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 **protons and electrons** and **different numbers of neutrons and different masses**.
Proton number / atomic number	The number of **protons** in the nucleus of an atom.
Nucleon number / mass number	The number of **protons and neutrons** 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 **weighted mean** mass of an atom of an element compared to 1/12 of the mass of an atom of carbon-12.
Cation	A **positively charged** ion with fewer electrons than protons.
Anion	A **negatively charged** 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 **two elements** only.
Diatomic molecules	Molecules composed of **two atoms** only.
Polyatomic ions	Ion containing more than one atoms.

- Anions to know
-
Ion	Formula
Nitrate	NO_3^-
Carbonate	CO_3^{2-}
Sulfate	SO_4^{2-}

Hydroxide	OH⁻

- Cations to know

Ion	Formula
Ammonium	NH_4^+
Zinc ion	Zn^{2+}
Silver ion	Ag^+

- 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
Soluble in water	• All common sodium, potassium and ammonium salts (also their carbonate and hydroxide salt) • All nitrates • Most common chlorides • Most common sulfates
Insoluble in water	• **Silver chloride, lead chloride** • **Lead sulfate, barium sulfate, calcium sulfate, strontium sulfate** • Most common carbonates • Most common hydroxides

2.1.3 Amount of substance

- Definitions

Term	Definition
Mole	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.
Molar mass / M	The mass in grams in each mole of the substance, measured in g mol⁻¹.
Hydrated	A crystalline compound that contains water (e.g. $CuSO_4 \cdot 5H_2O_{(s)}$).
Anhydrous	A crystalline compound containing no water (e.g. $CuSO_{4(s)}$).
Water of crystallisation	Water molecules that form part of the crystalline structure of a compound (e.g. H_2O in $CuSO_4 \cdot 5H_2O_{(s)}$).
Stoichiometry	The relative quantities of substances in a reaction.
Standard solution	A solution of known concentration.
Limiting reagent	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_A
    - 6.02×10^{23} mol⁻¹
    - The number of particles per mole
- Concentration (c)
    - Unit = mol dm⁻³ (aka molar / M) or g dm⁻³
    - mol dm⁻³: $c = \frac{n}{V} = \frac{\text{number of moles}}{\text{volume (in dm}^{-3})}$

- g dm^{-3}: $c = \frac{\text{mass (in g)}}{\text{volume (in dm}^{-3})}$
- Concentration in 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 1.01×10^5 Nm^{-2}
- Standard temperature and pressure (STP)
  - Temp = 0 °C / 273 K
  - pressure = 1 atm or 1.01×10^5 Nm^{-2}
- Molar gas volume / V$_m$
  - The volume per mole of gas at a stated temperature and pressure
  - Under RTP: 1 mol = 24 dm^3 = 24,000 cm^3
  - Under STP: 1 mol = 22.4 dm^3 = 22,400 cm^3
- Ideal gas equation
  - $pV = nRT$
  - p = pressure (Pa or N m^{-2})
  - V = volume (m^3)
  - n = amount of gas molecules (mol)
  - R = ideal gas constant (8.314 J mol^{-1} 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 = $\frac{\text{actual yield}}{\text{thereotical yield}} \times 100\%$
  - 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

Mass	• Use a digital mass balance • Choose a balance with a suitable resolution for the experiment
Volume of solution	• Use a measuring cylinder • Standard solution: use volumetric flask
Gas produced	• Use a gas syringe / measure mass lost on a balance and calculate the number of moles of gas produced

- Types of formulae

Formula	Meaning
Empirical formula	The **simplest whole number ratio** of atoms of each element present in a compound.
Molecular formula	The number and type of atoms of each element in a molecule (**if the elements are the same then combine them, e.g. not CH$_3$COOH, use C$_2$H$_4$O$_2$**).
Displayed (graphical) formula	Shows all the bonds in the structure.
Structural formula	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$^+$ ions (proton) into the solution
  - Common acids
    - HCl
    - H$_2$SO$_4$
    - HNO$_3$
    - CH$_3$COOH
- Bases
  - React with acid by **accepting H$^+$ ions (protons)** and neutralising the acid to form a salt
  - Common bases
    - Carbonates
    - Hydrogencarbonates
    - Metal oxides
    - Metal hydroxides
    - Ammonia (accept H$^+$ and form NH4$^+$ ions)
- Alkalis
  - Bases that dissolve in water and release OH$^-$ ions into the solution
  - Common alkalis
    - NaOH
    - KOH
    - NH$_3$
- Salt
  - When the H$^+$ in an acid is replaced by a positive ion
- Strong and weak acid
  - Both release H$^+$ ions / H$^+$ donor in aqueous solutions
  - Strong acid
    - **Completely dissociates** in aqueous solutions / releases all hydrogen atoms as H$^+$ ions
    - e.g. HCl(aq) $\rightarrow$ H$^+$(aq) + Cl$^-$(aq)
  - Weak acid
    - **Partially dissociates** in aqueous solutions / only releases a portion of available hydrogen atoms as H$^+$ ions
    - e.g. CH$_3$COOH(aq) $\rightleftharpoons$ H$^+$(aq) + CH$_3$COO$^-$(aq)
- Neutralisation
  - The reaction of acids with bases (including carbonates, metal oxides and alkalis) to form salts

- Ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
- 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 cm³) 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 cm³: ± 0.04 cm³, 25 cm³: ± 0.04 cm³, 50 cm³: ± 0.10 cm³
  - 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 cm³)
  - * Only use concordant results for calculating the mean titre

2.1.5 Redox

- Definitions

Term	Definition
Redox reactions	A reaction involving reduction and oxidation.
Oxidising agent	A reagent that **accepts / takes in** electrons.
Reducing agent	A reagent that **donates / gives out** electrons.
Oxidation number	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
O (normally)	-2
H (normally)	+1
F	-1
Group 1	+1
Group 2	+2

Group 3	+3

- Oxidation number for special cases

	Combined element	Oxidation number
	H in metal hydrides (e.g. NaH, CaH$_2$)	-1
•	O in peroxide ions (O$_2^{2-}$)	-1
	O bonded to F (e.g. F$_2$O)	+2

- Roman numerals in chemical names
  - Show oxidation number without sign
  - Nitrate = assume to be NO$_3^-$
  - Sulfate = assume to be SO$_4^{2-}$
  - e.g. chlorate(I) = ClO$^-$
- 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^{2+} in redox reactions)

2.2 Electrons, bonding and structure

2.2.1 Electron structure

- Definitions

	Term	Definition
	Atomic orbitals	A region around the nucleus that can hold up to two electrons with opposite spins.
	Sub-shells	A group of orbitals of the same type within a shell.
	Electron configuration	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 ($= 2n^2$)
1	2
2	8
3	18
4	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 → 2s → 2p …)
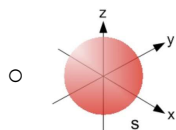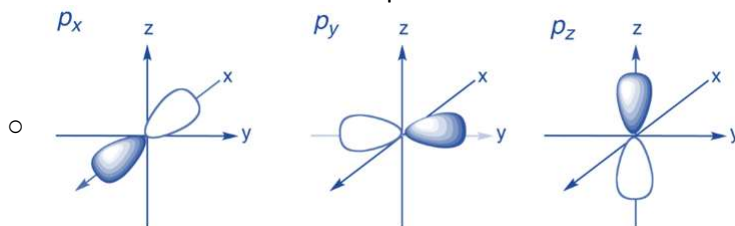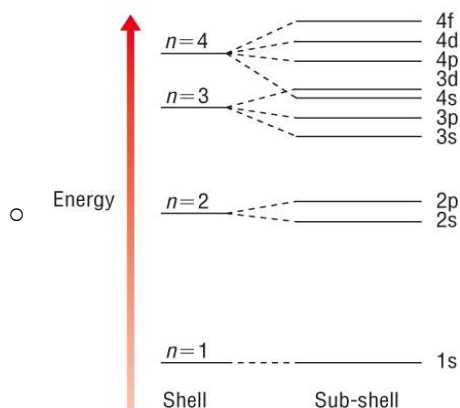
   * 4s is filled before 3d
- Inside each sub-shell
    - The orbitals all have the same energy within a sub-shell
    - One electron occupies each orbital before pairing starts to prevent any repulsion between paired electrons
    - Opposite spins within each orbital (one ↑ and one ↓) as both electrons are negatively charged and repel one another so this minimises repulsion
    - The paired electrons are easier to remove than the unpaired ones
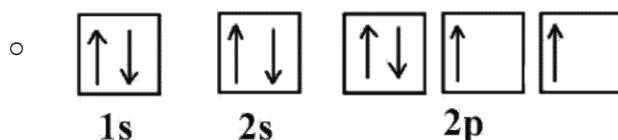
    - More than one orbital within a sub-shell = the orbitals are degenerate (all the same)
- Writing electron configuration of atoms
    - e.g. Li = $1s^2 2s^1$, F = $1s^2 2s^1 2p^5$
    - Shorthand notation: in terms of the previous noble gas + outer electron sub-shells
        - e.g. Krypton = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ = [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
Polarity	There is an uneven distribution of electrons.
Polar molecule	A molecule with an overall dipole, having taken into account any dipole across bonds and the shape of the molecule.
Bond angle	The angle between 2 bonds in an atom.
Electronegativity	A measure of the attraction of a bonded atom for the pair of electrons in a covalent bond.
Dipole	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, δ+, and

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

      calcium ion, Ca^{2+} $[2,8,8]^{2+}$

      chloride ion, Cl^- $[2,8,8]^-$
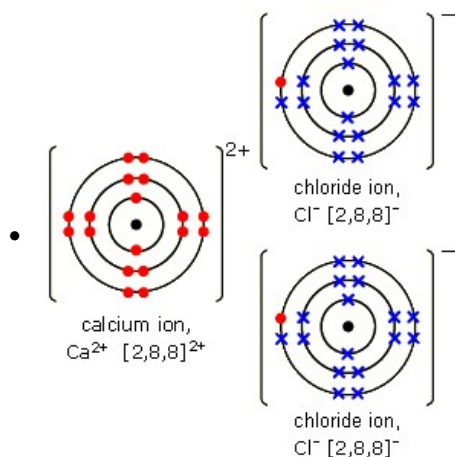
      chloride ion, Cl^- $[2,8,8]^-$
- Structure of ionic compounds
    - Each ion attracts oppositely charged ions strongly in **all directions**
    - Forms a **giant lattice structure** containing many ions
    - Every positive ion is surrounded by negative ions; every negative ion is surrounded by positive ions
    - Regular arrangement of ions = regular, predictable shapes depending on size of ions
        - NaCl = always cubic
        - $MgSO_4$, $CuSO_2$, etc. = not cubic
    -

      CHLORIDE ION Cl^- SODIUM ION Na^+
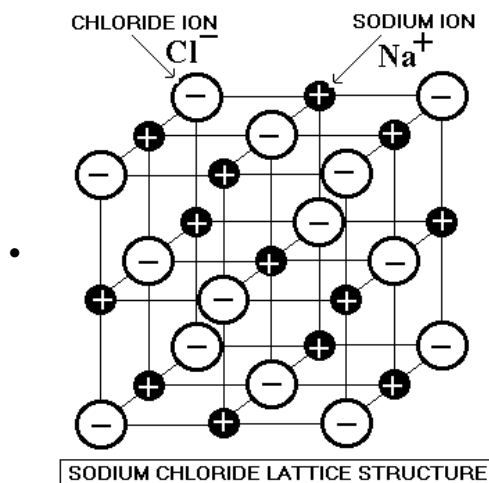
      SODIUM CHLORIDE LATTICE STRUCTURE
- Properties
    - High melting and boiling points
        - **Strong** electrostatic forces of attraction between oppositely charged ions in the **giant ionic lattice**
        - A high temperature is needed to provide the large amount of energy needed to overcome the 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
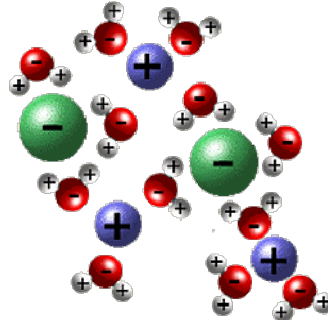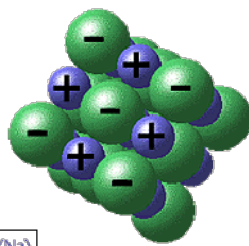
  sodium (Na)
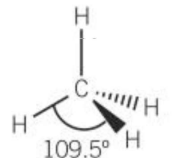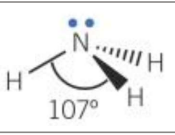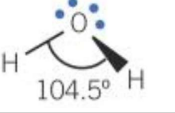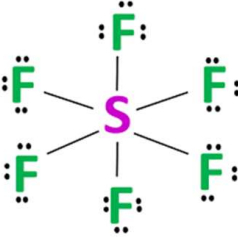 chlorine (Cl)
- • Does not conduct electricity in solid state
  - ○ Ions held in fixed positions
  - ○ No mobile charge carriers
- • Conduct electricity when dissolved or molten
  - ○ The solid ionic lattice breaks down
  - ○ Ions are free to move as mobile charge carriers
- • Covalent bonding
  - • 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 atomics 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
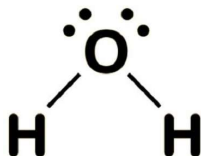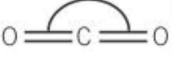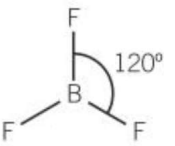
- • Multiple covalent bond
  - • The electrostatic attraction is between two / three shared pairs of electrons and the nuclei of the bonded atoms
- • Dative covalent bonds / coordinate bonds
  - • The shared pair of electrons is supplied by one of the bonding atoms only
  - • The shared pair is originally a lone pair of electrons on one of the bonded atoms
  - • e.g. ammonia molecule donates its lone pair of electrons to a H^+ ion to form NH_4^+ ion

-

Hydronium ion
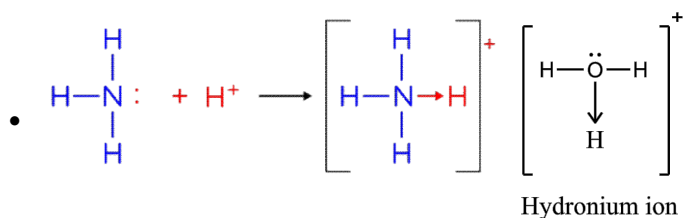
- Exceptions
  - Boron
    - Only 3 outer shell electrons can be paired → only forms 3 pairs
    - e.g. BF_3 only has 6 electrons around the boron atom
  - Phosphorus, sulfur, chlorine (expansion of the octet)
    - Outer electrons are in $n = 3$ shell which can hold up to 18 electrons
    - More electrons are available for bonding (can have more than 8 electrons in outer shell e.g. 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° 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	
3	Trigonal planar	
4 (no lone pairs)	Tetrahedral	
4 (1 lone pair)	Pyramidal	
4 (2 lone pairs)	Non-linear	
6	Octahedral	**Remember SF₆ as an example of this**

- Bond representations
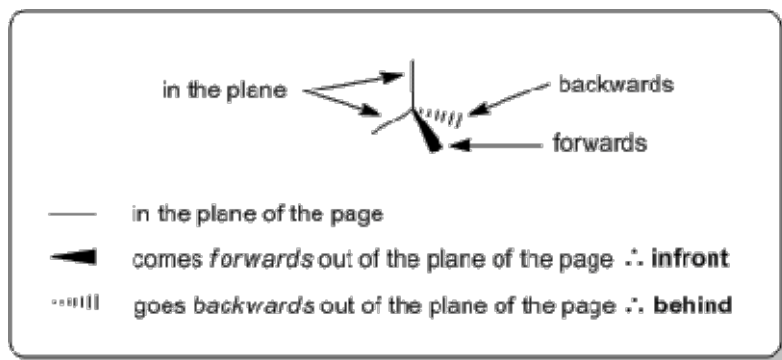
- Predicting molecular shape of ions
  - Ions with oxygen
    - Add an electron to an oxygen atom for every negative charge
    - Bonds can be single or double bond
  - Cations with hydrogen
    - Add positive charge by H^+ ions
  - Others
    - Add / remove electrons from the central atom to match the 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 $\rightarrow$ attraction increases
  - Atomic radius increases down the table $\rightarrow$ attraction decreases
  - **Fluorine is the most electronegative element**
- Predicting type of bond

Bond type	Electronegativity difference
Covalent	0

|	
Polar covalent	0 - 1.8
Ionic	> 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
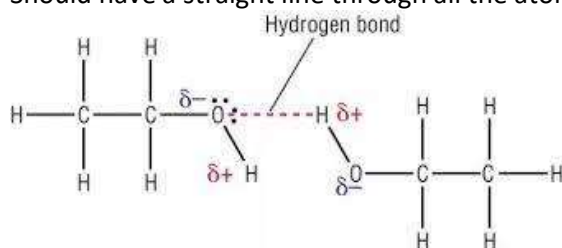 - e.g. overall dipole in H_2O, cancels out in CO_2 and methane
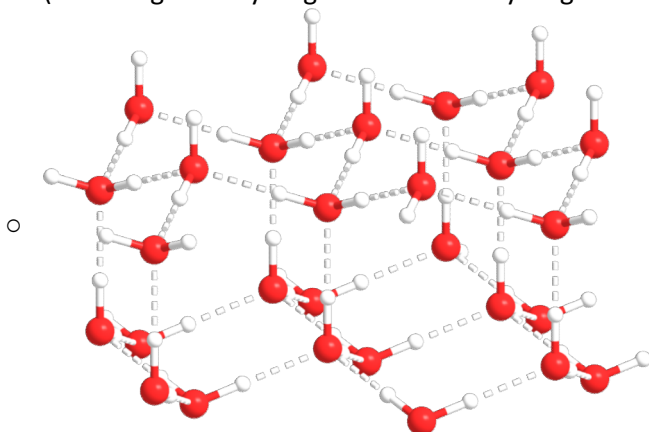 -
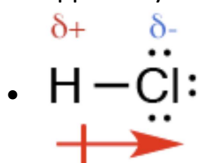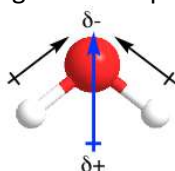
    H_2O, bend shape
    polar
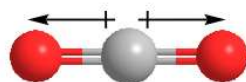
    CO_2, linear shape
    non-polar
- Types of intermolecular forces
  - London forces / induced dipole-dipole **interactions** / dispersion forces (van der Waals' forces)
  - Permanent dipole-dipole **interactions** (van der Waals' forces)
  - Hydrogen bonding (a special type of permanent dipole-dipole 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-shieled 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 δ+ 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 H_2O
  - 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°)
  -
  - 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
Periodicity	A repeating trend in physical and chemical properties of the elements across the periodic table.
Groups	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.
Periods	A horizontal row in the periodic table. Elements show trends in properties across a period.
Shielding effect	The repulsion between electrons in different inner shells. Shielding reduces the net attractive force between the positive nucleus on the outer shell electrons.
Metallic bonding	The strong electrostatic attraction between the regularly arranged metal cations and the delocalised valence electrons between them.
Delocalised electrons	Electrons shared between more than two electrons.
Giant metallic lattice	A three dimensional structure of positive ions and delocalised electrons, bonded together by strong metallic bonds.
Giant covalent lattice	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
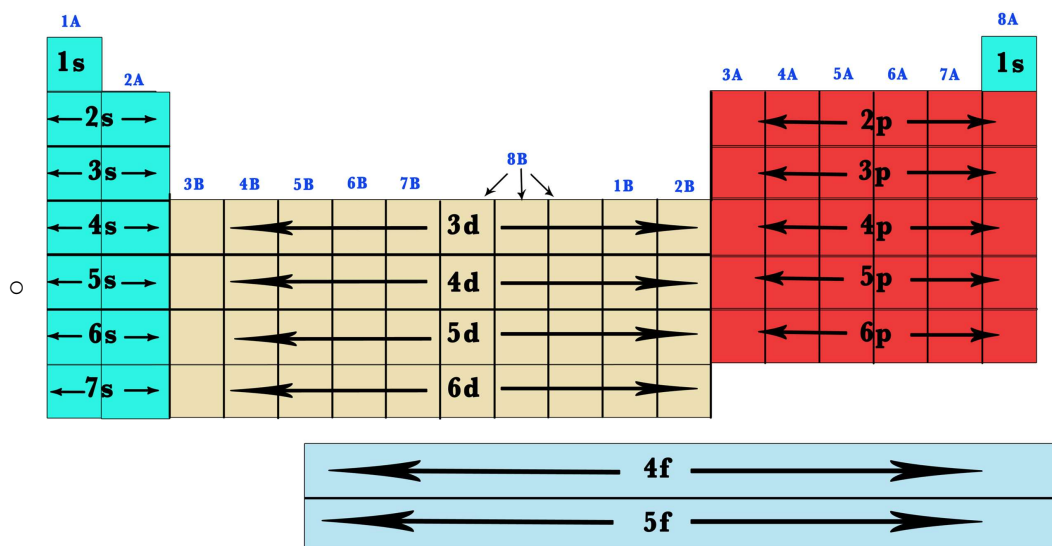 - In groups with similar properties
- Electron configuration pattern
  - Across period
    - Each period starts with an electron in a new highest energy shell
    - Period 2: 2s fills → 2p fills
    - Period 3: 3s fills → 3p fills
    - Period 4: only 4s and 4d occupied in $n = 4$ shell
- Blocks
  - * 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

Periodic table orbital blocks diagram:

1A — 1s
2A — 2s, 3s, 4s, 5s, 6s, 7s
3B, 4B, 5B, 6B, 7B, 8B, 1B, 2B — 3d, 4d, 5d, 6d
3A, 4A, 5A, 6A, 7A, 8A — 2p, 3p, 4p, 5p, 6p (8A top: 1s)
4f
5f

- 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 = kJ mol^{-1}
  - Equation: e.g. $Na(g) \rightarrow Na^+(g) + e^-$ (first ionisation energy = +496 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 → 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 → first ionisation energy increases
  - Falls when the p sub-shell is starting to be filled (e.g. Li → 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
-
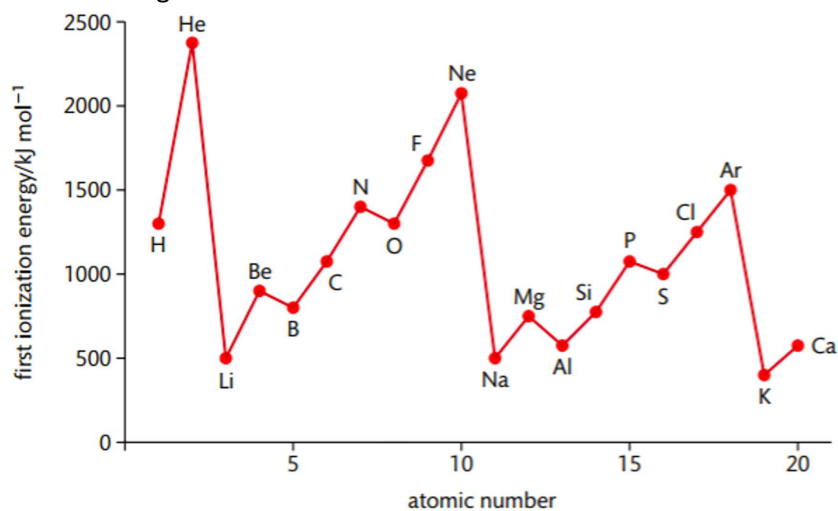
- First ionisation energy trend down a group
  - Decrease down a group
  - Atomic radius increases
  - More inner shells so shielding increases
  - * Increase in atomic radius and shielding outweighs the increasing nuclear charge
  - Nuclear attraction on outer electrons decreases → first ionisation energy decreases
- Successive ionisation energy pattern
  - Equation: e.g. $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$
  - 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 shall electrons to a shared pool of electrons which are delocalised throughout the whole structure
  - Cations life 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
-
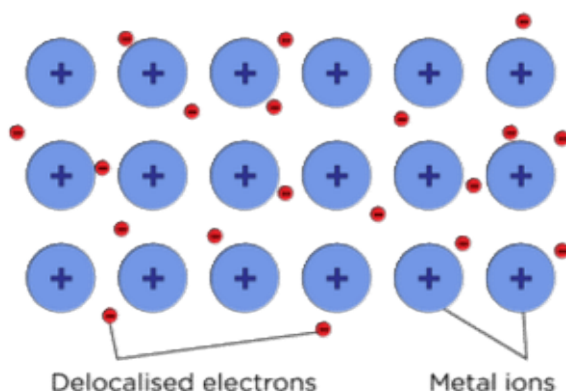
- Properties of metals

- 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$_2$, 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 ionsare 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
Oxidising agent	A reagent that oxidises another species
Reducing agent	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_2 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
  - $MO(s) + H_2O(l) \rightarrow M^{2+}(aq) + 2OH^-(aq)$
  - OH^- 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: $M^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow M(OH)_{2(s)}$
  - Solubility of hydroxides increases down the group so the solution can contain more OH^- ions and become more alkaline
    - $Mg(OH)_{2(s)}$ slightly soluble $\rightarrow$ low OH^- concentration, pH $\approx$ 10
    - $Ba(OH)_{2(s)}$ more soluble $\rightarrow$ higher OH^- concentration, pH $\approx$ 13
- Uses of Group 2 compounds as bases
  - $Ca(OH)_2$ in agriculture to neutralise acidic soil
    - Added to fields as lime
    - $Ca(OH)_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O(l)$
    - Sodium or potassium hydroxides are not suitable as they would kill soil organisms and plants (too alkaline)
  - $Mg(OH)_2$, $MgCO_3$ and $CaCO_3$ 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 $Mg(OH)_2$ in water
    - $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$
    - $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
    - 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

F_2	Gas	
Cl_2	Gas	Boiling point increases down the group
Br_2	Liquid	
I_2	Solid	
At_2	Solid	

- Appearance under different states

Halogen	Colour in natural state	Colour in aqueous solutions	Colour in organic solvents
F_2	Pale yellow **gas**	/	/

	Cl$_2$	Pale green **gas**	Pale green	Pale green
	Br$_2$	Red-brown **liquid**	Orange	Orange
	I$_2$	Shiny grey-black **solid**	**Brown**	**Violet**

- Redox reaction of halogens
    - Halogens all have s^{2}p^5 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$_2$ reacts with Br$^-$ (Cl$_2$(aq) + 2Br$^-$(aq) → 2Cl$^-$(aq) + Br$_2$(aq) orange)
        - Cl$_2$ reacts with I$^-$ (Cl$_2$(aq) + 2I$^-$(aq) → 2Cl$^-$(aq) + I$_2$(aq) violet)
        - Br$_2$ reacts with I$^-$ only (Br$_2$(aq) + 2I$^-$(aq) → 2Br$^-$(aq) + I$_2$(aq) violet)
        - I$_2$ 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$_2$ > Br$_2$ > I$_2$
- 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
    - $$Cl_2(aq) + H_2O(l) \rightarrow HClO(aq) + HCl(aq)$$

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$^-$)
    - 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**
    - $$Cl_2(aq) + 2NaOH(aq) \rightarrow NaClO(aq) + NaCl(aq) + H_2O(l)$$

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 (NH_4^+)
    - $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$
    - **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 H_2SO_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
       - $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$
     - 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
       - $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$
  2. Sulfate test
     - Add barium chloride (barium nitrate if halide test needed later) to the **solution** of the compound
     - If white precipitate forms then SO_4^{2-} is present
       - $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
  3. Halide test
     - Add aqueous silver nitrate ($AgNO_3$) to an **aqueous solution** of a halide
     - Silver halide precipitates as different colour
       - $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
       - 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 $NH_3(aq)$ only
       - AgBr = soluble in concentrated $NH_3(aq)$ only, insoluble in dilute $NH_3(aq)$
       - AgI = insoluble in dilute and concentrated $NH_3(aq)$
  - Correct sequence needed
    - Neither sulfate / halide produce bubbles with dilute acid → cannot have incorrect conclusion
    - $BaCO_3$ is white and insoluble in water so it gives a false positive result on carbonates as well in sulfate tests
    - Ag_2CO_3 and Ag_2SO_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
Enthalpy / H	Measure of heat energy in a chemical system
Chemical system	The atoms, molecules or ions making up the chemicals
Activation energy / E_a	The minimum energy required for a reaction to take place
Standard state	The physical state of a substance under standard conditions
Enthalpy change of reaction / $\Delta_r H$	The enthalpy change associated with a stated equation in the **molar quantities shown in a chemical equation**
Enthalpy change of formation / $\Delta_f H$	The enthalpy change that takes place when **1 mole of a compound** is formed from its elements
Enthalpy change of combustion / $\Delta_c H$	The enthalpy change that takes place when **1 mole of a substance** reacts completely with oxygen (complete combustion)
Enthalpy change of neutralisation / $\Delta_{neut} H$	The enthalpy change that accompanies the reaction of an acid by a base to form **1 mole of H$_2$O$_{(l)}$**
Enthalpy change of solution / dissolution	The enthalpy change when **1 mole of a substance** is completely dissolved in water
Hess's Law	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 beat 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
  -

Exothermic	Endothermic
ΔH is negative	ΔH is positive
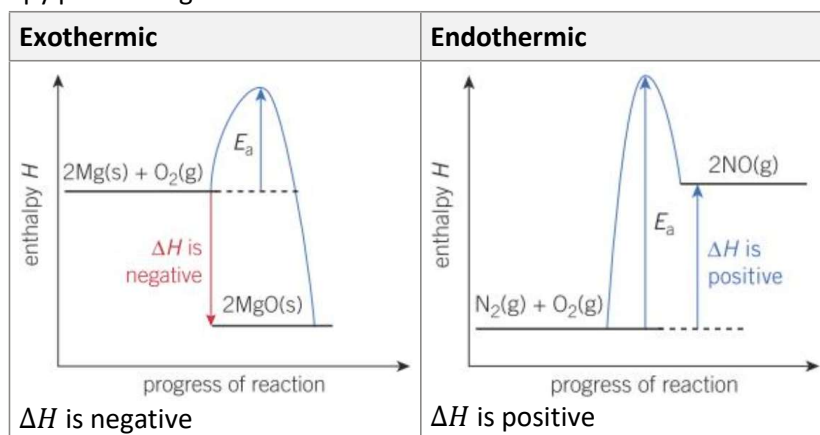
- * The activation energy can normally be omitted when there are > 1 energy changes
- Standard conditions
  - Shown with symbol $\ominus$ / °
  - Standard pressure = **100 kPa / 1×10⁵ N m⁻² / 1 atm**
  - Standard temperature = **298 K / 25 °C**
  - Standard concentration = **1 mol dm⁻³ / 1 M**
  - Substances 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 $= -\dfrac{q}{n}$
- 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
    - Weight 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

thermometer
insulating lid
mixed chemicals
polystyrene (insulated) cup
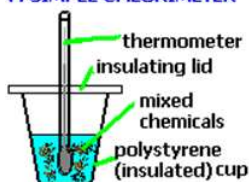
- Cooling curve correction
  - Add one reactant to the polystyrene cup
  - Take temperature of the solution every 30s until temperature stays constant
  - Add the other reactant + stir
  - Measure temperature every 30s until temperature has fallen for several mins
  - Plot a graph of temperature against time
  - Extrapolate cooling curve section back to when second reactant added
  - Find the theoretical ΔT at that point of time
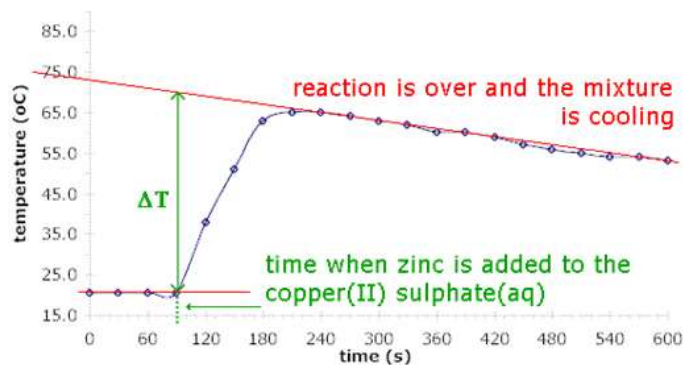
- Average bond enthalpy
  - The enthalpy change when **1 mole** of a bond is broken in the **gas state**
  - Limitations: actual bond enthalpy can vary depending on the chemical environment of the bond
- Endothermic / exothermic
  - Endothermic
    - Bond breaking is endothermic
    - More energy required when breaking bonds than energy released when making bonds
    - $\Delta H > 0$
  - Exothermic
    - Bond formation is exotmermic
    - More energy released when making bonds than energy required when breaking bonds
    - $\Delta H < 0$
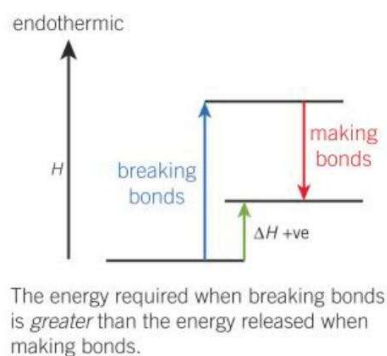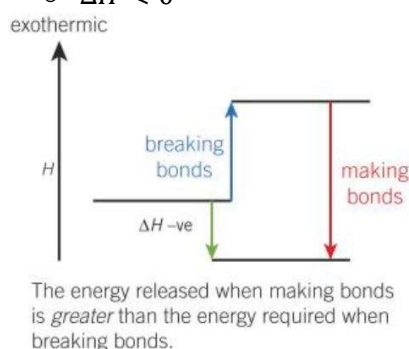
- Calculating enthalpy change from average bond enthalpies
  - $\Delta_r H = \Sigma(\text{bond enthalpies in reactants}) - \Sigma(\text{bond enthalpies in products})$
- Hess's Law
  -
- Working out enthalpy change using Hess's Law
  - Using enthalpy change of formation: $\Delta_r H = \Sigma\Delta_f H \text{ products} - \Sigma\Delta_f H \text{ reactants}$
  - 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
Intermediate	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
  - $\text{rate} = \dfrac{\text{change in concentration}}{\text{time}}$ (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
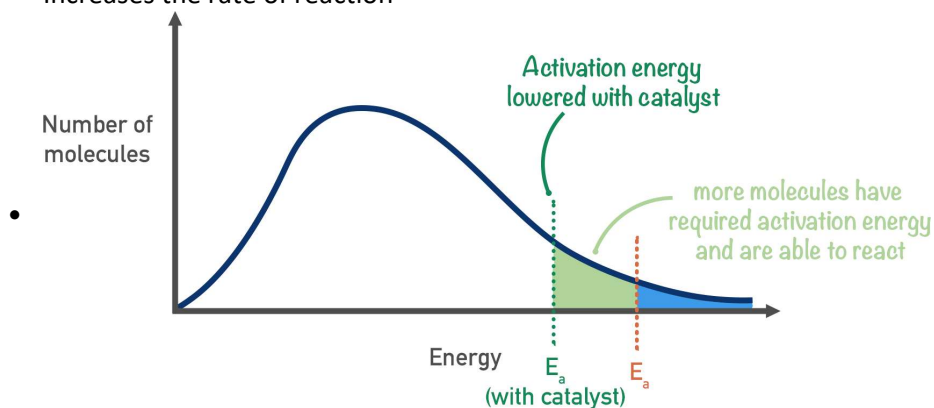 - Increase concentration / pressure = increase in rate of reaction

- 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 probably 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**

most molecules don't have the required activation energy and are unable to react

only molecules with required activation energy are able to react

Number of molecules

Energy

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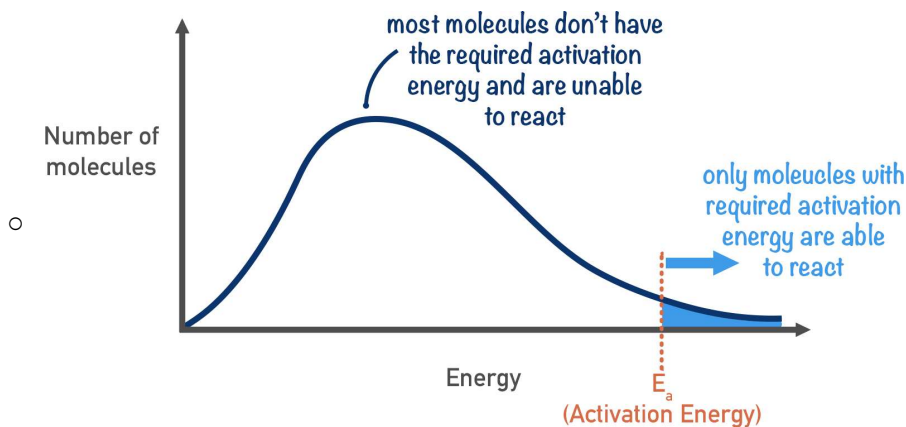
- Effect of change in temperature on Boltzmann distribution
  - Graph: higher temperature = lower peak, peak shifted to the right
  - **Larger area to the right of E_a → More molecules have energy $\geq E_a$** (major effect)
  - A greater proportion of collisions will lead to a reaction
  - More frequent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

T_1

T_2 (increased temperature)

Number of molecules

more molecules at T_2 have required activation energy and are able to react

Energy

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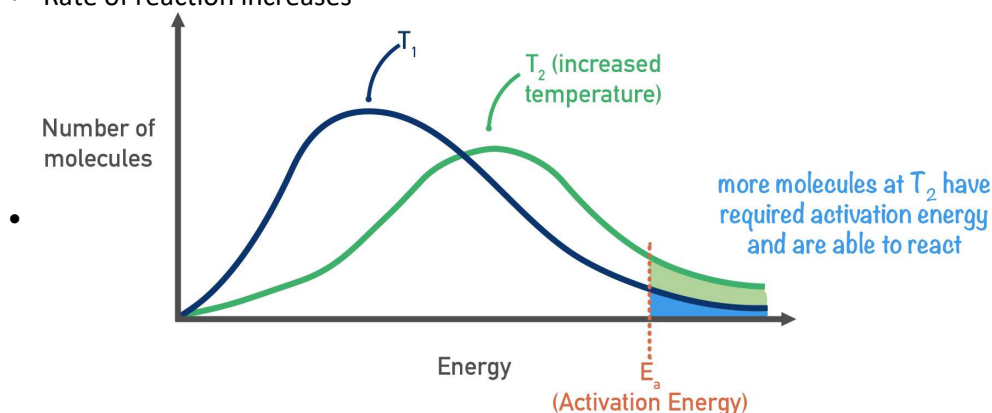
- Effect of catalyst on Boltzmann distribution
  - Larger area to the right of E_a → a greater proportion of molecules now have an energy $\geq$ the lower activation energy
  - A greater proportion of collisions will lead to a reaction
  - Increases the rate of reaction

Activation energy lowered with catalyst

Number of molecules

more molecules have required activation energy and are able to react

Energy

E_a
(with catalyst)

E_a

3.2.3 Chemical equilibrium

- Definitions

Term	Definition
Dynamic equilibrium	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
  - $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (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 H_2 and 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
  - $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$
  - [] = 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 **same functional group** but with **each successive member differing by CH$_2$**
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 **same molecular formula** but **different structural formulae**

- Alkyl group
  - General formula C_nH_{2n+1}
  - 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_nH_{2n+2}
  - Structural formula
    - The minimal detail that shows the arrangement of atoms in a molecule
    - e.g. for butane: $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

- 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
    -
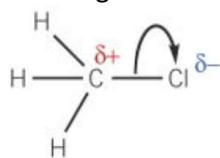 - Benzene
    -
- Types of covalent bond fission
  - Homolytic fission
    - **Each bonding atom receiving one electron** from the bonded pair forming 2 radicals
  - Heterolytic fission
    - **One bonding atom receiving both electrons** from the bonded pair
    - The atom that takes both electrons becomes a negative ion
    - The atom that does not take the electrons becomes a positive ion
    - e.g. $H_3C\text{-}Cl \rightarrow H_3C^+ + Cl^-$
- Radical
  - A species with **an unpaired electron**
  - Represented with a dot (•)
  - e.g. $H_3C\text{-}CH_3 \rightarrow H_3C• + •CH_3$
- Curly arrows
  - Showing the **movement of an electron pair**
  - Showing either heterolytic fission or formation of a covalent bond
  -
- Types of reaction
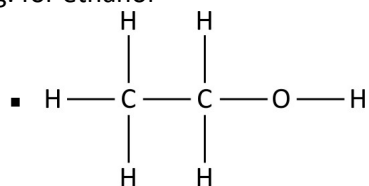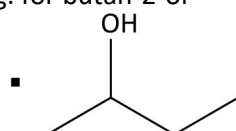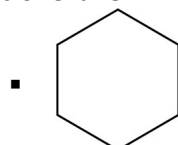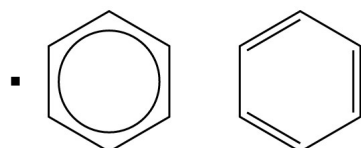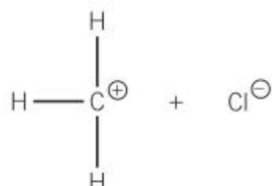
- Addition reaction
  - Two reactants join together to form one product
- Substitution reaction
  - An atom or group of atoms is replaced by a different atom or group of atoms
- Elimination reaction
  - Involves the removal of a small molecule from a larger one
  - One reactant molecule forms two products

4.1.2 Alkanes

- Definitions
-

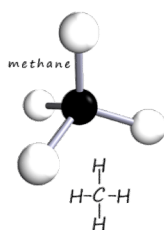| Term	Definition
Free radical	A species with an unpaired electron
Chain reaction	A reaction in which the propagation steps release new radicals that continue the reaction
Initiation	The first stage in a radical reaction in which radicals form when a covalent bond is broken by homolytic fission
Propagation	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 = σ-bond (sigma bond)
    - σ-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 σ-bond
- Shape of alkanes
  - Tetrahedral shape around each carbon atom, bond angle 109.5°
  - Each carbon atom surrounded by 4 electron pairs in four σ-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
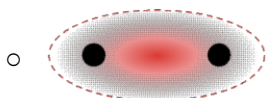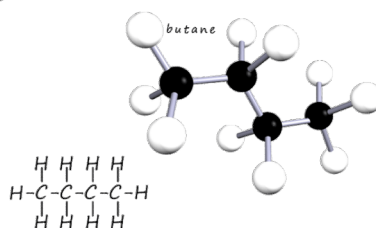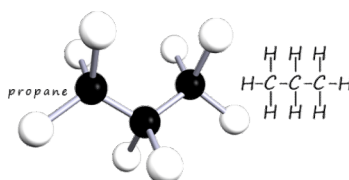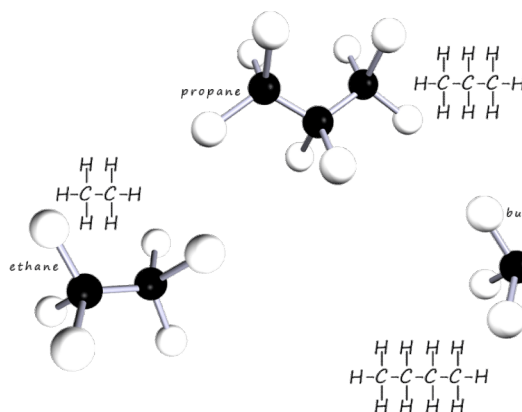
- More branching = lower boiling point
- More branches = fewer surface area of contact → weaker London forces
- The branches prevent the branched molecules getting as close together as straight-chain molecules → further decrease intermolecular forces
- Less energy is required to overcome the London forces
- Reactivity of alkanes
  - Low reactivity
  - C-C and C-H σ-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-CH₃ + X₂ → R-CH₂X + 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• + CH₄ → •CH₃ + HCl
    - Second propagation step
      - Each alkyl radical reacts with another halogen molecule → forming haloalkane + new halogen radical
      - •CH₃ + Cl₂ → CH₃Cl + Cl•
    - 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• + •Cl → Cl₂ / •CH₃ + •CH₃ → C₂H₆ / •CH₃ + •Cl → CH₃Cl
    - 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

- o 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 δ+ 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 **unsaturated alkene molecules** (monomers)

- Structure of C=C bond
  - Comprised of
    - o A σ-bond: **head on overlap** of orbitals directly between the bonding atoms
    - o A π-bond: **sideways overlap** of **adjacent p-orbitals** above and below the bonding carbon atoms
    - o The π-bond locks the two carbon atoms in position and prevents them from rotating around the double bond (restrict rotation)

  ⭐ o
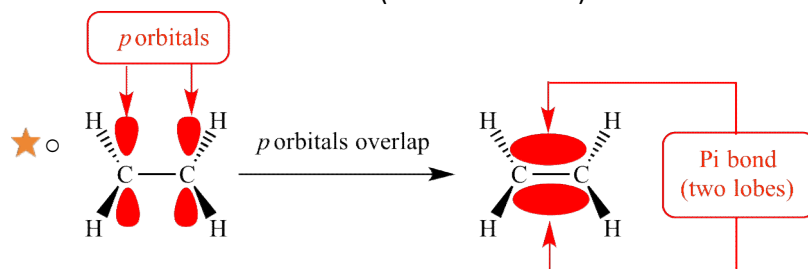
  - **Trigonal planar** shape around each carbon atom in the C=C bond (120° bond angle)
    - o 3 regions of electron density around each carbon atom
    - o The 3 regions repel each other as far apart as possible
- σ and π-bond difference

|	σ-bond	π-bond
Position of electron density	Between bonding atoms	Above and below bonding atoms
Overlap of orbitals	Head on overlap of orbitals	Sideways overlap of orbitals
Bond enthalpy / strength	Higher	Lower
Size	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 π-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
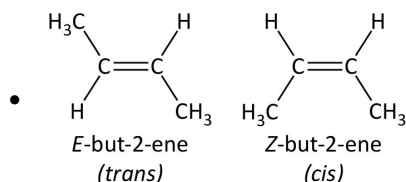
-
  E-but-2-ene   *Z*-but-2-ene
  (trans)   (cis)
- Identify E/Z isomers by Cahn-Ingold-Prelog (CIP) priority rules
  - Assigning priority
    - ○ Examine the atomic number of the atoms directly attached to the carbon atoms of the double bind
    - ○ Higher atomic number = higher priority
    - ○ Two 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 π-bond so it is broken more readily
    - ○ It is on the outside of the σ-bond so its electrons are more exposed
- Addition reactions of alkanes

Reaction	Condition	Detail
Hydrogenation	• Nickel catalyst • 423 K (150°C) • High pressure	• Alkene + hydrogen → alkene / $R-CH=CH_2 + H_2$ → $R-CH_2-CH_3$ • Type: hydrogenation / addition

Halogenation	• RTP	• Alkene + halogen → dihaloalkane e.g. $R-CH=CH_2 + Br_2$ → $R-CHBr-CH_2Br$
		• Type: electrophilic addition (see below for mechanism)
		• Reaction of alkenes with bromine can be used to test if the organic compound is unsaturated
		    • Bromine water added dropwise to alkene
		    • Bromine adds across the double bond
		    • The orange colour of bromine water disappears
		    • Added to an saturated compound: no addition reaction so no colour change

Addition with (gaseous) halogen halides	• Room temperature	• Alkene + halogen halide → haloalkane e.g. $R-CH=CH_2 + HBr$ → $R-CHBr-CH_3$ • Type: electrophilic addition (see below for mechanism) • Alkene is a gas: reaction takes place when the two gases are mixed • Alkene is a liquid: hydrogen halide bubbled through it • Can also react with concentrated hydrochloric or hydrobromic acid * **Two possible products**
Hydration	• Steam • Phosphoric acid (H_3PO_4) catalyst	• Alkene + $H_2O_{(g)}$ → alcohol • Type: hydration • $R-CH=CH_2 + H_2O$ → $R-CH(OH)-CH_3$ * **Two possible products**

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

-

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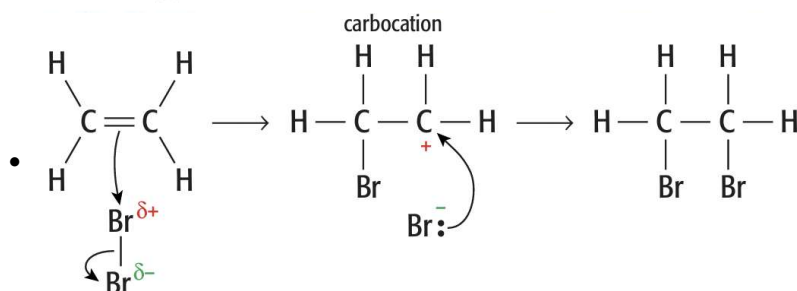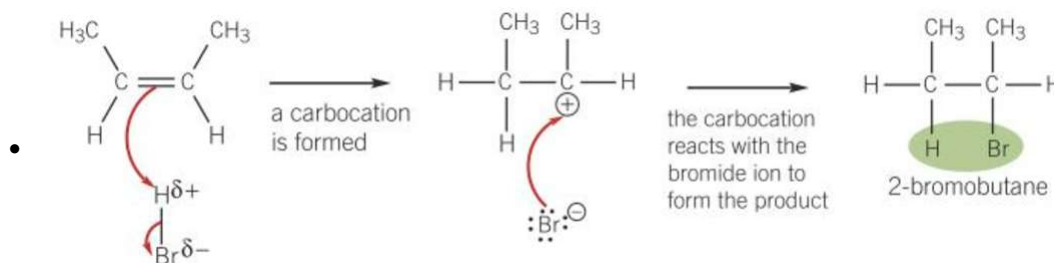
- Types of carbocations

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$^-$ 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**
    -
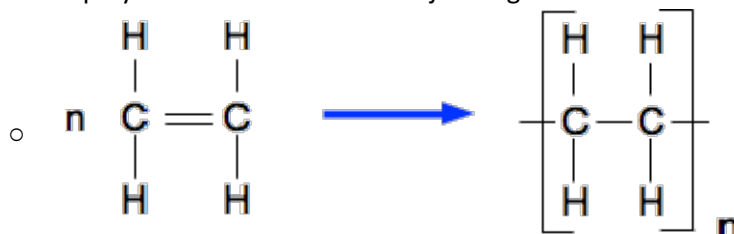
- Problems of waste polymers
  - Benefits of cheap oil-derived plastics are counteracted by problems for the environment of landfill
  - They are unreactive so they are non-biodegradable and cannot be broken down by species in nature
  - Non-biodegradable waste polymers can become a threat to wildlife
- 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_2 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 **water molecule** 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
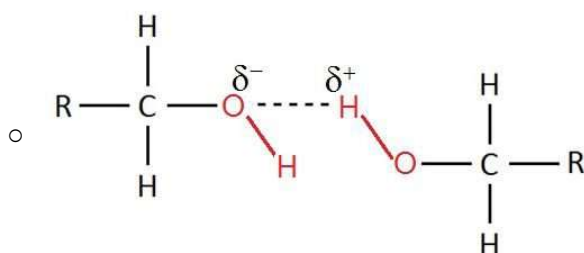
  - Greater water solubility than alkenes
    - Alkanes are non-polar so they cannot form hydrogen bonds with water
    - O-H bond in alcohol is polar and forms hydrogen bond with water
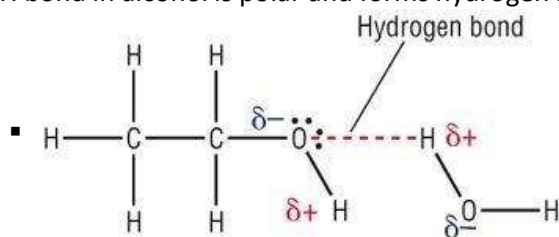
    - Longer carbon chain = less miscible in water
    - More -OH groups = more miscible in water
- Classifying alcohols
  - Primary: -OH group attached to a carbon atom attached to **2 hydrogen atoms + 1 alkyl group**
  - Secondary: -OH group attached to a carbon atom attached to **1 hydrogen atom + 2 alkyl 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
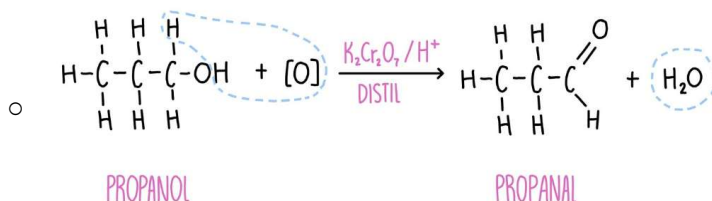- Oxidation of alcohols
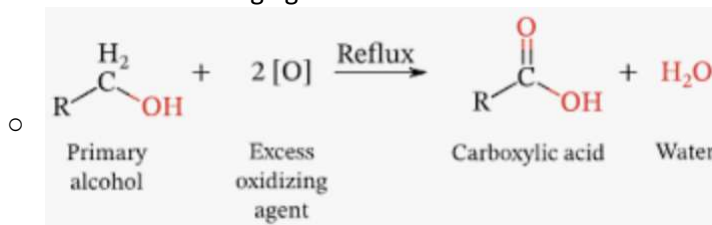 - Heat with an oxidising agent ([O])

- - Normally acidified dichromate (VI) ($Cr_2O_7^{2-}$ / H^+)
      - e.g. acidified potassium dichromate (VI) ($K_2Cr_2O_7$ / H_2SO_4)
  - Observations
    - Cr will be reduced
    - Reaction mixture turn from orange (Cr^{6+} in $Cr_2O_7^{2-}$) to green (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
   -

      PROPANOL → PROPANAL
  - 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
  -
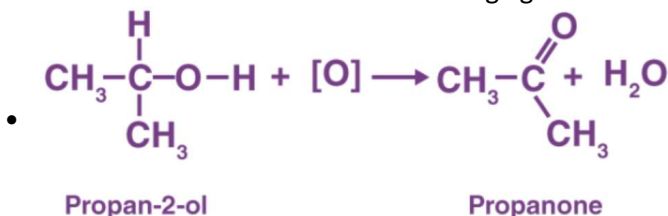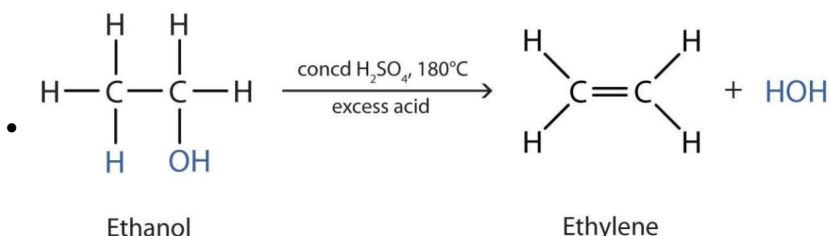

  Propan-2-ol → Propanone
- Oxidation of tertiary alcohols
  - Do not undergo oxidation reactions
  - Acidified dichromate (VI) ions remain orange when added to a tertiary alcohol
- Dehydration of alcohols
  - Heated under **reflux** with **acid catalyst** (e.g. concentrated H_2SO_4 / H_3PO_4)
  - Product = an alkene
  - Type = elimination reaction
  -

  Ethanol → Ethylene
- Substitution reaction of alcohols
  - Alcohols react with halide ions to form haloalkanes
  - Heated under **reflux** with **concentrated acid catalyst** & halide ion e.g. H_2SO_4 + 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

$$R-OH \quad + \quad NaX \quad \xrightarrow{H_2SO_4} \quad R-X \quad + \quad NaHSO_4 \quad + \quad H_2O$$
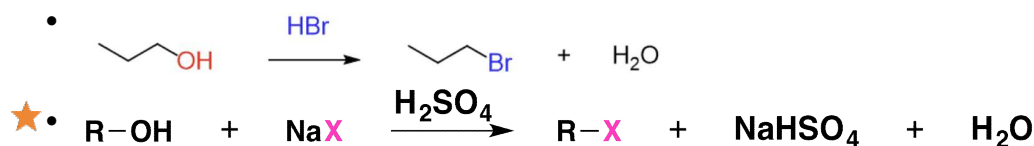
4.2.2 Haloalkanes

- Definitions

Term	Definition
Nucleophile	An atom or group of atoms which is attracted to an electron-deficient centre or atom, where it **donates a pair of electrons** to form a new covalent bond
Nucleophilic substitution	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
Hydrolysis	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
    - δ+ 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**
    - OH⁻ normally from NaOH
    - 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 δ+ 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
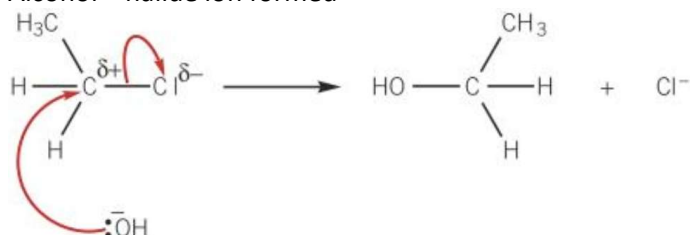
- Trend in reaction rates of hydrolysis of primary haloalkanes
    - C-F has the greatest bond enthalpy (strongest), C-I has the lowest bond enthalpy (weakest)
        - Going down the table = larger halogen atom = longer bond = bond becomes weaker
    - Rate: iodoalkanes > bromoalkanes > chloroalkanes > 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
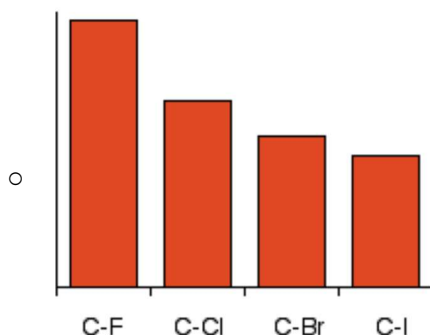
- Measuring rate of hydrolysis
  - Set up 3 test tubes of 1 cm^3 ethanol and couple drops of 1-chlorobutane / bromobutane / iodobutane
  - Put the test tubes + a test tube with silver nitrate in water bath at 60°C
  - Allow them to reach constant temperature (60°C)
  - Add 1 cm^3 of silver nitrate to 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. $CF_2Cl_2 \rightarrow CF_2Cl\bullet + Cl\bullet$
  - Chlorine radical formed is a very reactive intermediate and can react with an ozone molecule
    - Propagation step 1: $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
    - Propagation step 2: $ClO\bullet + O \rightarrow Cl\bullet + O_2$
    - (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: $NO \rightarrow N\bullet + O\bullet$
    - Propagation step 1: $N\bullet + O_3 \rightarrow \bullet NO + O_2$
    - Propagation step 2: $\bullet NO + O \rightarrow N\bullet + O_2$
    - Overall: $O_3 + O \rightarrow 2O_2$
  - Reaction with NO_2

- Initiation: $NO_2 \rightarrow NO\bullet + O\bullet$
- Propagation step 1: $NO\bullet + O_3 \rightarrow NO_2\bullet + O_2$
- Propagation step 2: $NO_2\bullet + O \rightarrow NO\bullet + O_2$
- Overall: $O_3 + O \rightarrow 2O_2$
- 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
Fractional distillation	The separation of components in a liquid mixture by their different boiling points into fractions with different compositions
Drying agent	An **anhydrous solid** 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
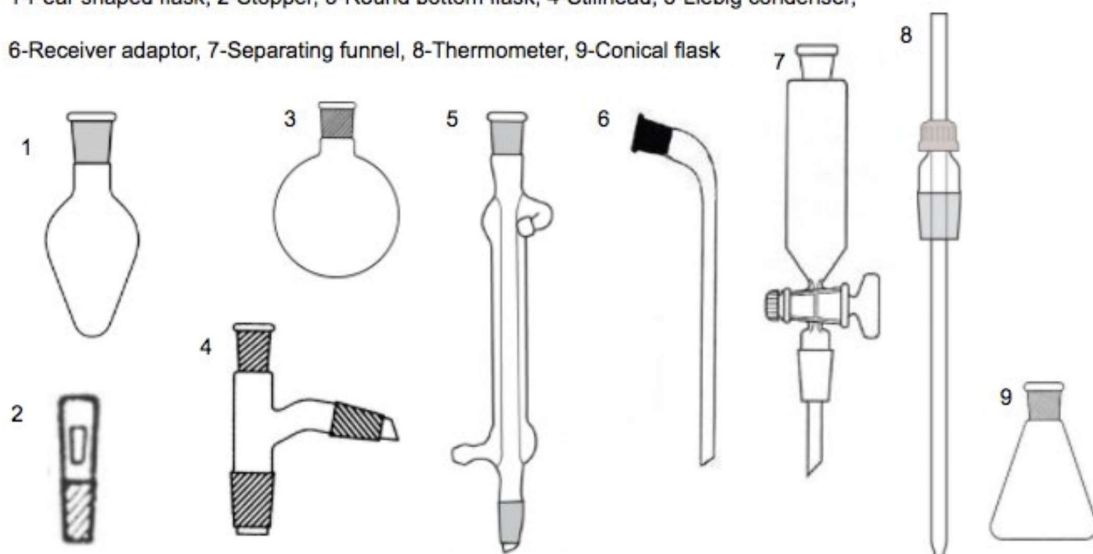

- Heating under reflux
  - To prepare organic solid without boiling off solvent, reactants or products
  - Water bath can be used rather than Bunsen if can be carried out below 100°C
  - Heating mantle can be used for flammable liquids
  - Anti-bumping granules added to liquid so it boils smoothly
    - 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)
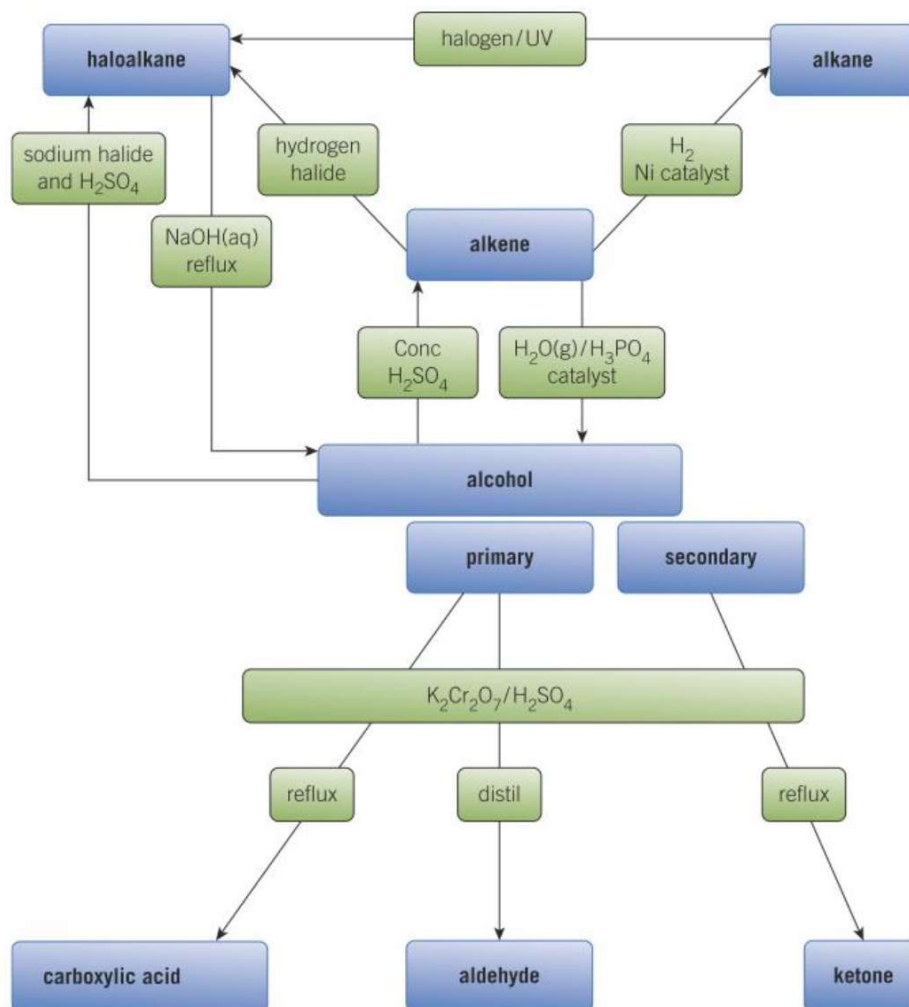
- Distillation
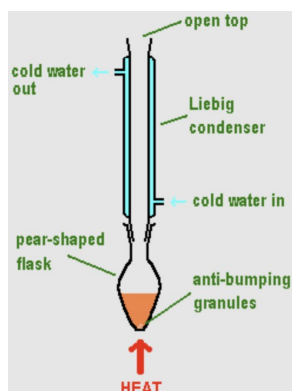
Aldehyde Preparation
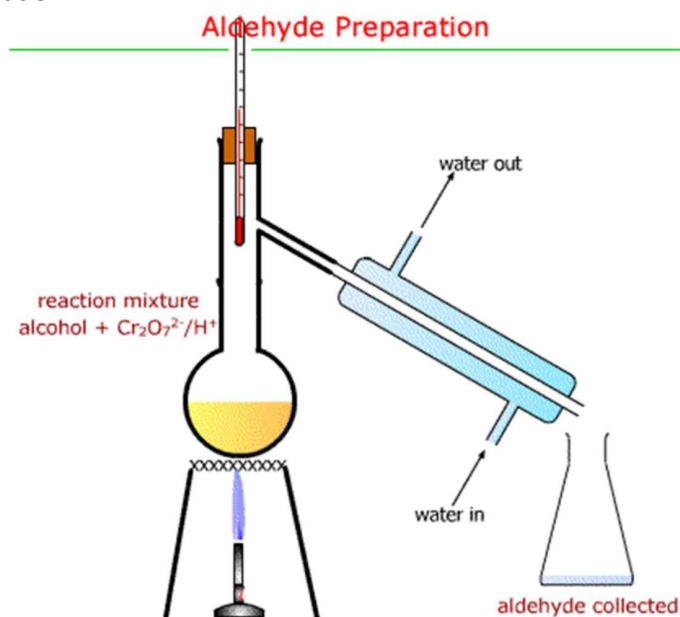
- Separates a pure liquid from impurities
- Flask clamped by neck
- Still head connected to the flask
- Condenser connected to rubber tubing for water (**water enters at the bottom**)
- Flask used to collect the distillate so the apparatus is not airtight
- Heat the mixture gently (make sure the temperature 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. $CaCl_2$ for drying hydrocarbons, $CaSO_4$ / $MgSO_4$ 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
  -

haloalkane ← halogen/UV → alkane

sodium halide and H_2SO_4

hydrogen halide

H_2 Ni catalyst

NaOH(aq) reflux

alkene

Conc H_2SO_4

$H_2O(g)/H_3PO_4$ catalyst

alcohol

primary — secondary

$K_2Cr_2O_7/H_2SO_4$

reflux — distil — reflux

carboxylic acid — aldehyde — ketone

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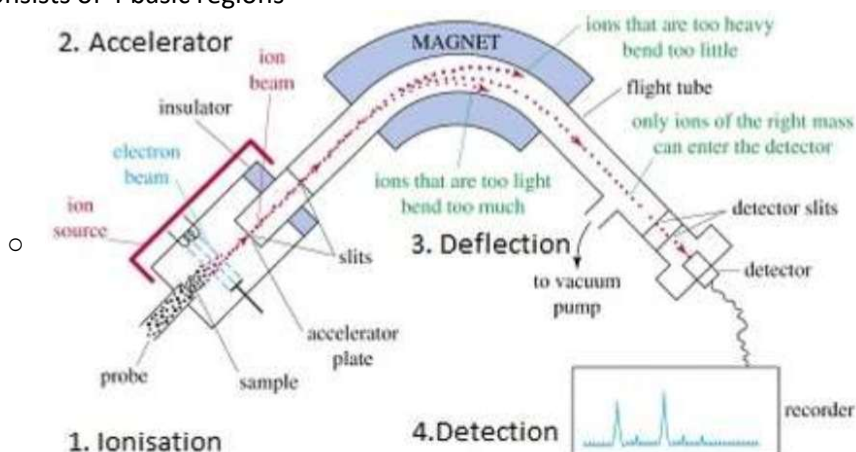 - Find the properties and reactions for each functional group

4.2.4 Analytical technique

- Definitions

Term	Definition
Fragmentation	The process in mass spectrometry that causes a positive ion to split into smaller pieces, one of which is a positive fragment ion
Fragment ions	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 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. CO_2, H_2O and 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 CO_2 emission to reduce global warming
- • Infrared spectroscopy
  - • Determine the functional groups present
  - • Sample placed in IR spectrometer
  - • IR radiation beams with wavenumber 200-4000 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 cm^{-1}** with **unique peaks to identify particular molecule**
  - • All organic compounds produce a peak 2850-3100 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)

15	CH_3^+	
29	$CH_3CH_2^+$	
31	CH_2OH^+	
41	C_3H_5, C_2H_3N	
43	$CH_3CH_2CH_2^+$ / CH_3CO / C_3H_7	
45	$CH_3CH_2O^+$	
49	$CH_3CH_2CH_2CH_2^+$	

- 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