

OCR (A) Chemistry A-level

Module 3: Period Table and Energy

Notes

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7.1 the periodic table

- Then: Mendeleev arranged in order of atomic mass & lined up those with similar properties. Gaps left where he thought elements would be found.
- Now: arranged in increasing atomic number, in vertical columns (groups) with same number of outer electrons + similar properties & horizontal rows (periods) giving number of highest energy electron shell
- Periodicity: repeating, periodic pattern across a period
- Electron configuration across a period: period 2: 2s then 2p, period 3: 3s then 3p, period 4: 3d filled but highest energy is 4: 4s then 4p
- Periodic table divided into blocks highest energy sub-shell s,p,d,f
- Group 1= alkali metals, 2=alkaline earth metals, 3-12=transition elements, 15=pnictogens, 16=chalcogens, 17=halogens, 18=noble gases

7.2 ionisation energies

- First ionisation energy: energy required to remove one electron from one mole of gaseous atoms, forming one mole gaseous $1+$ ions
- Factors affecting ionisation energies: atomic radius (greater distance nucleus to outer electrons=less attraction, big effect), nuclear charge (more protons, more attraction), electron shielding (shielding effect- inner shell electrons repel outer shell electrons → reduced attraction nucleus to outer electrons)
- Successive ionisation energies are greater: after 1st electron lost, remaining electrons pulled closer to nucleus, nuclear attraction increases so more energy needed
- Large increase successive ionisation energies → electron has been removed from shell closer to nucleus with less shielding
- Successive ionisation energies allow predictions about: no. electrons outer shell, group in periodic table → element can be identified
- Trends in IE: general increase across period, sharp decrease between end of a period to the start of the next
- Down a group: atomic radius increases, more inner shells so shielding increases, nuclear attraction on outer electrons decreases, 1st IE decreases
- Across a period: nuclear charge increases, same shell so similar shielding, nuclear attraction increases, atomic radius decreases, 1st IE increases. Exceptions period 2+3: group 2-3 fall (2p subshell higher energy than 2s, so 2p electron easier to remove) & group 5-6 fall (highest energy in 2p, but paired in 6- electrons repel making it easier for them to be removed)

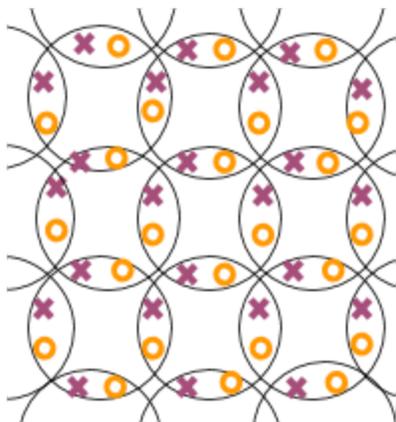
7.3 periodic trends in bonding + structure

- Elements near to metal/nonmetal divide (e.g. boron, silicon, germanium, arsenic, antimony) show in-between properties, called semimetals/metalloids
- Metals all solids at room temp except mercury, ranging properties of metals: tungsten-strong/hard, lead- soft, aluminium-light, osmium- very heavy
- Metallic bonding: strong electrostatic attraction between cations (+ve) and delocalised electrons. Cations fixed in position (maintains shape) & delocalised electrons mobile





- Metals w/ 2+ cations have 2x electrons
- Properties: electrical conductivity (electrons can move when voltage is applied), high mpt/bpt (high temp needed to overcome strong electrostatic attraction between cations/electrons) & insoluble (any interactions lead to reaction not dissolving)
- Giant covalent lattice: many billions of atoms held together by network strong covalent bonds (boron, carbon, silicon).
- Carbon (diamond) + silicon use 4 outer electrons forming covalent bonds with other atoms → tetrahedral, 109.5° , can be shown w/ dot+cross diagram



- Properties: high mpt/bpt (covalent bonds strong so high energy to break), insoluble in almost all solvents (bonds too strong to be broken by interactions w/ solvents), electrical conductivity (diamond/silicone no- no electrons not involved in bonding + graphene/graphite- yes)
- Graphene: single layer graphite, hexagonally arranged (planar 120°) carbons, conducts electricity & thinnest + strongest material in existence
- Graphite: parallel layers hexagonally arranged carbon atoms (planar 120°). Layers bonded by weak London forces, spare electron delocalised between layers → conducts electricity
- Periodic trend mpts period 2+3: increases group 1-14, sharp decrease 14-15, comparatively low 15-18

8.1 group 2

- Most common reactions of group 2 = redox. They act as reducing agents
- Reaction with oxygen: $2M(s) + O_2(g) \rightarrow 2MO(s)$ (Mg burns w/ white light, MgO = white) (M = generic group 2 metal)
- Reaction with water: $M(s) + 2H_2O(l) \rightarrow M(OH)_2 + H_2(g)$. Reaction more vigorous as reactivity increases down group





- Reaction with dilute acids: reactivity increases down group, metal + acid → salt + hydrogen e.g. $M(s) + 2HCl(aq) \rightarrow MCl_2(aq) + H_2(g)$
- Reactivity increases down group because: lose 2 electrons, requiring energy for 1st+2nd ionisation energies, these decrease down group b/c attraction decreases b/c atomic radius + shielding increase
- Oxides reaction with water: $MO(s) + H_2O(l) \rightarrow M^{2+}(aq) + 2OH^-(aq)$, only slightly soluble so once solution saturated, any further ions: $M^{2+}(aq) + 2OH^-(aq) \rightarrow M(OH)_2(s)$
- Solubility hydroxides increases down group → more OH^- ions → more alkaline (higher pH). Show this by experiment: add some oxide to test tube with water, shake (insufficient water so white ppt undissolved at bottom), measure pH
- Compounds in agriculture: $Ca(OH)_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O(l)$
- Compounds in medicine: antacids to treat indigestion, 'milk of magnesia' suspension of white $Mg(OH)_2$ in water. $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l) \quad \text{///} \quad CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

8.2 the halogens

- On earth occur dissolved in seawater OR combined with sodium/potassium as solid deposits
- Appearance and state at RTP:
 - F_2 : pale yellow gas (reacts w/ almost any substance)
 - Cl_2 : pale green gas
 - Br_2 : red-brown liquid
 - I_2 : shiny grey-black solid
 - At_2 never been seen (radioactive + decays rapidly)
- Trend in bpt down group: more electrons, stronger London forces, more energy to break intermolecular forces, bpt increases
- Most common reaction=redox, oxidising agents
- Halogen-halide displacement reactions:
 - 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
 - Solution in water: Cl=pale green, Br=orange, I=brown
 - Solution in cyclohexane (/nonpolar solvent) top layer: Cl=pale green, Br=orange, I=violet
- Trend in reactivity down group: atomic radius increases, more inner shells so shielding increases, less nuclear attraction to capture another electron, reactivity decreases
- Become weaker oxidising agents down group
- Disproportionation: redox reaction where same element is both oxidised + reduced,
 - e.g. $Cl_2(aq) + H_2O(l) \rightarrow HClO(aq) + HCl(aq)$ (bacteria killed by chloric (I) acid/ions, chloric (I) acid acts as weak bleach- indicator paper will turn red then white)
 - $Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) + NaClO$ (household bleach)





- Benefits of Cl in water: kills bacteria preventing disease e.g. cholera. Risks: can react with organic hydrocarbons (formed by decaying vegetation) to make chlorinated hydrocarbons- carcinogens, could use other methods purification

8.3 qualitative analysis

- Carbonate test: add dilute HNO_3 , test bubbles produced by bubbling through limewater \rightarrow white ppt
 - Eq: $\text{Na}_2\text{CO}_3 + 2\text{HNO}_3 \rightarrow 2\text{NaNO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ // $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}$
- Sulfate test: add barium chloride (not if testing for halides after)/nitrate \rightarrow white ppt
 - Eq: $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$
- Halide test: add aq AgNO_3 to aq halide sol, Cl=white, Br=cream, I=yellow, use aqueous dilute + concentrated ammonia to test solubility: Cl=soluble in dilute, Br=soluble in conc, I=insoluble in conc/dilute
 - Eq: $\text{Ag}^+ + \text{X}^- \rightarrow \text{AgX}(\text{s})$
- Barium meal- patient swallows water shaken with barium sulfate, white ppt coats inner lining of gut, X-ray taken \rightarrow can identify abnormalities e.g. ulcers/tumours
- Sequence of tests: carbonate, sulfate, halides because: neither halides/sulfates produce bubbles with acid, BaCO_3 is a white ppt so need to know it's not a carbonate 1st, $\text{Ag}_2\text{CO}_3 + \text{Ag}_2\text{SO}_4$ will form ppts
- Mixture of ions:
 - Carbonate: continue adding dilute nitric acid until all bubbling stops, meaning all carbonate ions have been removed & make sure to use dilute HNO_3
 - Sulfate: add excess $\text{Ba}(\text{NO}_3)_2$ to solution left from carbonate test, any sulfate ions will ppt out as barium sulfate, filter the solution to remove this & make sure not to use BaCl_2
 - Halide: same as normal- carbonate/sulfate ions have been removed
- Test for ammonium ion: add aq NaOH to sol, ammonia gas produced (bubbles unlikely since very soluble), warm mixture to release gas, may be able to smell, moist indicator paper \rightarrow blue
 - Eq: $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

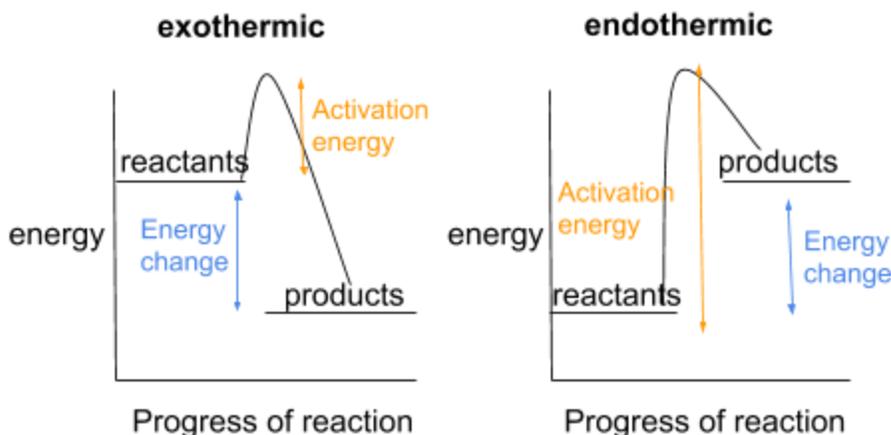
9.1 enthalpy changes

- Enthalpy (H): measure of heat energy in a chemical system
- Chemical system: the atoms, molecules or ions making up the chemicals
- Enthalpy change: $\Delta H = H(\text{products}) - H(\text{reactants})$ can be +ve/-ve
- system=chemicals, surroundings=apparatus, lab etc, universe=system and surroundings
- Enthalpy can be determined experimentally by measuring energy transfer between system/surroundings
- Exothermic: system releases heat energy to surroundings, ΔH -ve





- Endothermic: system takes in heat energy from surroundings, $\Delta H +ve$



- Activation energy (E_a): minimum energy required for a reaction to take place/energy required to break bonds, acting as a barrier to reaction
- Reactions with a small E_a take place rapidly because energy to break bonds readily available from surroundings. A very large E_a is such a large energy barrier reaction is very slow/doesn't happen
- Standard pressure=100kPa, standard temp=298K, standard conc=1 mol dm⁻³
- Standard state: physical state of a substance under standard conditions
- Enthalpy change of reaction: enthalpy change associated with a stated equation
- Enthalpy change of formation: formation of one mole of a compound from its elements (all elements have enthalpy change of formation of 0 KJmol⁻¹)
- Enthalpy change of combustion: complete combustion of one mol of a substance
- Enthalpy change of neutralisation: formation of one mol of water from neutralisation
 $\Delta_{\text{neut}}H$ (same for all neutralisation reactions $H^+ + OH^- \rightarrow H_2O$)

9.2 measuring enthalpy changes

- $q = mc\Delta T$
- Determination enthalpy change of combustion experimentally:
 - Measure certain volume of water, pour into beaker, record initial temperature
 - Add fuel to spirit burner + weigh
 - Place spirit burner under beaker + light & stir water with thermometer
 - Extinguish flame after about 3 mins + immediately record temp water
 - Re-weigh spirit burner
- Reasons experimental $\Delta_c H$ not accurate:
 - Less exothermic than expected: heat loss to surroundings, incomplete combustion fuel (black layer soot on beaker), evaporation fuel from wick
 - more/less exothermic: non-standard conditions
- To determine enthalpy change of reaction: carry out reaction in polystyrene cup with thermometer clamped so that it stands in it
- Cooling curves to correct heat loss in enthalpy experiments:
 - Add one reactant polystyrene cup
 - Take temperature sol every 30s until temperature stays constant





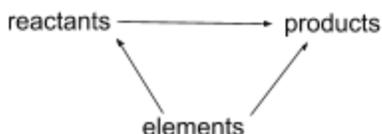
- Add other reactant + stir, measure temp every 30s until temp has fallen for several mins
- Plot graph temp against time
- To correct for cooling, extrapolate cooling curve section back to when second reactant added & draw vertical line to extrapolated curve
- For enthalpy change neutralisation, use total volume both reactants and moles of reactant not in excess

9.3 bond enthalpies

- Average bond enthalpy: energy required to break one mole specified type bond in gaseous molecule (always endothermic-energy is required to break bonds)
- Actual bond enthalpy can vary depending on chemical environment, the average takes different values into account
- Energy is released when bonds form- exothermic
- Enthalpy change of reaction can be found by calculating bond enthalpies bonds in reactants and products: $\Delta_r H = \Sigma(\text{bond enthalpies reactants}) - \Sigma(\text{bond enthalpies products})$ (need to be gaseous to be standard)

9.4 Hess' law and enthalpy cycles

- Allow enthalpy changes to be determined indirectly
- States that: if a reaction can take place by 2 routes & starting/finishing conditions are the same, the total enthalpy changes are the same
- If formation values given, elements ↑



- Impossible to work out enthalpy change of formation directly because elements would form many compounds alongside the one you're looking at
- If combustion values given, combustion products ↓



- For unfamiliar energy cycles, label enthalpies given & work out 2 routes to solve for unknown

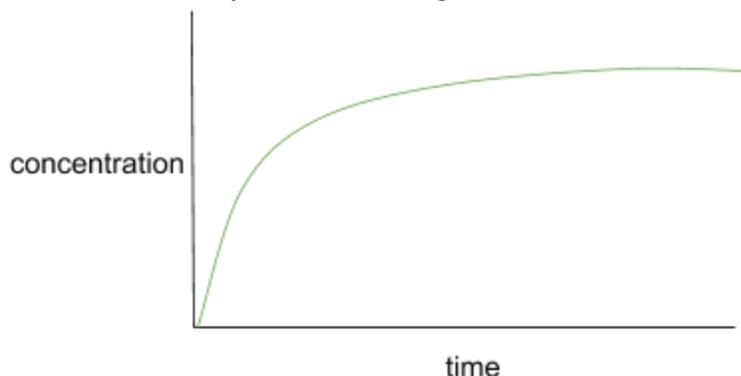
10.1 reaction rates

- Rate of a chemical reaction: measures how fast a reactant is being used up/product is being formed
- rate = change in conc ÷ time, units = $\text{mol dm}^{-3} \text{s}^{-1}$
- Rate is fastest at start (each reactant at its highest concentration), rate slows as reaction proceeds (reactants being used up so concentration decreases), once reactants used up, concentration doesn't change, rate = 0





- Conc-time graphs can be used to monitor rate of a chemical reaction. For concentration-time of a product, gradient steepest at start, becomes less steep as reaction proceeds + eventually becomes straight line



- Collision theory: two reacting particles must collide for a reaction to occur. Must collide with correct orientation & have sufficient energy to overcome E_a barrier
- Increase concentration → increased number of particles in same volume → more effective collisions in a given period of time → increased rate reaction
- Gas compressed into smaller volume → pressure is increased → same number of molecules occupy smaller volume → closer together → collide more frequently → more effective collisions in same time
- Progress reaction can be monitored by: removal reactant/formation product
- Monitoring reactions producing gases:
 - Monitoring gas collected: 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 against time plotted, gradient tangent at $t=0$ is initial rate
 - Monitoring loss of mass: 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

10.2 catalysts

- Catalyst: substance that changes the rate of a chemical reaction without undergoing any permanent change itself, by providing an alternative pathway of lower E_a
- Homogenous catalysts react with reactants to form intermediate, intermediate breaks down to give product & regenerates catalyst
- Heterogeneous catalysts work by the reactant molecules being adsorbed onto surface of catalyst, reaction takes place, then products leave surface of catalyst by desorption
- Catalytic converters- made of platinum, rhodium and palladium, on honeycomb mesh (large surface area). Exhaust gases passed over ($\text{CO} + \text{NO}$) & converted to non-toxic products ($\text{CO}_2 + \text{N}_2$, unburnt hydrocarbons → water + CO_2)
- Catalysts increase rate by lowering E_a → lower temperature is needed → less energy required → less electricity/fossil fuels used & increased profit





- Economic advantages outweigh costs associated with developing catalytic process
- Sustainability requires high atom economies + fewer pollutants (so fewer fossil fuels used)

10.3 the boltzmann distribution

- Features: curve starts at origin (no molecules have 0 energy), area under curve = total number of molecules, curve doesn't meet x-axis (no maximum energy)
- Higher temperature → peak is lower + shifted to right (more molecules have energy greater than E_a → greater proportion of collisions lead to reaction → increased rate. Collisions also more frequent but E_a has more of an effect)
- catalyst → lower E_a (E_c) to left on graph (→ greater proportion of molecules have energy greater than E_c → more molecules will form products on collision → rate increases)

10.4 dynamic equilibrium and le chatelier's principle

- Looks at reversible reactions
 - In equilibrium system: rate forward reaction = rate reverse reaction, concentration of reactants/products don't change
 - To be in equilibrium must be in closed system
 - Le chatelier's principle: when a system in equilibrium is subject to external change, the system re-adjusts itself to minimise the change
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- Equilibrium between CrO_4^{2-} (yellow) and $\text{Cr}_2\text{O}_7^{2-}$ (orange). Can show effect of changing concentration by experiment:
 - Add K_2CrO_4 (yellow) to beaker + add H_2SO_4 dropwise until no further change (→ orange), adding NaOH sol → yellow
 - When H_2SO_4 added, this increases the concentration H^+ (reactant), equilibrium shifts to right to decrease concentration of added reactant, this increases the rate of forwards reaction, more product is made, new equilibrium is established towards products
 - Adding NaOH , $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$, decrease in concentration of H^+ , decreases rate of forward reaction, equilibrium shifts to the left, increasing concentration of reactant, new equilibrium established towards reactants
 - forwards/reverse reactions have same enthalpy change but one will be + and one will be -, increased temperature shifts equilibrium in endothermic direction
 - CoCl_2 dissolves in water forming equilibrium of complexes pink/blue pink → blue ΔH +ve, experiment:
 - Dissolve CoCl_2 in boiling tube + add small amount HCl . put in iced water → pink (decrease in temperature, shifts in exothermic direction). Put in water bath → blue (increase in temperature, shifts in endothermic direction)
 - Increasing the pressure will shift the position of equilibrium to side with fewer moles of gas, reducing the pressure of the system e.g. 2NO_2 (brown) \rightleftharpoons N_2O_4 (colourless)
 - Two moles of NO_2 has 2x conc & pressure as one mole N_2O_4 in same container
 - Haber process: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ΔH -ve:





- Low temp → high yield of product but rate may be so slow equilibrium may not be established
- High pressure increases yield & forced molecules closer together, increasing conc + reaction rate. But, requires very strong container + large quantity energy → increased cost. Safety- failure of steelwork/seals could lead to hot gases (including toxic ammonia) leaking, endangering workforce + surrounding area
- Actual conditions: 350-500°C, 100-200 atm, iron catalyst (means lower temperature can be used so operating costs reduced)
- Only about 15% converted to ammonia, but $H_2 + N_2$ recycled repeatedly so nearly all is eventually converted

