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Expert A Level Chemistry Tuition

AQA A Level Chemistry

Paper 2: Organic and Physical Chemistry

7405/2 • 2 hours • 105 marks • 35% of A-level

COMPLETE REVISION GUIDE

Physical Chemistry (3.1.2 – 3.1.6 and 3.1.9) • Organic Chemistry (3.3)

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How to Use This Guide

This revision guide covers sections 3.1.2 – 3.1.6, 3.1.9 (Physical Chemistry) and 3.3 (all Organic Chemistry) for AQA A Level Chemistry Paper 2 (7405/2).

Each numbered box shows the spec point in italics, followed by a concise, exam-ready explanation. Key terms are highlighted in bold. Sections marked ★ A-LEVEL ONLY are not examined at AS.

Required Practicals are in orange boxes with methods, uncertainties, errors and improvements.

Good luck with your revision! – Chloe

Key Constants and Standard Values

Constant / Value	Symbol / Value	Notes
Avogadro constant	$N_A = 6.022 \times 10^{23}$ mol^{-1}	Given in AQA exams
Gas constant	$R = 8.314$ J K^{-1} mol^{-1}	Given in AQA exams
Specific heat capacity (water)	$c = 4.18$ J g^{-1} K^{-1}	Given if needed
Ionic product of water (25°C)	$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}	$K_w = [H^+][OH^-]$
Faraday constant	$F = 96{,}485$ C mol^{-1}	Charge per mole of electrons
Standard conditions	100 kPa, 298 K	For all standard enthalpy changes
Standard electrode (SHE)	$E^\ominus = 0.00$ V	Reference for all $E^\ominus$ values
Molar gas volume (RTP)	24.0 dm^3 mol^{-1}	At 298 K and 100 kPa

3.1.2 Amount of Substance Quick Notes

Formula / Equation	What It Means / When to Use It
$n = m / M$	Moles = mass (g) / molar mass (g mol^{-1})
$n = c \times V$	Moles = concentration (mol dm^{-3}) × volume (dm^3)
$n = V / 24{,}000$ or $n = V / 24$	Gas moles: volume in cm^3 ÷ 24,000 or dm^3 ÷ 24 at RTP
No. of particles = $n \times N_A$	Number of particles = moles × Avogadro constant
$pV = nRT$	Ideal gas: p (Pa), V (m^3), n (mol), R (8.314), T (K)
Conc (g dm^{-3}) = c (mol dm^{-3}) × M	Convert between concentration units

Unit Conversions for pV = nRT

- kPa × 1000 = Pa cm^3 ÷ 10^6 = m^3 dm^3 ÷ 1000 = m^3 °C + 273 = K

Yields and Atom Economy

Formula / Equation	What It Means / When to Use It
% yield = (actual / theoretical) × 100	Always < 100% (losses, side reactions, equilibrium)
Atom economy = (Mr desired product / ΣMr all reactants) × 100%	AQA uses REACTANTS in denominator (not products)

Equipment Uncertainties

- % uncertainty = (uncertainty / reading) × 100%
- Burette: ±0.05 cm³ per reading (±0.10 cm³ per titre, as two readings are taken)
- 25 cm³ pipette: ±0.06 cm³ 250 cm³ volumetric flask: ±0.10 cm³ Balance: ±0.001 g

3.1.3 Bonding Quick Notes

Shapes of Molecules and Ions (VSEPR)

- 2 electron pairs: linear, 180° ($BeCl_2$, CO_2)
- 3 electron pairs: trigonal planar, 120° (BF_3). With 1 lp: bent, ~118°
- 4 electron pairs: tetrahedral, 109.5° (CH_4, NH_4^+). With 1 lp: pyramidal, 107° (NH_3). With 2 lp: bent, 104.5° (H_2O)
- 5 electron pairs: trigonal bipyramidal, 90°/120° (PCl_5)
- 6 electron pairs: octahedral, 90° (SF_6)
- Lone pairs reduce bond angles by ~2.5° each. Repulsion: lp–lp > lp–bp > bp–bp

Intermolecular Forces (weakest to strongest)

- London forces < permanent dipole–dipole < hydrogen bonding
- London forces: present in ALL molecules. Increase with more electrons (higher Mr)
- H-bonding: requires H bonded to N, O, or F + lone pair on N/O/F of adjacent molecule
- Water anomalies: high b.p. (H-bonds); ice less dense than water (open H-bonded lattice)

Structure and Properties Quick Reference

- High m.p. + conducts when molten/dissolved → GIANT IONIC
- Very high m.p. + hard + doesn't conduct (unless graphite) → GIANT COVALENT
- High m.p. + conducts when solid + malleable → METALLIC
- Low m.p./b.p. + doesn't conduct → SIMPLE MOLECULAR

3.1.4 Energetics Quick Notes

Formula / Equation	What It Means / When to Use It
q = mcΔT	Energy (J) = mass (g) × c (J g^{-1} K^{-1}) × temp change
ΔH = –q / n	Enthalpy change (kJ mol^{-1}). – sign for direction
ΔrH = ΣΔfH(products) – ΣΔfH(reactants)	Hess's Law using enthalpies of formation
ΔrH = ΣΔcH(reactants) – ΣΔcH(products)	Hess's Law using enthalpies of combustion
ΔH = Σ(bonds broken) – Σ(bonds formed)	Mean bond enthalpies (gaseous species only, approximate)

- ΔfH⊖ of an element in its standard state = 0 by definition
- ΔcH⊖ is always negative (exothermic). ΔfH⊖ can be + or –
- Mean bond enthalpy values give APPROXIMATE ΔH – they are averages across different molecules

3.1.6 Chemical Equilibria and Kc Quick Notes

Formula / Equation	What It Means / When to Use It
$K_c = [C]^c[D]^d / [A]^a[B]^b$	For aA + bB ⇌ cC + dD. Products over reactants.

- Le Chatelier's: system shifts to OPPOSE the change
- Increase T → favours endothermic direction. Increase P → favours fewer moles of gas
- Catalyst: reaches equilibrium FASTER but does NOT change position or Kc
- Only TEMPERATURE changes the value of Kc
- Exothermic forward: increase T → Kc decreases. Endothermic forward: increase T → Kc increases
- Units of Kc: substitute (mol dm^{-3}) raised to the appropriate powers

3.1.2 Amount of Substance (also examined in Paper 1)

3.1.2.1	*Relative atomic mass and relative molecular mass in terms of ^{12}C. Relative formula mass for ionic compounds.*
	Relative atomic mass (Ar): weighted mean mass of an atom of an element compared to 1/12 the mass of a ^{12}C atom. **Relative molecular mass (Mr):** sum of Ar values for all atoms in a molecular formula (covalent compounds). **Relative formula mass:** sum of Ar values for all atoms in a formula unit (ionic compounds, e.g. NaCl).

3.1.2.2	*The Avogadro constant and the mole. Concentration of a substance in solution (mol dm^{-3}). Calculations using mass, Mr, moles and concentration.*
	Avogadro constant (NA): 6.022×10^{23} mol^{-1} (number of particles per mole). Given in exams. **Key formulae:** **n = m / M** (moles = mass / molar mass) **n = c × V** (moles = concentration × volume in dm^3) **Number of particles = n × NA** Always convert cm^3 to dm^3 by dividing by 1000.

3.1.2.3	*The ideal gas equation pV = nRT with variables in SI units.*
	pV = nRT p = pressure (**Pa**), V = volume (**m^3**), n = moles, R = 8.314 J K^{-1} mol^{-1} (given), T = temperature (**K**). **Unit conversions:** kPa × 1000 = Pa; $cm^3 \div 10^6 = m^3$; $dm^3 \div 1000 = m^3$; °C + 273 = K. Used to find Mr of a volatile liquid (given mass, T, P, V).

3.1.2.4	*Empirical and molecular formula. Calculate from composition by mass or percentage composition.*
	Empirical formula: simplest whole number ratio of atoms. **Molecular formula:** actual number of atoms in one molecule. **Method:** (1) Divide each mass/% by Ar. (2) Divide all by the smallest. (3) Multiply up to whole numbers if needed. **Molecular formula:** Mr ÷ empirical formula mass = multiplier.

3.1.2.5	*Balanced equations (full and ionic). Atom economy. Calculations: masses, gas volumes, percentage yields, concentrations.*
	Atom economy = (Mr desired product / ΣMr all reactants) × 100% (AQA uses reactants in the denominator). **Percentage yield = (actual yield / theoretical yield) × 100%** Yield < 100% due to: incomplete reactions, side reactions, losses during purification. High atom economy is economically and environmentally desirable (less waste). **Titration calculations:** use concordant titres → mean titre → moles of known → mole ratio → moles of unknown → concentration.

⭐ REQUIRED PRACTICAL 1: Make Up a Volumetric Solution and Carry Out a Simple Acid–Base Titration

Method:

1. Weigh accurately a known mass of solid acid (e.g. potassium hydrogen phthalate) using a balance (±0.001 g). Record mass before and after transfer (by difference).
2. Transfer the solid to a beaker. Rinse the weighing bottle into the beaker with distilled water to ensure complete transfer.
3. Dissolve in distilled water, stir, then transfer quantitatively to a 250 cm^3 volumetric flask using a funnel. Rinse the beaker, rod and funnel into the flask several times.
4. Make up to the 250 cm^3 graduation mark using a dropping pipette for the final additions. Stopper and invert to mix. This is the standard solution.
5. Pipette 25.0 cm^3 of the unknown NaOH solution into a conical flask. Add a suitable indicator (e.g. phenolphthalein).
6. Fill a burette with the standard acid. Record the initial reading. Titrate, adding acid dropwise near the end point, swirling continuously.
7. Record the final burette reading. Repeat to obtain at least two concordant titres (within 0.10 cm^3).
8. Calculate: mean titre → moles of acid → mole ratio → moles of NaOH → concentration of NaOH.

Sources of Uncertainty:

- Balance: ±0.001 g
- Volumetric flask (250 cm^3): ±0.10 cm^3
- Pipette (25 cm^3): ±0.06 cm^3
- Burette: ±0.05 cm^3 per reading (±0.10 cm^3 per titre)

Common Errors:

- Not all solid transferred to the volumetric flask (systematic – concentration too low)
- Overshooting the end point (random)
- Misreading the meniscus (parallax error)
- Not making up to the graduation mark accurately
- Rinsing the conical flask with NaOH (increases moles – systematic error)
- Note: a wet conical flask rinsed with distilled water does NOT cause an error

Improvements:

- Weigh by difference to account for any solid left in the weighing bottle
- Rinse all glassware into the volumetric flask thoroughly
- Use a dropping pipette for the final approach to the graduation mark
- Use a white tile under the conical flask to see the colour change clearly
- Rinse the burette with the acid solution before filling; rinse the pipette with the NaOH solution
- Add acid dropwise near the end point to avoid overshooting
- Repeat and use concordant titres (within 0.10 cm^3) to calculate a mean

3.1.3 Bonding (also examined in Paper 1)

3.1.3.1	*Ionic bonding: electrostatic attraction between oppositely charged ions in a lattice. Formulas of compound ions.*
	Ionic bonding: the **strong electrostatic attraction** between **oppositely charged ions** arranged in a **giant ionic lattice**. Formed by **electron transfer** from a metal to a non-metal. **Compound ions to know:** sulfate SO_4^{2-}, hydroxide OH^-, nitrate NO_3^-, carbonate CO_3^{2-}, ammonium NH_4^+. Predict ionic charge from position in the Periodic Table.

3.1.3.2	*Covalent and dative covalent bonds. Single, multiple and co-ordinate bonds.*
	Covalent bond: a **shared pair of electrons** between two non-metal atoms. The **strong electrostatic attraction** between the shared electrons and the two nuclei. **Multiple bonds:** double = 2 shared pairs; triple = 3 shared pairs. **Dative covalent (co-ordinate) bond:** both electrons in the shared pair come from **one atom**. Represented by an **arrow** from donor to acceptor (e.g. NH_4^+, Al_2Cl_6).

3.1.3.3	*Metallic bonding: attraction between delocalised electrons and positive ions in a lattice.*
	Metallic bonding: the **strong electrostatic attraction** between **positive metal ions (cations)** and a **sea of delocalised electrons**. Strength increases with: more delocalised electrons, smaller ionic radius, higher charge. This explains trends in m.p. and hardness of metals.

3.1.3.4	*Four types of crystal structure: ionic, metallic, macromolecular (giant covalent), molecular. Examples and properties.*
	Ionic (e.g. NaCl): high m.p., conducts when molten/dissolved, brittle. **Metallic (e.g. Mg):** high m.p., conducts when solid, malleable/ductile. **Giant covalent (e.g. diamond, graphite, SiO_2):** very high m.p., hard (except graphite), diamond doesn't conduct; graphite does (delocalised electrons in layers). **Simple molecular (e.g. I_2, ice):** low m.p./b.p., doesn't conduct. Weak intermolecular forces overcome on melting (NOT covalent bonds). Always link properties to the **type of bonding/structure** and what must be overcome.

3.1.3.5	*Shapes of simple molecules and ions with up to six electron pairs. VSEPR theory and bond angles.*
	VSEPR: electron pairs (bonding and lone) repel and arrange to be **as far apart as possible**. **Repulsion order:** lone pair–lone pair > lone pair–bond pair > bond pair–bond pair. **2 pairs:** linear, 180° ($BeCl_2$, CO_2). **3 pairs:** trigonal planar, 120° (BF_3). With 1 lp: bent, ~118°. **4 pairs:** tetrahedral, 109.5° (CH_4, NH_4^+). With 1 lp: pyramidal, 107° (NH_3). With 2 lp: bent, 104.5° (H_2O). **5 pairs:** trigonal bipyramidal, 90°/120° (PCl_5). **6 pairs:** octahedral, 90° (SF_6). Lone pairs reduce bond angles by ~2.5° each.

3.1.3.6	*Electronegativity and bond polarity. Polar bonds vs polar molecules.*
	Electronegativity: the power of an atom to attract the bonding pair of electrons in a covalent bond. Difference in electronegativity → **polar bond** (δ+ and δ–). A molecule is **polar** if the dipoles don't cancel. **Symmetric molecules** (e.g. CO_2, CCl_4) have polar bonds but are **non-polar overall**.

3.1.3.7	*Intermolecular forces: permanent dipole–dipole, London forces, hydrogen bonding. Effect on melting/boiling points.*
	London forces (induced dipole–dipole): present in ALL molecules. Strength increases with number of electrons (higher Mr). Temporary fluctuations in electron density induce dipoles in neighbouring molecules. **Permanent dipole–dipole:** between molecules with permanent dipoles. **Hydrogen bonding:** occurs when H is bonded to **N, O, or F** (highly electronegative atoms with lone pairs). Strongest intermolecular force. **Anomalous properties of water:** high b.p., ice is less dense than liquid water (open H-bonded lattice in ice).

3.1.4 Energetics (also examined in Paper 1)

3.1.4.1	*Enthalpy change (ΔH). Standard conditions (100 kPa, stated T). Define ΔcH⊖ and ΔfH⊖.*
	Enthalpy change (ΔH): heat energy change at constant pressure. **Exothermic:** ΔH negative (heat released). **Endothermic:** ΔH positive (heat absorbed). **Standard conditions:** 100 kPa and a stated temperature (usually 298 K). **ΔcH⊖:** enthalpy change when **one mole** of a substance is **completely burned** in excess oxygen under standard conditions. **ΔfH⊖:** enthalpy change when **one mole** of a compound is formed from its **elements in their standard states** under standard conditions. ΔfH⊖ of an element in its standard state = 0.

3.1.4.2	*Calorimetry: q = mcΔT. Calculate molar enthalpy changes from experimental results.*
	q = mcΔT where q = energy (J), m = mass of solution (g), c = specific heat capacity (given; for water, 4.18 J g^{-1} K^{-1}), ΔT = temperature change. **ΔH = –q / n** (kJ mol^{-1}). The negative sign accounts for direction (if solution heats up, reaction is exothermic). **Assumptions:** no heat loss; solution has density/heat capacity of water; all solute reacts.

3.1.4.3	*Hess's Law: calculate enthalpy changes from enthalpies of formation or combustion.*
	Hess's Law: total enthalpy change is independent of the route taken. **Using ΔfH⊖:** ΔrH⊖ = ΣΔfH⊖(products) – ΣΔfH⊖(reactants) **Using ΔcH⊖:** ΔrH⊖ = ΣΔcH⊖(reactants) – ΣΔcH⊖(products) Draw an enthalpy cycle showing two routes from reactants to products.

3.1.4.4	*Mean bond enthalpy. Calculate approximate ΔH for gaseous reactions. Explain why values differ from Hess's Law.*
	Mean bond enthalpy: average energy required to break one mole of a particular type of bond in the gaseous state, averaged across different molecules. **ΔH = Σ(bonds broken) – Σ(bonds formed)** Bonds broken = endothermic (+). Bonds formed = exothermic (–). **Why values differ from Hess's Law:** mean bond enthalpies are **averages** – actual values depend on molecular environment. Only strictly valid for **gaseous** reactions.

⭐ REQUIRED PRACTICAL 2: Measurement of an Enthalpy Change

Method:

1. Common examples: neutralisation (NaOH + HCl), displacement (Zn + $CuSO_4$), dissolution (NH_4NO_3 or KCl in water), combustion of alcohols (spirit burner).
2. FOR NEUTRALISATION/DISPLACEMENT/DISSOLUTION: measure a known volume of solution (e.g. 25 cm^3 of 1.0 mol dm^{-3} $CuSO_4$) into a polystyrene cup with a lid.
3. Record the initial temperature every minute for 2–3 minutes to establish a baseline.
4. Add the second reagent (e.g. excess Zn powder) at a known time. Stir continuously and record the temperature every minute for a further 5–6 minutes.
5. Plot temperature vs time. Extrapolate both lines back to the time of mixing to find the true ΔT (correcting for heat loss).
6. Calculate $q = mc\Delta T$, then $\Delta H = -q/n$ (kJ mol^{-1}). Assign correct sign.
7. FOR COMBUSTION: weigh a spirit burner, burn the alcohol under a copper calorimeter containing a known mass of water, record the temperature rise, reweigh the burner. Calculate q and ΔH.

Sources of Uncertainty:

- Thermometer: ±0.5°C (standard) or ±0.1°C (digital)
- Measuring cylinder: ±0.5 cm^3 (or pipette for greater precision)
- Balance: ±0.001 g
- Polystyrene cup loses heat to surroundings

Common Errors:

- Heat loss to the surroundings (systematic – ΔT too small, ΔH less exothermic than true value)
- Assuming the specific heat capacity and density of the solution are the same as pure water
- Not using excess of one reagent (incomplete reaction)
- For combustion: significant heat loss to the air, incomplete combustion, evaporation of alcohol
- Heat absorbed by the cup, thermometer and stirrer (not accounted for)

Improvements:

- Use a polystyrene cup with a lid to reduce heat loss
- Use a plotting/extrapolation method (temperature vs time graph) to correct for heat loss
- Use a digital thermometer (±0.1°C) for more precise temperature readings
- Use excess of the solid/second reagent to ensure complete reaction of the solution
- Stir continuously for even heat distribution
- For combustion: use a draught shield, minimise distance between burner and calorimeter
- Repeat and take a mean value for ΔH

3.1.5 Kinetics (Paper 2 only)

3.1.5.1	*Collision theory: reactions only occur when collisions take place between particles with sufficient energy (activation energy). Define activation energy. Explain why most collisions do not lead to a reaction.*

Activation energy (Ea): the **minimum energy** required for a collision between particles to result in a chemical reaction.

Most collisions do not lead to a reaction because:

- The particles do not have **sufficient energy** (≥ Ea) – the collision is not energetic enough to break the necessary bonds.
- The particles do not collide with the correct **orientation** – the reactive parts of the molecules must come into contact.

Only a small fraction of all collisions are **successful collisions** (i.e. have both sufficient energy AND correct orientation).

3.1.5.2	*Maxwell–Boltzmann distribution of molecular energies in gases. Draw and interpret distribution curves for different temperatures.*

The **Maxwell–Boltzmann distribution** shows the **range of kinetic energies** of molecules in a gas at a given temperature.

Key features of the curve:

- Starts at the origin (no molecules have zero energy).
- Rises to a **peak** (the most probable energy).
- Has a long **tail** to the right (a few molecules have very high energies).
- The area under the curve = total number of molecules (constant).
- **No maximum energy** – the curve never touches the x-axis on the right.

At higher temperature:

- The peak shifts **right** and becomes **lower** (flatter and broader).
- The **area under the curve remains the same** (same number of molecules).
- The area to the **right of Ea increases significantly** – more molecules have energy ≥ Ea.

3.1.5.3	*Rate of reaction. Qualitative effect of temperature on rate. Use Maxwell–Boltzmann distribution to explain why a small temperature increase leads to a large increase in rate.*

Rate of reaction: the change in concentration of a reactant or product per unit time.

A **small increase in temperature** causes a **large increase in rate** because:

- At higher temperature, molecules have **more kinetic energy** on average.
- The Maxwell–Boltzmann distribution shifts right – the proportion of molecules with energy **≥ Ea increases significantly**.
- This means many **more molecules** can undergo successful collisions per unit time.
- The increase in collision frequency (molecules move faster) also contributes, but the **main factor** is the much greater proportion of molecules exceeding Ea.

Exam tip: always refer to the **proportion of molecules with energy ≥ Ea**, not just "molecules have more energy".

3.1.5.4	*Qualitative effect of changes in concentration and pressure on collision frequency and rate.*

Increasing concentration (in solution) or **increasing pressure** (for gases):

- There are **more particles per unit volume**.
- Particles are **closer together**.
- Collisions occur **more frequently**.
- Therefore the **rate of reaction increases** (more successful collisions per unit time).

Note: increasing concentration/pressure does **not** change the proportion of molecules with energy ≥ Ea – it only increases the **frequency** of collisions.

3.1.5.5	*A catalyst increases rate without being changed in composition or amount. Catalysts provide an alternative route of lower activation energy. Use Maxwell–Boltzmann to explain.*

A **catalyst** increases the rate of reaction by providing an **alternative reaction pathway** with a **lower activation energy (Ea)**.

Using the Maxwell–Boltzmann distribution:

- The distribution curve is **unchanged** (same temperature, same distribution of energies).
- But the **Ea is lower** (the Ea line moves to the left on the diagram).
- Therefore a **greater proportion** of molecules now have energy ≥ the new, lower Ea.
- More successful collisions occur per unit time → faster rate.

Important points:

- A catalyst is **not consumed** – it is regenerated at the end of the reaction.
- A catalyst does **not change ΔH** – the overall enthalpy change is the same.
- A catalyst does **not change the position of equilibrium** or the value of K – it only helps equilibrium be reached **faster**.
- A catalyst does **not change the Maxwell–Boltzmann distribution** itself – only the Ea changes.

⭐ REQUIRED PRACTICAL 3: Investigation of How the Rate of a Reaction Changes with Temperature

Method:

1. A common example is the reaction of sodium thiosulfate with hydrochloric acid: $Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$. The sulfur produced makes the solution go cloudy.
2. Draw a black cross on a piece of white paper. Place a conical flask on top of the cross.
3. Measure a fixed volume of sodium thiosulfate solution (e.g. 25 cm^3) into the flask. Place in a water bath at the first temperature (e.g. 20°C). Allow to equilibrate for at least 3 minutes.
4. Measure a fixed volume of dilute HCl (e.g. 5 cm^3) and warm to the same temperature.
5. Add the HCl to the thiosulfate, start the timer immediately, and swirl to mix.
6. Look down through the solution at the cross. Stop the timer when the cross is no longer visible (the solution is sufficiently cloudy).
7. Record the time. Calculate rate = 1/time.
8. Repeat at several different temperatures (e.g. 25, 30, 35, 40, 45, 50°C), keeping all volumes and concentrations the same.
9. Plot rate (1/time) vs temperature to show the relationship.

Sources of Uncertainty:

- Thermometer: ±0.5°C
- Stopwatch: ±0.5 s (plus human reaction time in judging when cross disappears)
- Measuring cylinder: ±0.5 cm^3
- Judgement of when the cross disappears is subjective

Common Errors:

- Temperature not equilibrated before mixing (reagents at different temperatures – actual reaction temperature is unknown)
- Inconsistent judgement of when the cross disappears (different people may judge differently)
- Temperature changing during the reaction (not maintained at the target temperature throughout)
- Not using the same volumes and concentrations for each experiment (unfair comparison)
- Looking at the cross from different angles between experiments

Improvements:

- Allow both solutions to equilibrate in the water bath for at least 3–5 minutes before mixing
- Use the same person to judge the end point throughout the experiment (consistency)
- Always look down at the cross from the same height and angle
- Use a thermostatted water bath to maintain constant temperature during the reaction
- Use a light sensor and data logger instead of the human eye for a more objective end point
- Use the same volumes, concentrations and total volume for every experiment
- Repeat at each temperature and take a mean time
- Use at least 5 different temperatures across a reasonable range (e.g. 20–50°C) for a reliable graph

3.1.6 Chemical Equilibria and Kc (also examined in Paper 1)

3.1.6.1	*Reversible reactions and dynamic equilibrium. Le Chatelier's principle. Compromise conditions in industry.*
	Dynamic equilibrium (closed system): forward rate = reverse rate; concentrations remain constant. **Le Chatelier's principle:** if a system at equilibrium is disturbed, it shifts to **oppose the change**. **Temperature:** increase favours the **endothermic** direction. **Concentration:** increase in [reactant] shifts right. **Pressure:** increase shifts towards **fewer moles of gas**. **Catalyst:** no effect on position or K – just reaches equilibrium faster. **Industrial compromise:** e.g. Haber process – moderate T (~450°C) for reasonable rate, high P (~200 atm) for yield, iron catalyst.

3.1.6.2	*Kc for homogeneous systems. Construct expressions, calculate values, predict effect of temperature.*
	For $aA + bB \rightleftharpoons cC + dD$: **$K_c = [C]^c[D]^d / [A]^a[B]^b$** Products over reactants, raised to stoichiometric coefficients. **Only temperature changes Kc.** Changes in concentration or a catalyst do NOT change Kc. **Exothermic forward:** increasing T **decreases** Kc. **Endothermic forward:** increasing T **increases** Kc. Use an **ICE table** (Initial, Change, Equilibrium) to find equilibrium concentrations. Calculate units by substituting (mol dm^{-3}) raised to appropriate powers.

3.1.9 Rate Equations

★ A-LEVEL ONLY

3.1.9.1a	*Rate equations: rate = k[A]^m[B]^n. Orders (0, 1, 2). Rate constant k. Arrhenius equation k = Ae $^{-Ea/RT}$.*
	Rate equation: rate = k[A]^m[B]^n – determined **experimentally only** (cannot be deduced from the balanced equation). **Order** with respect to A = power m. **Overall order** = m + n. Orders are 0, 1, or 2. **Rate constant (k):** varies with temperature. Increasing T increases k (more successful collisions). **Arrhenius equation:** k = Ae$^{-Ea/RT}$ where A = Arrhenius constant, Ea = activation energy, R = 8.314, T in K. Rearranged: **ln k = –Ea/RT + ln A** (form y = mx + c). Plot **ln k vs 1/T** → straight line, gradient = **–Ea/R**. **Units of k:** zero order = mol dm^{-3} s^{-1}; first order = s^{-1}; second order = dm^3 mol^{-1} s^{-1}.

3.1.9.1b	*Determining order from data: concentration–time graphs, initial rate method, rate–concentration graphs.*
	From initial rate data: double [A] and observe the effect on rate. No change = zero order; rate doubles = first; rate quadruples = second. **Concentration–time graphs:** zero order = straight line; first order = exponential decay (constant half-life); second order = steeper initial drop. **Rate–concentration graphs:** zero order = horizontal line; first order = straight through origin; second order = curve through origin. **Half-life:** if constant → first order. For zero order, gradient of conc–time graph = –k. **Rate-determining step (rds):** the slowest step. Species in the rate equation appear in or before the rds.

3.1.9.2	*Use orders to deduce the rate-determining step and mechanism. Rate equation is experimentally determined.*
	Species in the rate equation = species involved in (or before) the rds. If rate = k[A][B] → rds involves one A and one B. If rate = k[A]^2 → rds involves two molecules of A. If a species appears in the overall equation but NOT in the rate equation → it is involved in a **fast step after the rds**. The proposed mechanism must: (1) have the rds consistent with the rate equation, (2) sum to give the overall equation.

⭐ REQUIRED PRACTICAL 7: Measuring the Rate of Reaction

Method:

1. METHOD A – INITIAL RATE (e.g. iodine clock): prepare a series of flasks with different concentrations of one reactant (e.g. KI), keeping others constant. Add distilled water to maintain constant total volume.
2. Add a fixed amount of $Na_2S_2O_3$ and starch indicator. Add the final reagent (e.g. H_2O_2 or acidified H_2O_2), start timer, swirl.
3. Record time for solution to turn blue/black. Rate ≈ 1/time for each experiment.
4. Plot rate vs [varied reactant] to determine order.
5. METHOD B – CONTINUOUS MONITORING (e.g. Mg + HCl): place acid in a flask on a balance (or connected to a gas syringe). Add Mg ribbon, start timer.
6. Record mass loss (or gas volume) at regular intervals (e.g. every 30 s).
7. Plot concentration (or volume) vs time. Draw tangents at different times to find rate at those times.
8. Determine order from the shape of the graph (or by measuring half-lives).

Sources of Uncertainty:

- Stopwatch: ±0.5 s (reaction time)
- Measuring cylinders: ±0.5 cm^3
- Balance: ±0.01 g
- Thermometer: ±0.5°C

Common Errors:

- Temperature not controlled (rate depends on temperature – all experiments must be at same T)
- Inconsistent mixing/swirling between experiments
- Difficulty judging exact colour change in clock reaction (subjective end point)
- Not keeping total volume constant when varying concentration (dilution effect)
- Gas escaping before apparatus connected (for gas collection method)

Improvements:

- Use a thermostatted water bath to control temperature
- Keep total volume constant by adding distilled water
- Use consistent swirling/mixing technique for all experiments
- For clock reactions: use a white tile to see colour change clearly
- For gas collection: connect apparatus quickly and ensure airtight seals
- Repeat each experiment and take a mean time
- Plot appropriate graphs and draw lines of best fit

SECTION 3.3: ORGANIC CHEMISTRY

3.3.1 Introduction to Organic Chemistry

3.3.1.1	*Nomenclature: empirical, molecular, general, structural, displayed, skeletal formulae. Homologous series and functional groups. IUPAC naming up to 6C chains/rings.*
	Empirical formula: simplest whole number ratio (e.g. CH_2O). **Molecular formula:** actual atoms (e.g. $C_6H_{12}O_6$). **General formula:** for a homologous series (e.g. C_nH_{2n+2} for alkanes). **Structural formula:** shows grouping (e.g. CH_3CH_2OH). **Displayed formula:** shows every bond. **Skeletal formula:** zigzag carbon backbone; C and H on chain not shown; heteroatoms shown. **Homologous series:** same functional group, same general formula, differ by CH_2. Similar chemical properties, gradual trend in physical properties.

3.3.1.2	*Reaction mechanisms: free-radical (dot notation, no curly arrows), and curly arrow mechanisms from lone pairs or bonds.*
	Free-radical mechanisms: radicals shown with a single dot (e.g. Cl•). Curly arrows NOT used. **Curly arrow mechanisms:** arrow starts from a **lone pair** or a **bond** (region of electron density), and points to where the electrons move to. Shows bond formation or breaking. **Heterolytic fission:** both electrons go to one atom → ions formed. **Homolytic fission:** one electron to each atom → radicals formed.

3.3.1.3	*Isomerism: structural isomers (chain, position, functional group) and stereoisomers (E/Z isomerism with CIP priority rules).*
	Structural isomers: same molecular formula, different structural formula. Types: **chain** (different carbon skeleton), **position** (same group, different position), **functional group** (different functional groups). **Stereoisomers:** same structural formula, different spatial arrangement. **E/Z isomerism:** requires restricted rotation (C=C) and two different groups on each C of the double bond. **Z (zusammen):** higher priority groups on same side. **E (entgegen):** opposite sides. Priority by **CIP rules** (higher atomic number = higher priority).

3.3.2 Alkanes

3.3.2.1	*Alkanes are saturated hydrocarbons. Fractional distillation of crude oil.*
	Saturated: only single C–C and C–H bonds. General formula: C_nH_{2n+2}. **Fractional distillation:** crude oil heated, vapours rise up the column. Fractions collected at different heights based on **boiling point range**. Shorter chains = lower b.p. = higher up the column.

3.3.2.2	*Cracking: thermal (high P, high T, alkenes) and catalytic (zeolite catalyst, motor fuels, aromatics). Economic reasons.*
	Thermal cracking: high temperature (~1000°C), high pressure. Produces **alkenes** (for polymers/plastics). **Catalytic cracking:** zeolite catalyst, lower temperature, slight pressure. Produces **branched alkanes** and **aromatics** (for motor fuels). **Economic reasons:** demand for short-chain fractions (petrol) exceeds supply from distillation; long-chain fractions have lower demand; cracking converts low-demand fractions into high-demand products.

3.3.2.3	*Combustion of alkanes. Pollutants (NOx, CO, carbon, unburned HC). Catalytic converters. SO_2 removal.*
	Complete combustion: alkane + O_2 → CO_2 + H_2O. **Incomplete:** produces CO (toxic), C (particulates), unburned hydrocarbons. **NOx:** formed at high engine temperatures (N_2 + O_2 → 2NO). Causes acid rain and smog. **Catalytic converters:** 2CO + 2NO → $2CO_2$ + N_2 (Pt/Pd/Rh catalyst). **SO_2 removal** from flue gases: CaO + SO_2 → $CaSO_3$ or $CaCO_3$ + SO_2 → $CaSO_3$ + CO_2.

3.3.2.4	*Free-radical substitution of methane with chlorine: initiation, propagation, termination steps.*
	Initiation: Cl_2 → 2Cl• (UV light, homolytic fission) **Propagation:** Cl• + CH_4 → CH_3• + HCl, then CH_3• + Cl_2 → CH_3Cl + Cl• **Termination:** any two radicals combine (e.g. Cl• + Cl• → Cl_2, CH_3• + Cl• → CH_3Cl, CH_3• + CH_3• → C_2H_6). **Limitations:** further substitution (CH_2Cl_2, $CHCl_3$, CCl_4) → mixture of products.

3.3.3 Halogenoalkanes

3.3.3.1	*Nucleophilic substitution of halogenoalkanes with OH^-, CN^- and NH_3. Mechanisms. Bond enthalpy and rate.*
	Halogenoalkanes have polar C–X bonds (δ+C attracts nucleophiles). **With OH^- (aq KOH, reflux):** R–X + OH^- → R–OH + X^- (alcohol). **With CN^- (KCN in ethanol/water, reflux):** R–X + CN^- → R–CN + X^- (nitrile, **C chain +1**). **With NH_3 (excess, heat in sealed tube):** R–X + 2NH_3 → R–NH_2 + NH_4X (primary amine). **Mechanism (SN2 for primary):** curly arrow from nucleophile lone pair to δ+C; simultaneously C–X bond breaks. **Reactivity:** C–I > C–Br > C–Cl (C–I has lowest bond enthalpy, weakest, easiest to break).

3.3.3.2	*Elimination with KOH in ethanol. Concurrent substitution and elimination. Role of OH^- as nucleophile and base.*
	With ethanolic KOH (reflux): R–X + KOH → alkene + H_2O + KX (elimination). OH^- acts as a **base** (removes H^+ from the carbon adjacent to C–X). **Concurrent reactions:** with **aqueous** KOH → substitution (alcohol); with **ethanolic** KOH → elimination (alkene). The solvent determines the reaction pathway. **Mechanism:** curly arrow from OH^- to H on adjacent C; C–H breaks, electrons form C=C, C–X breaks simultaneously.

3.3.3.3	*Ozone depletion: CFCs, Cl radicals catalyse decomposition of ozone. Legislation and alternatives.*
	Ozone (O_3) in the upper atmosphere absorbs harmful **UV radiation**. **CFCs** (chlorofluorocarbons) release Cl• radicals when UV breaks C–Cl bonds: Cl• + O_3 → ClO• + O_2, then ClO• + O_3 → 2O_2 + Cl• Cl• is a **catalyst** – regenerated, destroys many O_3 molecules. Scientific evidence led to **legislation banning CFCs**. Replaced by chlorine-free alternatives (HFCs).

3.3.4 Alkenes

3.3.4.1	*Alkenes are unsaturated hydrocarbons with a C=C double bond (centre of high electron density).*
	General formula: C_nH_{2n}. The C=C consists of a σ-bond (head-on overlap) and a π-bond (sideways p-orbital overlap). The π-bond is a region of **high electron density** above and below the bond, attracting **electrophiles**. Restricted rotation about C=C causes E/Z isomerism.

3.3.4.2	*Electrophilic addition: HBr, H_2SO_4, Br_2. Mechanisms. Major/minor products. Bromine test for unsaturation.*
	With HBr: alkene + HBr → halogenoalkane. **Markovnikov's rule:** H adds to C with more H's → more stable carbocation (tertiary > secondary > primary) → **major product**. **With H_2SO_4:** alkene + H_2SO_4 → alkyl hydrogen sulfate. Then hydrolysis with water → alcohol (industrial route). **With Br_2:** alkene + Br_2 → dibromoalkane. **Test for unsaturation:** bromine water is **decolourised** (orange → colourless). **Mechanism:** curly arrow from C=C π-bond to δ+H (or δ+Br). Heterolytic fission of H–Br (or Br–Br). Carbocation intermediate formed. Then nucleophilic attack by Br^- (or HSO_4^-).

3.3.4.3	*Addition polymers from alkenes. Repeat units. Naming. PVC and plasticisers. Polymers are unreactive.*
	Addition polymerisation: many alkene monomers join, C=C opens to form C–C. No by-products (100% atom economy). **Repeat unit:** draw monomer with double bond opened, continuation bonds at each end. **Poly(chloroethene) = PVC:** rigid but can be softened with **plasticisers** (small molecules that sit between chains and reduce intermolecular forces, increasing flexibility). **Addition polymers are unreactive:** strong C–C backbone, no polar functional groups, so resistant to chemical attack and **non-biodegradable**.

3.3.5 Alcohols

3.3.5.1	*Alcohol production: hydration of alkenes (acid catalyst) and fermentation of glucose. Biofuels. Carbon neutrality.*
	Hydration of alkenes: ethene + steam, H_3PO_4 catalyst, 300°C, 60 atm. Fast, continuous, pure product but uses non-renewable crude oil feedstock. **Fermentation:** glucose → $2C_2H_5OH + 2CO_2$ (yeast, 25–37°C, anaerobic). Batch process, slow, impure, needs fractional distillation. But uses **renewable** feedstock. **Biofuel:** ethanol from fermentation. Claimed to be **carbon neutral** (CO_2 released on burning = CO_2 absorbed during crop growth). **Not truly carbon neutral** due to energy used in farming, transport, distillation.

3.3.5.2	*Oxidation of alcohols: primary → aldehyde/carboxylic acid, secondary → ketone, tertiary → no reaction. Tests for aldehydes.*
	Primary alcohol + $K_2Cr_2O_7/H_2SO_4$: → **Aldehyde** (distil immediately to remove before further oxidation). → **Carboxylic acid** (reflux with excess oxidising agent). **Secondary alcohol → ketone** (reflux or distil). **Tertiary → no reaction** (no H on the C bearing OH). Orange dichromate turns **green** (Cr^{3+}) when oxidation occurs. **Tests for aldehydes (not ketones):** Fehling's/Benedict's = **brick-red precipitate**. Tollens' (ammoniacal $AgNO_3$) = **silver mirror**.

3.3.5.3	*Elimination: acid-catalysed dehydration of alcohols to alkenes. Mechanism. Use of alkenes to make polymers from non-crude-oil sources.*
	Alcohol + conc. H_2SO_4 (or conc. H_3PO_4), heat → alkene + H_2O (dehydration/elimination). **Mechanism:** H^+ protonates the OH. Curly arrow from C–H bond to form C=C. H_2O leaves. **Significance:** alkenes from this route can make **addition polymers without using crude oil** (if the alcohol comes from fermentation of renewable crops).

⭐ REQUIRED PRACTICAL 5: Distillation of a Product from a Reaction

Method:

1. Typically: preparation of cyclohexene from cyclohexanol by acid-catalysed elimination.
2. Add cyclohexanol (~10 cm^3) to a round-bottomed flask with anti-bumping granules. Add a few drops of concentrated phosphoric acid (catalyst).
3. Set up for distillation: flask + thermometer + condenser + collection flask.
4. Heat gently. Collect the distillate at the correct boiling point range (cyclohexene: ~83°C).
5. Transfer the distillate to a separating funnel. Wash with sodium carbonate solution (to remove acid impurities). Vent regularly.
6. Separate the organic layer (top). Wash with water. Separate again.
7. Dry the organic product with anhydrous calcium chloride. Filter off the drying agent.
8. Redistil if needed, collecting the fraction at the correct boiling point.
9. Record the boiling point and compare with the literature value.

Sources of Uncertainty:

- Thermometer: ±0.5°C
- Measuring cylinder: ±0.5 cm^3
- Boiling point range of collected fraction

Common Errors:

- Not heating gently enough (bumping/loss of product) or too strongly (charring)
- Not washing the organic layer sufficiently (acid impurities remain)
- Incomplete drying (water contamination lowers purity and affects boiling point)
- Loss of volatile product during transfers between vessels
- Collecting fractions at wrong temperature range (impure product)

Improvements:

- Use anti-bumping granules to prevent bumping
- Wash with Na_2CO_3 to neutralise acid, then with water
- Use anhydrous drying agent and allow sufficient time
- Minimise the number of transfers to reduce losses
- Record boiling point – sharp b.p. close to literature value indicates purity
- Calculate percentage yield: actual mass / theoretical mass × 100%

3.3.6 Organic Analysis

3.3.6.1	*Identification of functional groups by test-tube reactions.*
	Alkene: bromine water **decolourised** (orange → colourless). **Alcohol:** burns cleanly; reacts with PCl_5 to give steamy white HCl fumes. **Aldehyde:** Fehling's = brick-red ppt; Tollens' = silver mirror; acidified $K_2Cr_2O_7$ goes orange → green. **Ketone:** no reaction with Fehling's, Tollens', or $K_2Cr_2O_7$. **Carboxylic acid:** turns blue litmus red; fizzes with Na_2CO_3 (CO_2 produced – limewater goes milky).

⭐ REQUIRED PRACTICAL 6: Tests for Alcohol, Aldehyde, Alkene and Carboxylic Acid

Method:

1. Prepare small samples of each unknown in separate clean test tubes.
2. TEST FOR ALKENE: add bromine water. If decolourised (orange → colourless) = alkene present.
3. TEST FOR ALCOHOL: add a few drops to PCl_5. Steamy white fumes (HCl) = –OH group present. Or: warm with acidified $K_2Cr_2O_7$ – orange to green = primary/secondary alcohol.
4. TEST FOR ALDEHYDE: warm with Fehling's solution. Brick-red precipitate = aldehyde. OR warm with Tollens' reagent in a clean glass tube. Silver mirror = aldehyde. Ketones give no reaction with either.
5. TEST FOR CARBOXYLIC ACID: add Na_2CO_3 (or $NaHCO_3$). Effervescence (CO_2) = carboxylic acid. Test gas with limewater (turns milky). Also turns blue litmus red.
6. Record all observations systematically in a table.

Sources of Uncertainty:

- Visual judgement of colour changes and precipitate formation
- Volume of reagents added (consistency)

Common Errors:

- Cross-contamination between test tubes (false positives)
- Not warming Fehling's/Tollens' sufficiently (slow reactions give false negatives)
- Using dirty glassware for Tollens' test (silver mirror won't form on dirty glass)
- Confusing a colour change with a precipitate

Improvements:

- Use clean test tubes for every test – especially clean glass for Tollens'
- Warm Fehling's and Tollens' gently in a water bath (not direct flame for Tollens')
- Use small, consistent quantities of reagents
- Record observations immediately
- Carry out tests in a logical order: alkene first, then functional group tests

3.3.6.2	*Mass spectrometry: molecular formula from precise atomic masses.*
	High-resolution mass spec measures Mr to many decimal places, distinguishing compounds with same integer Mr. **M^+ peak** = molecular ion → gives Mr. Common fragment losses: −15 (CH_3), −17 (OH), −28 (CO), −29 (CHO), −31 (CH_2OH), −45 (OC_2H_5).

3.3.6.3	*Infrared spectroscopy: bond absorptions, fingerprinting, functional group identification. Link to global warming.*
	Key IR absorptions: O–H alcohol (broad, ~3230–3550 cm^{-1}), O–H acid (very broad, ~2500–3300 cm^{-1}), C=O (~1680–1750 cm^{-1}), C–H (~2850–2960 cm^{-1}), N–H (~3300–3500 cm^{-1}). **Fingerprint region** (below ~1500 cm^{-1}) is unique to each compound. **Global warming link:** CO_2, CH_4, and H_2O vapour absorb IR radiation. Bonds in these molecules vibrate at frequencies matching IR wavelengths, trapping heat in the atmosphere (greenhouse effect).

3.3.7 Optical Isomerism

★ A-LEVEL ONLY

3.3.7	*Optical isomerism: chirality, asymmetric carbon, enantiomers (non-superimposable mirror images), racemic mixtures.*
	Optical isomerism occurs when a molecule has a **chiral centre** (carbon bonded to **four different groups**). **Enantiomers:** non-superimposable mirror images. Identical physical properties but rotate plane-polarised light in **opposite directions**. **Racemic mixture (racemate):** 50:50 mix of both enantiomers → **no net optical rotation** (rotations cancel). Racemic mixtures form when: a planar intermediate (e.g. carbocation or trigonal planar carbonyl) is attacked **equally from both sides**.

3.3.8 Aldehydes and Ketones

★ A-LEVEL ONLY

3.3.8	*Aldehydes and ketones: oxidation, reduction ($NaBH_4$), nucleophilic addition (KCN), tests (Fehling's, Tollens'). Mechanisms.*
	Aldehydes are readily oxidised to carboxylic acids; **ketones** are not. **Tests:** Fehling's (brick-red ppt with aldehyde, no change with ketone). Tollens' (silver mirror with aldehyde). **Reduction ($NaBH_4$ in aqueous solution):** aldehyde → primary alcohol; ketone → secondary alcohol. [H] in equations. **Mechanism:** nucleophilic addition – H^- (from $NaBH_4$) attacks δ+C of C=O. **Reaction with KCN then dilute acid → hydroxynitrile.** Mechanism: CN^- attacks δ+C of C=O (nucleophilic addition). The C=O π-bond breaks, electrons go to O. Then protonation by H^+ from dilute acid. **Chirality:** if the carbonyl was not already at a chiral centre, the product has a **new chiral centre** → **racemic mixture** (CN^- attacks equally from both sides of the planar C=O). **KCN is extremely toxic** – handle in fume cupboard, wear gloves, have safety protocols.

3.3.9 Carboxylic Acids and Derivatives

★ A-LEVEL ONLY

3.3.9.1	*Carboxylic acids and esters: weak acids, esterification, hydrolysis (acid and alkaline). Biodiesel. Soap. Vegetable oils/fats.*
	Carboxylic acids are **weak acids** but strong enough to liberate CO_2 from carbonates: $2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + H_2O + CO_2$. **Esterification:** $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$ (acid catalyst, reflux). Esters have fruity smells; used as solvents, plasticisers, perfumes, food flavourings. **Acid hydrolysis of esters:** $RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$ (reversible, dilute acid, reflux). **Alkaline hydrolysis:** $RCOOR' + NaOH \rightarrow RCOONa + R'OH$ (**irreversible**). Fats/oils + NaOH → **soap** (sodium salt of long-chain carboxylic acid) + **glycerol**. **Biodiesel:** methyl esters of long-chain carboxylic acids, made from vegetable oils + methanol + catalyst.

3.3.9.2	*Acylation: acyl chlorides and acid anhydrides with water, alcohols, ammonia, primary amines. Mechanisms. Aspirin. Advantages of anhydrides.*
	Acyl chlorides (RCOCl) and **acid anhydrides ($(RCO)_2O$)** react with nucleophiles via **nucleophilic addition–elimination**: **+ Water:** → carboxylic acid + HCl (or carboxylic acid). **+ Alcohol:** → ester + HCl (or carboxylic acid). **+ Ammonia:** → amide + HCl (or carboxylic acid). **+ Primary amine:** → N-substituted amide + HCl (or carboxylic acid). **Mechanism (acyl chlorides):** nucleophile attacks δ+C of C=O. C=O π-bond breaks. Cl^- leaves (addition-elimination). **Aspirin manufacture:** ethanoic anhydride preferred over ethanoyl chloride because it is **cheaper, less corrosive, reacts less vigorously** (safer), and produces ethanoic acid (not HCl) as by-product.

⭐ REQUIRED PRACTICAL 10: Preparation of a Pure Organic Solid and Liquid

Method:

1. SOLID (e.g. aspirin): weigh 2-hydroxybenzoic acid (salicylic acid) into a flask. Add ethanoic anhydride and a few drops of conc. H_3PO_4 (catalyst). Heat in a water bath at 80–90°C for 15 min.
2. Allow to cool. Add cold distilled water to decompose excess anhydride. Cool in ice bath until crystals form. Scratch flask to encourage crystallisation.
3. Filter under reduced pressure (Buchner funnel). Wash crystals with cold water.
4. Recrystallise: dissolve in minimum hot ethanol, add warm water, cool slowly, then ice-cool. Filter, wash, dry.
5. Measure melting point and compare with literature value (aspirin: 135°C).
6. LIQUID (e.g. preparation and purification of a liquid product): carry out the reaction, then purify by washing in a separating funnel, drying with anhydrous salt, and distilling. Record boiling point.

Sources of Uncertainty:

- Balance: ±0.001 g
- Thermometer: ±0.5°C
- Melting point apparatus: ±1°C

Common Errors:

- Not heating under reflux for long enough (incomplete reaction)
- Adding water too quickly to hot mixture (splattering)
- Not cooling sufficiently before filtering (product dissolves, lower yield)
- Impure product: broad melting point range or m.p. below literature value
- Losses during recrystallisation and transfer

Improvements:

- Heat for the full time to ensure complete reaction
- Add water slowly to the cooled mixture
- Cool thoroughly in ice and scratch flask to maximise crystallisation
- Recrystallise using minimum hot solvent for maximum purity
- Dry completely before weighing and measuring melting point
- A sharp m.p. close to literature value = high purity

3.3.10 Aromatic Chemistry

★ A-LEVEL ONLY

3.3.10.1	*Benzene bonding: delocalised π-system. Evidence from enthalpy of hydrogenation. More stable than cyclohexa-1,3,5-triene. Substitution preferred over addition.*
	Benzene (C_6H_6): 6 carbon atoms, each sp^2 hybridised, in a planar hexagonal ring. Each C has one p-orbital perpendicular to the ring → overlap to form a **delocalised π-system** above and below the plane. **Evidence:** enthalpy of hydrogenation of benzene is **152 kJ mol^{-1} less exothermic** than predicted for cyclohexatriene. This is the **delocalisation (stabilisation) energy**. **Bond lengths:** all C–C bonds equal (140 pm), intermediate between single (154) and double (134). **Substitution preferred:** addition would destroy the stable delocalised ring. Substitution preserves it.

3.3.10.2	*Electrophilic substitution: nitration (with NO_2^+ generation) and Friedel-Crafts acylation ($AlCl_3$ catalyst). Mechanisms.*
	Nitration: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$. Conc. H_2SO_4 + conc. HNO_3 at **below 55°C**. **Electrophile generation:** $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$. **Friedel-Crafts acylation:** $C_6H_6 + RCOCl \rightarrow C_6H_5COR + HCl$ (catalyst: $AlCl_3$). **Electrophile generation:** $RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$. **Mechanism (both):** (1) Electrophile attacks delocalised π-system (curly arrow from ring to E^+). (2) Intermediate with H still attached. (3) H^+ lost, ring restored (curly arrow from C–H back into ring). $AlCl_3$ regenerated. **Nitration is important** for making explosives and amines (reduce NO_2 to NH_2).

3.3.11 Amines

★ A-LEVEL ONLY

3.3.11.1	*Amine preparation: from halogenoalkanes with NH_3, and reduction of nitriles. Aromatic amines from nitro compounds.*
	From halogenoalkanes: $RX + 2NH_3 \rightarrow RNH_2 + NH_4X$ (excess NH_3, sealed tube, heat). Further substitution → secondary, tertiary amines, quaternary ammonium salts. **From nitriles:** $RCN + 4[H] \rightarrow RCH_2NH_2$ ($LiAlH_4$ in dry ether, or H_2/Ni). Carbon chain extended by 1. **Aromatic amines:** $ArNO_2 + 6[H] \rightarrow ArNH_2 + 2H_2O$ (Sn + conc. HCl, reflux). Used in dye manufacture.

3.3.11.2	*Amines as weak bases. Difference in base strength: aliphatic > NH_3 > aromatic.*
	Amines are **weak bases** (lone pair on N accepts H^+). **Basicity order: aliphatic amine > ammonia > aromatic amine.** **Aliphatic amines:** alkyl group is electron-donating (+I effect) → increases electron density on N → lone pair more available for protonation. **Aromatic amines:** N lone pair is **delocalised into the benzene ring** → less available → weaker base.

3.3.11.3	*Amines as nucleophiles: with halogenoalkanes (to form 1°, 2°, 3° amines and quaternary salts), with acyl chlorides and acid anhydrides. Mechanisms.*
	With halogenoalkanes: nucleophilic substitution. $RNH_2 + R'X \rightarrow R'NHR + HX$ (and further substitution). Quaternary ammonium salts (R_4N^+) are used as **cationic surfactants** (positively charged head, long hydrocarbon tail). **With acyl chlorides/acid anhydrides:** nucleophilic addition-elimination. Produces **amides** ($RCONHR' + HCl$). **Mechanism:** lone pair on N attacks δ+C of C=O (or δ+C of C–X). Show curly arrows from lone pair.

3.3.12 Polymers

★ A-LEVEL ONLY

3.3.12.1	*Condensation polymers: from dicarboxylic acids + diols (polyesters, e.g. Terylene), dicarboxylic acids + diamines (polyamides, e.g. nylon 6,6, Kevlar), amino acids. Repeat units and linkages.*
	Condensation polymerisation: monomers join with loss of a small molecule (H_2O). **Polyesters** (e.g. Terylene/PET): dicarboxylic acid + diol → **ester linkage (–COO–)** + H_2O. **Polyamides** (e.g. nylon 6,6, Kevlar): dicarboxylic acid + diamine → **amide linkage (–CONH–)** + H_2O. **From amino acids:** self-condensation → polypeptide with **peptide bonds (–CONH–)**. You must be able to draw repeat units from monomers and vice versa.

3.3.12.2	*Biodegradability and disposal. Polyalkenes non-biodegradable. Polyesters/polyamides can be hydrolysed.*
	Polyalkenes (addition polymers) are **non-biodegradable** – no polar functional groups, so resistant to hydrolysis and microbial attack. **Polyesters and polyamides** (condensation polymers) **can be hydrolysed** (ester/amide bonds broken by water/acid/alkali) → **biodegradable**. **Disposal methods:** landfill (slow degradation), incineration (energy recovery but CO_2/toxic gases), recycling (sorting by type, reprocessing).

3.3.13 Amino Acids, Proteins and DNA

★ A-LEVEL ONLY

3.3.13.1	*Amino acids: acidic and basic properties, zwitterion formation.*
	Amino acids have **–NH_2** (basic) and **–COOH** (acidic) groups. At neutral pH, the amino acid exists as a **zwitterion**: $^{+}NH_3$–CHR–COO^{-} (internal salt). **In acid:** $^{+}NH_3$–CHR–COOH (positive ion, both groups protonated). **In alkali:** NH_2–CHR–COO^{-} (negative ion, both groups deprotonated). High melting points (ionic interactions in solid state); soluble in water.

3.3.13.2	*Proteins: peptide links, primary/secondary/tertiary structure, hydrogen bonding, S–S bonds. Hydrolysis. Chromatography and Rf values.*
	Peptide bond (–CONH–): formed by condensation between –COOH of one amino acid and –NH_2 of another (+ H_2O lost). **Primary structure:** sequence of amino acids. **Secondary:** α-helix or β-pleated sheet (maintained by **H-bonds** between C=O and N–H of peptide bonds). **Tertiary:** overall 3D shape (maintained by H-bonds, ionic interactions, van der Waals, and **disulfide bridges (S–S)**). **Hydrolysis:** heat protein with 6 mol dm^{-3} HCl under reflux → individual amino acids. **Chromatography:** separate amino acids by TLC. Locate with **ninhydrin** or UV light. **Rf = distance by spot / distance by solvent front.** Compare with standards.

3.3.13.3	*Enzymes: proteins with stereospecific active sites. Drugs as enzyme inhibitors.*
	Enzymes are biological catalysts (proteins). The **active site** is stereospecific – it has a complementary shape to the substrate (lock-and-key model). Only **one enantiomer** of a chiral substrate fits. **Enzyme inhibitors (drugs):** molecules that **block the active site**, preventing the substrate from binding. Computer modelling helps design drugs with the correct shape to fit the active site.

3.3.13.4	*DNA: nucleotides (phosphate + 2-deoxyribose + base), polymer backbone, double helix, complementary base pairing by H-bonding.*
	Nucleotide = phosphate + 2-deoxyribose (pentose sugar) + base (A, C, G, or T). **DNA strand:** polymer of nucleotides linked by covalent bonds between phosphate and sugar → sugar-phosphate backbone with bases attached. **Double helix:** two complementary strands held together by **hydrogen bonds** between base pairs: **A–T** (2 H-bonds) and **C–G** (3 H-bonds). Complementary base pairing enables replication.

3.3.13.5	*Cisplatin as an anticancer drug. Prevents DNA replication by ligand replacement with guanine N. Benefits vs adverse effects.*
	Cisplatin [$PtCl_2(NH_3)_2$] is a square planar Pt(II) complex used in cancer treatment. **Mechanism:** Cl ligands are replaced by bonds to **N atoms on guanine** bases in DNA (ligand substitution). This **cross-links** the two DNA strands, preventing them from separating for replication → cancer cell cannot divide. **Adverse effects:** cisplatin also affects healthy, rapidly dividing cells (e.g. hair, gut lining) → side effects (nausea, hair loss). Society must balance **benefits** (treating cancer) vs **risks** (side effects).

3.3.14 Organic Synthesis

★ A-LEVEL ONLY

3.3.14	*Organic synthesis: multi-step routes (up to 4 steps). Green chemistry principles: fewer steps, high atom economy, no solvent, non-hazardous starting materials.*
	You must know all reactions in the specification and be able to **chain them together** in multi-step syntheses. **Key routes:** alkene → alcohol → halogenoalkane → nitrile → carboxylic acid/amine. Alcohol → aldehyde → carboxylic acid. Halogenoalkane → alcohol/alkene/amine. **Green chemistry aims:** fewer steps (less waste), high atom economy, avoid hazardous solvents/reagents, use renewable feedstocks.

3.3.15 NMR Spectroscopy

★ A-LEVEL ONLY

3.3.15	*NMR spectroscopy: ^{13}C and ^{1}H NMR. Chemical shift (δ). Integration. (n+1) rule. TMS standard. Deuterated solvents.*
	^{13}C NMR: number of peaks = number of different **carbon environments**. Simpler spectra than ^{1}H. **^{1}H NMR:** number of peaks = number of different **proton environments**. Peak area (integration) = relative number of H atoms. **(n+1) rule:** peak split into n+1 lines by n adjacent non-equivalent H atoms. Singlet (0 neighbours), doublet (1), triplet (2), quartet (3). **Chemical shift (δ):** position on spectrum (in ppm). Depends on molecular environment. Use data booklet. **TMS (tetramethylsilane, $Si(CH_3)_4$):** used as standard (δ = 0). Chosen because: 12 equivalent H atoms (one strong peak), δ = 0 is away from most other signals, inert, volatile (easily removed), miscible with most solvents. **Deuterated solvents** (e.g. $CDCl_3$) used because D (^{2}H) is NMR-inactive and doesn't produce interfering peaks. **D_2O shake:** O–H and N–H peaks disappear (H exchanged for D).

3.3.16 Chromatography

★ A-LEVEL ONLY

3.3.16	*Chromatography: TLC, column chromatography, GC. Rf values and retention times. GC-MS.*
	Chromatography separates components between a **mobile phase** (moving) and a **stationary phase** (fixed). **TLC:** stationary = solid on plate, mobile = solvent. **Rf = distance by substance / distance by solvent front** (0 to 1). **Column chromatography:** stationary = solid packed in column, mobile = solvent flowing down. **Gas chromatography (GC):** stationary = solid/liquid in column, mobile = carrier gas. Separates by **retention time**. Separation depends on **balance** between solubility in mobile phase and retention by stationary phase. **GC-MS:** GC separates the mixture, then each component enters a mass spectrometer for identification. Used in forensics and drug testing.

⭐ REQUIRED PRACTICAL 12: Separation of Species by Thin-Layer Chromatography

Method:

1. Draw a pencil line (baseline) about 1 cm from the bottom of a TLC plate. Do NOT use pen (ink will run).
2. Using a capillary tube, apply small spots of each sample and known standards onto the baseline, evenly spaced. Label in pencil.
3. Place the plate in a beaker containing a shallow layer of solvent (mobile phase). The solvent level must be BELOW the baseline.
4. Cover the beaker with a lid (to saturate the atmosphere with solvent vapour and prevent uneven evaporation).
5. Allow the solvent to rise up the plate by capillary action. Remove the plate when the solvent front is near the top.
6. Immediately mark the solvent front with a pencil line.
7. If spots are colourless (e.g. amino acids), visualise using a locating agent: UV lamp, ninhydrin spray, or iodine vapour.
8. Measure the distance from the baseline to the centre of each spot, and the distance to the solvent front.
9. Calculate Rf = distance moved by substance / distance moved by solvent front.
10. Compare Rf values with known standards to identify substances.

Sources of Uncertainty:

- Ruler: ±0.5 mm (for measuring distances)
- Difficulty locating the exact centre of diffuse spots
- Variation in Rf if temperature or solvent composition changes

Common Errors:

- Baseline drawn in ink (dissolves and runs with solvent)
- Spots too large or too concentrated (streaking, poor separation)
- Solvent level above the baseline (spots dissolve directly into solvent instead of being carried up)
- Not covering the beaker (uneven solvent evaporation, curved solvent front)
- Allowing plate to remain in solvent too long (spots run off the top)

Improvements:

- Use pencil for baseline and labels (insoluble in solvent)
- Apply small, concentrated spots using a capillary tube
- Ensure the solvent level is below the pencil baseline
- Cover the beaker with a watch glass or lid
- Remove the plate promptly when solvent front nears the top
- Run known standards alongside unknowns on the same plate for reliable comparison
- Repeat in different solvents if separation is poor

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