

## 2.1 Atoms and reactions

### 2.1.1 Atomic structure and isotopes

- Definitions

Term	Definition
Isotopes	Atoms of the same element with the same number of <b>protons and electrons</b> and <b>different numbers of neutrons and different masses</b> .
Proton number / atomic number	The number of <b>protons</b> in the nucleus of an atom.
Nucleon number / mass number	The number of <b>protons and neutrons</b> in the nucleus of an atom.
Relative isotopic mass / $A$	The mass of an isotope of an element compared to 1/12th of the mass of an carbon-12 atom.
Relative atomic mass / $A_r$ / $A_R$	The <b>weighted mean</b> mass of an atom of an element compared to 1/12 of the mass of an atom of carbon-12.
Cation	A <b>positively charged</b> ion with fewer electrons than protons.
Anion	A <b>negatively charged</b> ion with more electrons than protons.

- Properties of isotopes

- Same chemical reactions
  - Same electron configuration & the same number of protons
  - Number of neutrons has no effect on reactions of an element
- Small differences in physical properties
  - Higher mass isotopes = higher melting and boiling point + higher density

- Mass and charge of sub-atomic particles

Particle	Relative charge	Relative mass
Proton / $p^+$	1+	1
Neutron / $n$	0	1
Electron / $e^-$	1-	1/1836

- Determining relative atomic mass and relative isotopic mass (for ions with single charges)

- Mass spectrometer
- Records abundance of ions of different isotopes and their mass-to-charge ratio ( $m/z$  ratio)
- Value of relative isotopic mass can be worked out from  $m/z$  ratio and hence relative atomic mass

### 2.1.2 Compounds, formulae and equations

- Definitions

Term	Definition
Binary compounds	Compounds that contains <b>two elements</b> only.
Diatomic molecules	Molecules composed of <b>two atoms</b> only.
Polyatomic ions	Ion containing more than one atoms.

- Anions to know

Ion	Formula
Nitrate	$\text{NO}_3^-$
Carbonate	$\text{CO}_3^{2-}$
Sulfate	$\text{SO}_4^{2-}$

<b>Hydroxide</b>	OH <sup>-</sup>
------------------	-----------------

- Cations to know

Ion	Formula
<b>Ammonium</b>	NH <sub>4</sub> <sup>+</sup>
<b>Zinc ion</b>	Zn <sup>2+</sup>
<b>Silver ion</b>	Ag <sup>+</sup>

- ✍ • Writing ionic equations
  - We can only dissociate the **aqueous compounds**
  - Split all chemicals into ions
  - Cancel out spectator ions
  - ★ • No aqueous compound = no ionic equation
- Solubility

Solubility	Compounds
<b>Soluble in water</b>	<ul style="list-style-type: none"> <li>• All common sodium, potassium and ammonium salts (also their carbonate and hydroxide salt)</li> <li>• All nitrates</li> <li>• Most common chlorides</li> <li>• Most common sulfates</li> </ul>
<b>Insoluble in water</b>	<ul style="list-style-type: none"> <li>• <b>Silver chloride, lead chloride</b></li> <li>• <b>Lead sulfate, barium sulfate, calcium sulfate, strontium sulfate</b></li> <li>• Most common carbonates</li> <li>• Most common hydroxides</li> </ul>

### 2.1.3 Amount of substance

- Definitions

Term	Definition
<b>Mole</b>	A mole is the amount of a substance that contains the Avogadro number of elementary particles / the amount of a substance that contains the same amount of particles as 12 g of carbon-12.
<b>Molar mass / <i>M</i></b>	The mass in grams in each mole of the substance, measured in g mol <sup>-1</sup> .
<b>Hydrated</b>	A crystalline compound that contains water (e.g. CuSO <sub>4</sub> ·5H <sub>2</sub> O <sub>(s)</sub> ).
<b>Anhydrous</b>	A crystalline compound containing no water (e.g. CuSO <sub>4(s)</sub> ).
<b>Water of crystallisation</b>	Water molecules that form part of the crystalline structure of a compound (e.g. H <sub>2</sub> O in CuSO <sub>4</sub> ·5H <sub>2</sub> O <sub>(s)</sub> ).
<b>Stoichiometry</b>	The relative quantities of substances in a reaction.
<b>Standard solution</b>	A solution of known concentration.
<b>Limiting reagent</b>	The reactant that is not in excess and will be used up in the reaction.

- Amount of substance
  - Symbol *n*
  - Measured in moles (symbol mol)
  - \* Always use **decimals (not fractions)** in **every step** of a calculation
- Avogadro constant / N<sub>A</sub>
  - 6.02×10<sup>23</sup> mol<sup>-1</sup>
  - The number of particles per mole
- Concentration (*c*)
  - Unit = mol dm<sup>-3</sup> (aka molar / M) or g dm<sup>-3</sup>
  - mol dm<sup>-3</sup>:  $c = \frac{n}{V} = \frac{\text{number of moles}}{\text{volume (in dm}^{-3}\text{)}}$

- $\text{g dm}^{-3}: c = \frac{\text{mass (in g)}}{\text{volume (in dm}^{-3}\text{)}}$
- Concentration in  $\text{mol dm}^{-3} = \frac{\text{concentration in g dm}^{-3}}{M_r}$
- Room temperature and pressure (RTP)
  - Temp = 20 °C / 293 K
  - pressure = 1 atm or  $1.01 \times 10^5 \text{ Nm}^{-2}$
- Standard temperature and pressure (STP)
  - Temp = 0 °C / 273 K
  - pressure = 1 atm or  $1.01 \times 10^5 \text{ Nm}^{-2}$
- Molar gas volume /  $V_m$ 
  - The volume per mole of gas at a stated temperature and pressure
  - Under RTP: 1 mol =  $24 \text{ dm}^3 = 24,000 \text{ cm}^3$
  - Under STP: 1 mol =  $22.4 \text{ dm}^3 = 22,400 \text{ cm}^3$
- Ideal gas equation
  - $pV = nRT$
  - $p$  = pressure (Pa or  $\text{N m}^{-2}$ )
  - $V$  = volume ( $\text{m}^3$ )
  - $n$  = amount of gas molecules (mol)
  - $R$  = ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
  - $T$  = temperature (**K not °C**)
  - Rearranged:  $\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$
- Ideal gas assumptions
  - Random motion in straight lines
  - Molecules behave as rigid spheres
  - Pressure is due to collisions between the molecules and the walls of the container
  - Elastic collisions between the molecules and between the molecules and the walls of the container
  - Temperature of the gas  $\propto$  average KE of the molecules
  - The molecules occupy an entirely negligible volume
  - No intermolecular forces between the gas molecules
- Percentages yield
  - Percentage yield =  $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$
  - Actual yield: the amount of the product obtained from a reaction
  - Theoretical yield: the yield resulting from complete conversion of reactants into products
  - Reasons for < 100% percentage yield
    - Reaction did not go to completion
    - Side reactions may have taken place along the main reaction
    - Purification of the product may result in the loss of some products
- Atom economy
  - Atom economy =  $\frac{\text{sum of masses of useful product(s)}}{\text{sum of masses of all products or reactants}} \times 100\%$   
 $= \frac{\text{sum of molar masses of useful products}}{\text{sum of molar masses of all products or reactants}} \times 100\%$
- Benefits of high atom economy
  - More efficient industrial process
  - Preserve raw materials
  - Reduce waste
- Means to improve sustainability
  - Use processes with high atom economy and fewer steps
  - Redesign methods to use less hazardous starting materials
  - Use milder reaction conditions / better catalysts / less hazardous solvents
- Experimental techniques

Variable measured	Method

<b>Mass</b>	<ul style="list-style-type: none"> <li>• Use a digital mass balance</li> <li>• Choose a balance with a suitable resolution for the experiment</li> </ul>
<b>Volume of solution</b>	<ul style="list-style-type: none"> <li>• Use a measuring cylinder</li> <li>• Standard solution: use volumetric flask</li> </ul>
<b>Gas produced</b>	<ul style="list-style-type: none"> <li>• Use a gas syringe / measure mass lost on a balance and calculate the number of moles of gas produced</li> </ul>

- Types of formulae

Formula	Meaning
<b>Empirical formula</b>	The <b>simplest whole number ratio</b> of atoms of each element present in a compound.
<b>Molecular formula</b>	The number and type of atoms of each element in a molecule ( <b>if the elements are the same then combine them, e.g. not CH<sub>3</sub>COOH, use C<sub>2</sub>H<sub>4</sub>O<sub>2</sub></b> ).
<b>Displayed (graphical) formula</b>	Shows all the bonds in the structure.
<b>Structural formula</b>	A molecular formula that shows not only what atoms are present but also how they are joined together.

## 2.1.4 Acids

- Acids
  - When dissolved in water an acid releases H<sup>+</sup> ions (proton) into the solution
  - Common acids
    - HCl
    - H<sub>2</sub>SO<sub>4</sub>
    - HNO<sub>3</sub>
    - CH<sub>3</sub>COOH
- Bases
  - React with acid by **accepting H<sup>+</sup> ions (protons)** and neutralising the acid to form a salt
  - Common bases
    - Carbonates
    - Hydrogencarbonates
    - Metal oxides
    - Metal hydroxides
    - Ammonia (accept H<sup>+</sup> and form NH<sub>4</sub><sup>+</sup> ions)
- Alkalis
  - Bases that dissolve in water and release OH<sup>-</sup> ions into the solution
  - Common alkalis
    - NaOH
    - KOH
    - NH<sub>3</sub>
- Salt
  - When the H<sup>+</sup> in an acid is replaced by a positive ion
- Strong and weak acid
  - Both release H<sup>+</sup> ions / H<sup>+</sup> donor in aqueous solutions
  - Strong acid
    - **Completely dissociates** in aqueous solutions / releases all hydrogen atoms as H<sup>+</sup> ions
    - e.g. HCl(aq) → H<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)
  - Weak acid
    - **Partially dissociates** in aqueous solutions / only releases a portion of available hydrogen atoms as H<sup>+</sup> ions
    - e.g. CH<sub>3</sub>COOH(aq) ⇌ H<sup>+</sup>(aq) + CH<sub>3</sub>COO<sup>-</sup>(aq)
- Neutralisation
  - The reaction of acids with bases (including carbonates, metal oxides and alkalis) to form salts

- Ionic equation:  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
- Preparing standard solution
  - Solid weighed accurately **using a balance with 2 dp or more**
  - Dissolve solid in a beaker
    - Use less distilled water than needed to fill the volumetric flask to the mark
  - Transfer the solution to (250 cm<sup>3</sup>) volumetric flask
    - Rinse the beaker and transfer washings to the flask so the last traces of the solution is transferred to the volumetric flask
  - Volumetric flask is filled to the graduation line
    - Add distilled water a drop at a time using a dropping pipette
    - Keep adding until the bottom of the meniscus lines up exactly with the mark
  - Mix the solution thoroughly
    - Volumetric flask is sealed with a stopper and inverted several times
- Titration
  - Add measured volume of one solution to conical flask using pipette
    - Typical tolerances: 10 cm<sup>3</sup>:  $\pm 0.04 \text{ cm}^3$ , 25 cm<sup>3</sup>:  $\pm 0.04 \text{ cm}^3$ , 50 cm<sup>3</sup>:  $\pm 0.10 \text{ cm}^3$
  - Add other solution to burette, record initial reading
  - Add a few drops of indicator to conical flask (phenolphthalein / methyl orange)
  - Run solution from burette into conical flask until it reaches the end point
    - Swirl the flask while the solution is added
  - Record final reading
  - Titre = final reading - initial reading
  - First titre carried out quickly to get approximate titre
  - Repeat accurately by adding solution dropwise as the end point is approached
  - Carry out until two accurate titres are concordant (within 0.1 cm<sup>3</sup>)
  - \* Only use concordant results for calculating the mean titre

## 2.1.5 Redox

- Definitions

Term	Definition
<b>Redox reactions</b>	A reaction involving reduction and oxidation.
<b>Oxidising agent</b>	A reagent that <b>accepts / takes in</b> electrons.
<b>Reducing agent</b>	A reagent that <b>donates / gives out</b> electrons.
<b>Oxidation number</b>	A measure of the number of electrons that an atom uses to bond with atoms of another element. Oxidation numbers are derived from a set of rules.

- Oxidation number (oxidation state) rules
  - Elements
    - **Always 0**
    - Any bonding is to atoms of the same element in pure elements
  - Compound and ions
    - Each atom in a compound has an oxidation number
    - Sign is placed before the number
    - Sum of oxidation numbers in a compound / ion = total charge
- Fixed oxidation numbers

Combined element	Oxidation number
<b>O (normally)</b>	-2
<b>H (normally)</b>	+1
<b>F</b>	-1
<b>Group 1</b>	+1
<b>Group 2</b>	+2

Group 3	+3
---------	----

- Oxidation number for special cases

Combined element	Oxidation number
H in metal hydrides (e.g. NaH, CaH <sub>2</sub> )	-1
O in peroxide ions (O <sub>2</sub> <sup>2-</sup> )	-1
O bonded to F (e.g. F <sub>2</sub> O)	+2

- Roman numerals in chemical names
  - Show oxidation number without sign
  - Nitrate = assume to be NO<sub>3</sub><sup>-</sup>
  - Sulfate = assume to be SO<sub>4</sub><sup>2-</sup>
  - e.g. chlorate(I) = ClO<sup>-</sup>
- Redox reaction
  - Oxidation
    - Gain of oxygen
    - Loss of hydrogen
    - Loss of electrons
    - Increase in oxidation number
  - Reduction
    - Loss of oxygen
    - Gain of hydrogen
    - Gain of electrons
    - Decrease in oxidation number
  - \* Oxidation and reduction always **happen together**
- Redox reaction of acids
  - Metal + acid → salt + hydrogen
  - Metal oxidised (oxidation number increases from 0 to ...)
  - Hydrogen in acid reduced (oxidation number decreases from +1 to 0)
  - (Iron is normally Fe<sup>2+</sup> in redox reactions)

## 2.2 Electrons, bonding and structure

### 2.2.1 Electron structure

- Definitions

Term	Definition
<b>Atomic orbitals</b>	A region around the nucleus that can hold up to two electrons with opposite spins.
<b>Sub-shells</b>	A group of orbitals of the same type within a shell.
<b>Electron configuration</b>	A shorthand method for showing how electrons occupy sub-shells in an atom.

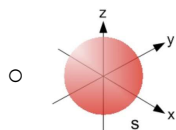
- Number of electrons that can fit in each shell

Shell number $n$	Number of electrons ( $= 2n^2$ )
<b>1</b>	2
<b>2</b>	8
<b>3</b>	18
<b>4</b>	32

- Types of orbitals

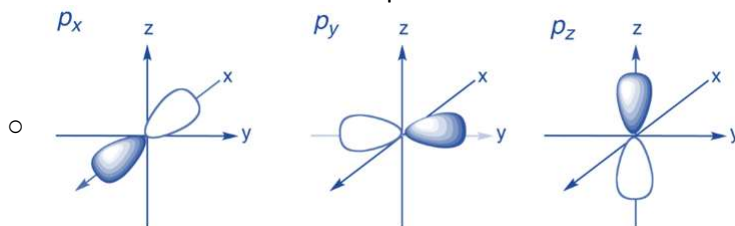
- s-orbitals

- **Spherical** shape
- Each shell from  $n = 1$  contains 1 s-orbital
- Greater shell number  $n$  = greater radius of its s-orbital



- p-orbitals

- **Dumb-bell** shape
- Three separate p-orbitals at right angles to one another:  $p_x$ ,  $p_y$ ,  $p_z$
- Each shell from  $n = 2$  contains 3 p-orbitals
- Greater shell number  $n$  = its p-orbital is further from the nucleus



- d-orbitals

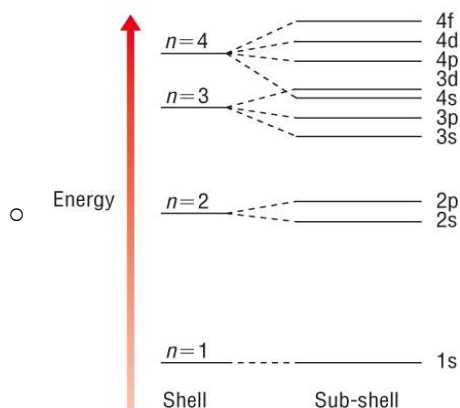
- Each shell from  $n = 3$  contains 5 d-orbitals

- f-orbitals

- Each shell from  $n = 4$  contains 7 f-orbitals

- Filling of sub shells and orbitals

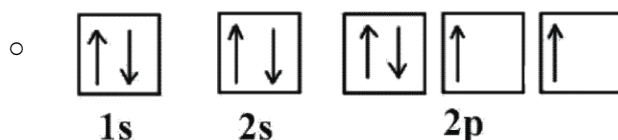
- Sub shells fill in the order of increasing energy ( $1s \rightarrow 2s \rightarrow 2p \dots$ )



\* 4s is filled before 3d

- Inside each sub-shell
  - The orbitals all have the same energy within a sub-shell
  - One electron occupies each orbital before pairing starts to prevent any repulsion between paired electrons
  - Opposite spins within each orbital (one  $\uparrow$  and one  $\downarrow$ ) as both electrons are negatively charged and repel one another so this minimises repulsion
  - The paired electrons are easier to remove than the unpaired ones

### Oxygen



- More than one orbital within a sub-shell = the orbitals are degenerate (all the same)
- Writing electron configuration of atoms
  - e.g. Li =  $1s^2 2s^1$ , F =  $1s^2 2s^2 2p^5$
  - Shorthand notation: in terms of the previous noble gas + outer electron sub-shells
    - e.g. Krypton =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$  = [Ar]  $3d^{10} 4s^2 4p^6$
    - **Always show outer shell electrons**
  - (4s can be written before 3d)
- Exceptions of atom electron configurations
  - Chromium: [Ar]  $3d^5 4s^1$
  - Copper: [Ar]  $3d^{10} 4s^1$
  - Chromium and copper do not follow the expected pattern
    - Half-filled / fully filled d sub-shell gives **additional stability**
- Electron configuration of ions
  - The highest energy subshell gain or lose electrons
  - d-block elements
    - 4s is at a lower energy level than 3d sub-shell so it is filled first
    - Once filled the energy level of 3d falls below 4s so 4s empties before 3d

## 2.2.2 Bonding and structure

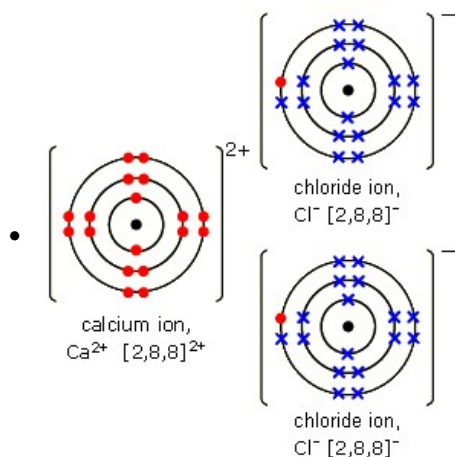
- Definitions

Term	Definition
<b>Polarity</b>	There is an uneven distribution of electrons.
<b>Polar molecule</b>	A molecule with an overall dipole, having taken into account any dipole across bonds and the shape of the molecule.
<b>Bond angle</b>	The angle between 2 bonds in an atom.
<b>Electronegativity</b>	A measure of the attraction of a bonded atom for the pair of electrons in a covalent bond.
• <b>Dipole</b>	A separation in electrical charge so that one atom of a polar covalent bond, or one end of a polar molecule, has a small positive charge, $\delta^+$ , and

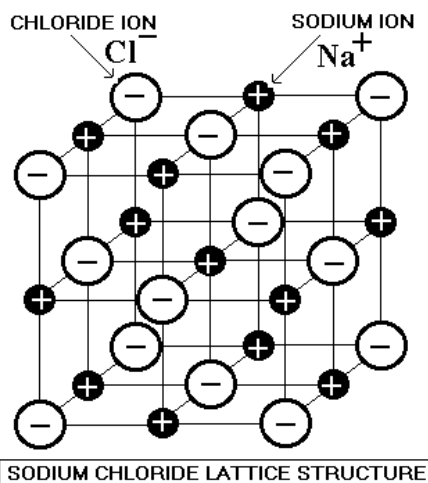


	the other has a small positive charge, $\delta^-$ .
<b>Intermolecular forces</b>	An attractive force between molecules. Can be London forces, permanent dipole-dipole interactions or hydrogen bonding.
<b>Giant ionic lattice</b>	A three dimensional structure of oppositely charged ions, bonded together by strong ionic bonds.
<b>Simple molecular lattice</b>	A three dimensional structure of molecules, bonded together by weak intermolecular forces.

- Ionic bonding
  - The electrostatic attraction between positive and negative ions
  - Occurs between atoms that have a **big difference in electronegativity** (usually metals and non-metals)
- Dot and cross diagram



- Structure of ionic compounds
  - Each ion attracts oppositely charged ions strongly in **all directions**
  - Forms a **giant lattice structure** containing many ions
  - Every positive ion is surrounded by negative ions; every negative ion is surrounded by positive ions
  - Regular arrangement of ions = regular, predictable shapes depending on size of ions
    - NaCl = always cubic
    - MgSO<sub>4</sub>, CuSO<sub>2</sub>, etc. = not cubic

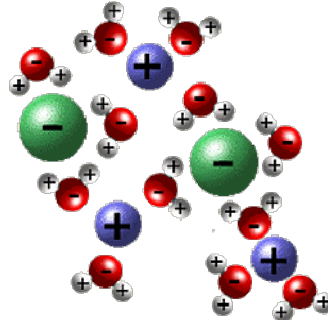
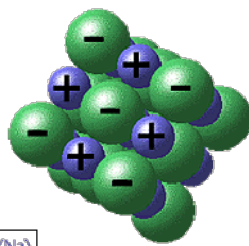


- Properties
  - High melting and boiling points
    - **Strong** electrostatic forces of attraction between oppositely charged ions in the **giant ionic lattice**
    - A high temperature is needed to provide the large amount of energy needed to overcome the strong electrostatic attraction
    - Higher for ions with greater ionic charges due to stronger attraction between ions
      - \* Ionic substances with complex ions: can decompose before they reach melting point
  - Dissolve in polar solvents (e.g. water)

- Salvation / hydration
  - Polar solvent molecules attract the ions
  - Anions to positive dipole, cations to negative dipole
  - Energy is released in the process
  - Molecules break down the lattice + surround each ion in solution
- Strong ionic bond must be overcome for the substance to dissolve
  - Energy to do this is supplied by solvating / hydrating the ions / absorbed from the surroundings
- If the compound is made of ions with strong charges the attraction can be too strong to be broken down → less soluble
- Solubility depends on
  - Relative strengths of attractions within the lattice
  - Attraction between ions + water molecules

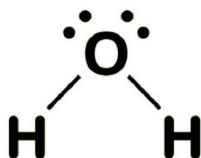
NaCl crystal structure

NaCl in water

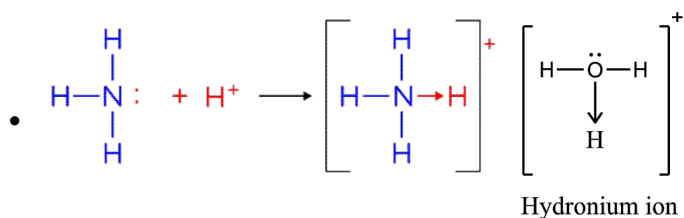


sodium (Na)  
chlorine (Cl)

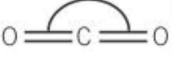
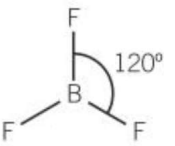
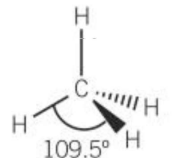
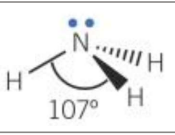
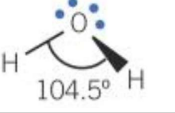
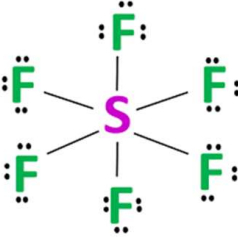
- Does not conduct electricity in solid state
  - Ions held in fixed positions
  - No mobile charge carriers
- Conduct electricity when dissolved or molten
  - The solid ionic lattice breaks down
  - Ions are free to move as mobile charge carriers
- Covalent bonding
  - The **strong** electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms
  - Occur between atoms that have a **small difference in electronegativity**
  - Formed when the atomic orbitals of the two atoms overlap and combine to form a new orbital (still holding 2 electrons max)
- Covalent substance structure
  - Attraction is localised between the shared pair of electrons and the nuclei of the bonded atoms only
  - Results in small molecules consisting two or more atoms (simple molecular lattice if solid)
- Lone pairs / non-bonding pair
  - Paired electrons that are not shared



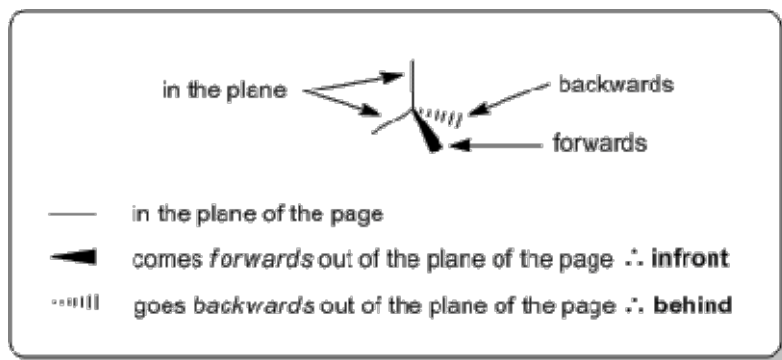
- Multiple covalent bond
  - The electrostatic attraction is between two / three shared pairs of electrons and the nuclei of the bonded atoms
- Dative covalent bonds / coordinate bonds
  - The shared pair of electrons is supplied by one of the bonding atoms only
  - The shared pair is originally a lone pair of electrons on one of the bonded atoms
  - e.g. ammonia molecule donates its lone pair of electrons to a  $\text{H}^+$  ion to form  $\text{NH}_4^+$  ion



- Exceptions
  - Boron
    - Only 3 outer shell electrons can be paired → only forms 3 pairs
    - e.g.  $\text{BF}_3$  only has 6 electrons around the boron atom
  - Phosphorus, sulfur, chlorine (expansion of the octet)
    - Outer electrons are in  $n = 3$  shell which can hold up to 18 electrons
    - More electrons are available for bonding (can have more than 8 electrons in outer shell e.g.  $\text{ClF}_7$ )
- Average bond enthalpy
  - A measurement of covalent bond strength
  - Higher average bond enthalpy = stronger covalent bond
- Molecule shape and bond angles
  - Electron pairs around the central atom repel each other as far apart as possible
  - Lone pairs repel more strongly than bonded pairs
  - They repel bonded pairs slightly closer together → reducing the bond angle
    - 4 pairs / regions: bond angle reduced by approx.  $2.5^\circ$  per lone pair
  - The greater the number of electron pairs the smaller the bond angle
  - (Mention the number of bonded pairs and lone pairs)

Electron pairs / regions	Name	Shape and bond angle
2	Linear	$180^\circ$ 
3	Trigonal planar	
4 (no lone pairs)	Tetrahedral	
4 (1 lone pair)	Pyramidal	
4 (2 lone pairs)	Non-linear	
6	Octahedral	 <p>Remember <math>\text{SF}_6</math> as an example of this</p>

- Bond representations



- Predicting molecular shape of ions
  - Ions with oxygen
    - Add an electron to an oxygen atom for every negative charge
    - Bonds can be single or double bond
  - Cations with hydrogen
    - Add positive charge by  $H^+$  ions
  - Others
    - Add / remove electrons from the central atom to match the charge
    - Pair up surrounding atoms and count bonded pairs and lone pairs
- Electronegativity
  - A measure of the attraction of a bonded atom for the pair of electrons in a covalent bond
  - Measured using Pauling electronegativity values (higher = attract bonded electrons more strongly)

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

- Important electronegativity values

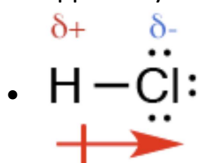
Element	Electronegativity
Fluorine	4.0
Oxygen	3.5
Chlorine	3.0
Nitrogen	3.0
Carbon	2.5
Hydrogen	2.1

- Electronegativity pattern
  - Electronegativity increases across the periodic table and up the periodic table
  - Across the periodic table the nuclear charge increases and the atomic radius decreases → attraction increases
  - Atomic radius increases down the table → attraction decreases
  - **Fluorine is the most electronegative element**
- Predicting type of bond

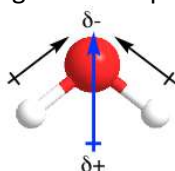
Bond type	Electronegativity difference
Covalent	0

<b>Polar covalent</b>	0 - 1.8
<b>Ionic</b>	> 1.8

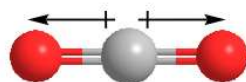
- Pure covalent bond
  - Non-polar bond
  - The bonded electron is shared equally between the bonded atoms
  - Happen when:
    - The bonded atoms are the same
    - The bonded atoms have same / similar electronegativity (e.g. carbon and hydrogen)
- Polar covalent bonds
  - Polar bond
  - The bonded electron pair is shared unequally between the bonded atom
  - When the bonded atoms are different and have different electronegativity values
  - Form permanent dipole: small positive ( $\delta+$ ) / negative charge ( $\delta-$ ) on the two bonded atoms, oppositely charged on each



- Polar / non-polar molecules
  - Polar molecules require polar bonds with dipoles that **do not cancel out** due to their direction
  - If the molecule is symmetrical in 3D **and** the polarities cancel out the molecule is non-polar
  - e.g. overall dipole in  $\text{H}_2\text{O}$ , cancels out in  $\text{CO}_2$  and methane



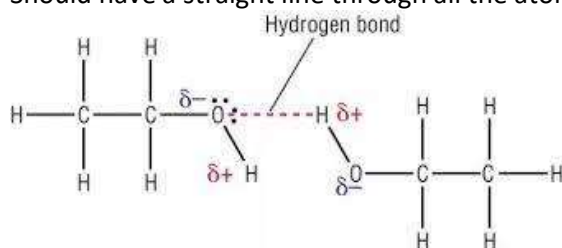
$\text{H}_2\text{O}$ , bend shape  
**polar**



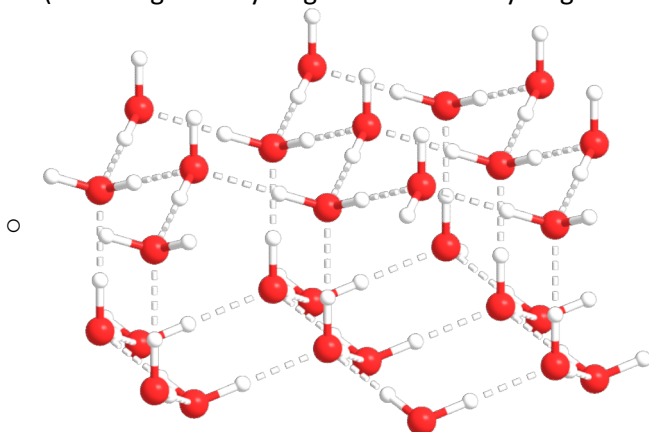
$\text{CO}_2$ , linear shape  
**non-polar**

- Types of intermolecular forces
  - London forces / induced dipole-dipole **interactions** / dispersion forces (van der Waals' forces)
  - Permanent dipole-dipole **interactions** (van der Waals' forces)
  - Hydrogen bonding (a special type of permanent dipole-dipole interactions)
- London forces / induced dipole-dipole interactions
  - Exist between all molecules, only temporary
  - Creation
    - Movement of electrons produces changing dipole in a molecule
    - There is an uneven distribution of electrons which causes an instantaneous dipole
    - At any instant an instantaneous dipole will exist but position shifts constantly
    - Instantaneous dipole induces a dipole on a neighbouring molecule
    - The induced dipole induces dipoles on further molecules, they then attract one another
    - Electrons move and the dipole is gone and the attraction disappears and re-appears elsewhere
  - Very weak - the weakest of all intermolecular forces
    - The **only intermolecular** force that exist between non-polar simple covalent molecules
    - They have very low melting and boiling points (normally gases / volatile liquids under room temperature)
- London forces strength pattern
  - Stronger down the periodic table
  - More electrons in each molecule
  - Larger instantaneous + induced dipoles
  - Greater induced dipole-dipole interactions
  - Stronger attractive forces between molecules
- Permanent dipole-dipole interactions
  - Act between **permanent dipoles** in polar molecules

- Permanent dipole-dipole interactions is much stronger than London forces
  - Polar molecules have both London forces and permanent dipole-dipole interactions
  - Mean melting and boiling point of polar molecules is much greater
- Hydrogen bond
  - Occurs when a highly de-shielded hydrogen in one molecule is attracted to a lone pair on a **N, O or F** atom in another molecule
    - Highly de-shielded hydrogen: a hydrogen atom directly bonded to an **very electronegative atom (N, O or F)**
  - A lone pair of electrons on an electronegative atom forms bond with the  $\delta^+$  of a hydrogen atom in a different molecule
  - Strongest type of intermolecular attractions
    - Molecules with hydrogen bonds between them have relatively high melting and boiling points
    - More hydrogen bond = greater increase in melting and boiling points
- Hydrogen bond diagram
  - Shown by a dotted line between lone pair + hydrogen atom
  - Should have a straight line through all the atoms involved



- Anomalous properties of  $\text{H}_2\text{O}$ 
  - Solid less dense than liquid
    - Each water molecule can form **4 hydrogen bonds** (2 lone pairs + 2 hydrogen atoms in O-H bond)
    - Hydrogen bonds extend outwards and hold water molecules apart in an **open lattice structure**
    - Water molecules form an tetrahedral lattice full of holes
    - Water molecules in ice are further apart than in water
    - (Bond angle for hydrogen involved in hydrogen bond is  $180^\circ$ )



- Relatively high melting and boiling points
  - Has hydrogen bond (much stronger) + PDD + IDD between molecules
  - A large quantity of energy is needed to break hydrogen bonds
  - When ice lattice breaks the arrangement of hydrogen bonds is broken
  - When water boils hydrogen bonds break completely
- Simple molecular substance
  - Made of simple molecules (small units with a definite number of atoms)
  - Simple molecules form a regular structure called a simple molecular lattice in the solid state
    - Shape of the lattice is determined by the packing pattern of the molecules
    - Molecules held together by weak intermolecular forces
    - Atoms within each molecule bonded together by strong covalent bonds (intramolecular forces)

- Properties of non-polar simple molecular substances
  - Low melting and boiling point
    - Only weak London forces between molecules
    - Weak intermolecular forces can be broken by energy present at low temperatures
  - Solubility
    - Non-polar solvent
      - Tend to be soluble
      - Intermolecular forces form between the molecules and the solvent
      - Weaken the intermolecular forces in the simple molecular lattice
      - The intermolecular forces break and the compound dissolves
    - Polar solvent
      - Tend to be insoluble
      - Little interaction between the lattice and the solvent molecules
      - Intermolecular bonding in solvent too strong to be broken
  - Non-conductors of electricity
    - No free electrons or mobile ions in simple molecular substances, cannot complete a circuit
    - No mobile charge carriers
- Properties of polar simple covalent substance
  - Higher melting and boiling point
    - Permanent dipole-dipole interactions are stronger than London forces
    - More energy is required to break them
  - Solubility
    - Hard to predict
    - Usually soluble polar solvents: polar solute/solvent molecules can attract each other
    - If they contain a significant non-polar region they may also be soluble in non-polar solvents
    - Solubility depends on strength of dipole
  - Electrical conductivity
    - Can conduct electricity if they can ionise and form mobile ions

## 3.1 The periodic table

### 3.1.1 Periodicity

- Definitions

Term	Definition
<b>Periodicity</b>	A repeating trend in physical and chemical properties of the elements across the periodic table.
<b>Groups</b>	A vertical column in the periodic table. Elements in a group have similar chemical properties and their atoms have the same number of outer shell electrons.
<b>Periods</b>	A horizontal row in the periodic table. Elements show trends in properties across a period.
<b>Shielding effect</b>	The repulsion between electrons in different inner shells. Shielding reduces the net attractive force between the positive nucleus on the outer shell electrons.
<b>Metallic bonding</b>	The strong electrostatic attraction between the regularly arranged metal cations and the delocalised valence electrons between them.
<b>Delocalised electrons</b>	Electrons shared between more than two electrons.
<b>Giant metallic lattice</b>	A three dimensional structure of positive ions and delocalised electrons, bonded together by strong metallic bonds.
<b>Giant covalent lattice</b>	A three dimensional structure of atoms, bonded together by strong covalent bonds.

- History

- Then

- Mendeleev arranged the elements in order of atomic mass
    - Swapped elements to line up to arrange them into groups of similar properties
    - Gaps left where he thought elements would be found
    - Predicted properties for missing elements
    - Newly discovered elements filled in the gap and matched the predicted properties

- Now

- Arranged in increasing atomic number
    - In vertical columns (groups) with same number of outer electrons + similar properties and horizontal rows (periods) giving number of highest energy electron shell

- Arrangement

- In the order of increasing atomic number
  - Periodicity: in periods showing repeating trends in physical and chemical properties e.g. metals → non-metals
  - In groups with similar properties

- Electron configuration pattern

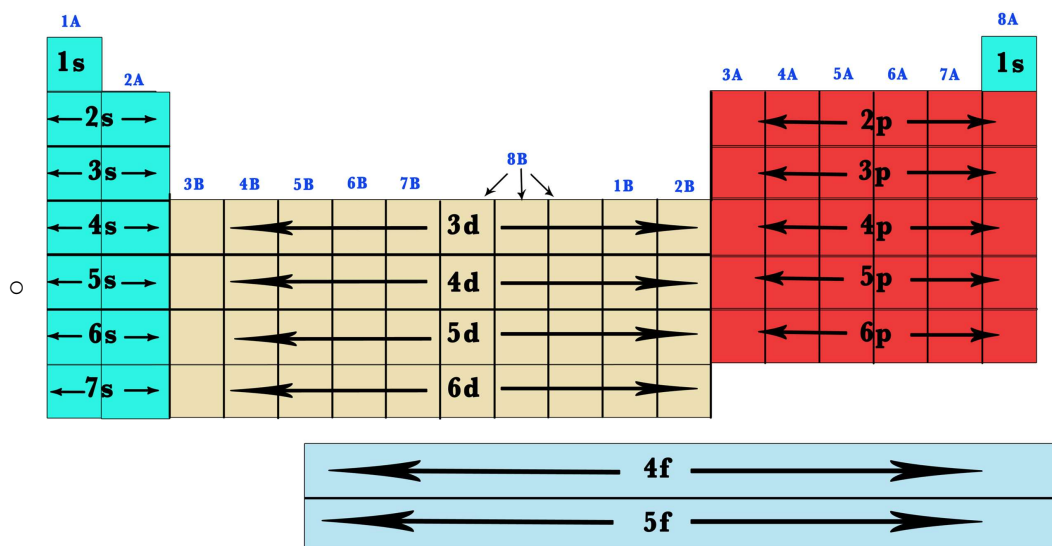
- Across period

- Each period starts with an electron in a new highest energy shell
    - Period 2: 2s fills → 2p fills
    - Period 3: 3s fills → 3p fills
    - Period 4: only 4s and 4d occupied in  $n = 4$  shell

- Blocks

- \* s/p/d/f-block meaning: the **highest energy / outer electron** is in a s/p/d/f-orbital
  - S, p, d and f block



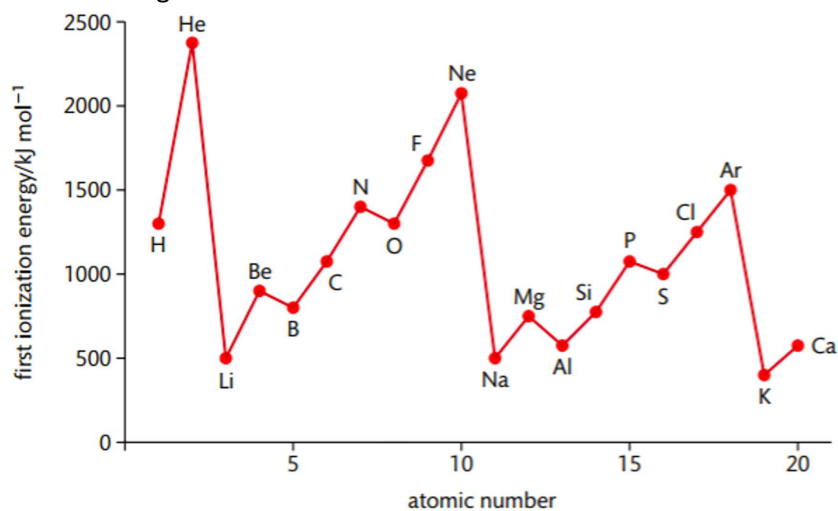


- Name of groups

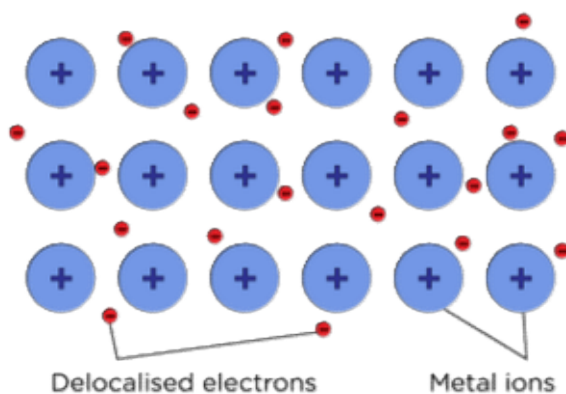
Group number	Name
1	Alkali metal
2	Alkaline earth metals
3-12	Transition elements
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases

- First ionisation energy
  - Energy required to remove one electron from each **atom** in one mole of **gaseous** atoms of an element, forming one mole of **gaseous**  $1+$  ions
  - Unit =  $\text{kJ mol}^{-1}$
  - Equation: e.g.  $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$  (first ionisation energy =  $+496 \text{ kJ mol}^{-1}$ )
- Factors affecting ionisation energy
  - Atomic radius
    - Greater distance between nucleus and outer electrons = less nuclear attraction
    - Large effect on ionisation energy as force of attraction falls sharply with increasing distance
    - \* Effect of increase atomic radius outweighs the effect of increasing nuclear charge
  - Nuclear charge
    - More protons in nucleus (greater nuclear charge) = greater attraction between the nucleus and the outer electrons = increase in ionisation energy
  - Electron shielding
    - Shielding effect: electrons are negatively charged so inner shell electrons repel outer-shell electrons
    - Reduces the attraction between nucleus and outer electrons  $\rightarrow$  reduce ionisation energy
    - \* Effect of shielding outweighs the effect of increasing nuclear charge
- First ionisation energy trends across a period
  - Increases across a period
    - Nuclear charge increases
    - Same number of shells so similar shielding
    - Atomic radius decreases
    - Nuclear attraction increases  $\rightarrow$  first ionisation energy increases
  - Falls when the p sub-shell is starting to be filled (e.g.  $\text{Li} \rightarrow \text{Be}$ )
    - $2p / 3p$  sub-shell has a higher energy than  $2s / 3s$  sub-shell so the electron is easier to remove
    - \* Still larger than IE before the decrease

- Falls when pairing of electrons in p sub-shell starts (e.g. N → O)
  - Paired electrons in one of the p orbitals repel one another so it is easier to remove an electron from the atom
- \* Still larger than IE before the decrease



- First ionisation energy trend down a group
  - Decrease down a group
  - Atomic radius increases
  - More inner shells so shielding increases
  - \* Increase in atomic radius and shielding outweighs the increasing nuclear charge
  - Nuclear attraction on outer electrons decreases → first ionisation energy decreases
- Successive ionisation energy pattern
  - Equation: e.g.  $\text{Mg}^+(\text{g}) \rightarrow \text{Mg}^{2+}(\text{g}) + \text{e}^-$
  - Larger than the previous one
    - After the first electron is lost the remaining electrons are pulled closer to the nucleus
    - Nuclear attraction on the remaining electrons increases so more energy needed
  - Large increase when shell change
    - Shell closer to the nucleus → stronger nuclear attraction and less shielding so more energy needed
    - Going to a more inner shell = extremely large increase
  - Smaller but still large increase when going to a new sub-shell / sub-shell become half filled
  - Can be used to work out the number of electrons in each shell + group number of the element
- Metallic bonding structure
  - Regularly arranged metal cations sitting in a sea of delocalised electrons
  - Each atom donate its negative outer shell electrons to a shared pool of electrons which are delocalised throughout the whole structure
  - Cations left behind = nucleus + inner shell electrons
  - Cations are fixed in position
  - Delocalised electrons are mobile and free to move throughout the structure
  - Forms a giant metallic lattice



- Properties of metals

- All conduct electricity
  - Delocalised electrons can move through the structure and carry charge through the structure when a voltage is applied across a metal
  - More delocalised electrons → more electrons can move → better conductivity
  - Conducts electricity both in solid state and when molten
- Most have high melting and boiling points
  - Depends on the strength of metallic bonds
    - Greater cation charge = stronger attractive forces as more electrons are delocalised and forces between electrons + cations are stronger
    - Larger ions = weaker attractive forces due to larger atomic radius decreasing the charge density
  - High temperature needed to provide the large amount of energy to overcome strong electrostatic attraction between the cations and the electrons
  - Melting and boiling points decrease down the group
- Dissolve in liquid metals only
  - Similar force between particles
  - Any interaction between polar / non-polar solvent + solute lead to a reaction rather than dissolving
    - Forces between particles are too large so it is not energetically favourable for them to mix
- Giant covalent structures
  - **Boron, carbon allotropes, and silicon (Si, SiO<sub>2</sub>, SiC)**
  - A network of atoms bonded by strong covalent bonds to form a giant covalent lattice
- Diamond / silicon
  - 4 outer shell electrons of each atom form 4 covalent bonds with other carbon / silicon atoms
  - Tetrahedral structure
  - 109.5° bond angle due to electron-pair repulsion
  - High melting and boiling points
    - Atoms held together by strong covalent bonds
    - High temperatures are needed to provide the large quantity of energy needed to break the strong covalent bonds
  - Non-conductors of electricity
    - All 4 outer-shell electrons involved in covalent bond so no charged particles or mobile ions are available for conducting electricity
- Graphite
  - Flat 2D sheets of hexagonally arranged carbon atoms (trigonal planar 120°)
  - Layers bonded by weak London forces
  - Very hard as there are no points of weakness in the structure
  - High melting and boiling points
    - Atoms held together by strong covalent bonds
    - High temperatures are needed to provide the large quantity of energy needed to break the strong covalent bonds
  - Can conduct electricity
    - One electron from each carbon atom is delocalised and is available for conductivity
- Graphene
  - Single layer of graphite
  - Hexagonally arranged (trigonal planar 120°) carbons
  - One of the thinnest + strongest material in existence (atoms held together by strong covalent bond)
  - High melting and boiling points
    - Atoms held together by strong covalent bonds
    - High temperatures are needed to provide the large quantity of energy needed to break the strong covalent bonds
  - Can conduct electricity
    - One electron from each carbon atom is delocalised
    - They can move and conduct electricity
- Applications of graphene

- Electronics
  - Flexible displays
  - Wearables
  - Other next-generation electronic devices
- Atomic radii trend across a period
  - Atomic radii decreases across the period
  - Positive charge in nucleus and negative charge in the valence shell both increases
  - Shielding remains similar as the number of shells doesn't change
  - The attraction between the nucleus and the valence electrons increases
- Melting / boiling point trend across a period
  - Increases from Group 1 to 14
  - Sharp decrease between Group 14 to 15 - change from giant to simple molecular structures
  - Comparatively low from Group 15 to 18
    - The exact boiling points depend on the type of covalent bonding
    - Giant covalent bonding = very high melting and boiling points
    - Simple covalent bonding = depends on strength of intermolecular forces (London forces) which depends on the mass of the nucleus
    - Smaller molecular radius = lower boiling points (hence Group 18 has the lowest boiling points)

### 3.1.2 Group 2

- Definitions

Term	Definition
• <b>Oxidising agent</b>	A reagent that oxidises another species
<b>Reducing agent</b>	A reagent that reduces another species

- Comparison to Group 1 elements
  - Better electrical conductivity
    - More outer shell electrons → 2 electrons delocalised from each metal atom instead of 1
    - More delocalised electrons to move and carry electric current
  - Higher melting and boiling points
    - **More outer shell electrons** → 2 electrons delocalised from each metal atom instead of 1
    - Higher charge on metal cation
    - Stronger attraction between the metal ions and the delocalised electrons
- Redox reaction of Group 2 elements
  - Two outer shell in the outer s sub-shell
  - Lose two electrons to form 2+ ion with an electron configuration of a noble gas
  - Another species gain these two electrons and is reduced
    - Reducing agent as it reduce another species
- Redox with oxygen
  - $M(s) + O_2(g) \rightarrow 2MO(s)$
  - Each metal atom's oxidation number increases from 0 on LHS to +2 in MO on RHS
  - Each O decreases from 0 in  $O_2(g)$  on LHS to -2 in MO(s) on RHS
- Redox with water
  - $M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$
  - Each metal atom increases from 0 in M(s) on LHS to +2 in  $M(OH)_2(aq)$  on RHS
  - 2 hydrogen atoms in  $H_2O$  decreases from +1 in  $H_2O(l)$  on LHS to 0 in  $H_2(g)$  on RHS
  - The other 2 H atoms do not change their oxidation state and forms  $M(OH)_2(aq)$
  - Observations
    - More vigorous fizzing / bubbling down the group
    - Metal being more soluble down the group / dissolve faster down the group
    - Solution has a higher pH / more alkaline down the group
- Redox with dilute acids
  - Metal + acid → salt + hydrogen
  - Oxidation number change
    - Each metal atom increases from 0 in metal on LHS to +2 in salt on RHS

- Each H decreases from +1 in acid on LHS to 0 in H<sub>2</sub> on RHS
- \* **Barium / calcium / strontium sulfate** are **insoluble in water** so reaction stops quickly after the metal solid is coated with insoluble sulfate
- Reactivity trend
  - Reactivity increases down the group
  - First and second ionisation energy decreases down the group / easier to remove outer shell electrons
    - Increased atomic radius
    - Increased shielding
    - The effect of increasing nuclear charge is outweighed by the effects of increasing atomic radius and shielding
    - Attraction between the nucleus and outer electrons decreases
- Reaction of Group 2 oxides with water
  - $\text{MO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{M}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$
  - OH<sup>-</sup> ions are released and form alkaline solutions of the metal hydroxide
  - Hydroxides only slightly soluble in water
  - When the solution become saturated, addition of further metal oxide causes some ions to come out of the solution and form a solid precipitate:  $\text{M}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{M(OH)}_{2(\text{s})}$
  - Solubility of hydroxides increases down the group so the solution can contain more OH<sup>-</sup> ions and become more alkaline
    - $\text{Mg(OH)}_{2(\text{s})}$  slightly soluble → low OH<sup>-</sup> concentration, pH ≈ 10
    - $\text{Ba(OH)}_{2(\text{s})}$  more soluble → higher OH<sup>-</sup> concentration, pH ≈ 13
- Uses of Group 2 compounds as bases
  - $\text{Ca(OH)}_2$  in agriculture to neutralise acidic soil
    - Added to fields as lime
    - $\text{Ca(OH)}_{2(\text{s})} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$
    - Sodium or potassium hydroxides are not suitable as they would kill soil organisms and plants (too alkaline)
  - $\text{Mg(OH)}_2$ ,  $\text{MgCO}_3$  and  $\text{CaCO}_3$  are used as antacids in treating indigestion
    - They are weak bases that neutralise excess stomach acids (HCl) that causes the indigestion
    - e.g. milk of magnesia = suspension of  $\text{Mg(OH)}_2$  in water
    - $\text{Mg(OH)}_{2(\text{s})} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_{2(\text{aq})} + 2\text{H}_2\text{O(l)}$
    - $\text{CaCO}_{3(\text{s})} + 2\text{HCl(aq)} \rightarrow \text{CaCl}_{2(\text{aq})} + \text{H}_2\text{O(l)} + \text{CO}_{2(\text{g})}$
    - KOH and NaOH are not suitable as ingesting them would cause poisoning and potentially death

### 3.1.3 The halogens

- Trend in boiling points
  - Boiling point increases down the group
  - Halogens exist as diatomic molecules at RTP
  - Number of electron shells in the atom increases going down the group
  - The atom gets bigger + heavier
  - Number of electrons in the diatomic molecules increases
  - Stronger induced dipole-dipole interactions
  - More energy required to break the intermolecular forces

<b>F<sub>2</sub></b>	Gas	Boiling point increases down the group
<b>Cl<sub>2</sub></b>	Gas	
<b>Br<sub>2</sub></b>	Liquid	
<b>I<sub>2</sub></b>	Solid	
<b>At<sub>2</sub></b>	Solid	

- Appearance under different states

Halogen	Colour in natural state	Colour in aqueous solutions	Colour in organic solvents
F <sub>2</sub>	Pale yellow gas	/	/

• Cl <sub>2</sub>	Pale green <b>gas</b>	Pale green	Pale green
Br <sub>2</sub>	Red-brown <b>liquid</b>	Orange	Orange
I <sub>2</sub>	Shiny grey-black <b>solid</b>	<b>Brown</b>	<b>Violet</b>

- Redox reaction of halogens
  - Halogens all have s<sup>2</sup>p<sup>5</sup> electron configuration in their outer shell
  - They gain 1 electron to form 1- ion during redox reactions and gain the electron configuration of the nearest noble gas (reduced)
  - Another species loses electrons to halogen atoms so it is oxidised
  - Halogens are oxidising agents as they oxidise other species
  - Halide ions combine with metal ions to form white (ionic) solids which are **mostly soluble**
- Halogen-halide displacement reactions
  - Solution of hydrogen added to other halide solutions
  - If the halogen added is more reactive than the halide in the solution
    - It will displace the halide in the solution
    - The solution changes colour (from ... to ...)
  - Results
    - Cl<sub>2</sub> reacts with Br<sup>-</sup> (Cl<sub>2</sub>(aq) + 2Br<sup>-</sup>(aq) → 2Cl<sup>-</sup>(aq) + Br<sub>2</sub>(aq) orange)
    - Cl<sub>2</sub> reacts with I<sup>-</sup> (Cl<sub>2</sub>(aq) + 2I<sup>-</sup>(aq) → 2Cl<sup>-</sup>(aq) + I<sub>2</sub>(aq) violet)
    - Br<sub>2</sub> reacts with I<sup>-</sup> only (Br<sub>2</sub>(aq) + 2I<sup>-</sup>(aq) → 2Br<sup>-</sup>(aq) + I<sub>2</sub>(aq) violet)
    - I<sub>2</sub> doesn't react at all
  - Element displaced can be identified by adding cyclohexane (non-polar solvent, dissolve more readily) + mix
    - Use the colour of the top layer to identify the element being displaced
  - Show reactivity: Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>
- Trend in reactivity
  - Reactivity decreases down the group
  - Atomic radius increases
  - More inner shells so shielding increases
  - Effect of increasing nuclear charge is outweighed by increasing atomic radius and shielding
  - Less nuclear attraction between the nucleus and the outer shell
  - Harder for elements to capture an electron from another species and form 1- ions
- Disproportionation
  - A redox reaction in which the same element is both oxidised and reduced
- Chlorinating water
  - Chlorine reacted with water
 
$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HClO}(\text{aq}) + \text{HCl}(\text{aq})$$
  - |   |   |    |           |
|---|---|----|-----------|
| 0 | → | -1 | reduction |
| 0 | → | +1 | oxidation |
  - Used in water treatment systems to kill harmful bacteria
  - Bacteria killed by chloric(I) acid (HClO) and chlorate(I) ions (ClO<sup>-</sup>)
  - Chloric(I) acid also acts as a weak bleach e.g. indicator paper will turn red then white
- Benefits and risk of chlorinating water
  - Benefits
    - Kill bacteria in water treatment
    - Reduces the risk of waterborne diseases
  - Risks
    - Hazards of toxic chlorine gas → respiratory irritant in small concentrations, can be fatal if in large concentrations
    - Formation of chlorinated hydrocarbons may cause cancer
- Manufacturing bleach
  - React chlorine with **cold and dilute aqueous NaOH solution**

$$\text{Cl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaClO}(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
  - |   |   |    |           |
|---|---|----|-----------|
| 0 | → | -1 | reduction |
| 0 | → | +1 | oxidation |

- NaClO solution = bleach
- Halide test
  - See 3.1.4

### 3.1.4 Qualitative analysis

- Test for cations
  - Test for ammonium ion ( $\text{NH}_4^+$ )
    - $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$
    - **Aqueous sodium hydroxide** added to a **solution** of ammonium ion
    - Ammonia gas is produced (unlikely to see bubbles as it is very soluble in water)
    - Ammonia can be smelled / turns damp red litmus paper blue
- Test for anions (must be in this order)
  1. Carbonate test
    - Add dilute **nitric acid (not HCl or  $\text{H}_2\text{SO}_4$  if doing sulfate or halide test later)** to the **solid or solution** being tested
    - If there are bubbles then the compound could be a carbonate
      - $2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
    - Check the gas produced by bubbling it through lime water (calcium hydroxide)
    - Lime water will turn cloudy if the gas is carbon dioxide as a white precipitate of calcium carbonate forms
      - $\text{CO}_2(\text{g}) + \text{Ca}(\text{OH})_2(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$
  2. Sulfate test
    - Add barium chloride (barium nitrate if halide test needed later) to the **solution** of the compound
    - If white precipitate forms then  $\text{SO}_4^{2-}$  is present
      - $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
  3. Halide test
    - Add aqueous silver nitrate ( $\text{AgNO}_3$ ) to an **aqueous solution** of a halide
    - Silver halide precipitates as different colour
      - $\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightarrow \text{AgX}(\text{s})$
      - AgCl = white
      - AgBr = cream
      - AgI = yellow
    - Add aqueous ammonia to test the solubility of the precipitate (colours can be difficult to tell apart)
      - AgCl = soluble in dilute and concentrated  $\text{NH}_3(\text{aq})$  only
      - AgBr = soluble in concentrated  $\text{NH}_3(\text{aq})$  only, insoluble in dilute  $\text{NH}_3(\text{aq})$
      - AgI = insoluble in dilute and concentrated  $\text{NH}_3(\text{aq})$
- Correct sequence needed
  - Neither sulfate / halide produce bubbles with dilute acid → cannot have incorrect conclusion
  - $\text{BaCO}_3$  is white and insoluble in water so it gives a false positive result on carbonates as well in sulfate tests
  - $\text{Ag}_2\text{CO}_3$  and  $\text{Ag}_2\text{SO}_4$  both insoluble in water and form precipitates in the test so it gives a false positive result for carbonates and sulfates in halide tests

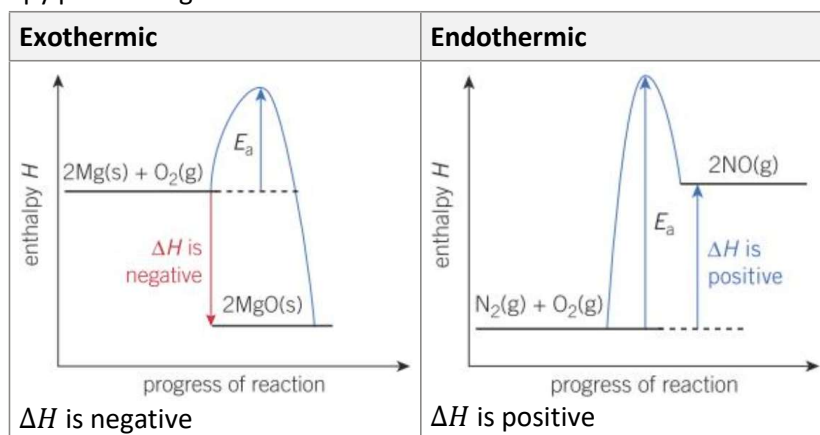
## 3.2 Physical chemistry

### 3.2.1 Enthalpy changes

- Definitions

Term	Definition
<b>Enthalpy / <math>H</math></b>	Measure of heat energy in a chemical system
<b>Chemical system</b>	The atoms, molecules or ions making up the chemicals
<b>Activation energy / <math>E_a</math></b>	The minimum energy required for a reaction to take place
<b>Standard state</b>	The physical state of a substance under standard conditions
<b>Enthalpy change of reaction / <math>\Delta_r H</math></b>	The enthalpy change associated with a stated equation in the <b>molar quantities shown in a chemical equation</b>
<b>Enthalpy change of formation / <math>\Delta_f H</math></b>	The enthalpy change that takes place when <b>1 mole of a compound</b> is formed from its elements
<b>Enthalpy change of combustion / <math>\Delta_c H</math></b>	The enthalpy change that takes place when <b>1 mole of a substance</b> reacts completely with oxygen (complete combustion)
<b>Enthalpy change of neutralisation / <math>\Delta_{\text{neut}} H</math></b>	The enthalpy change that accompanies the reaction of an acid by a base to form <b>1 mole of <math>\text{H}_2\text{O}_{(l)}</math></b>
<b>Enthalpy change of solution / dissolution</b>	The enthalpy change when <b>1 mole of a substance</b> is completely dissolved in water
<b>Hess's Law</b>	The enthalpy change in a chemical reaction is independent of the route it takes

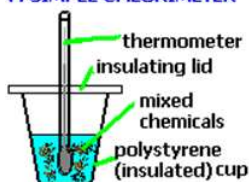
- (standard ... = under standard conditions : 298 K & 100 kPa, with all reactants and products in their standard states)
- Enthalpy change
  - $\Delta H = H(\text{products}) - H(\text{reactants})$
  - Can be positive (endothermic) or negative (exothermic)
- Conservation of energy
  - When a chemical reaction involving an enthalpy change takes place heat energy is transferred between the system and the surroundings
    - System = chemicals
    - Surroundings = apparatus, lab, etc. (everything that is not the system)
    - universe = system + surroundings
- Types of reactions
  - Exothermic reaction
    - Energy transferred from the system to the surroundings
  - Endothermic reaction
    - Energy transferred from the surroundings to the system
- Enthalpy profile diagrams



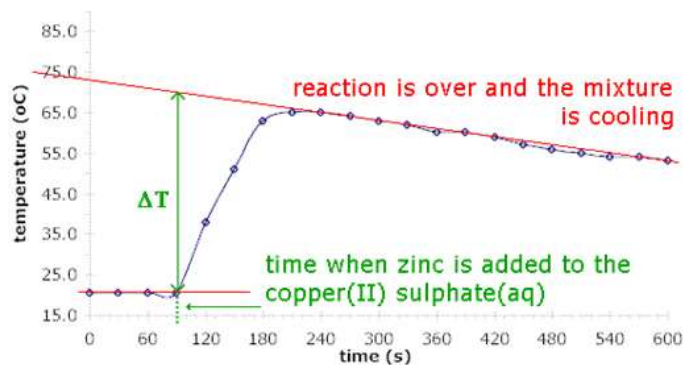


- \* The activation energy can normally be omitted when there are > 1 energy changes
- Standard conditions
  - Shown with symbol  $\ominus / ^\circ$
  - Standard pressure = **100 kPa /  $1 \times 10^5 \text{ N m}^{-2}$  / 1 atm**
  - Standard temperature = **298 K / 25 °C**
  - Standard concentration = **1 mol dm<sup>-3</sup> / 1 M**
  - Substances will be in their **normal physical states**
- Measuring energy changes
  - Use the equation  $q = mc\Delta T$
  - Energy change for the **system** =  $-q$
- Determine enthalpy change of combustion
  - Measure certain volume of water, pour water into beaker
  - Record initial temperature of water using a thermometer
  - Add fuel to spirit burner + weigh spirit burner and fuel together
  - Place spirit burner under beaker + light the burner
  - Stir water with thermometer
  - Extinguish flame after about 3 mins
  - Immediately record water temperature
  - Re-weigh spirit burner
  - Work out the mass of fuel burnt hence the amount of fuel burnt in moles
  - Work out energy change with  $q = mc\Delta T$
  - Enthalpy change of combustion =  $-\frac{q}{n}$
- Reasons for inaccuracies
  - Heat loss to surroundings → less exothermic than expected
  - Incomplete combustion fuel (black layer soot on calorimeter) → less exothermic than expected
  - Non-standard conditions → more or less exothermic than expected
  - Evaporation of fuel
    - Less exothermic
    - Seems to have used more fuel than actual
    - Weigh the spirit burner before
    - Extinguish the spirit burner ASAP after the experiment
- Determine enthalpy change of reaction
  - Carry out reaction in polystyrene cup with thermometer clamped so that it stands in it
  - Surroundings = the reaction solution (may assume density and specific are close to those of water)
  - Enthalpy change of neutralisation
    - Make one reactant excess so the amount of water formed is fixed
    - In theory all acid and alkali should **release the same amount of energy** but in reality it isn't due to the different strengths of acid / alkali species

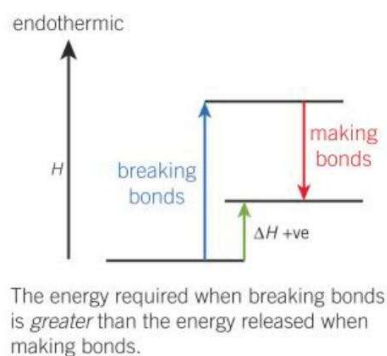
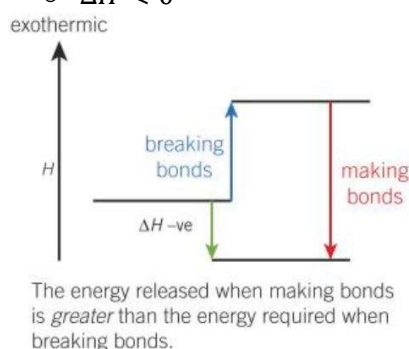
A SIMPLE CALORIMETER



- Cooling curve correction
  - Add one reactant to the polystyrene cup
  - Take temperature of the solution every 30s until temperature stays constant
  - Add the other reactant + stir
  - Measure temperature every 30s until temperature has fallen for several mins
  - Plot a graph of temperature against time
  - Extrapolate cooling curve section back to when second reactant added
  - Find the theoretical  $\Delta T$  at that point of time



- Average bond enthalpy
  - The enthalpy change when **1 mole** of a bond is broken in the **gas state**
  - Limitations: actual bond enthalpy can vary depending on the chemical environment of the bond
- Endothermic / exothermic
  - Endothermic
    - Bond breaking is endothermic
    - More energy required when breaking bonds than energy released when making bonds
    - $\Delta H > 0$
  - Exothermic
    - Bond formation is exothermic
    - More energy released when making bonds than energy required when breaking bonds
    - $\Delta H < 0$



- Calculating enthalpy change from average bond enthalpies
  - $\Delta_r H = \Sigma(\text{bond enthalpies in reactants}) - \Sigma(\text{bond enthalpies in products})$
- Hess's Law
  -
- Working out enthalpy change using Hess's Law
  - Using enthalpy change of formation:  $\Delta_r H = \Sigma \Delta_f H \text{ products} - \Sigma \Delta_f H \text{ reactants}$
  - Using enthalpy change of combustion:  $\Delta_r H = \Sigma \Delta_c H \text{ reactants} - \Sigma \Delta_c H \text{ products}$

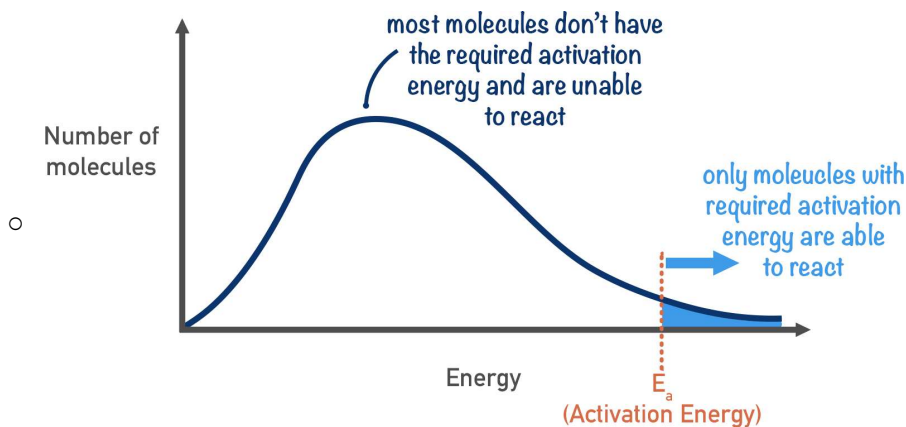
### 3.2.2 Reaction rates

- Definitions

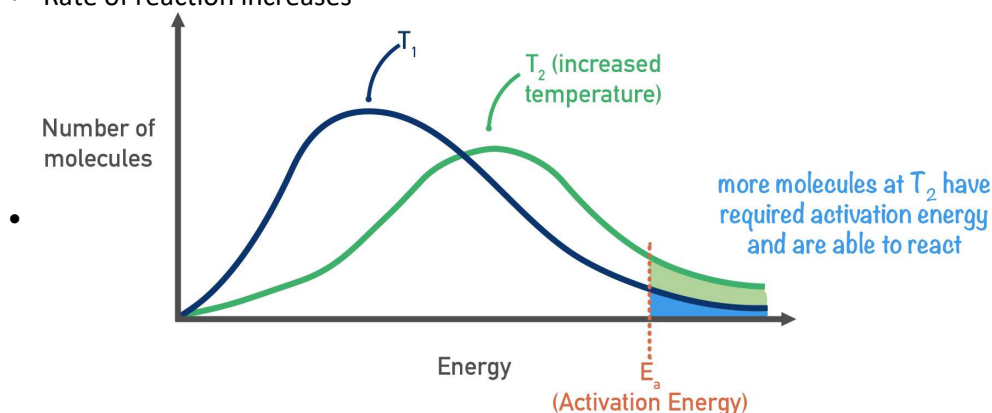
Term	Definition
• <b>Intermediate</b>	A species formed during a reaction that reacts further and is not present in the final products

- Rate of reaction
  - Measures how fast a reactant is being used up / a product is being formed
  - $\text{rate} = \frac{\text{change in concentration}}{\text{time}}$  (units =  $\text{mol dm}^{-3} \text{s}^{-1}$ )
- The collision theory
  - Two reacting particles must **collide** with the **correct orientation** and have **sufficient energy** to overcome the activation energy barrier of the reaction
  - Most collisions between particles are unsuccessful and **do not** result in a chemical reaction
- Effect of change in concentration / pressure on rate of reaction
  - Increase concentration / pressure = increase in rate of reaction

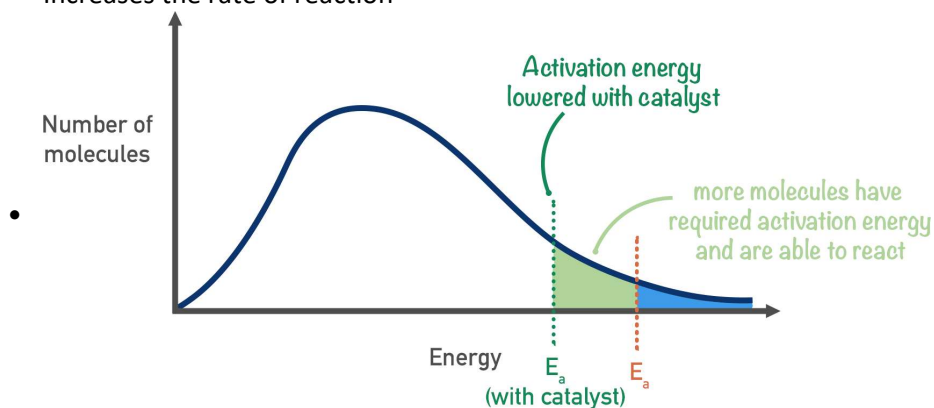
- Increases the number of particles in the same volume
  - The particles are closer together and collide **more frequently**
  - In a given period of time** there will be **more effective collisions**
  - (The proportion of collisions that are successful does not change)
- Measuring rates of reaction by amount of gas produced
  - Reactant added to conical flask + bung replaced
  - Initial volume of gas recorded
  - Catalyst added + bung replaced, start stopwatch
  - Volume of gas recorded at regular intervals until reaction is complete (no more gas produced)
  - Graph of total volume of gas produced against time plotted
  - Gradient of tangent at  $t = 0$  is the initial rate
- Measuring rates of reaction by mass loss
  - Add reactants to conical flask on a balance
  - Mass is recorded initially & at regular intervals until no more mass lost
  - Plot a graph of mass against time
  - Gradient of tangent at  $t = 0$  is the initial rate
- Catalyst
  - Increases the rate of reaction without being used up by the overall reaction
  - Allowing a reaction to proceed via a different route with **lower activation energy**
  - May react with a reactant to form an intermediate or provide a surface on which the reaction can take place
- Types of catalysts
  - Homogenous
    - The catalyst is in the **same physical state** as the reactants
  - Heterogeneous
    - The catalyst is in a **different physical state** from the reactants
- Economic importance of catalysts
  - Obtain industrial products faster
    - Increase profit
  - Operate industrial processes at lower temperatures and pressures
    - Reduce the amount of energy needed
    - Less electricity / fossil fuels used
- Problems of catalysts
  - Catalysts do not last forever and need to be replaced periodically
    - Waste need to be disposed of responsibly
    - Many catalysts are toxic and need to be disposed of very carefully to prevent damage to the environment
- Boltzmann distribution
  - Not all molecules in a substance have the same amount of energy
  - Particles to the right of the  $E_a$**  have enough energy to react
  - Distribution graph
    - Area under curve = total number of molecules
    - Peak = most probable energy of a molecule
    - No molecules have zero energy (**graph starts at origin**)
    - No maximum energy for a molecule (**the curve does not meet the x-axis at high energy**)
    - The shape is **positively skewed**



- Effect of change in temperature on Boltzmann distribution
  - Graph: higher temperature = lower peak, peak shifted to the right
  - **Larger area to the right of  $E_a$  → More molecules have energy  $\geq E_a$**  (major effect)
  - A greater proportion of collisions will lead to a reaction
  - More frequent collisions as the molecules gain more KE and are moving faster (minor effect)
  - Rate of reaction increases



- Effect of catalyst on Boltzmann distribution
  - Larger area to the right of  $E_a$  → a greater proportion of molecules now have an energy  $\geq$  the lower activation energy
  - A greater proportion of collisions will lead to a reaction
  - Increases the rate of reaction



### 3.2.3 Chemical equilibrium

- Definitions

Term	Definition
• <b>Dynamic equilibrium</b>	When the rates of forward and backward reactions are equal

- Dynamic equilibrium conditions
  - In a **closed system** for **reversible reactions**
  - The rate of the forward reaction is equal to the rate of the reverse reaction
  - The amount of reactants and products are constant

- Effect of concentration changes on position of equilibrium
  - Increase in concentration of reactants / decrease in concentration of products
    - Rate of forward reaction increases
    - Equilibrium shifts to the right, more products formed
  - Increase in concentration of products / decrease in concentration of reactants
    - Rate of backward reaction increases
    - Equilibrium shifts to the left, more reactants formed
- Effect of changes in temperature on position of equilibrium
  - Increase in temperature
    - Favours the endothermic reaction
  - Decrease in temperature
    - Favours the exothermic reaction
  - (Equilibrium shifts to ..., there are more ..., less ..., the yield ...)
  - \* Forward and backward reactions have the same magnitude of enthalpy change but opposite signs
- Effect of changes in pressure on position of equilibrium
  - Increasing the pressure
    - ... is favoured because it reduces the number of moles of gas in the mixture (fewer moles of gas on that side)
    - Shift the position of equilibrium to side with fewer moles of gas
    - Reduces the pressure of the system
  - Decreasing the pressure
    - ... is favoured because it increases the number of moles of gas in the mixture (more moles of gas on that side)
    - Shift the position of equilibrium to side with more moles of gas
    - Increases the pressure of the system
- Effect of catalyst on equilibrium
  - Increases the rate of both forward and reverse reactions in an equilibrium **by the same amount**
  - **Do not** change the position of equilibrium
  - Allow equilibrium to be **achieved faster**
- Investigating changes in position of equilibrium
  - Observe colour change
  - Change in concentration
    - Add more reactants / products to the mixture
  - Change in temperature
    - Heat using boiling water bath
    - Cool using iced water
- Haber process
  - $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$  (Forward = exothermic)
  - Lower temperature
    - Higher yield of product
    - Rate may be too slow that equilibrium may not be established
    - Not used
  - High pressure
    - Increases yield & forces molecules closer together
    - Increases concentration + reaction rate
    - Requires very strong container + large quantity of energy → higher cost
    - Failure of steelwork / seals could lead to hot gases (including toxic ammonia) leaking → endangering the workforce and the surrounding area → safety concerns
  - Operate under compromise conditions of 400-500°C, 100-200 atm and iron catalysts
    - Gives a reasonable rate without shifting the equilibrium position too far away from ammonia and back to the reactants
    - Iron catalyst: increases the rate so lower temperatures can be used and operating cost is lowered
    - Only about 15% of the reactants is converted to ammonia, but  $\text{H}_2$  and  $\text{N}_2$  are recycled

repeatedly so nearly all reactants are eventually converted

- Industrial process conditions
    - Lower temperature / pressure: rate might be too slow
    - Higher temperature / pressure: safety risk / high cost / high energy use
  - The equilibrium constant /  $K_c$ 
    - For reaction  $aA + bB \rightleftharpoons cC + dD$
    - $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
    - $[\ ]$  = concentration of ...
    - $[A]$ ,  $[B]$ ,  $[C]$ ,  $[D]$  = equilibrium concentration of the reactants and products of this equilibrium
    - **Only solutions** should appear in the equation for  $K_c$ 
      - Include liquid if they have a similar amount to the solutions
  - Value of  $K_c$ 
    - $< 1$ 
      - Position of equilibrium is towards the LHS
      - Greater concentration for reactants
    - $= 1$ 
      - Position of equilibrium is halfway between reactants and products
    - $> 1$ 
      - Position of equilibrium is towards the RHS
      - Greater concentration for products
  - Effect of temperature change on  $K_c$ 
    - Forward reaction is exothermic
      - $K_c$  decreases when temperature increases
    - Forward reaction is endothermic
      - $K_c$  increases when temperature increases
- \* If the direction of reaction is not specified take it as the forward reaction by default

## 4.1 Basic concepts and hydrocarbons

### 4.1.1 Basic concepts of organic chemistry

- Definitions

Term	Definition
Functional group	A group of atoms responsible for the characteristic reactions of a compound
Homologous series	A series of organic compounds having the <b>same functional group</b> but with <b>each successive member differing by CH<sub>2</sub></b>
Saturated	All carbon to carbon bonds are single bonds
Unsaturated	Contain carbon to carbon multiple bonds (C=C or C≡C)
Hydrocarbons	Substances containing carbon and hydrogen atoms only
Isomerism	Compounds with the same molecular formula but different arrangements of atoms in space
Structural isomers	Compounds with the <b>same molecular formula</b> but <b>different structural formulae</b>

- Alkyl group

- General formula C<sub>n</sub>H<sub>2n+1</sub>
- Found on side chains of organic molecules

- Types of hydrocarbons

- Aliphatic
  - A compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings
- Alicyclic
  - An aliphatic compound arranged in non-aromatic rings with or without side chains
- Aromatic
  - A compound containing a **benzene ring**

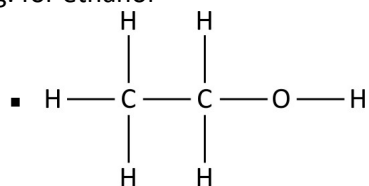
- Stem prefix

Number of carbon atoms	Prefix
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pen-
6	Hex-
7	Hept-
8	Oct-
9	Non-
10	Dec-

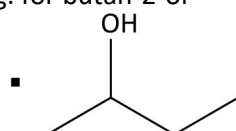
- Types of formulae

- General formula
  - The simplest algebraic formula of a member of a homologous series
  - e.g. for an alkane: C<sub>n</sub>H<sub>2n+2</sub>
- Structural formula
  - The minimal detail that shows the arrangement of atoms in a molecule
  - e.g. for butane: CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> or CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>

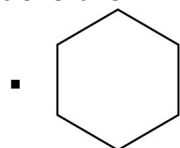
- Displayed formula
  - The relative positioning of atoms and the bonds between them
  - e.g. for ethanol



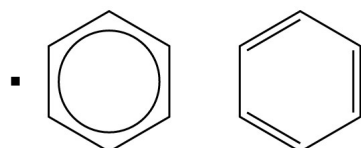
- Skeletal formula
  - The simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups
  - e.g. for butan-2-ol



- Cyclohexane



- Benzene



- Types of covalent bond fission

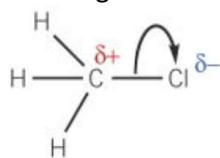
- Homolytic fission
  - **Each bonding atom receiving one electron** from the bonded pair forming 2 radicals
- Heterolytic fission
  - **One bonding atom receiving both electrons** from the bonded pair
  - The atom that takes both electrons becomes a negative ion
  - The atom that does not take the electrons becomes a positive ion
  - e.g.  $\text{H}_3\text{C}-\text{Cl} \rightarrow \text{H}_3\text{C}^+ + \text{Cl}^-$

- Radical

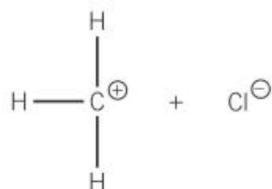
- A species with **an unpaired electron**
- Represented with a dot (•)
- e.g.  $\text{H}_3\text{C}-\text{CH}_3 \rightarrow \text{H}_3\text{C}\cdot + \cdot\text{CH}_3$

- Curly arrows

- Showing the **movement of an electron pair**
- Showing either heterolytic fission or formation of a covalent bond



heterolytic fission



- Types of reaction



- Addition reaction
  - Two reactants join together to form one product
- Substitution reaction
  - An atom or group of atoms is replaced by a different atom or group of atoms
- Elimination reaction
  - Involves the removal of a small molecule from a larger one
  - One reactant molecule forms two products

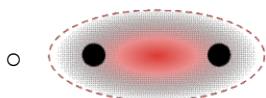
### 4.1.2 Alkanes

- Definitions

Term	Definition
Free radical	A species with an unpaired electron
Chain reaction	A reaction in which the propagation steps release new radicals that continue the reaction
Initiation	The first stage in a radical reaction in which radicals form when a covalent bond is broken by homolytic fission
Propagation	The steps that continue a free radical reaction, in which a radical reacts with a reactant molecule to form a new molecule and another radical, causing a chain reaction
Termination	The step at the end of a radical substitution when two radicals combine to form a molecule

- Bonding in alkanes

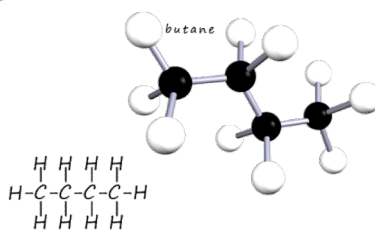
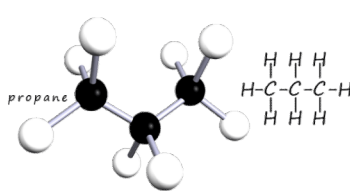
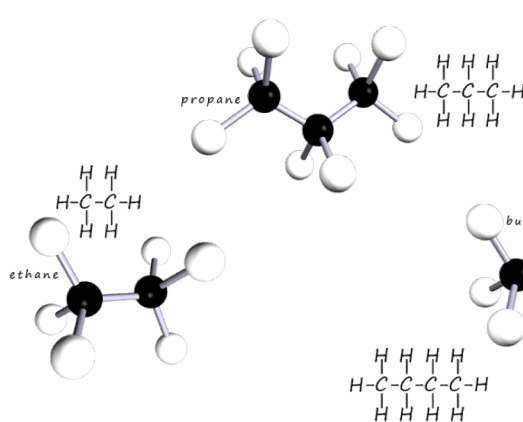
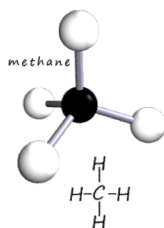
- Saturated hydrocarbons
- Only carbon and hydrogen atoms joined together by single covalent bonds
- Bond type =  $\sigma$ -bond (sigma bond)
  - $\sigma$ -bond = **heads on** overlap of orbitals directly between the bonding atoms
  - One orbital from each bonding atom, each containing one electron
  - Positioned on a line directly between bonding atoms



- Atoms can rotate freely around the  $\sigma$ -bond

- Shape of alkanes

- Tetrahedral shape around each carbon atom, bond angle  $109.5^\circ$
- Each carbon atom surrounded by 4 electron pairs in four  $\sigma$ -bonds
- The electron pairs repel each other as far away as possible



- Effect of chain length on boiling points
  - Longer chain length = higher boiling point
  - Increased chain length = greater surface area of contact + more electrons
  - Stronger London forces
  - More energy is required to overcome the London forces
- Effect of branching on boiling points

- More branching = lower boiling point
- More branches = fewer surface area of contact → weaker London forces
- The branches prevent the branched molecules getting as close together as straight-chain molecules → further decrease intermolecular forces
- Less energy is required to overcome the London forces
- Reactivity of alkanes
  - Low reactivity
  - C-C and C-H  $\sigma$ -bonds are strong
  - C-C bonds are non-polar
  - C-H bond can be considered non-polar as the electronegativities of C and H are very similar
- Combustion of alkanes
  - Complete combustion (sufficient oxygen present)
    - Equation:  $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$
  - Incomplete combustion (insufficient oxygen present)
    - Hydrogen atom always oxidised to water
    - Combustion of carbon may be incomplete so carbon (soot) or carbon monoxide is formed instead of  $CO_2$
    - Carbon monoxide is toxic + colorless and odorless so it is difficult to spot
    - CO combines irreversibly to haemoglobin and replace oxygen so oxygen cannot pass round the body and the person can suffocate
  - Alkane is a good source of fuel
    - Release large amounts of energy when burned
    - Easy to transport
- Methane and chlorine reaction
  - Equation:  $R-CH_3 + X_2 \rightarrow R-CH_2X + HX$
  - Type: free radical substitution
  - Step 1: initiation
    - The halogen-halogen bond is broken by **homolytic fission** to form 2 free radicals
    - Energy for bond fission is provided by UV radiation
    - e.g.  $Cl_2 \xrightarrow{u.v.} 2Cl\bullet$
  - Step 2: propagation (halogen radical intermediate react with original reactants)
    - One free radical reacts to produce another different free radical
    - Always in 2 steps
    - First propagation step
      - A halogen radical reacts with a C-H bond in the methane → forming an alkyl radical + a hydrogen halide molecule
      - $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$
    - Second propagation step
      - Each alkyl radical reacts with another halogen molecule → forming haloalkane + new halogen radical
      - $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
    - A halogen radical acts as an catalyst and is recreated
  - Step 3: termination
    - Two free radicals combine and their unpaired electrons pair up to form a covalent bond between the 2 species
    - $Cl\bullet + \bullet Cl \rightarrow Cl_2$  /  $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$  /  $\bullet CH_3 + \bullet Cl \rightarrow CH_3Cl$
    - Both radicals are removed from the reaction mixture so the reaction stops
  - (Same equation for bromine atoms)
- Limitations of radical substitution in synthesis
  - Further substitution
    - The propagation step can continue many times as it is a chain reaction
    - Conditions can be altered to favour the termination step and limit the number of substitutions
  - Substitution at different positions in a carbon chain
    - Longer chain = a mixture of monosubstituted isomers by substitution at different positions of the chain

- Different chains can also undergo further substitution
- Produces different termination products (more than one possible termination step)

### 4.1.3 Alkenes

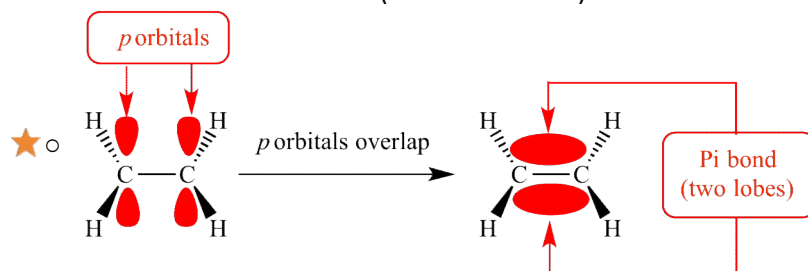
- Definitions

Term	Definition
Electrophile	An atom or group of atoms which is attracted to an electron-rich centre of atom, where it accepts a pair of electrons to form a new covalent bond, usually a cation or an atom or molecule with $\delta+$ charge
Electrophilic addition	An addition reaction in which the first step is attack by an electrophile on a region of high electron density
Addition polymerisation	Formation of a very long molecular chain, by repeated addition reactions of many <b>unsaturated alkene molecules</b> (monomers)

- Structure of C=C bond

- Comprised of

- A  $\sigma$ -bond: **head on overlap** of orbitals directly between the bonding atoms
- A  $\pi$ -bond: **sideways overlap of adjacent p-orbitals** above and below the bonding carbon atoms
- The  $\pi$ -bond locks the two carbon atoms in position and prevents them from rotating around the double bond (restrict rotation)



- **Trigonal planar** shape around each carbon atom in the C=C bond ( $120^\circ$  bond angle)
  - 3 regions of electron density around each carbon atom
  - The 3 regions repel each other as far apart as possible

- $\sigma$  and  $\pi$ -bond difference

	$\sigma$ -bond	$\pi$ -bond
<b>Position of electron density</b>	Between bonding atoms	Above and below bonding atoms
<b>Overlap of orbitals</b>	Head on overlap of orbitals	Sideways overlap of orbitals
<b>Bond enthalpy / strength</b>	Higher	Lower
<b>Size</b>	Larger	Smaller

- Stereoisomer

- Compounds with the **same structural formula** but with a **different arrangement in space**

- E/Z isomerism / geometrical isomerism

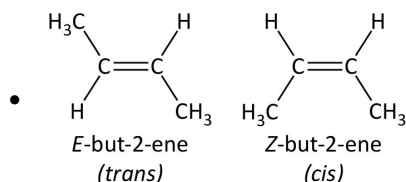
- An type of stereoisomerism
- Different groups attached to each carbon atom of a C=C double bond may be arranged differently in space because of the restricted rotation about the C=C bond
- Rotation about a double bond is restricted (due to the  $\pi$ -bond) so the groups attached to each carbon atom are fixed relative to each other

- Conditions for E/Z isomerism

- A C=C double bond
- **Two different groups** to be attached to **each carbon atom** of the double bond

- *Cis-trans* isomerism

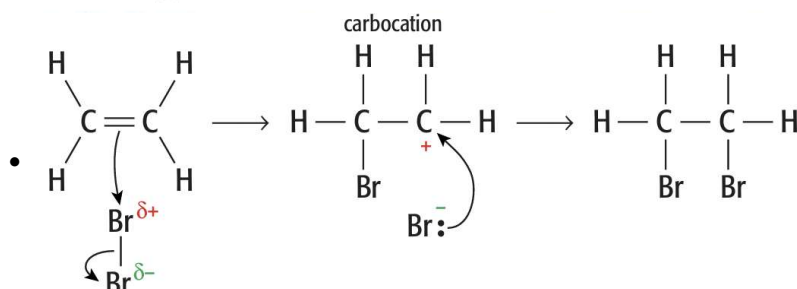
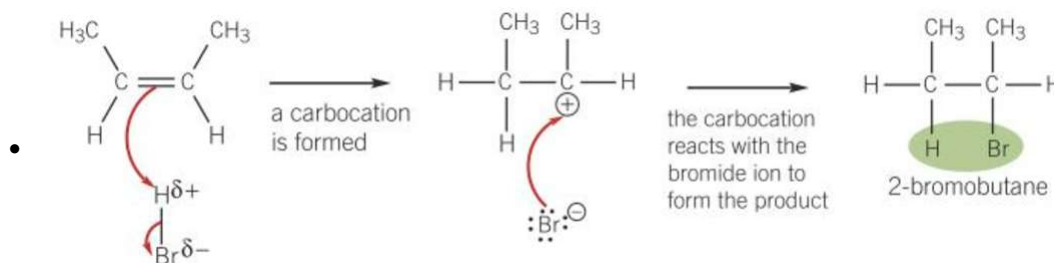
- A special case of E/Z isomerism
- **One of the attached groups on each carbon atom of the double bond must be the same**
- Same group on same side = cis, same group on different sides = trans



- Identify E/Z isomers by Cahn-Ingold-Prelog (CIP) priority rules
  - Assigning priority
    - Examine the atomic number of the atoms directly attached to the carbon atoms of the double bond
    - Higher atomic number = higher priority
    - Two same atoms attached to the carbon atom
      - Find the first point of difference
      - Higher atomic number at first point of difference = higher priority
  - The groups of higher priority are on the **same side = Z isomer**
  - The groups of higher priority are **diagonally placed across the double bond = E isomer**
- Reactivity of alkenes
  - Much more reactive than alkanes
  - Relative low bond enthalpy of the  $\pi$ -bond so it is broken more readily
    - It is on the outside of the  $\sigma$ -bond so its electrons are more exposed
- Addition reactions of alkenes

Reaction	Condition	Detail
<b>Hydrogenation</b>	<ul style="list-style-type: none"> <li>Nickel catalyst</li> <li>423 K (150°C)</li> <li>High pressure</li> </ul>	<ul style="list-style-type: none"> <li>Alkene + hydrogen <math>\rightarrow</math> alkane / <math>R-CH=CH_2 + H_2 \rightarrow R-CH_2-CH_3</math></li> <li>Type: hydrogenation / addition</li> </ul>
<b>Halogenation</b>	<ul style="list-style-type: none"> <li>RTP</li> </ul>	<ul style="list-style-type: none"> <li>Alkene + halogen <math>\rightarrow</math> dihaloalkane e.g. <math>R-CH=CH_2 + Br_2 \rightarrow R-CHBr-CH_2Br</math></li> <li>Type: electrophilic addition (see below for mechanism)</li> <li>Reaction of alkenes with bromine can be used to test if the organic compound is unsaturated               <ul style="list-style-type: none"> <li>Bromine water added dropwise to alkene</li> <li>Bromine adds across the double bond</li> <li>The orange colour of bromine water disappears</li> <li>Added to an saturated compound: no addition reaction so no colour change</li> </ul> </li> </ul>
<b>Addition with (gaseous) halogen halides</b>	<ul style="list-style-type: none"> <li>Room temperature</li> </ul>	<ul style="list-style-type: none"> <li>Alkene + halogen halide <math>\rightarrow</math> haloalkane e.g. <math>R-CH=CH_2 + HBr \rightarrow R-CHBr-CH_3</math></li> <li>Type: electrophilic addition (see below for mechanism)</li> <li>Alkene is a gas: reaction takes place when the two gases are mixed</li> <li>Alkene is a liquid: hydrogen halide bubbled through it</li> <li>Can also react with concentrated hydrochloric or hydrobromic acid</li> <li><b>* Two possible products</b></li> </ul>
<b>Hydration</b>	<ul style="list-style-type: none"> <li>Steam</li> <li>Phosphoric acid (<math>H_3PO_4</math>) catalyst</li> </ul>	<ul style="list-style-type: none"> <li>Alkene + <math>H_2O_{(g)} \rightarrow</math> alcohol</li> <li>Type: hydration</li> <li><math>R-CH=CH_2 + H_2O \rightarrow R-CH(OH)-CH_3</math></li> <li><b>* Two possible products</b></li> </ul>

- Electrophilic addition mechanisms
  - Electrophile =  $\delta^+$  atom (accepts the  $\pi$ -electrons from the double bond)
  - Electron pair in the  $\pi$ -bond is attracted to the  $\delta^+$  atom  $\rightarrow$  double bond breaks
  - A bond forms between the  $\delta^+$  atom and a carbon atom from the double bond
  - The bond in the molecule breaks by heterolytic fission, electron pair goes to the  $\delta^-$  atom
  - An anion and a carbocation (positively charged carbon atom) are formed
  - They react to form the addition product



• Types of carbocations

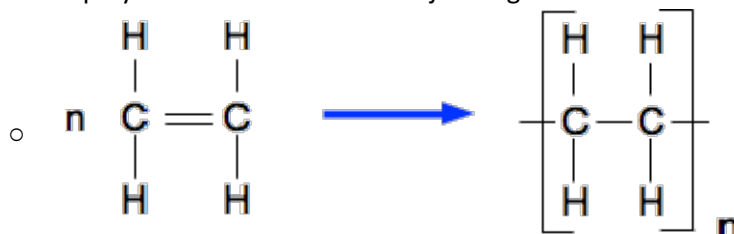
Type	Definition
Primary	1 alkyl group attached to the positively charged carbon atom
Secondary	2 alkyl groups attached to the positively charged carbon atom
Tertiary	3 alkyl groups attached to the positively charged carbon atom

• Using Markownikoff's rule to predict formation of major organic product

- For **unsymmetrical alkanes**
- The hydrogen attaches itself to the carbon atom with the **larger number of hydrogen atoms**
- Stability: tertiary carbocation > secondary carbocation > primary carbocation
- Major product = halide / OH<sup>-</sup> ion attached to the **most stable carbocation**

• Addition polymerisation of alkenes

- Short chain monomers join together to form long chain polymers **under high pressure**
- Double bond of the alkene is replaced by single bonds to form a repeating unit + bond with other monomers to form the polymer
- Addition polymers as the short chains join together to form **a single product**



• Problems of waste polymers

- Benefits of cheap oil-derived plastics are counteracted by problems for the environment of landfill
- They are unreactive so they are non-biodegradable and cannot be broken down by species in nature
- Non-biodegradable waste polymers can become a threat to wildlife

• Reducing the effect of waste polymers

- Choose plastic items that are made from polymers that can be recycled
- Re-use plastic items at many time as possible
- Try to recycle plastic items

• Ways of processing waste polymers

- Recycle
  - High cost of collection and re-processing
  - The different types of polymer have to be separated
- Combustion to release heat energy for generating electricity
  - Toxic fumes produced from burning halogenated polymers
    - HCl is removed during the combustion of chlorine containing haloalkanes

- CO produced during incomplete combustion
  - Can be removed by scrubbing
  - Greenhouse gases can be released which causes global warming
- Organic feedstock
  - Use the waste for the production of useful organic compounds
  - New technology can convert waste into hydrocarbons
  - Hydrocarbons can then be turned back into polymers
- New types of polymers
  - Biodegradable polymers
    - Broken down by microorganisms into water, CO<sub>2</sub> and organic compounds
    - Compostable polymer degrade and leave no visible or toxic residues
    - e.g. can be used as bin liners for food waste
  - Photodegradable polymers
    - Contain weak bonds that break when they absorb light energy
  - Benefits
    - Conserve fossil fuel reserves
    - Reduce pollution from disposing polymers

## 4.2 Alcohols, haloalkanes and analysis

### 4.2.1 Alcohols

- Definitions

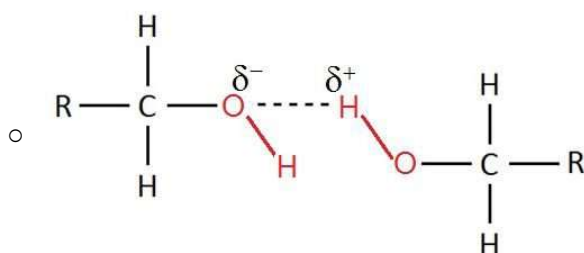
Term	Definition
Dehydration	A <b>water molecule</b> is removed from the starting material

- Alcohol structure

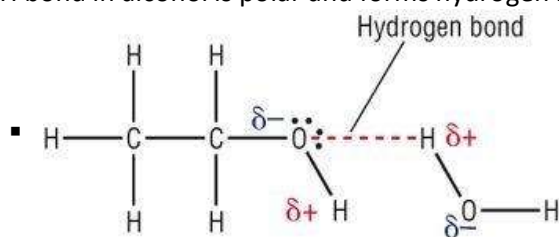
- Functional group = -OH (hydroxyl group)
- Has **polar and non-polar** parts
  - The O-H bond is **polar** (oxygen is more electronegative than hydrogen)
  - The side chain is **non-polar**
  - so alcohol can mix with both polar and non-polar liquids

- Alcohol properties

- Less volatile + higher melting point than alkanes
  - Induced dipole-dipole interactions between the non-polar side chains
  - Strong hydrogen bonds** + permanent dipole-dipole interactions between alcohol molecules hold them together (stronger than London forces)
  - Extra heat energy is required to break the strong hydrogen bonds



- Greater water solubility than alkenes
  - Alkanes are non-polar so they cannot form hydrogen bonds with water
  - O-H bond in alcohol is polar and forms hydrogen bond with water



- Longer carbon chain = less miscible in water
- More -OH groups = more miscible in water

- Classifying alcohols

- Primary: -OH group attached to a carbon atom attached to **2 hydrogen atoms + 1 alkyl group**
- Secondary: -OH group attached to a carbon atom attached to **1 hydrogen atom + 2 alkyl groups**
- Tertiary: -OH group attached to a carbon atom attached to **no hydrogen atoms + 3 alkyl groups**

- (Complete) combustion of alcohols

- Alcohol + oxygen → carbon dioxide + water
- Exothermic reaction
  - A large quantity of energy released in the form of heat
  - Burn with a clear blue flame
- More carbon atoms in the alcohol chain = more heat energy released per mole
- Alcohols undergo complete combustion more often due to the oxygen atom in the molecule

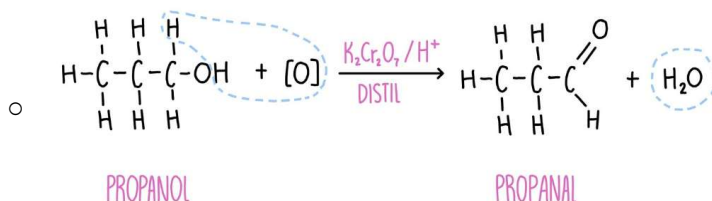
- Oxidation of alcohols

- Heat with an oxidising agent ([O])

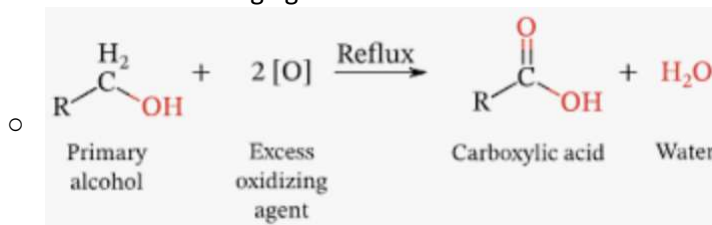
- Normally acidified dichromate (VI) ( $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$ )
- e.g. acidified potassium dichromate (VI) ( $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ )
- Observations
  - Cr will be reduced
  - Reaction mixture turn from orange ( $\text{Cr}^{6+}$  in  $\text{Cr}_2\text{O}_7^{2-}$ ) to green ( $\text{Cr}^{3+}$ )

- Oxidation of primary alcohols

- Gentle heating + **distil** = aldehyde formed
  - Aldehyde distilled out of the reaction mixture as it forms to prevent any further reaction (distil)
  - Acidified dichromate (VI) ions change colour from orange to green

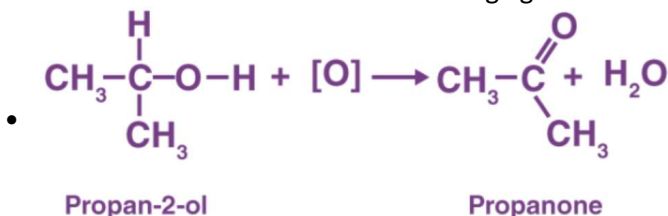


- Heated strongly + **reflux** + **excess of acidified potassium dichromate (VI)** = carboxylic acid
  - Reflux = ensure that all aldehyde formed initially also oxidised to carboxylic acid
  - Excess of oxidising agent = ensure that all alcohol is oxidised



- Oxidation of secondary alcohols

- Oxidised to ketones with an oxidising agent (acidified dichromate (VI) ions)
- Ketones cannot be further oxidised
- Heated under **reflux** with the oxidising agent to ensure that the reaction goes to completion

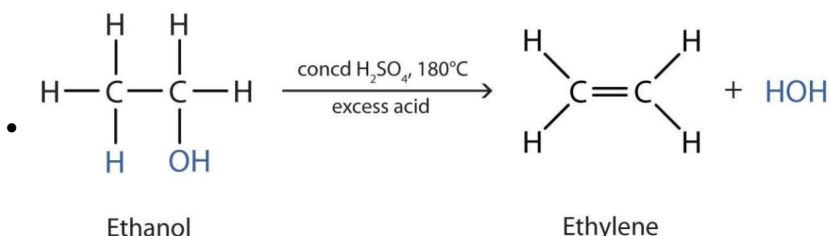


- Oxidation of tertiary alcohols

- Do not undergo oxidation reactions
- Acidified dichromate (VI) ions remain orange when added to a tertiary alcohol

- Dehydration of alcohols

- Heated under **reflux** with **acid catalyst** (e.g. concentrated  $\text{H}_2\text{SO}_4$  /  $\text{H}_3\text{PO}_4$ )
- Product = an alkene
- Type = elimination reaction

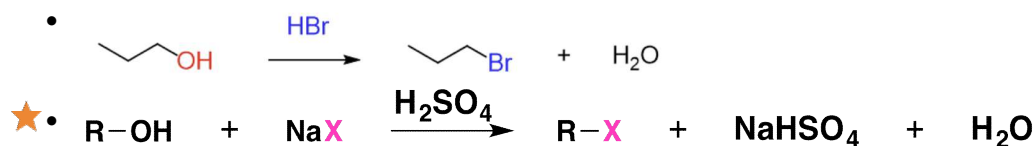


- Substitution reaction of alcohols

- Alcohols react with halide ions to form haloalkanes
- Heated under **reflux** with **concentrated acid catalyst** & halide ion e.g.  $\text{H}_2\text{SO}_4 + \text{NaBr}$ 
  - Acid need to be concentrated to minimise back reactions
- Used to produce hydrogen halide in situ when carrying out chemical reactions



Alcohols can be converted to Alkyl Halides with HX acids



## 4.2.2 Haloalkanes

### Definitions

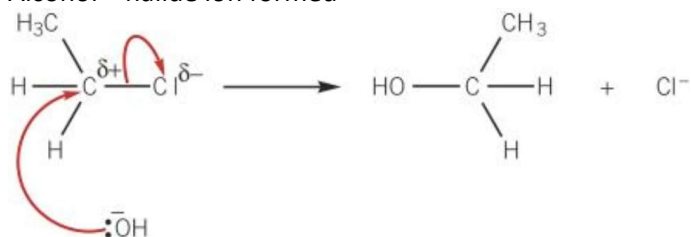
Term	Definition
<b>Nucleophile</b>	An atom or group of atoms which is attracted to an electron-deficient centre or atom, where it <b>donates a pair of electrons</b> to form a new covalent bond
<b>Nucleophilic substitution</b>	A reaction in which a nucleophile is attracted to an electron-deficient centre or atom, where it donates a pair of electrons to form a new covalent bond
<b>Hydrolysis</b>	A reaction with water that breaks a chemical compound into two compounds, the H and OH in a water molecule becomes incorporated into the two compounds

### Reactivity of haloalkanes

- Reactivity: alkenes > haloalkanes > alkanes
- Halogen atoms are more electronegative than carbon atoms so the carbon-halogen bond is polar
- $\delta+$  on carbon can attract nucleophiles (contain a lone pair of electrons)
- The nucleophile replaces the halogen atom
- A new compound with a different functional group is formed

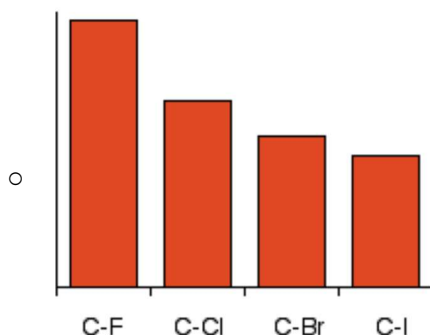
### Hydrolysis mechanism

- Nucleophilic substitution**
- $\text{OH}^-$  normally from NaOH
- $\text{OH}^-$  (nucleophile) approaches the carbon atom attached to the halogen from the opposite side of halogen to minimise repulsion
- A lone pair on OH attracted & donated to  $\delta+$  carbon atom
- New bond formed between oxygen atom of OH and the carbon atom
- Carbon-halogen bond breaks by heterolytic fission**
- Alcohol + halide ion formed



### Trend in reaction rates of hydrolysis of primary haloalkanes

- C-F has the greatest bond enthalpy (strongest), C-I has the lowest bond enthalpy (weakest)
  - Going down the table = larger halogen atom = longer bond = bond becomes weaker
- Rate: iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes
  - Increases as strength of carbon-halogen bond decreases
  - Less energy is needed to break the carbon-halogen bond to start the reaction so the activation energy is lower



- Measuring rate of hydrolysis
  - Set up 3 test tubes of 1 cm<sup>3</sup> ethanol and couple drops of 1-chlorobutane / bromobutane / iodobutane
  - Put the test tubes + a test tube with silver nitrate in water bath at 60°C
  - Allow them to reach constant temperature (60°C)
  - Add 1 cm<sup>3</sup> of silver nitrate to each test tube quickly + start stop watch
  - Observe time taken for precipitate to form
    - Chlorine = white, bromine = cream, iodine = yellow
  - Speed: iodobutane > bromobutane > chlorobutane
- CFCs
  - Shorthand for chlorofluorocarbons
    - Compounds containing carbon with chlorine and fluorine atoms attached
- Uses of CFCs
  - CFCs are non-flammable and not very toxic so they have a lot of uses
    - Refrigerants
    - Propellants for aerosols
    - Generating foamed plastics
    - Solvents for dry cleaning and for general degreasing purposes
- Problems associated with CFCs
  - Global warming
  - Breakdown of ozone layers in the atmosphere
- Ozone layer
  - Ozone continually formed and broken down by the action of UV radiation
  - Initially very high energy UV breaks oxygen molecules into oxygen radicals:  $O_2 \rightarrow 2O$
  - A steady state then set up where rate of ozone formation is the same as the rate of ozone being broken down:  $O_2 + O \rightleftharpoons O_3$
  - Equilibrium disturbed by human activities e.g. production and use of CFCs
- How CFCs break down ozone
  - CFCs remain stable until they reach the stratosphere
  - In the stratosphere UV breaks carbon-halogen bond by homolytic fission to form radicals (initiates the breakdown of ozone)
    - Photodissociation (Initiation): e.g.  $CF_2Cl_2 \rightarrow CF_2Cl\cdot + Cl\cdot$
  - Chlorine radical formed is a very reactive intermediate and can react with an ozone molecule
    - Propagation step 1:  $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$
    - Propagation step 2:  $ClO\cdot + O \rightarrow Cl\cdot + O_2$
    - (Overall:  $O_3 + O \rightarrow 2O_2$ )
    - There is a significant amount of  $O_3$  and free oxygen atoms in the upper atmosphere for reaction
  - Chlorine radical can go on in chain reaction to break down other ozone molecules
- How nitrogen oxide break down ozone
  - Reaction with NO
    - Initiation:  $NO \rightarrow N\cdot + O\cdot$
    - Propagation step 1:  $N\cdot + O_3 \rightarrow \cdot NO + O_2$
    - Propagation step 2:  $\cdot NO + O \rightarrow N\cdot + O_2$
    - Overall:  $O_3 + O \rightarrow 2O_2$
  - Reaction with  $NO_2$

- Initiation:  $\text{NO}_2 \rightarrow \text{NO}\cdot + \text{O}\cdot$
- Propagation step 1:  $\text{NO}\cdot + \text{O}_3 \rightarrow \text{NO}_2\cdot + \text{O}_2$
- Propagation step 2:  $\text{NO}_2\cdot + \text{O} \rightarrow \text{NO}\cdot + \text{O}_2$
- Overall:  $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$
- Alternatives for CFCs
  - Replace the C-Cl bond with stronger C-F bond
    - Hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) can be used
    - Still volatile, non-toxic and non-flammable
    - Still damage the ozone layer
  - Replace the C-Cl bond with a C-H bond
    - Use hydrocarbons
    - The C-H bond is much weaker and the molecules don't persist until they reach the upper atmosphere
    - They are very flammable

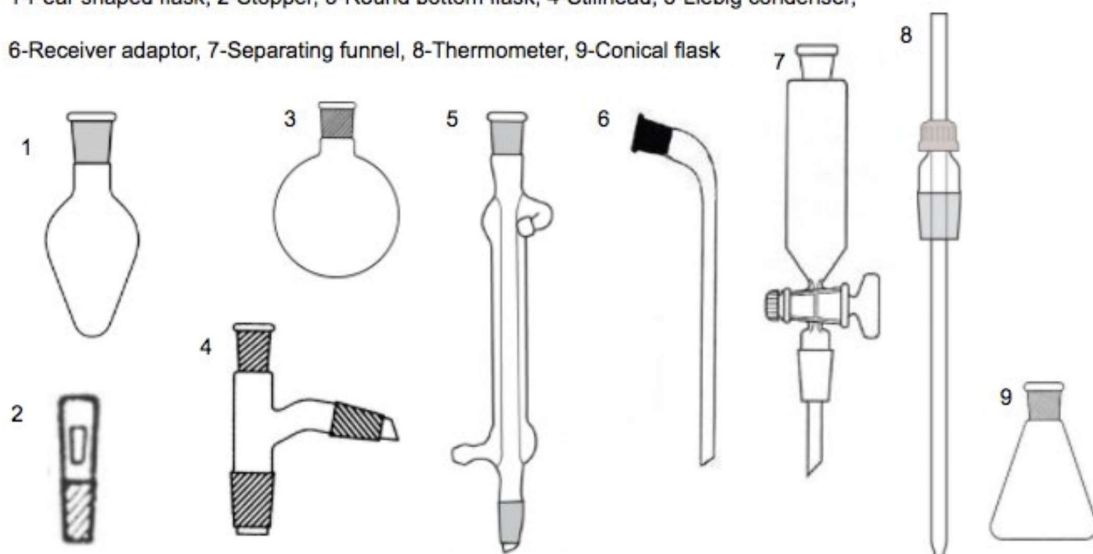
### 4.2.3 Organic synthesis

- Definitions

Term	Definition
<b>Fractional distillation</b>	The separation of components in a liquid mixture by their different boiling points into fractions with different compositions
<b>Drying agent</b>	An <b>anhydrous solid</b> that readily absorbs water from the mixture to become hydrated

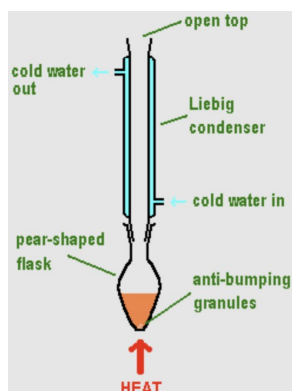
- Quickfit apparatus set

1-Pear shaped flask, 2-Stopper, 3-Round bottom flask, 4-Stillhead, 5-Liebig condenser, 6-Receiver adaptor, 7-Separating funnel, 8-Thermometer, 9-Conical flask

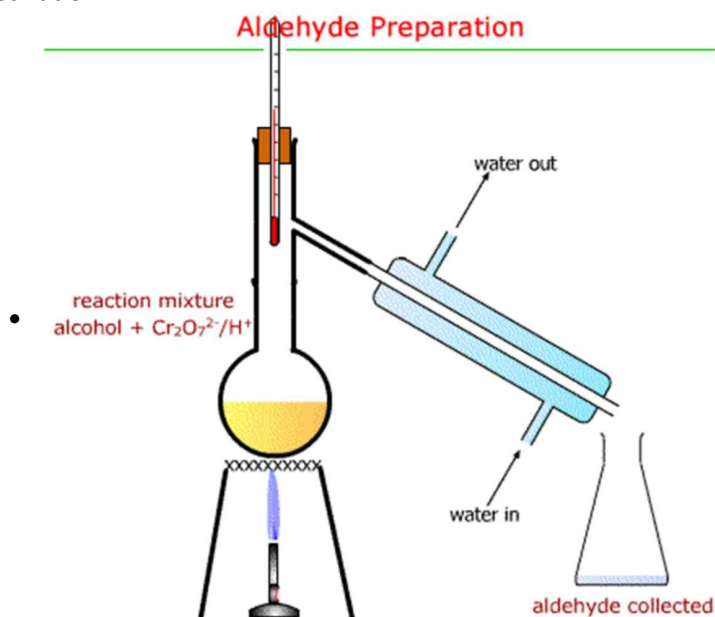


- Heating under reflux

- To prepare organic solid without boiling off solvent, reactants or products
- Water bath can be used rather than Bunsen if can be carried out below 100°C
- Heating mantle can be used for flammable liquids
- Anti-bumping granules added to liquid so it boils smoothly
  - Otherwise large bubbles will form at bottom so the glassware vibrate / jump
- Glass joints greased lightly so apparatus comes apart easily after experiment
- Condensers should be clamped loosely as the outer jacket is very fragile + kept in upright position
- Never put stopper in top-closed system or pressure would build up and the apparatus would explode
- Rubber tubing used to connect the inlet of condenser to tap and outlet to the sink (water always enters the condenser at the bottom and leaves at the top)

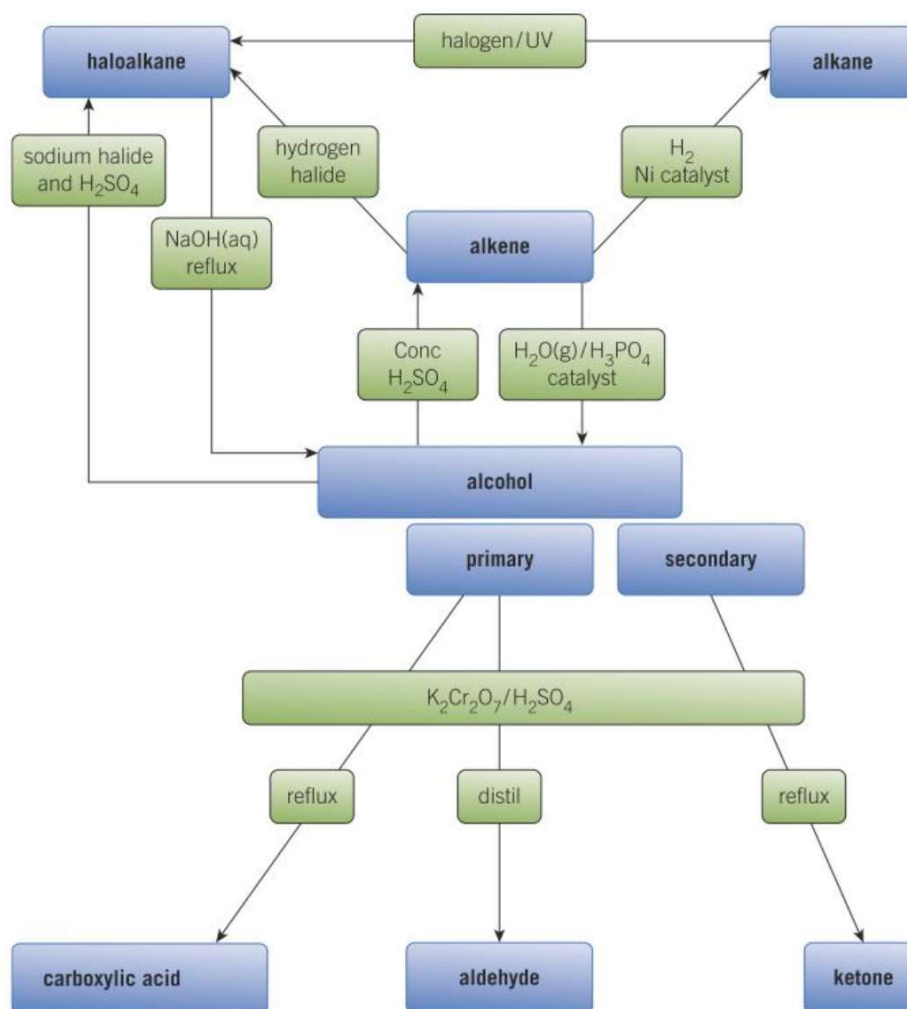


- Distillation



- Separates a pure liquid from impurities
- Flask clamped by neck
- Still head connected to the flask
- Condenser connected to rubber tubing for water (**water enters at the bottom**)
- Flask used to collect the distillate so the apparatus is not airtight
- Heat the mixture gently (make sure the temperature doesn't reach the boiling point of the less volatile compound)
- Purifying organic products using a separating funnel
  - When there are two layers inside the collection flask: one organic layer, one aqueous / water layer
  - Ensure tap of the separating funnel is closed
  - Pour in mixture and place a stopper in the top of the funnel + invert to mix the contents
  - Allow layers to settle
  - Can't tell the layers: add water to the mixture, the layer that increase in volume is the aqueous layer
  - Place conical flask under the separating funnel
  - Remove stopper + open the tap until whole lower layer has left the funnel
  - If the top layer is accidentally poured then pour the content in the first conical flask back into the separating funnel and restart
  - Repeat this several times until the bottom layer is almost completely removed
- Redistillation
  - Organic compounds may have relatively close boiling points so the sample may still have some impurities left over
  - Carry out a second distillation (or more)
  - Only collect product with the exact boiling point of the target compound
  - Try to not overheat the mixture
  - Narrower boiling point range = purer product
- Drying an organic product

- There may be water left in the organic product
- Add organic liquid to conical flask
- Add some drying agent with spatula + swirl the contents
  - e.g.  $\text{CaCl}_2$  for drying hydrocarbons,  $\text{CaSO}_4$  /  $\text{MgSO}_4$  for general drying
- Put a stopper on to prevent product from evaporating away
- Leave for about 10 minutes
- If the solid stuck in a lump water is still present so add more drying agent until it becomes a fine powder
- After all the water is absorbed the organic mixture can be separated by filtration / simply decanting the liquid
- Synthetic routes



- Predicting properties of organic compounds
  - Find all functional groups
  - Find the properties and reactions for each functional group

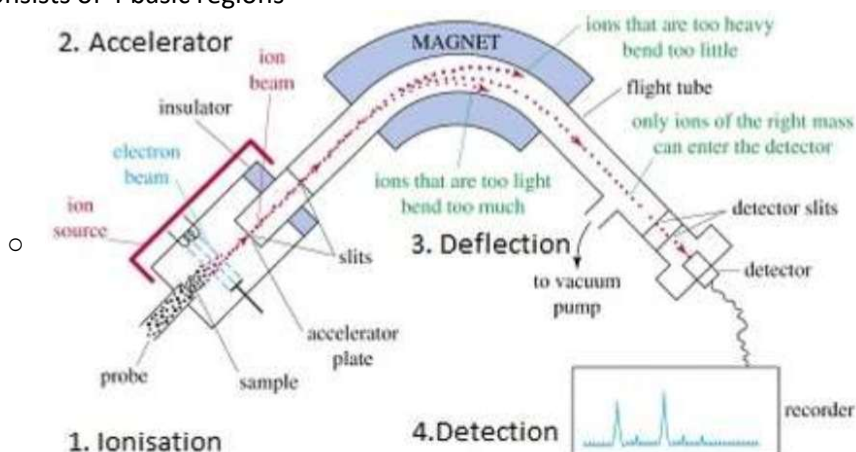
#### 4.2.4 Analytical technique

- Definitions

Term	Definition
<b>Fragmentation</b>	The process in mass spectrometry that causes a positive ion to split into smaller pieces, one of which is a positive fragment ion
<b>Fragment ions</b>	Ions formed from the breakdown of the molecular ion in a mass spectrometer

- Vibrations in bonds
  - Bonds vibrate at a particular frequency
    - Stretch: moving along the line between atoms so the distance between them changes
    - Bend: results in change in bond angle
  - Bonds only absorb radiation with the same frequency as the natural frequency of the bond

- The frequency of the light depends on bond strength, bond length and atomic masses at both ends of the bond
  - Most bonds absorb at a frequency of  $300 - 4000 \text{ cm}^{-1}$ , i.e. IR radiation
- Absorbing IR radiation causes covalent bonds to absorb energy and vibrate more
- Greenhouse effect
  - Most of the Sun's radiation is **short wave** and is relatively unaffected by atmospheric gases
  - They pass through the atmosphere to the Earth's surface and some is reflected as **long wave** radiation
  - C=O, O-H and C-H bonds absorb radiation in the IR range which causes bond in gas molecules to vibrate
    - e.g.  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  molecules
  - The vibrating bonds eventually re-emit the energy as radiation that increases the temperature of the atmosphere close to the Earth's surface
  - This creates incentives to reduce  $\text{CO}_2$  emission to reduce global warming
- Infrared spectroscopy
  - Determine the functional groups present
  - Sample placed in IR spectrometer
  - IR radiation beams with wavenumber  $200\text{-}4000 \text{ cm}^{-1}$  is passed through the sample
  - Molecules absorb some IR + emerging beam is analysed to identify frequencies absorbed
  - IR spectroscopy is usually connected to a computer that plots a graph of transmittance against wavenumber
  - The computer uses the fingerprint region to identify the compound
    - Fingerprint region: region **below  $1500 \text{ cm}^{-1}$**  with **unique peaks to identify particular molecule**
  - All organic compounds produce a peak  $2850\text{-}3100$  from C-H bond
  - Look at other peaks to identify other bonds present
- Uses of IR spectroscopy in real life
  - Remote sensors analyse IR spectra of vehicle emissions to detect pollutants
  - IR-based breathalysers pass beams of IR through breathed out gas + detect IR absorbance
    - Detecting C-O bonds in alcohol molecules
    - O-H bond is present in water vapour breathed out so it is not used
    - Blood test taken if the result suggests that the person is too drunk to drive safely
- Mass spectroscopy
  - Used to analyse **gaseous** samples
  - Consists of 4 basic regions



- Some molecular ions break down into smaller fragments by fragmentation
- Analysing the structure from a mass spectrum
  - $M_r$  = the  $m/z$  value of the **rightmost peak**
  - There might be a small peak after  $M^+$  peak called the  $M+1$  peak due to the presence of carbon-13 isotope
  - Other peaks are due to fragment ions
- Common  $m/z$  values for fragment ions

$m/z$ value	Ion (remember to include the + charge)
-------------	--

<b>15</b>	$\text{CH}_3^+$
<b>29</b>	$\text{CH}_3\text{CH}_2^+$
<b>31</b>	$\text{CH}_2\text{OH}^+$
<b>41</b>	$\text{C}_3\text{H}_5$ , $\text{C}_2\text{H}_3\text{N}$
<b>43</b>	$\text{CH}_3\text{CH}_2\text{CH}_2^+$ / $\text{CH}_3\text{CO}$ / $\text{C}_3\text{H}_7$
<b>45</b>	$\text{CH}_3\text{CH}_2\text{O}^+$
<b>49</b>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+$

- Identifying the organic compound
  - Elemental analysis: empirical formula
  - Mass spectrometry: determine molecular mass + identify sections of the molecule
  - IR spectrometry: identify bonds + functional groups present