

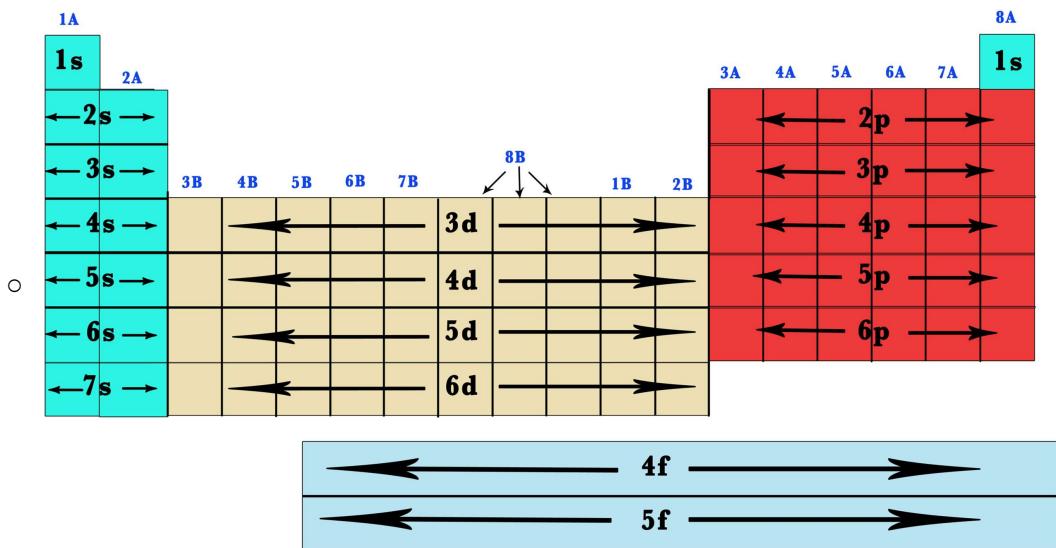
3.1.1 Periodicity

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 and 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 atoms / ions.
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.

The periodic table

- History
 - Then
 - Mendeleev arranged the elements in order of atomic mass
 - Swapped elements 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 electron** is in a s/p/d/f-orbital
 - S, p, d and f block



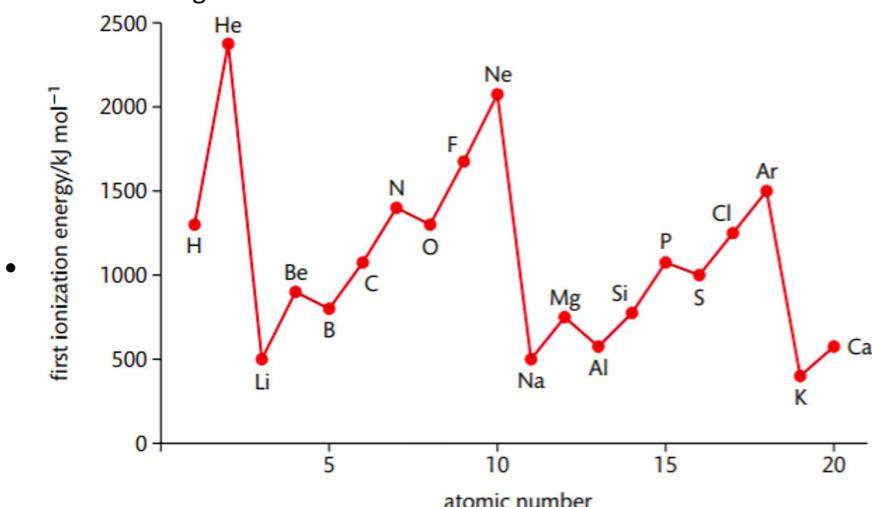
- Name of groups

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

Ionisation energy

- 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: $\text{X(g)} \rightarrow \text{X}^+(\text{g}) + \text{e}^-$
- 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
 - Nuclear charge (weakest effect, outweighed)
 - 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
- 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 \rightarrow 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

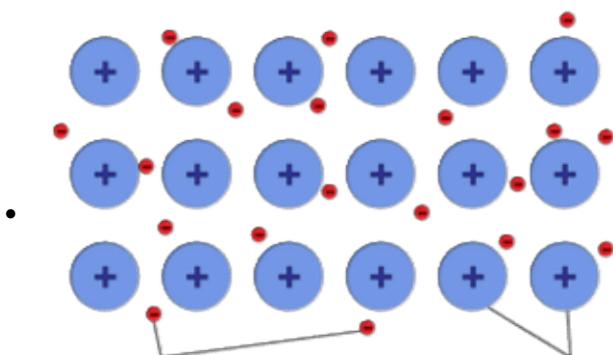
- Falls when pairing of electrons in p sub-shell starts (e.g. N \rightarrow O)
 - Paired electrons in one of the p orbitals repel one another so it is easier to remove an electron from the atom
 - Still larger than IE before the decrease

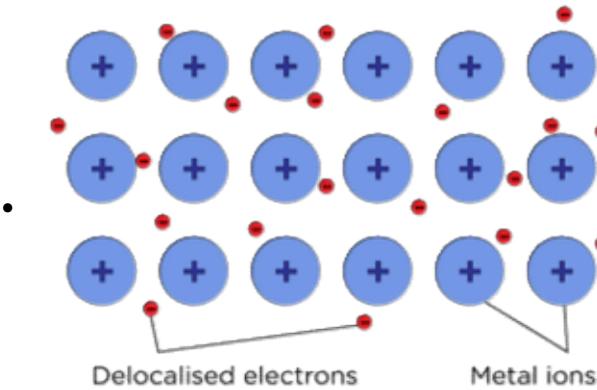


- First ionisation energy trend down a group
 - Decrease down a group
 - Atomic radius increases
 - More inner shells so shielding increases
 - Increase in atomic radius and shielding outweighs the increasing nuclear charge
 - Nuclear attraction on outer electrons decreases \rightarrow first ionisation 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 as atomic radius drops
 - Less shielding present as there are now less inner shells between electron & nucleus
 - Stronger nuclear attraction 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 bond

- Metallic bonding structure
 - Regularly arranged metal cations sitting in a sea of delocalised electrons
 - Each atom donates its negative outer shell electrons to a shared pool of electrons which are delocalised throughout the whole structure
 - Cations left behind = nucleus + inner shell electrons
 - Cations are fixed in position
 - Delocalised electrons are mobile and free to move throughout the structure
 - Forms a giant metallic lattice





- Properties of metals
 - All conduct electricity
 - Delocalised electrons can move through the structure and carry charge through the structure when a voltage is applied across a metal
 - More delocalised electrons → more electrons can move → better conductivity
 - Conducts electricity both in solid state and when molten**
 - Most have high melting and boiling points
 - Depends on the strength of metallic bonds
 - Greater cation charge = stronger attractive forces as more electrons are delocalised and forces between electrons + cations are stronger
 - Larger ions = weaker attractive forces due to larger atomic radius decreasing the charge density
 - High temperature needed to provide the large amount of energy to overcome strong electrostatic attraction between the cations and the electrons
 - Melting and boiling points decrease down the group
 - Dissolve in liquid metals only
 - Similar force between particles
 - Any interaction between polar / non-polar solvent + solute lead to a reaction rather than dissolving
 - Forces between particles are too large so it is not energetically favourable for them to mix

Giant covalent structures

- Giant covalent structures
 - Boron, carbon allotropes, and silicon (Si, SiO₂, SiC)**
 - A network of atoms bonded by strong covalent bonds to form a giant covalent lattice
- Diamond / silicon
 - 4 outer shell electrons of each atom form 4 covalent bonds with other carbon / silicon atoms
 - Tetrahedral structure
 - 109.5° bond angle due to electron-pair repulsion
 - High melting and boiling points
 - Atoms held together by strong covalent bonds
 - High temperatures are needed to provide the large quantity of energy needed to break the strong covalent bonds
 - Non-conductors of electricity
 - All 4 outer-shell electrons involved in covalent bond so no charged particles or mobile ions are available for conducting electricity
- Graphite
 - Flat 2D sheets of hexagonally arranged carbon atoms (trigonal planar 120°)
 - Layers bonded by weak London forces → they can slide over each other easily so graphite is soft
 - 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
 - Very hard as there are no points of weakness in the structure
 - 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

Periodic trends in properties

- Atomic radii trend across a period
 - Atomic radii decreases across the period
 - Positive charge in nucleus and negative charge in the outer shell both increases
 - Shielding remains similar as the number of shells doesn't change
 - The attraction between the nucleus and the outer 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

Group 2 properties and reactions

- Comparison to Group 1 elements
 - Better electrical conductivity
 - More outer shell electrons \rightarrow 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** \rightarrow 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 electrons are both 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 due to H_2 being produced at a faster rate
 - 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 \rightarrow 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 shell electrons decreases
- Reaction of Group 2 oxides with water
 - $MO(s) + H_2O(l) \rightarrow M^{2+}(aq) + 2OH^-(aq) \rightarrow M(OH)_2(aq)$
 - 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

- $\text{Mg(OH)}_{2(s)}$ slightly soluble \rightarrow low OH^- concentration, $\text{pH} \approx 10$
- $\text{Ba(OH)}_{2(s)}$ more soluble \rightarrow higher OH^- concentration, $\text{pH} \approx 13$
- Uses of Group 2 compounds as bases
 - Ca(OH)_2 in agriculture to neutralise acidic soil
 - Added to fields as lime
 - $\text{Ca(OH)}_2(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + 2\text{H}_2\text{O}(l)$
 - Sodium or potassium hydroxides are not suitable as they would kill soil organisms and plants (too alkaline)
 - 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
 - $\text{Mg(OH)}_2(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + 2\text{H}_2\text{O}(l)$
 - $\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$
 - KOH and NaOH are not suitable as ingesting them would cause poisoning and potentially death

3.1.3 The halogens

Physical properties

- 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
• Br_2	Liquid	increases down the group
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 reactions

- Redox reaction of halogens
 - Halogens all have s^2p^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 halogen added to other halide solutions
 - If the halogen added is more reactive than the halide ion in the solution
 - It will displace the halide ion in the solution
 - The solution changes colour (from ... to ...)
 - Results
 - Cl_2 reacts with Br^- ($Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$ orange)
 - Cl_2 reacts with I^- ($Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$ violet)
 - Br_2 reacts with I^- only ($Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$ 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 attraction between the nucleus and the outer shell
- Harder for elements to capture an electron from another species and form 1- ions

Disproportionation reactions

- Disproportionation
 - A redox reaction in which the same element is both oxidised and reduced
- Chlorinating water

$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HClO}(\text{aq}) + \text{HCl}(\text{aq})$$

• 0	→	-1	reduction
0	→	+1	oxidation

 - Used in water treatment systems to kill harmful bacteria
 - Bacteria killed by chloric(I) acid (HClO) and chlorate(I) ions (ClO^-)
 - 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 which is carcinogenic
- Manufacturing bleach
 - React chlorine with **cold and dilute aqueous NaOH solution**
$$\text{Cl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaClO}(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

• 0	→	-1	reduction
0	→	+1	oxidation

 - NaClO solution = bleach
- Halide test
 - See 3.1.4

3.1.4 Qualitative analysis

Test for cations

- Test for ammonium ion (NH_4^+)
 - $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$
 - **Aqueous sodium hydroxide** added to a **solution** of ammonium ion and **warm** the solution
 - 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

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
 - $2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 - Check the gas produced by bubbling it through lime water (calcium hydroxide)
 - Lime water will turn cloudy if the gas is carbon dioxide as a white precipitate of calcium carbonate forms
 - $\text{CO}_2(\text{g}) + \text{Ca}(\text{OH})_2(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$
2. Sulfate test
 - Add barium chloride (barium nitrate if halide test needed later) to the **solution** of the compound
 - If white precipitate forms then SO_4^{2-} is present
 - $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
 - BaSO_4 is insoluble in water
3. Halide test
 - Add aqueous silver nitrate (AgNO_3) to an **aqueous solution** of a halide
 - Silver halide precipitates as different colour
 - $\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightarrow \text{AgX}(\text{s})$
 - AgCl = white
 - AgBr = cream
 - AgI = yellow
 - Add aqueous ammonia to test the solubility of the precipitate (colours can be difficult to tell apart)
 - AgCl = soluble in both dilute and concentrated $\text{NH}_3(\text{aq})$
 - AgBr = soluble in concentrated $\text{NH}_3(\text{aq})$ only, insoluble in dilute $\text{NH}_3(\text{aq})$
 - AgI = insoluble in dilute and concentrated $\text{NH}_3(\text{aq})$
- Correct sequence needed
 - Neither sulfate / halide produce bubbles with dilute acid \rightarrow 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

3.2.1 Enthalpy changes

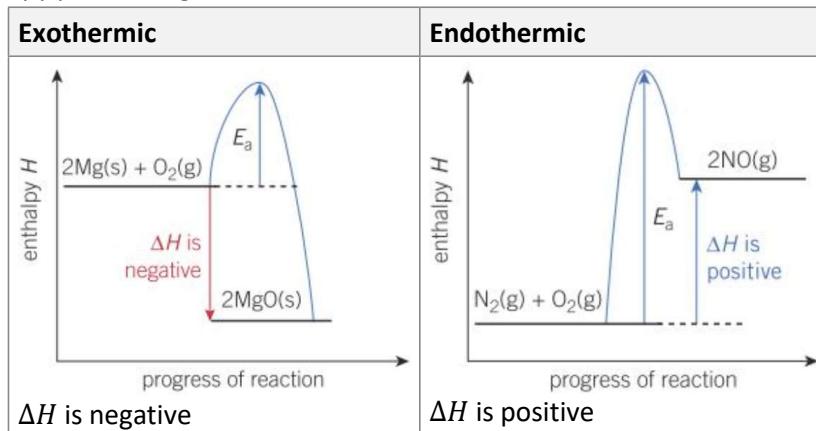
Definitions

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 the 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
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 $H_2O(l)$
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 changes

- Enthalpy change
 - $\Delta H = H(\text{products}) - H(\text{reactants})$
 - Can be positive (endothermic) or negative (exothermic)
- Types of reactions
 - Exothermic reaction
 - Energy transferred from the system to the surroundings
 - Endothermic reaction
 - Energy transferred from the surroundings to the system
- Enthalpy profile diagrams



* The activation energy can normally be omitted when there are > 1 energy changes

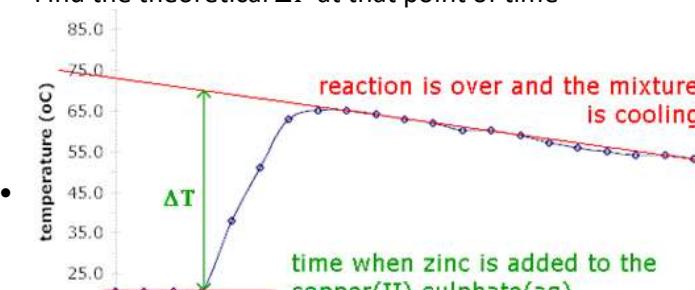
- Standard conditions
 - Shown with symbol $\ominus / ^\circ$
 - Standard pressure = **100 kPa / $1 \times 10^5 \text{ N m}^{-2}$ / 1 atm**

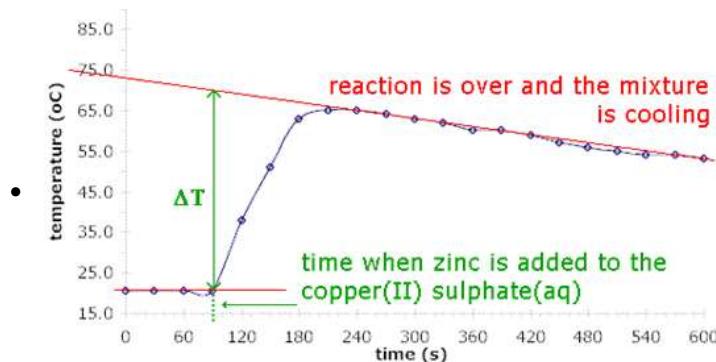
- Standard temperature = **298 K / 25 °C**
- Standard concentration = **1 mol dm⁻³ / 1 M**
- Substances will be in their **normal physical states (standard states)**
- Measuring energy changes
 - Use the equation $q = mc\Delta T$
 - Energy change for the **system** = $-q$
- Determine enthalpy change 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
 - Record the maximum temperature reached
 - Re-weigh spirit burner
 - Work out the mass of fuel burnt hence the amount of fuel burnt in moles
 - Work out energy change with $q = mc\Delta T$
 - Enthalpy change of combustion = $-\frac{q}{n}$
- Reasons for inaccuracies
 - Heat loss to surroundings → less exothermic than expected
 - Incomplete combustion of 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
 - Extinguish the spirit burner ASAP after the experiment + reweigh the spirit burner
- 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 heat capacity are the same as water)

A SIMPLE CALORIMETER

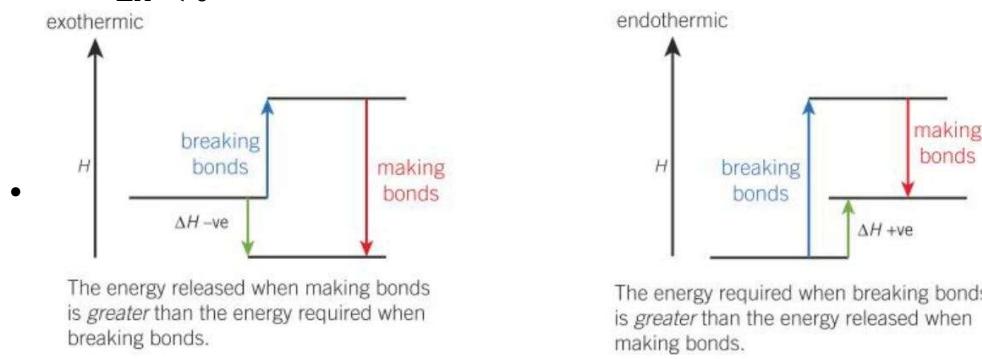


- Determining the enthalpy change of neutralisation
 - Make one reactant excess so the amount of water formed is fixed
 - In theory all acid and alkali should **release the same amount of energy** but in reality it isn't due to the different strengths of acid / alkali species
- Cooling curve correction
 - 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 exothermic
 - More energy released when making bonds than energy required when breaking bonds
 - $\Delta H < 0$



- Calculating enthalpy change from average bond enthalpies
 - $\Delta_r H = \Sigma(\text{bond enthalpies in reactants}) - \Sigma(\text{bond enthalpies in products})$
- 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

- Rate of reaction
 - Measures how fast a reactant is being used up / a product is being formed
 - $$\text{rate} = \frac{\text{change in concentration}}{\text{time}} \quad (\text{units} = \text{mol dm}^{-3} \text{ s}^{-1})$$
- Measuring rates of reaction by mass loss
 - Add reactants to conical flask on a digital mass balance + start stopwatch timer
 - Mass is recorded initially & at regular intervals (state a value e.g. 10s) until no more mass lost
 - Plot a graph of mass against time
 - **Gradient of tangent at $t = 0$ is the initial rate**

The collision theory

- 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 to react
 - 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)

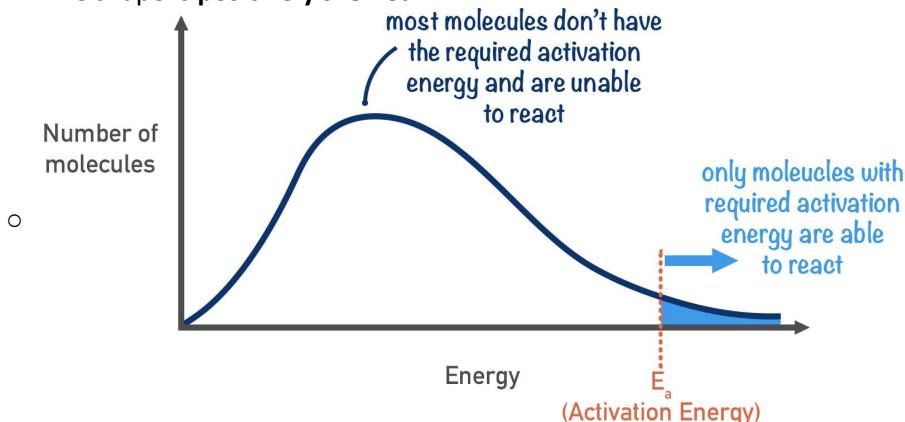
Catalyst

- 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
- Benefits of catalysts
 - Obtain industrial products faster
 - Increase profit
 - Operate industrial processes at lower temperatures and pressures
 - Reduce energy demand as less electricity and fuel is used
 - Reduce CO₂ emissions due to burning fossil fuels
 - Different reactions can be used
 - Choose reactions with greater atom economy / less toxic solvents / less toxic reactants
- Problems of catalysts
 - Catalysts do not last forever and need to be replaced periodically
 - Waste need to be disposed of responsibly

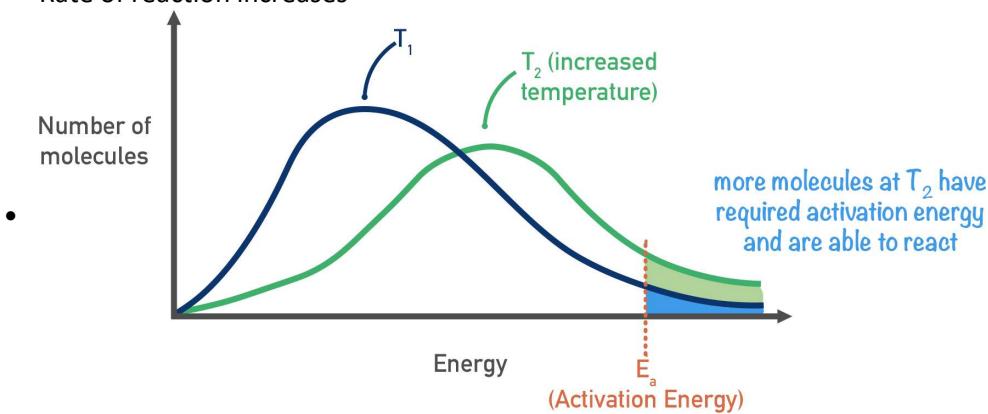
- Many catalysts are toxic and need to be disposed of very carefully to prevent damage to the environment

Boltzmann distribution

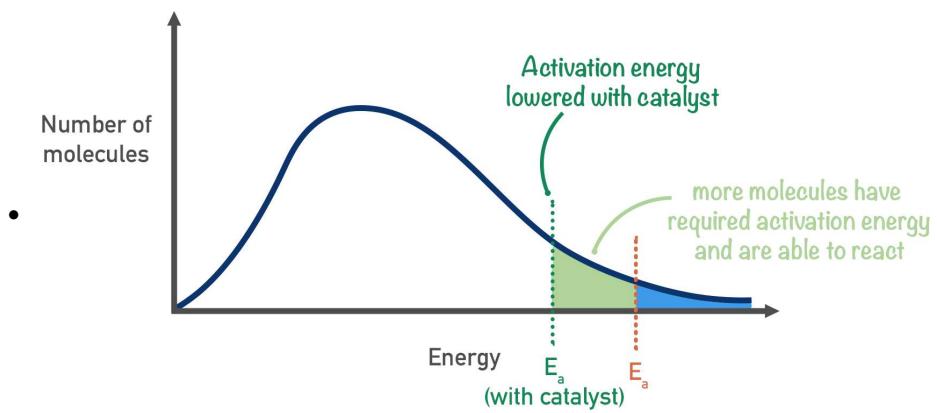
- Boltzmann distribution
 - Not all molecules of a substance have the same amount of energy
 - **Only particles to the right of the E_a** have enough energy to react
 - Distribution graph
 - Area under curve = total number of molecules
 - Peak = most probable energy of a molecule
 - No molecules have zero energy (**graph starts at origin**)
 - No maximum energy for a molecule (**the curve does not meet the x-axis at high energy**)
 - The shape is **positively skewed**



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



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



3.2.3 Chemical equilibrium

Definitions

Term	Definition
Dynamic equilibrium	When the rates of forward and backward reactions are equal in a closed system

Dynamic equilibrium and Le Chatelier's Principle

- 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 (favoured)
 - 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 ...)**
 - 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 ...)**
 - 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

Industrial processes

- 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
 - Increase yield & 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 + higher yield can be pursued
 - 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

- The equilibrium constant / K_c
 - For reaction $aA + bB \rightleftharpoons cC + dD$
 - $$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
 - $[]$ = concentration of ...
 - $[A], [B], [C], [D]$ = equilibrium concentration of the reactants and products of this equilibrium
 - **Only solutions** should appear in the equation for K_c
 - Include liquid if they have a similar amount to the solutions
- Value of K_c
 - < 1
 - Position of equilibrium is towards the LHS
 - Greater concentration of reactants
 - $= 1$
 - Position of equilibrium is halfway between reactants and products
 - > 1
 - Position of equilibrium is towards the RHS
 - Greater concentration of 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