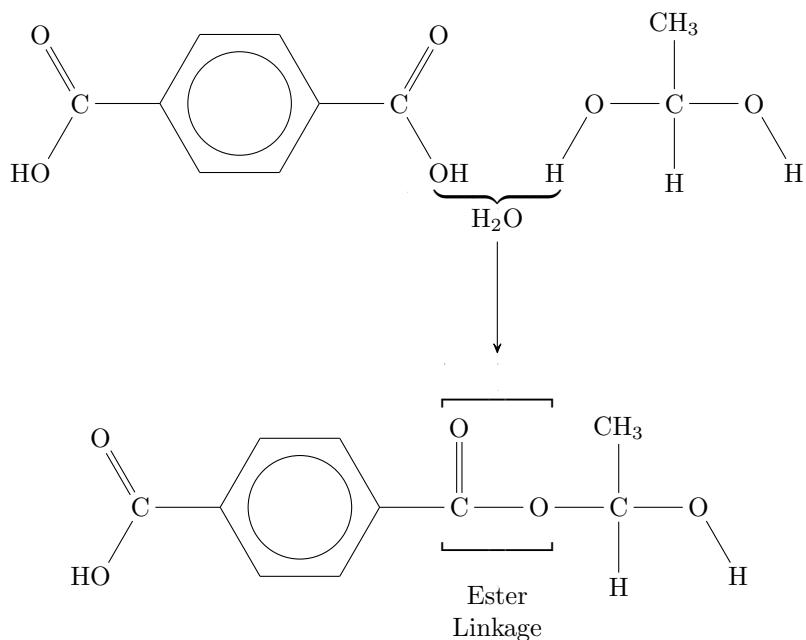


- **Polyesters from a diol and a dicarboxylic acid**

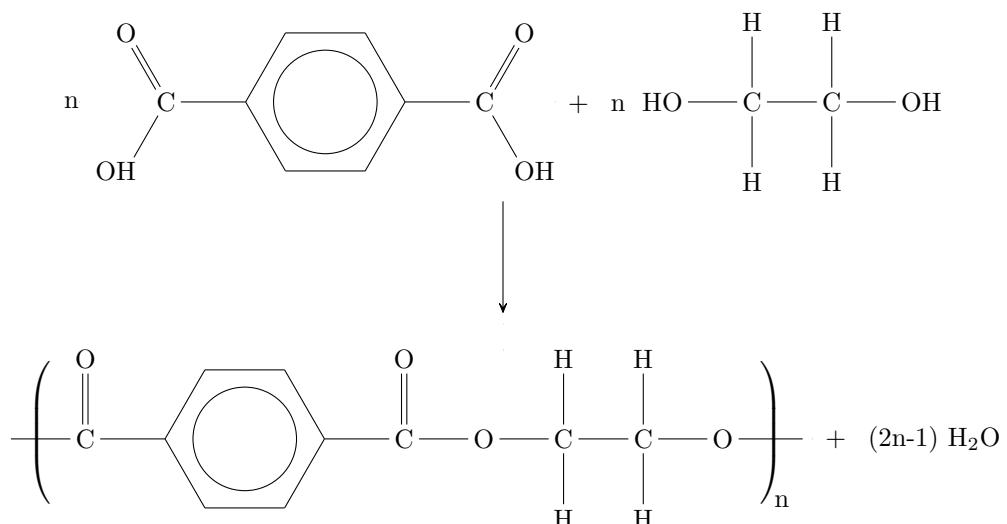
Polyesters can also form from a molecule with two alcohol functional groups and a molecule with two carboxylic acid functional groups. Each molecule bonds to the other by **condensation polymerisation** forming ester linkage. Below shows the reaction of 1,4 dibenzoic acid and ethane-1,1-diol to form terylene.



One of the carboxylic acid functional groups bonds with the alcohol group from the diol causing a dehydration and forming a C-O bond.



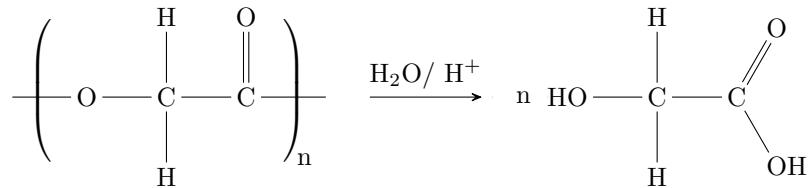
For a large number of diols and dicarboxylic acid you form a polymer chain. The example below shows the formation of the polymer polyethylene terephthalate also known as terylene:



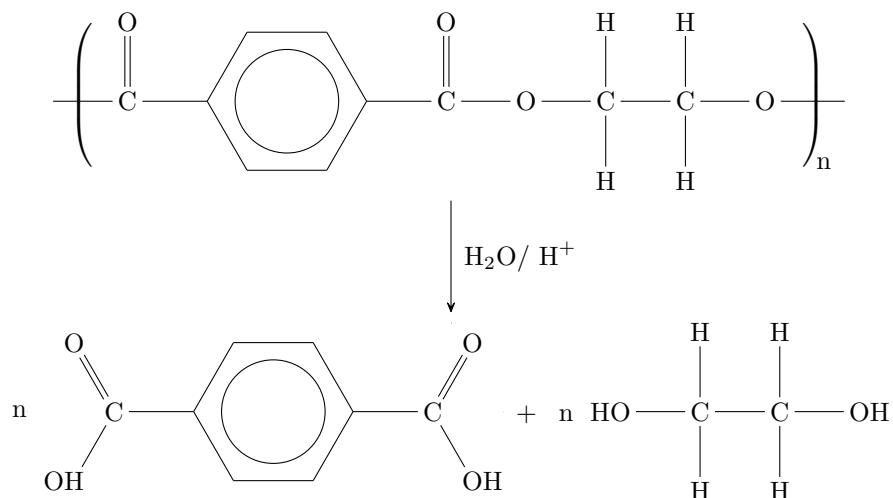
11.16.2 Hydrolysis of Polyesters

- Acid Hydrolysis

Hydrolysis of polyesters is essentially the inverse of condensation polymerisation, water is added to reform the monomer molecule(s). When there is a single R group in the repeating unit, a monomer with a carboxylic acid and alcohol functional group will form. For example, the acid hydrolysis of polyglycolic acid is shown to reproduce the glycolic acid monomer:

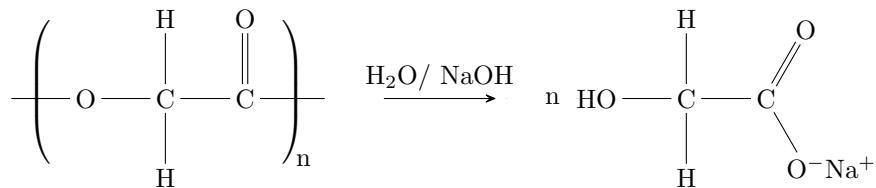


When the repeating unit consists of two R groups, a diol and a dicarboxylic acid forms. The acid hydrolysis of terylene is shown

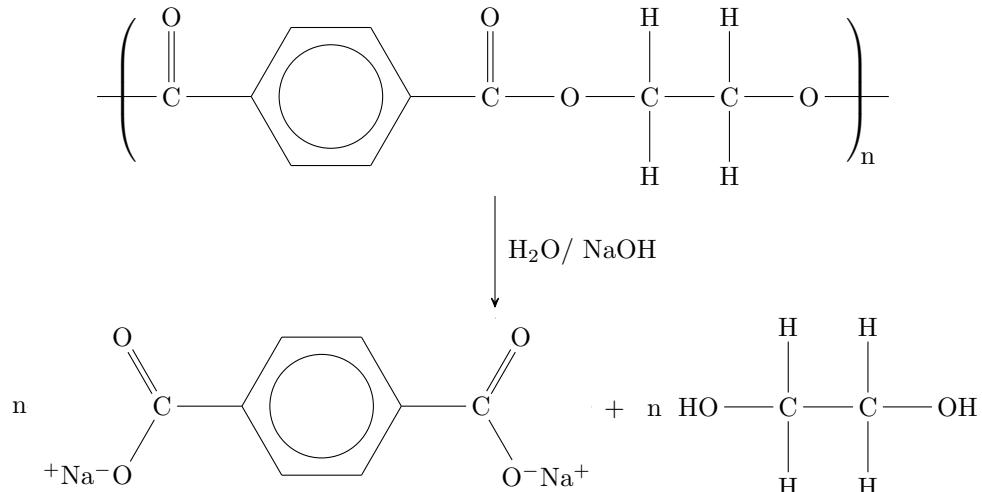


- Alkali Hydrolysis

Hydrolysis doesn't always occur in an acid environment. When alkali hydrolysis occurs, the carboxylic functional group cannot be oxidised, hence a carboxylate ion forms. the alkali hydrolysis of polyglycolic acid with sodium hydroxide NaOH is shown.



In a similar case, When the repeating unit contains two R groups, The dicarboxylic acid molecule cannot be oxidised and becomes a dicarboxylate ion. the alkali hydrolysis of terylene with sodium hydroxide is shown below.

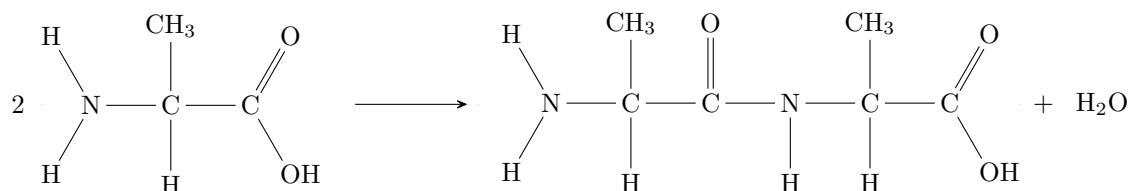


11.17 Polyamides

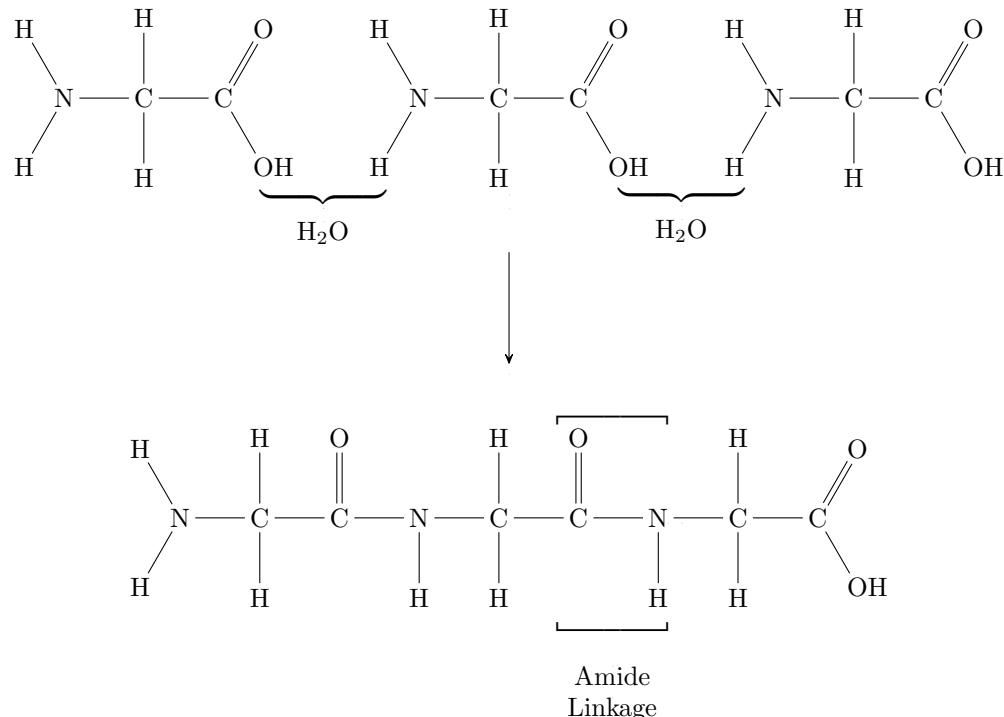
11.17.1 Polyamides by polymerisation

- Polyesters from an amino acid

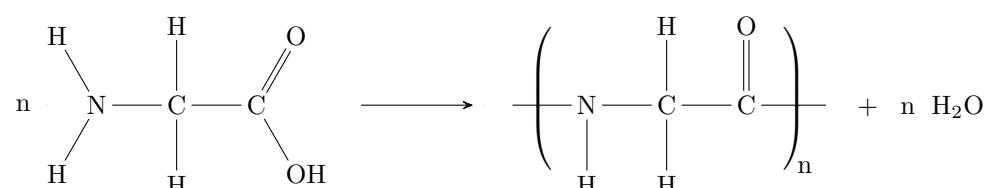
Polyamides are bonded together by **amide linkage** by **condensation polymerisation**. A monomer with a carboxylic and amine functional group also known as an amino acid can bond by amide linkage making a polypeptide or proteins. The following example shows the condensation reaction of 2-aminopropanoic acid



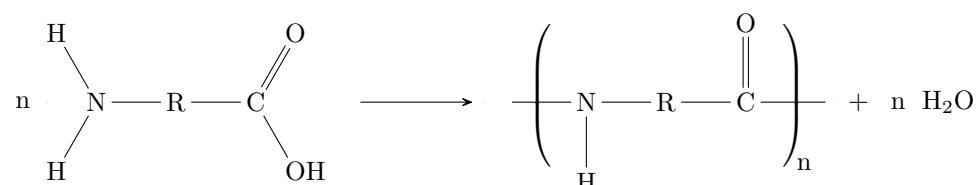
Ester linkage can form by removing an OH and a H from a carboxylic acid and an amine respectively creating a N-O single bond. It can be thought of as a dehydration reaction.



Incidentally, for a large amount of amino acid molecules n , the polypeptide or protein forms. The simplest example is of polyaminoethanoic acid.

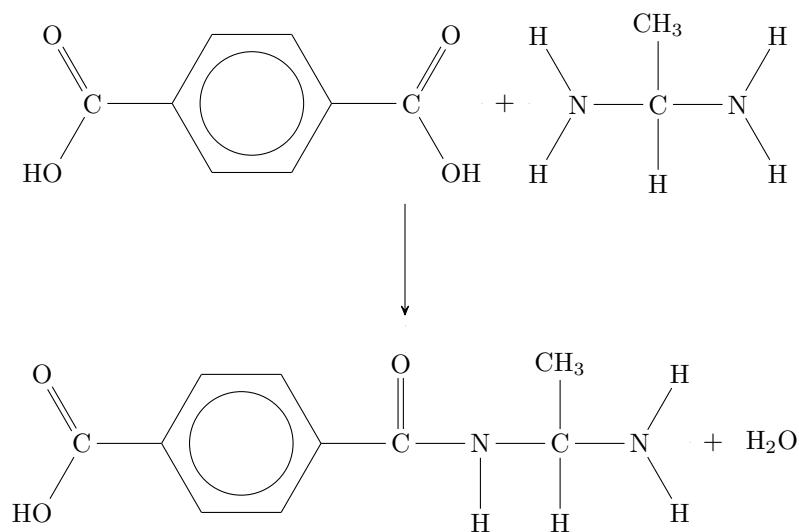


For a general organic structure R:

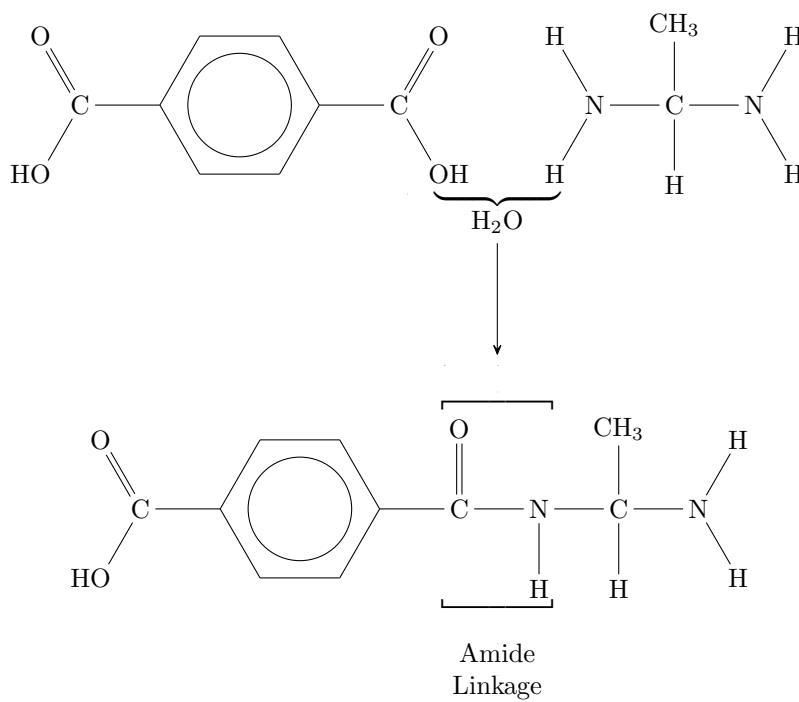


• Polyamides from a diamine and a dicarboxylic acid

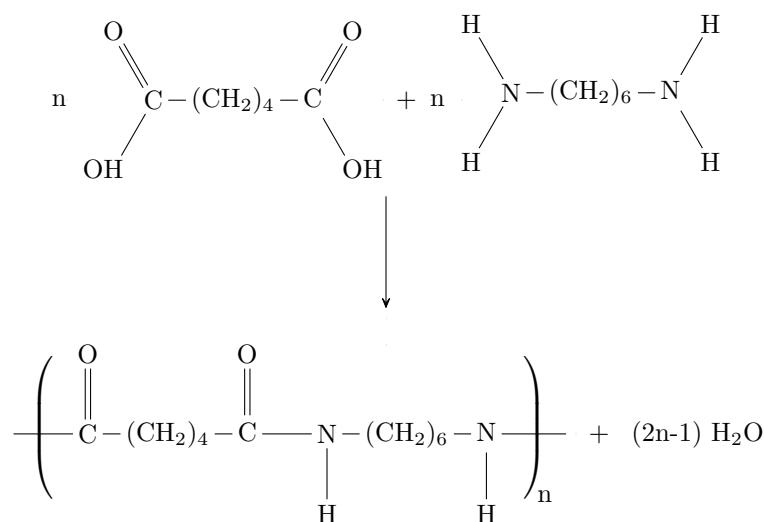
Polyamides can also form from a molecule with two amine functional groups and a molecule with two carboxylic acid functional groups. Each molecule bonds to the other by **condensation polymerisation** forming amide linkage. Below shows the reaction of 1,4-dibenzoic acid and ethane-1,1-diamine.



One of the carboxylic acid functional groups bonds with the amine group from the diamine causing a dehydration and forming a C-N single bond.

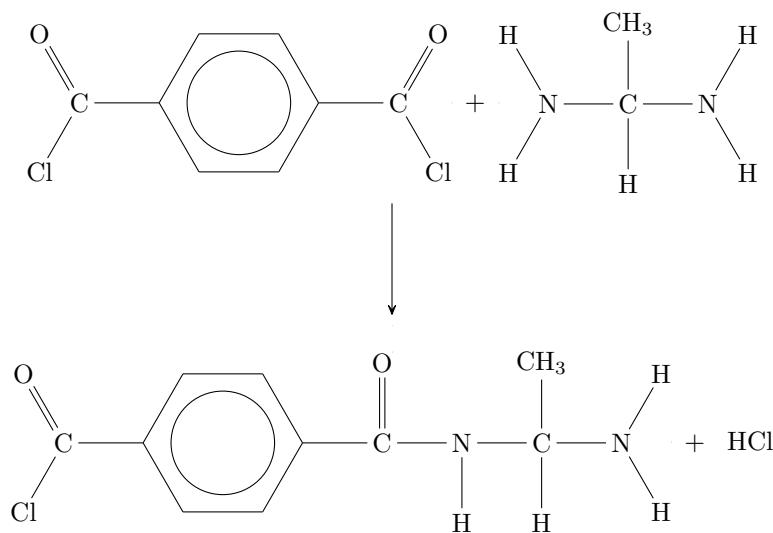


The most common polyamide is nylon-6,6. It is formed in a condensation polymerisation reaction between 1,6-diaminohexane and hexanedioic acid.

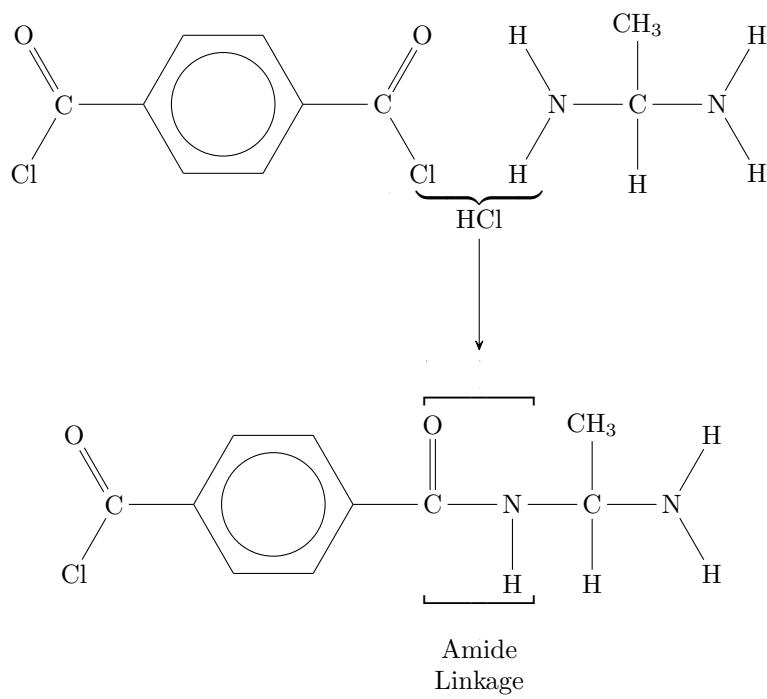


- Polyamides from a diamine and a diacyl chloride

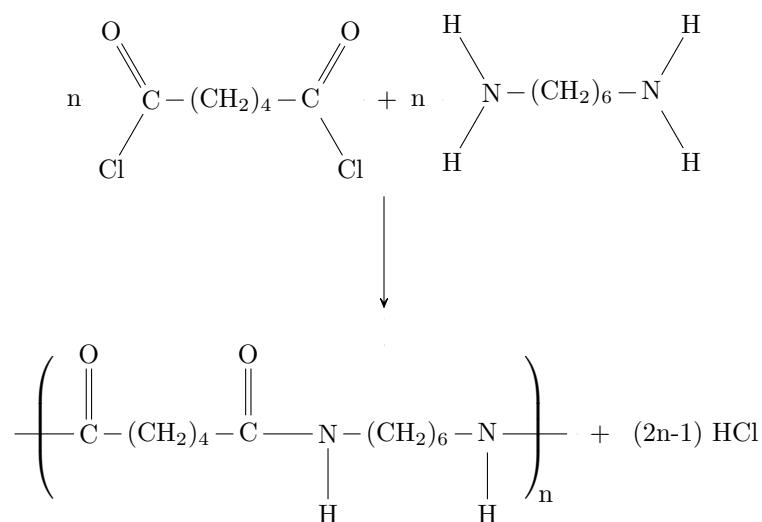
Polyamides can also form from a molecule with two amine functional groups and a molecule with two acyl chloride acid functional groups. Each molecule bonds to the other by **condensation polymerisation** forming amide linkage. Below shows the reaction of benzene-1,4-dioyl chloride and ethane-1,1-diamine.



One of the acyl chloride functional groups bonds with the amine group from the diamine causing a dehydration and forming a C-N single bond.



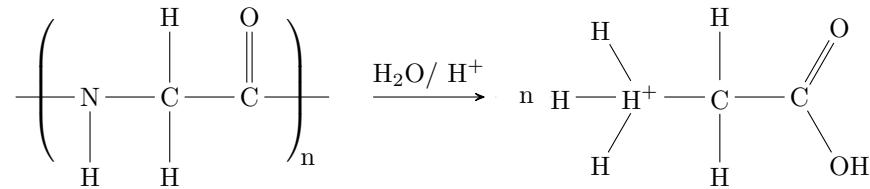
The most common polyamide is nylon-6,6. It is formed in a condensation polymerisation reaction between 1,6-diaminohexane and hexanedioyl chloride.



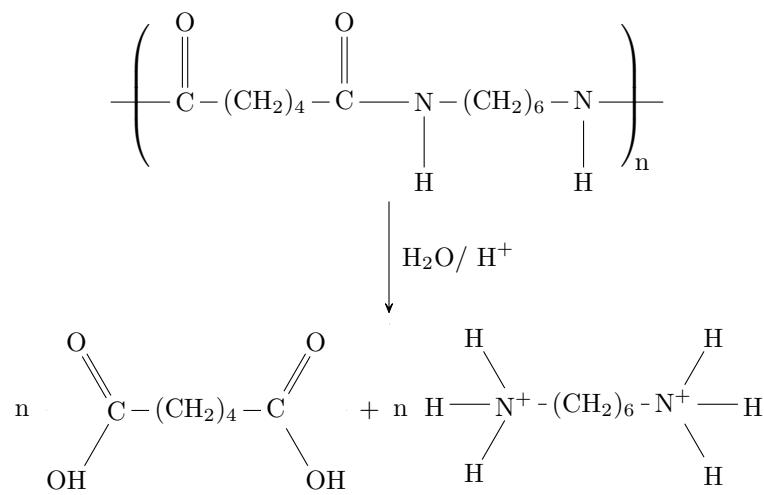
11.17.2 Hydrolysis of Polyamides

- Acid Hydrolysis

Hydrolysis of polyamides is very similar to that of polyesters - water is added to reform the monomer molecule(s). When there is a single R group in the repeating unit, a monomer with a carboxylic acid and alcohol functional group will form. For example, the acid hydrolysis of polyaminoethanoic acid is shown to reproduce the aminoethanoic acid monomer:

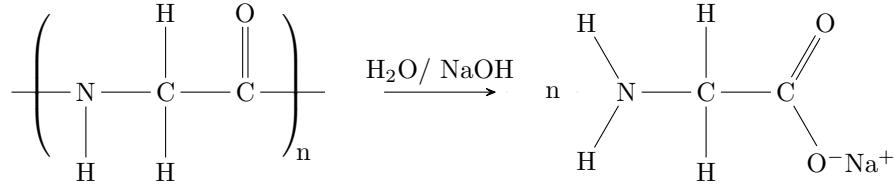


When the repeating unit consists of two R groups, a diol and a dicarboxylic acid forms. The acid hydrolysis of nylon is shown.

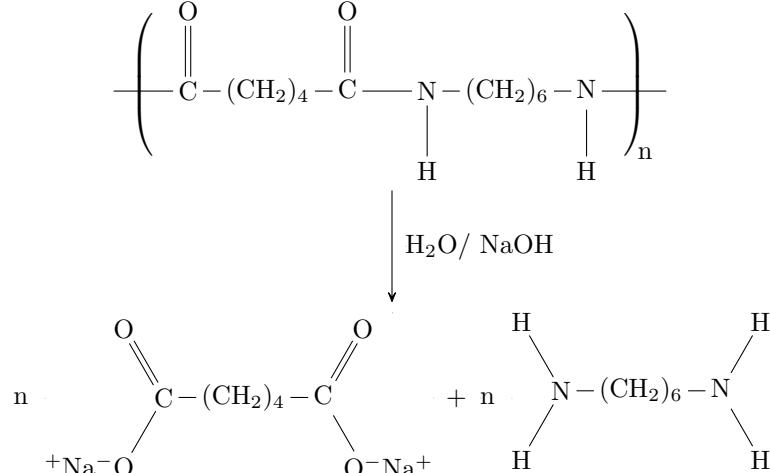


- Alkali Hydrolysis

Hydrolysis doesn't always occur in an acid environment. When alkali hydrolysis occurs, the carboxylic functional group cannot be oxidised, hence a carboxylate ion forms. the alkali hydrolysis of polyaminoethanoic acid with sodium hydroxide NaOH is shown.



In a similar case, When the repeating unit contains two R groups, The dicarboxylic acid molecule cannot be oxidised and becomes a dicarboxylate ion. the alkali hydrolysis of nylon with sodium hydroxide is shown below.

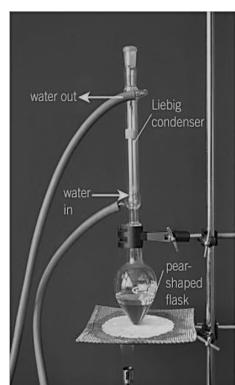


Chapter 12

Synthesis

12.1 Preparing an Organic Liquid

In organic synthesis, quick-fit apparatus is used that includes a pear-shaped flask, receiver, screw-tap adapter, condenser and a still head. The purpose of this equipment is to create perfect seals between equipment whilst being able to come apart easily.



Reflux



Distillation



Separating Funnel

12.1.1 Heating under Reflux

Heating under reflux is a procedure used when preparing an organic liquid without boiling off the solvent, reactants or products. It is predominantly used when rates of reactions are too slow at room temperature, so heat overcomes the activation energy.

- The method is used for temperatures greater than 100 degrees Celsius, anything below, a water bath can be used.
- When heating flammable liquids a mantle must be used so that there is no naked flame present from the Bunsen burner should the apparatus crack.
- A pear-shaped flask is clamped where the reaction mixture and anti-bumping granules are added to prevent large bubbles from forming and creating vibrations in the flask.
- A condenser is placed on top of the flask which prevents any substances from the flask to boil off. Additionally, grease is placed in between the flask and condenser so the equipment comes apart easily. When placing the condenser, it should be rotated to ensure a good seal.
- The condenser is kept vertical and only loosely clamped as it is very fragile.
- Rubber tubing is used to flow water through the outer jacket of the condenser. Water will always flow from the bottom to ensure the outer jacket is always full.
- Heating under reflux prevents volatile components from escaping. Any vapour that leaves the flask is condensed when it meets the outer jacket where it condenses and meets drips back into the flask.

12.1.2 Distillation

Chemical reactions do not always go to completion or by-products are produced. Distillation is used to purify the organic liquid by separating it from the solvents, by-products and any impurities.

- A pear-shaped flask is clamped by the neck which has a T still-head adaptor connected on top. Like in reflux, grease is used to ensure the apparatus comes apart easily.
- A second clamp is placed at a receiver adapter where the condenser will be attached. This prevents the condenser from needing a clamp as it is very fragile.
- The horizontal condenser is placed with rubber tubing supplying water from the bottom end. This cools the pure organic product into a liquid where it will drop into a collecting flask.
- A thermometer is placed in the flask to control the temperature. The temperature of the flask should be regulated to suit the boiling point of the organic product. The liquid with the lowest boiling point is the most volatile and will boil first leaving behind less volatile components.
- Sometimes a mixture may contain organic liquids with similar boiling points. In this case we **redistill** the mixture after cleaning it out, this time at the boiling point of the product you are trying to obtain.

12.1.3 Purifying the Organic Product

When preparing an organic liquid, water may be obtained with the product. A separating funnel is used to separate the two immiscible layers.

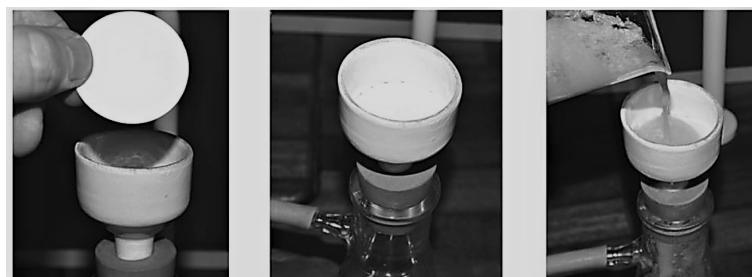
- I Ensure the tap of the separating funnel is closed. Pour the mixture that needs to be separated in the funnel with a stopper on top.
- II Invert to mix the mixture inside the funnel and allow the layers to separate.
- III Add water to the mixture to identify which layer is the organic layer. The layer which increases in volume is the aqueous layer.
- IV Place a conical flask under the separating funnel, remove the stopper and open the tap to remove the bottom layer. Using a second flask collect the other layer.
- V One flask will now contain a pure organic liquid and the other will contain the aqueous layer.
 - When using acids, the impure product may contain acid impurities. These can be removed by adding aqueous sodium carbonate and shaking.
 - The carbonate will react with acid producing carbon dioxide - at this point the stopper must be opened slowly to remove any gas pressure.
 - the salt produced becomes part of the aqueous layer and can be filtered out by the separating funnel.

12.1.4 Drying by Anhydrous Salt

There may still be some traces of water in the organic product which can be removed by a drying agent. A drying agent is an anhydrous inorganic salt that readily takes up water to become hydrated. Examples are anhydrous calcium sulphate CaSO_4 or magnesium sulphate MgSO_4 .

- I Add the organic liquid into a flask. Using a spatula, add the drying agent and mix the contents. Place a stopper on the flask to prevent any products from evaporating away. leave for 10 minutes.
- II If the solid has stuck together, there is still water present and additional drying agent must be added.
- III Decant the liquid into another flask. The pure organic liquid should be clear.

12.2 Preparing an Organic Solid.



12.2.1 Filtration under Reduced Pressure

Filtration under reduced pressure is a technique used to separate a solid from a solvent or liquid.

- I A pressure tubing is connected at one end to a vacuum outlet or pump and the other end to a Buchner flask which has fitted a Buchner funnel, ensuring there is a tight fit (this is usually obtained using a rubber bung). Check for good suction by placing your hand over the funnel.
- II Once the flask is set up, place a filter paper inside the Buchner funnel and wet it with same solvent used in preparing the solid.
- III To filter the sample, slowly pour the reaction mixture onto the filter paper. Rinse out the flask once so that all the solid crystals collect in the funnel.
- IV Rinse the Buchner flask with more solvent and leave under pressure for a few minutes until the crystals start to dry.



12.2.2 Recrystallisation

the solid crystal obtained after filtration under pressure will contain impurities which can be removed by recrystallisation

- I Pour a chosen solvent into a conical flask. If the solvent is flammable, place in a water bath, if not, heat the solvent using a Bunsen burner. In a second beaker, pour the impure solid.
- II Slowly add the solvent into the impure sample until it fully dissolves. The smaller the volume of the solvent used, the better. Allow the solution to cool.
- III Once the solution is cooled, crystals of the desired products should form. When crystals stop forming, filter by reduced pressure

12.2.3 Determining Melting point

Chemists use the melting point of a solid to determine whether it is pure. A pure organic solid usually has a melting range of 1 or 2 degrees - that is from the temperature it starts and finishes to melt. An impure sample will melt over a larger range and has a lower melting point

- I the sample used must be completely dry and free flowing. This can be done using filtration under pressure.
- II Hold one end of a glass-capillary tube in a hot flame. Rotate the tube until the tube is fully sealed.
- III By pushing the open end of the capillary into the sample, by force, fill the tube with 3mm depth of crystal.

At this point, the sample is ready to have its melting point measured. There are two ways of doing this, the first uses an electrically heated melting point apparatus.

- I Place the capillary tube into a sample hole with a 0-300 degrees celcius thermometer in the melting point apparatus.
- II Using a rapid heating setting, start to heat the sample whilst observing it. once the solid is seen melting, record the melting point
- III Allow the apparatus to cool and prepare a second sample to heat up again. As the melting point is approached, raise the temperature slowly so a more accurate determination is obtained.

An alternative method uses an oil bath or Thiele tube:

- I Set up the thiele tube or oil bath with an attached capillary tube containing the sample to a thermometer.
- II Place the thermometer into the thermometer hole of the Thiele tube or clamp if using an oil bath.
- III Using a micro-burner, slowly heat the side arm of the Thiele tube whilst observing the solid. Record the temperature at which the solid melts and repeat by raising the temperature slowly closer to the melting point to obtain an accurate value.



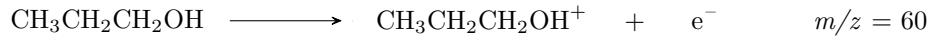
Chapter 13

Analysis

13.1 Mass Spectroscopy

13.1.1 Molecular Ion

Mass spectroscopy is used in organic analysis to determine the molecular mass and gain some insight into the structure of a compound. When the organic compound is placed in the mass spectrometer, it loses an electron to form a **molecular ion**. A mass spectrometer measures the mass to charge ratio or m/z value which gives the molecular mass of the compound. For propan-1-ol:



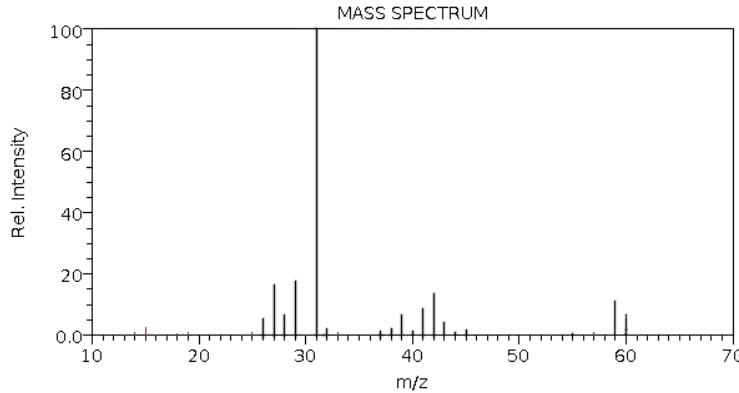
The molecular ion peak M^+ gives the molecular mass, to locate this peak on a mass spectrum, it will often be the second highest peak. The last peak is called the $\text{M}+1$ peak. This peak arises from the presence of a carbon-13 isotope. About 1.1% of carbon is the carbon-13 isotope so the $\text{M}+1$ peak should have a much lower relative intensity.

13.1.2 Fragmentation

In a mass spectrometer, smaller pieces called fragments form fragment ions from the original organic molecule. The simplest fragmentation breaks a molecular ion into a positively charged fragment and a radical. The mass spectrometer will only detect charged ions so the radical won't appear on the mass spectrum.



Below shows the mass spectrum for propan-1-ol



13.2 Infrared Spectroscopy

13.2.1 Bond Frequencies

Atoms in molecules are constantly in motion as the energy in covalent bonds between atoms vibrate naturally. These bonds can absorb infrared (IR) radiation. This can cause two different types of vibrations:

I A bond can stretch - that is the distance between the atoms can increase and then decrease in harmonic motion.

II the bond angle can change - the bond angle can increase and successively decrease in a constant motion.

The vibrations vary based on the mass of the atoms - heavier atoms vibrate slower than lighter ones; as well as the strength of the bond - stronger bonds vibrate faster than weaker ones.

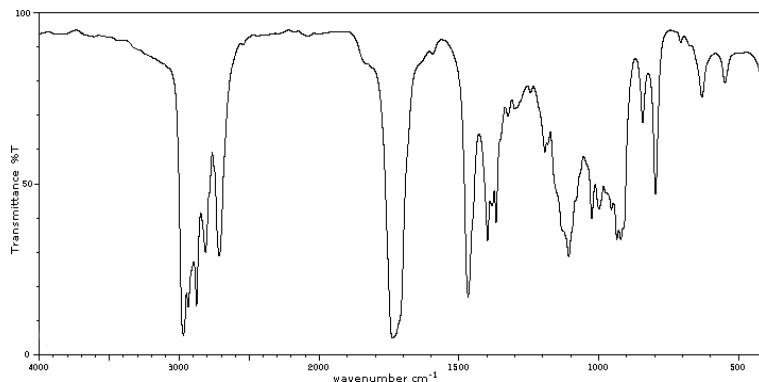
A bond will only absorb the frequency of infrared light that has the same natural bond frequency at which it vibrates. Frequency values are very large so instead a more convenient scale called the *wavenumber* is used (wavenumber has units cm^{-1}).

An example of bonds absorbing infrared light occurs in the atmosphere. Water, carbon dioxide and methane absorb the longer IR radiation emitted by the sun and re-emit the energy in the atmosphere that leads to the global warming.

13.2.2 Identifying functional groups

Chemists use this effect as a means of identifying functional groups in organic compounds using an **infrared spectrometer**:

- I A sample under investigation is placed into an infrared spectrometer where a beam of IR radiation in the range of 200-4000 cm⁻¹ is passed through the same.
- II The molecule absorbs the frequencies that relate to the frequencies of the bond vibrations and the unabsorbed radiation is analysed to identify which frequencies have been absorbed.
- III A graph of a percentage transmittance is plotted to identify ‘peaks’ that relate to the functional groups of that compound such as the one shown below.



The **fingerprint region** of the spectrum below 1500 cm⁻¹ contains unique peaks which can be used to identify the molecule under investigation.

It should also be recognised that all organic compounds produce a characteristic peak in the 2850-3100 range as the result of the carbon-hydrogen bonds C-H in the compound - this peak can be confused with alcohols O-H peak.

13.2.3 Applications

Many pollutants can be identified by their IR spectral fingerprints; remote sensors use IR spectra to determine the presences and intensity of carbon monoxide, carbon dioxide and hydrocarbons. IR based breathalysers detect the presence of the OH functional group to test whether a driver has had any intake of ethanol.

13.3 Chromatography

Chromatography is used to separate components from a mixture of substances. Chromatography always consists of two phases:

- **Stationary phase** - this phase does not move and is normally a solid or liquid
- **Mobile phase** - this phase does move and is normally a liquid or gas

13.3.1 Thin Layer Chromatography

Thin Layer Chromatography (TLC) is an analytical technique used to indicate how many components are in a mixture. This is a quick and inexpensive form of chemical analysis.

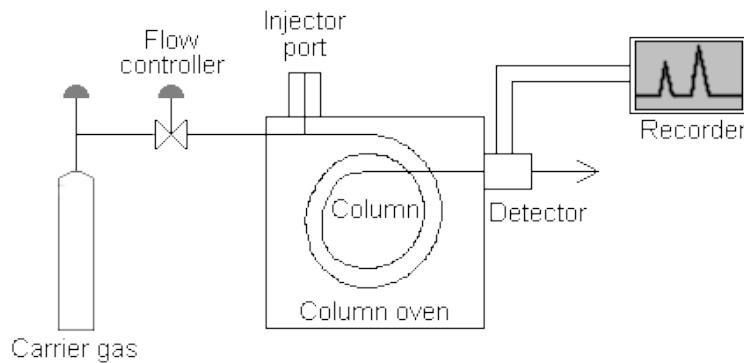
In TLC, a plastic sheet or glass is coated with an **absorbent** that acts as the stationary phase - this is usually silica. The different substances in the mixture have different affinities with the absorbent and will bind with different strengths with the mobile phase, the solvent. The different components will have different relative **adsorptions** with the stationary phase - that is the stationary phase will hold on to different substances differently.

• Retention Factor

When analysing a thin layer chromatogram, a **retention factor** R_f is calculated to compare the components to known R_f values. The retention factor can be calculated by the formula:

$$R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent front}}$$

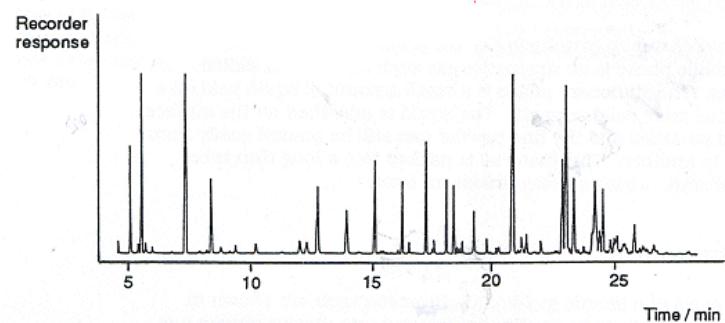
It is common to run a TLC sample of components that may be present to make it easier to identify which component is which substance.



13.3.2 Gas Chromatography

In gas chromatography, the stationary phase is a high boiling point liquid and the mobile phase is an inert gas like helium or neon. A small amount of a volatile mixture is injected into the chromatograph and is carried by the mobile phase through column where the stationary phase is located.

The components slow down as they interact with the stationary phase differently - the more soluble the solvent the slower it moves through the column, hence the components are separated by solubility. Each component reaches the detector in different times, this is called the **retention time** - the lowest retention time reaches the detector first and is the least soluble.



- **Retention Time**

The figure above shows a chromatogram with the retention time of various components. A gas chromatogram can be used to identify specific components of a known retention time. This technique is often used to test for drugs in urine samples.

- **Peak Integration**

Peak integration is a method used to determine the concentrations of components in a sample. The areas under each peak represent the concentration according to a **calibration curve**. A calibration curve can be plotted, sometimes called external calibration, to convert area into concentration. This curve must be plotted by data from a chromatogram of known concentrations.

13.4 Nuclear Magnetic Resonance

13.4.1 NMR spectroscopy

Nuclei have a property called **nuclear spin**, similar to they electrons have spin. This has significance if the nucleus has an odd number off nucleons such as hydrogen-1 and carbon-13. The nucleus has two different spin states with different energies. When the right magnetic field strength is applied and radio radiation frequency is applied, the nucleus absorbs the energy and rapidly flips between spin states.

Typically, the frequency of radio used is proportional the strength of the magnetic field. Very strong superconducting magnets are used and must be cooled to 4K by liquid helium. This allows NMR spectrometers to operatee at 100,200 or 400 MHz.

Electrons that surround the nucleus shift the energy used in NMR which casues a frequency shift. This shift is measured on a scale called the **chemical shift** δ ppm and is measured relative to teteramethylsilane (TMS) ($\text{CH}_3)_4\text{Si}$ which has a chemical shift of 0 ppm

• Carrying out an NMR Spectrum

- I When carrying out an NMR spectrum, a sample is dissolved in a solvent placed in a thin NMR tube with a small amount of TMS.
- II The sample is spun to even out impurities in the magnetic field from within the sample.
- III The spectrometer is zeroed against the TMS and the sample is given pulses of radio waves in a constant magnetic field
- IV After analysis, the solvent can be evaporated to recover the sample.

• Deuterated Solvents

Molecules of most solvents contain carbon and hydrogen which will produce signals in an NMR spectrum. Instead solvents can be deuterated by using the hydrogen-2 isotope which does not come up on NMR spectra. deuterated trichloromethane CDCl_3 is a commonly used solvent but still produces a peak in ^{13}C NMR.

13.4.2 ^{13}C NMR

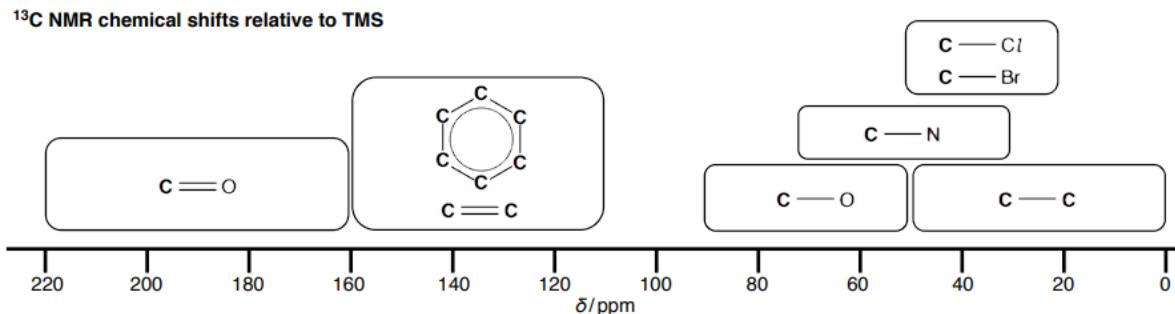
Carbon-13 NMR provides two pieces of information about a molecule.

- The number of carbon environments present given by the number of peaks
- the types of carbon environments present determined by the chemical shift of the peak relative to TMS.

The chemical environment of a carbon atom is determined by its position within the molecule.

- carbon atoms that are bonded to different atoms or functional groups will have different chemical shift and can be differentiated.
- If the molecule is symmetrical such that two carbon atoms are bonded to same groups and atoms, they will absorb radiation at the same chemical shift and produce a single peak as one environment

The spectrum below shows the four main types of carbon environments that appear on an NMR spectrometer for ^{13}C although these ranges vary depending on the solvent, concentrations and substituents.



13.4.3 ^1H NMR

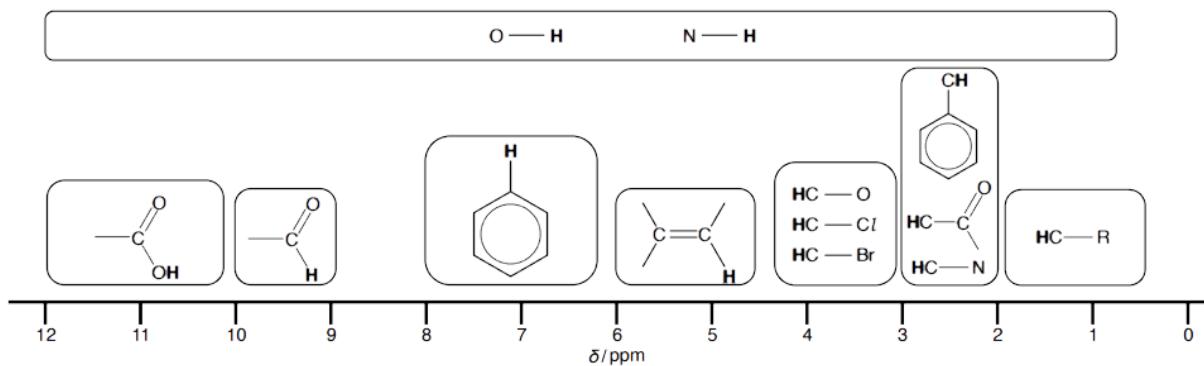
^1H NMR or proton NMR works very similar to carbon-13 NMR. It reveals four main pieces of information.

- The number of proton environments present given by the number of peaks
- the types of proton environments present determined by the chemical shift of the peak relative to TMS.
- The relative numbers of each type of proton from peak integration.
- The number of non-equivalent protons adjacent to a given proton from spin-spin splitting pattern

• Equivalent and Non-Equivalent Protons

- *Equivalent* environments is a term used when two or more protons absorb at the same chemical shift increasing the size of the peak.
- *Non-equivalent* environments are where different protons absorb at different chemical shifts producing different peaks.

¹H NMR chemical shifts relative to TMS



- Peak Integration

In carbon-13 NMR, the area under peaks does *not* indicate how many carbons are present under each environment. In proton NMR, areas under peaks give the relative number of protons. The NMR spectrometer measures this area by an **integration trace**, mathematically.

- Spin-Spin Coupling

In proton NMR, peaks are split into sub-peaks to form a splitting pattern by **spin-spin splitting**. The rule for spin coupling is as follows:

- For an n number of protons attached to an adjacent carbon atom, spin-spin coupling will produce $n+1$ sub-peaks on a proton NMR spectrum.

Spin-spin coupling will often occur in pairs. Two proton environments are paired if the splitting pattern matches the number of protons on its adjacent carbon atoms which provides a mean of identifying the structure of the molecule.

n	$n+1$	Splitting pattern	Relative peak areas within splitting	Pattern	Structural feature
0	1	singlet	1		no H on adjacent atoms
1	2	doublet	1:1		adjacent CH
2	3	triplet	1:2:1		adjacent CH ₂
3	4	quartet	1:3:3:1		adjacent CH ₃

- Hydroxyl and Amino Protons

The amino and hydroxyl functional groups that occur in alcohols, phenols, carboxylic acids, amides, amines and amino acids are involved in hydrogen bonding and absorb at variable chemical shifts which can make identifying them very difficult.

- Proton Exchange

Chemists have derived an easier way to identify hydroxyl and amino groups using a method called proton exchange

I A proton NMR is run as normal

II A small volume of deuterium oxide is added D₂O to the mixture and shaken. The NMR is run again.

Deuterium exchanges hydrogen-1 protons with deuterium in hydroxy and amino groups so that they will not appear on an NMR spectrum. This provides a means of identifying them by comparing the two spectra. the following equilibria is set up.



13.5 Chemical Tests

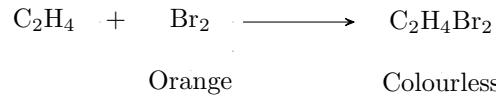
13.5.1 Test for Alkenes

The test for the presence of a carbon-carbon double bond also known as the alkene functional group is the following.

I **Test** - add bromine water drop-wise

II **Observation** - a colour change from orange to colourless

Alkenes exclusively undergo electrophilic addition reactions with bromine. Bromine water is naturally orange, as the bromine reacts to form a haloalkane the solution becomes colourless.



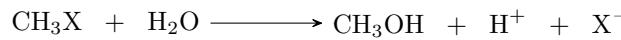
13.5.2 Test for Haloalkanes

The test for the presence of a halogen-carbon bond also known as the haloalkane functional group is the following.

I **Test** - add silver nitrate and ethanol and warm to 50 degrees Celsius in a water bath.

II **Observation** - a chlorine-carbon bond will produce a white precipitate, a bromine-carbon bond will produce a cream precipitate and finally an iodine-carbon bond will produce a yellow precipitate.

the reaction that occurs is hydrolysis. Ethanol acts as a solvent and allows the water and haloalkane to mix where the nucleophilic substitution can take place, in the following reaction.



The halogen X will bond with the a silver ions provided from the aqueous silver nitrate to form a silver-halogen precipitate.



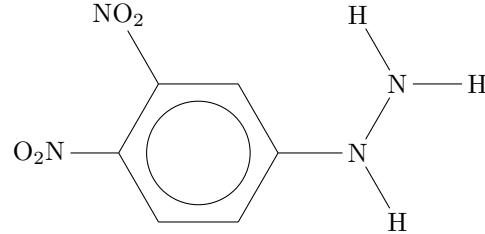
13.5.3 Test for Carbonyls

The test for the presence of a carbon-oxygen double bond C=O or the carbonyl functional group is as follows

I **Test** - add 2,4-dinitrophenylhydrazine (2,4-DNP).

II **Observation** - an orange precipitate will form.

2,4-DNP is sometimes referred to as Brady's reagent and is normally dissolved in sulfuric acid and methanol as a pale orange solution - solid 2,4-DNP is very hazardous as it becomes explosive. the structure of 2,4-DNP is shown below:



13.5.4 Test for Aldehydes

The test for the presence of an aldehyde functional group, CHO is shown below

I **Test** - add Tollen's reagent and warm in a water bath at 50 degrees Celsius.

II **Observation** - A silver mirror precipitate forms.

Tollen's reagent consists of silver nitrate and aqueous ammonia. The aqueous silver ion act as an oxidises agent - the silver ions are reduced to silver and the aldehyde is oxidised to a carboxylic acid.

Reduction of Silver Ions



Oxidation of Aldehyde



13.5.5 Test for Primary/Secondary Alcohols and Aldehydes

The test for the presence of an aldehyde functional group, CHO and primary or secondary alcohols is shown

I **Test** - add acidified potassium dichromate (*VI*) (usually by dilute sulfuric acid) and warm in a water bath.

II **Observation** - Colour change from orange to green.

The reaction is an oxidation reaction and occurs as a result of the oxidation of the dichromate (*VII*) ions to chromate (*III*) ions which has an associated colour change.



13.5.6 Test for Carboxylic acids

The test for the presence of a carboxylic acid functional group COOH is shown

I **Test** - add aqueous sodium carbonate.

II **Observation** - effervesence can be seen. The gas produced will turn lime water cloudy.

The reaction that occurs is a neutralisation reaction as the carboxylic acid acts as a weak acid with the carbonate ions that act as the base. Other organic compounds such as alcohols and phenols are not acidic enough to undergo this reaction. The gas produced is carbon dioxide.

