

AS Chemistry 9701: full syllabus summary (all topics in one document)

This summary covers every AS topic in the Cambridge International AS and A Level Chemistry (9701) syllabus, in syllabus order. Each section gives the key facts in short bullet points, the definitions you must learn word for word in boxes, and the equations and mechanisms that examiners ask for most often. Use it for revision once you have studied each topic in full; our separate topic notes on each area (atomic structure, bonding and shapes, energetics, redox, periodicity, the halogens, nitrogen and sulfur, organic chemistry and spectroscopy) go into more depth and include longer practice sets.

Values such as bond energies, electronegativities and infrared absorption ranges are printed in the 9701 Data Booklet. Where a number below depends on the booklet, always use the value the booklet or the question gives you.

1. Atomic structure

Particles in the atom

Particle	Relative mass	Relative charge	Location
Proton	1	+1	Nucleus
Neutron	1	0	Nucleus
Electron	1/1836 (negligible)	-1	Shells (orbitals) around the nucleus

- Almost all the mass of an atom is in the tiny nucleus; most of the volume is occupied by electrons.
- Proton number (atomic number, Z) = number of protons. Nucleon number (mass number, A) = protons + neutrons.
- In an electric field, protons are deflected towards the negative plate, electrons towards the positive plate (much more strongly, because they are so light), and neutrons are not deflected. The angle of deflection is proportional to charge/mass.
- Ions: a positive ion has lost electrons; a negative ion has gained electrons. The number of protons does not change.

Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons.

- Isotopes have the same chemical properties (same electron arrangement) but slightly different physical properties, such as density and rate of diffusion, because their masses differ.

Electrons, energy levels and orbitals

- Electrons occupy principal quantum shells ($n = 1, 2, 3 \dots$). Shells divide into sub-shells: s, p, d



(and f).

- An orbital is a region of space that can hold up to two electrons with opposite spins. s sub-shell: 1 orbital (2 electrons); p: 3 orbitals (6 electrons); d: 5 orbitals (10 electrons).
- Shapes: s orbitals are spherical; p orbitals are dumb-bell shaped, arranged along the x, y and z axes.
- Filling order: 1s 2s 2p 3s 3p 4s 3d 4p. The 4s fills before 3d because it is at slightly lower energy in atoms of potassium and calcium, but 4s electrons are lost first when transition metal atoms form ions.
- Electrons occupy orbitals singly, with parallel spins, before pairing (this reduces repulsion).
- Exceptions: chromium is $[\text{Ar}] 3d^5 4s^1$ and copper is $[\text{Ar}] 3d^{10} 4s^1$.
- Examples: Fe is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$; Fe^{3+} is $[\text{Ar}] 3d^5$.
- A free radical is a species with one or more unpaired electrons.

Ionisation energy

First ionisation energy: the energy required to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous $1+$ ions.

Example: $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$

- Successive ionisation energies always increase, because each electron is removed from an increasingly positive ion. A big jump shows the next electron comes from a shell closer to the nucleus. Counting the electrons before the first big jump gives the group number.
- Three factors: nuclear charge (more protons, higher IE); distance of the outer electron from the nucleus (further, lower IE); shielding by inner electrons (more shielding, lower IE).
- Down a group, IE decreases: the outer electron is further away and more shielded, which outweighs the increased nuclear charge.
- Across a period, IE generally increases: nuclear charge increases, shielding is similar and the atomic radius decreases.
- Dips across Period 3: Mg to Al (the 3p electron of Al is higher in energy and slightly shielded by 3s); P to S (S has a paired 3p electron, and repulsion between the paired electrons makes it easier to remove).
- Atomic radius decreases across a period (increasing nuclear charge, same shell) and increases down a group (more shells).
- Positive ions are smaller than their atoms; negative ions are larger than their atoms.

2. Atoms, molecules and stoichiometry

Relative atomic mass, A_r : the weighted mean mass of an atom of an element compared with 1/12 of the mass of an atom of carbon-12.

Relative isotopic mass: the mass of an atom of an isotope compared with 1/12 of the mass of an atom of carbon-12.

The mole: the amount of substance containing 6.02×10^{23} particles (the Avogadro constant, L or N_A).

- Relative molecular mass (M_r) is used for molecules; relative formula mass for ionic compounds. Both are found by adding the A_r values.
- From a mass spectrum: $A_r = \Sigma(\text{isotopic mass} \times \text{abundance}) / \Sigma(\text{abundance})$.
- Key equations:
 - $n = m / M$ (amount in mol = mass in g / molar mass in g mol^{-1})
 - $c = n / V$ (concentration in mol dm^{-3} , volume in dm^3 ; $1 \text{ dm}^3 = 1000 \text{ cm}^3$)
 - For gases at room conditions, $n = V / 24.0$ (V in dm^3), using the molar gas volume from the Data Booklet.
 - $pV = nRT$ (p in Pa, V in m^3 , T in K, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)
- Empirical formula: the simplest whole-number ratio of atoms of each element in a compound. Molecular formula: the actual number of atoms of each element in one molecule.
- To find an empirical formula: divide mass (or percentage) by A_r , divide by the smallest, and round to whole numbers (multiply if you get values like 1.5 or 1.33).
- Percentage yield = $(\text{actual yield} / \text{theoretical yield}) \times 100$.
- Atom economy = $(M_r \text{ of desired product} / \text{sum of } M_r \text{ of all products}) \times 100$.
- Limiting reagent: the reactant that is used up first; it decides the amount of product.
- Ionic equations show only the species that change; spectator ions are left out. Example: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$.
- Learn the formulae of common ions: NO_3^- , CO_3^{2-} , SO_4^{2-} , OH^- , NH_4^+ , Zn^{2+} , Ag^+ , HCO_3^- , PO_4^{3-} .

Worked example: relative atomic mass from isotopes

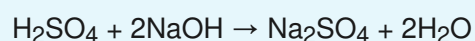
A sample of chlorine contains 75.8% ^{35}Cl and 24.2% ^{37}Cl .

$$A_r = (35 \times 75.8 + 37 \times 24.2) / 100 = (2653 + 895.4) / 100 = 35.5$$

The answer must lie between the two isotopic masses and closer to the more abundant isotope. Check this every time.

Worked example: titration

25.0 cm^3 of sodium hydroxide is neutralised by 20.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ sulfuric acid. Find the concentration of the NaOH.



$$n(\text{H}_2\text{SO}_4) = 0.100 \times 20.0/1000 = 2.00 \times 10^{-3} \text{ mol, so } n(\text{NaOH}) = 4.00 \times 10^{-3} \text{ mol.}$$

$$c(\text{NaOH}) = 4.00 \times 10^{-3} / (25.0/1000) = 0.160 \text{ mol dm}^{-3}.$$

Worked example: empirical and molecular formula

A compound contains 40.0% carbon, 6.7% hydrogen and 53.3% oxygen by mass. Its M_r is 60.

Moles in 100 g: C = $40.0/12.0 = 3.33$; H = $6.7/1.0 = 6.7$; O = $53.3/16.0 = 3.33$.

Divide by the smallest (3.33): C 1, H 2, O 1. Empirical formula CH_2O , with empirical formula mass 30.

$60 / 30 = 2$, so the molecular formula is $\text{C}_2\text{H}_4\text{O}_2$.

- Water of crystallisation: heat a hydrated salt to constant mass; the mass lost is water. Find the mole ratio of anhydrous salt to water to get x in, for example, $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$.
- Back titration: when a solid reacts slowly or is insoluble, add a known excess of acid and titrate the acid left over; the difference gives the amount that reacted.
- Always check the mole ratio from the balanced equation before converting between substances. Most lost marks in mole calculations come from skipping this step or from forgetting to convert cm^3 to dm^3 .

3. Chemical bonding

Electronegativity and bond polarity

Electronegativity: the power of an atom to attract electrons to itself in a covalent bond.

- Electronegativity increases across a period (greater nuclear charge, smaller radius) and decreases down a group (larger radius, more shielding). Fluorine is the most electronegative element.
- A covalent bond between atoms of different electronegativity is polar ($\delta+$ and $\delta-$). A large difference in electronegativity gives ionic bonding.

Ionic, covalent and metallic bonding

Ionic bonding: the electrostatic attraction between oppositely charged ions.

Covalent bond: the electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms.

Metallic bonding: the electrostatic attraction between positive metal ions and a sea of delocalised electrons.

- A dative covalent (coordinate) bond is a covalent bond in which both shared electrons come from the same atom. Examples: NH_4^+ , H_3O^+ , and Al_2Cl_6 (the dimer of aluminium chloride in the vapour).
- Some atoms can expand their octet using d orbitals (in Period 3 and below): PCl_5 , SF_6 , SO_2 . Others have fewer than eight outer electrons: BF_3 , BeCl_2 .
- Sigma (σ) bonds form by head-on (end-to-end) overlap of orbitals; the electron density lies between the nuclei. Pi (π) bonds form by sideways overlap of p orbitals; the electron density is above and below the bond axis. A double bond is one σ and one π bond; a triple bond is one σ and two π bonds.
- Hybridisation: sp^3 (tetrahedral, as in alkanes), sp^2 (trigonal planar, as in ethene), sp (linear, as in

ethyne).

- **Bond energy:** the energy needed to break one mole of a particular covalent bond in the gaseous state. **Bond length:** the distance between the nuclei of two bonded atoms. Shorter bonds are generally stronger.

Shapes of molecules (VSEPR)

Electron pairs around the central atom repel and move as far apart as possible. Lone pairs repel more strongly than bonding pairs (lone pair/lone pair > lone pair/bond pair > bond pair/bond pair), so each lone pair closes the bond angle by about 2 to 2.5°.

Bonding pairs	Lone pairs	Shape	Bond angle	Example
2	0	Linear	180°	CO ₂ , BeCl ₂
3	0	Trigonal planar	120°	BF ₃
4	0	Tetrahedral	109.5°	CH ₄ , NH ₄ ⁺
3	1	Trigonal pyramidal	107°	NH ₃
2	2	Non-linear (bent)	104.5°	H ₂ O
5	0	Trigonal bipyramidal	90° and 120°	PCl ₅
6	0	Octahedral	90°	SF ₆

- A double bond counts as one region of electron density when working out shape (CO₂ is linear).
- A molecule with polar bonds is non-polar overall if it is symmetrical so the dipoles cancel (CO₂, CCl₄, BF₃).

Intermolecular forces

- **Instantaneous dipole-induced dipole forces** (London dispersion forces) act between all molecules. Electrons move, creating a temporary dipole that induces a dipole in a neighbour. They are stronger for molecules with more electrons and for long, unbranched molecules with greater surface contact.
- **Permanent dipole-permanent dipole forces** act between polar molecules, such as HCl or propanone.
- **Hydrogen bonding** occurs when hydrogen is bonded to N, O or F. The δ⁺ hydrogen is attracted to a lone pair on an N, O or F atom of a neighbouring molecule. It is the strongest intermolecular force.
- Hydrogen bonding explains the anomalously high boiling points of H₂O, NH₃ and HF, the relatively high surface tension and viscosity of water, and why ice is less dense than liquid water (an open lattice in which each H₂O forms up to four hydrogen bonds).
- All intermolecular forces are much weaker than covalent, ionic or metallic bonds.

4. States of matter

Gases

- Ideal gas assumptions: molecules have negligible volume compared with the container; there are no intermolecular forces; collisions are perfectly elastic.
- Real gases behave most ideally at **high temperature** (molecules have enough energy to overcome attractions) and **low pressure** (molecules are far apart, so their own volume is small compared with the container).
- Deviations are largest for polar or large molecules with strong intermolecular forces, at low temperature and high pressure.
- $pV = nRT$ can find M_r of a volatile liquid: $M_r = mRT / (pV)$.

Worked example: $pV = nRT$

0.240 g of a gas occupies 100 cm³ at 100 kPa and 300 K. Find M_r .

$V = 100 \times 10^{-6} = 1.00 \times 10^{-4} \text{ m}^3$; $p = 1.00 \times 10^5 \text{ Pa}$.

$n = pV / RT = (1.00 \times 10^5 \times 1.00 \times 10^{-4}) / (8.31 \times 300) = 10.0 / 2493 = 4.01 \times 10^{-3} \text{ mol}$.

$M = 0.240 / 4.01 \times 10^{-3} = 59.8 \text{ g mol}^{-1}$, so $M_r \approx 60$.

Liquids and solids

- When a liquid is heated, energy is used to overcome intermolecular forces during melting and boiling, so temperature stays constant during a change of state.
- Vapour pressure increases with temperature; a liquid boils when its vapour pressure equals the external pressure.

Lattice type	Particles and forces	Example	Typical properties
Giant ionic	Ions held by strong ionic bonds	NaCl, MgO	High melting point; conducts when molten or in solution; often soluble in water; brittle
Simple molecular	Molecules held by weak intermolecular forces	I ₂ , ice	Low melting point; does not conduct
Giant molecular (covalent)	Atoms held by strong covalent bonds	Diamond, graphite, SiO ₂	Very high melting point; insoluble; non-conductor (except graphite)
Giant metallic	Positive ions in a sea of delocalised electrons	Copper	Conducts as solid and liquid; malleable and ductile

- Graphite: layers of hexagonal rings, each carbon bonded to three others; one delocalised electron per carbon allows conduction along the layers; weak forces between layers.
- Diamond: each carbon bonded tetrahedrally to four others; very hard; no free electrons.
- Graphene is a single layer of graphite; fullerenes (such as C₆₀) are simple molecules of carbon. Both have delocalised electrons.
- Choosing materials: compare properties (strength, conductivity, melting point) with the structure and bonding.

5. Chemical energetics

Enthalpy changes

- Enthalpy change (ΔH) is the heat energy transferred at constant pressure. Exothermic: ΔH negative, energy released to the surroundings, temperature rises. Endothermic: ΔH positive, energy taken in, temperature falls.
- Standard conditions: 298 K and 101 kPa, with substances in their standard states (and solutions at 1.00 mol dm^{-3}). Shown by the symbol $\ominus$.
- On a reaction pathway diagram, the activation energy (E_a) is the gap from reactants up to the top of the energy hump; ΔH is the gap from reactants to products.

Standard enthalpy change of reaction, $\Delta H_r^\ominus$: the enthalpy change when the amounts shown in the equation react under standard conditions.

Standard enthalpy change of formation, $\Delta H_f^\ominus$: the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.

Standard enthalpy change of combustion, $\Delta H_c^\ominus$: the enthalpy change when one mole of a substance is burned completely in oxygen under standard conditions.

Standard enthalpy change of neutralisation, $\Delta H_{\text{neut}}^\ominus$: the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.

Standard enthalpy change of atomisation, $\Delta H_{\text{at}}^\ominus$: the enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions.

- $\Delta H_f^\ominus$ of an element in its standard state is zero by definition.
- Calorimetry: $q = mc\Delta T$ (q in J, m = mass of solution or water in g, $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$), then $\Delta H = -q / n$, converted to kJ mol^{-1} . Remember the sign: a temperature rise means ΔH is negative.
- Sources of error in combustion calorimetry: heat loss to the surroundings, incomplete combustion, evaporation of fuel from the wick. Experimental values are usually less exothermic than data-book values.

Hess's law and bond energies

Hess's law: the total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are the same.

- Using enthalpies of formation: $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$.
- Using enthalpies of combustion: $\Delta H_r = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$.
- Using bond energies: $\Delta H = \sum (\text{bonds broken}) - \sum (\text{bonds made})$. Bond breaking is endothermic, bond making is exothermic.
- Answers from bond energies differ from data-book values because bond energies are **average** values taken over many compounds, and because the method assumes all species are gaseous.

Worked example: Hess's law with formation data

Find ΔH_r for $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$, given ΔH_f : $\text{C}_2\text{H}_4 = +52 \text{ kJ mol}^{-1}$, $\text{C}_2\text{H}_6 = -85 \text{ kJ mol}^{-1}$.
 $\Delta H_r = (-85) - (+52 + 0) = -137 \text{ kJ mol}^{-1}$. (Values for illustration; use the data given in a question.)

Drawing energy cycles

- For formation data, put the elements at the bottom of the cycle; arrows go up (or down) from the elements to both reactants and products.
- For combustion data, put the combustion products (CO_2 and H_2O) at the bottom; arrows go down from both reactants and products.
- Going against the direction of an arrow means reversing the sign of that enthalpy change. Multiply each value by the number of moles in the equation.
- Hess's law lets us find enthalpy changes that cannot be measured directly, such as the formation of methane from carbon and hydrogen, or the conversion of anhydrous copper(II) sulfate to the hydrated salt.

6. Electrochemistry: redox

Oxidation is loss of electrons or an increase in oxidation number. **Reduction** is gain of electrons or a decrease in oxidation number.

Oxidising agent: a species that accepts electrons (and is itself reduced). **Reducing agent:** a species that donates electrons (and is itself oxidised).

Oxidation number rules

- Elements: 0. Simple ions: the charge on the ion.
- Sum of oxidation numbers = 0 in a compound, or the overall charge in an ion.
- Usual values: F -1 ; O -2 (except in peroxides, -1 , and with F); H $+1$ (except in metal hydrides, -1); Group 1 $+1$; Group 2 $+2$.
- Roman numerals in names give the oxidation number: iron(III) chloride is FeCl_3 ; sodium chlorate(V) is NaClO_3 ; manganate(VII) is MnO_4^- .

Balancing redox equations

- Write the two half-equations. Balance atoms other than O and H; balance O with H_2O ; balance H with H^+ ; balance charge with electrons.
- Multiply so the electrons are equal, then add and cancel.
- Example: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ and $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ give $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$.
- Alternatively, use changes in oxidation number: the total increase must equal the total decrease.
- A **disproportionation** reaction is one in which the same element is both oxidised and reduced, for example $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$ (chlorine goes from 0 to -1 and $+1$).

7. Equilibria

Dynamic equilibrium and Le Chatelier's principle

Dynamic equilibrium: in a closed system, the rate of the forward reaction equals the rate of the reverse reaction, so the concentrations of reactants and products remain constant.

Le Chatelier's principle: if a change is made to a system in dynamic equilibrium, the position of equilibrium moves to minimise (oppose) the change.

- Concentration: adding a reactant moves the position of equilibrium to the right.
- Pressure (gases only): increasing pressure moves equilibrium to the side with fewer gas molecules.
- Temperature: increasing temperature moves equilibrium in the endothermic direction. Temperature is the only factor that changes the value of K .
- A catalyst does not change the position of equilibrium or K ; it increases the forward and reverse rates equally, so equilibrium is reached faster.

Equilibrium constants

- For $aA + bB \rightleftharpoons cC + dD$: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, using equilibrium concentrations in mol dm^{-3} . Work out units each time.
- K_p uses partial pressures: $p_A = \text{mole fraction of A} \times \text{total pressure}$, and mole fraction = moles of A / total moles of gas.
- Solids are not included in K_c or K_p expressions for heterogeneous equilibria (and solids and liquids are left out of K_p).
- A large K means the equilibrium lies to the right (mostly products).
- Calculations: use an ICE-style table (initial, change, equilibrium) of moles, then divide by volume.

Worked example: K_c

1.00 mol of H_2 and 1.00 mol of I_2 are heated in a 1.00 dm^3 flask; at equilibrium 1.56 mol of HI is present. $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

HI formed = 1.56 mol, so H_2 and I_2 used = 0.78 mol each; each has 0.22 mol left.

$$K_c = 1.56^2 / (0.22 \times 0.22) = 2.4336 / 0.0484 = 50 \text{ (no units, since the moles cancel).}$$

Worked example: K_p

For $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, an equilibrium mixture at 200 kPa contains 0.20 mol H_2 , 0.20 mol I_2 and 1.60 mol HI.

Total moles = 2.00. Partial pressures: $\text{H}_2 = (0.20/2.00) \times 200 = 20 \text{ kPa}$; $\text{I}_2 = 20 \text{ kPa}$; $\text{HI} = (1.60/2.00) \times 200 = 160 \text{ kPa}$.

$$K_p = 160^2 / (20 \times 20) = 25\,600 / 400 = 64 \text{ (no units, as the pressure units cancel).}$$

Industrial equilibria

Process	Equation	Typical conditions
Haber process	$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, ΔH negative	About 450 °C, about 200 atm (2×10^4 kPa), iron catalyst
Contact process	$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, ΔH negative	About 450 °C, 1 to 2 atm, vanadium(V) oxide catalyst

- The temperatures are a compromise: a low temperature gives a higher yield (exothermic forward reaction) but too slow a rate.
- Higher pressure would give a higher yield of ammonia but costs more and needs stronger equipment; for the Contact process the yield is already high at low pressure.

Acids and bases (Brønsted-Lowry)

Brønsted-Lowry acid: a proton (H^+) donor. **Brønsted-Lowry base:** a proton acceptor.

- Conjugate pairs differ by one H^+ . In $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$ are conjugate pairs.
- A strong acid is fully dissociated in water (HCl , HNO_3 , H_2SO_4). A weak acid is only partly dissociated (ethanoic acid): $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$.
- At the same concentration a weak acid has a higher pH, lower electrical conductivity and reacts more slowly with metals and carbonates than a strong acid, because $[\text{H}^+]$ is lower.
- Strong bases are fully dissociated (NaOH); weak bases only partly react with water (NH_3).
- Neutralisation: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$. Titration curves: strong acid/strong base has a sharp vertical section around pH 7; choose an indicator whose colour change falls within the steep part (phenolphthalein for a weak acid with strong base, methyl orange for a strong acid with weak base).

8. Reaction kinetics

- Rate of reaction = change in concentration of a reactant or product per unit time ($\text{mol dm}^{-3} \text{s}^{-1}$). On a concentration-time graph, the rate is the gradient of the tangent.
- Collision theory: particles must collide with energy equal to or greater than the activation energy, and in the correct orientation.

Activation energy, E_a : the minimum energy that colliding particles must have for a reaction to occur.

Catalyst: a substance that increases the rate of a reaction by providing an alternative route with a lower activation energy, and is chemically unchanged at the end.

- Increasing concentration (or gas pressure) increases the frequency of collisions, so more successful collisions per second.
- Increasing surface area of a solid increases the frequency of collisions.
- Boltzmann distribution:** a graph of number of molecules against energy. It starts at the origin, rises to a peak (most probable energy), and has a long tail that approaches but never meets the

energy axis. The area under the curve equals the total number of molecules.

- Raising the temperature moves the peak to the right and lowers it; the area stays the same. Many more molecules now have energy $\geq E_a$, so the rate increases greatly (much more than the small increase in collision frequency).
- A catalyst moves E_a to the left on the Boltzmann distribution, so a larger proportion of molecules have enough energy to react; the curve itself is unchanged.
- Homogeneous catalysts are in the same phase as the reactants; heterogeneous catalysts are in a different phase (for example iron in the Haber process). Catalysts are used in industry to lower the operating temperature and save energy.

Measuring rates in the laboratory

- Collect a gas in a gas syringe and record its volume at regular intervals (for example magnesium with acid, or calcium carbonate with acid).
- Record the loss of mass on a balance as a gas escapes (use a cotton wool plug to stop spray but let the gas out).
- Follow a colour change with a colorimeter, or time how long a precipitate takes to hide a cross under the flask (sodium thiosulfate with acid).
- The initial rate is the gradient of the tangent drawn at time zero. A steeper initial gradient means a faster reaction; the final amount of product depends only on the limiting reagent, not on the rate.

9. The Periodic Table: chemical periodicity (Period 3)

Physical trends across Period 3 (Na to Ar)

- Atomic radius decreases: nuclear charge increases while electrons enter the same shell.
- Ionic radius: Na^+ to Si^{4+} decrease (same electron arrangement, increasing nuclear charge); P^{3-} to Cl^- are much larger (an extra shell) and also decrease.
- First ionisation energy generally increases, with dips at Al and S (see Topic 1).
- Electrical conductivity increases from Na to Al (more delocalised electrons per ion), is low for Si (a semiconductor) and very low for P to Ar (simple molecules, no free electrons).
- Melting point rises from Na to Si, then falls sharply. Na, Mg, Al: metallic bonding gets stronger (more delocalised electrons, smaller, more highly charged ions). Si: giant covalent structure, highest. P_4 , S_8 , Cl_2 , Ar: simple molecular with weak intermolecular forces; S_8 is highest of these because it has the most electrons.

Reactions of the elements

- With oxygen: $4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O}$ (yellow flame); $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ (brilliant white flame); $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$; $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$; $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ (blue flame).
- With chlorine: $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$; $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$; $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$ (Al_2Cl_6); $\text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4$; P + Cl_2 gives PCl_3 and PCl_5 .
- With water: $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$ (vigorous, pH about 13 to 14); magnesium reacts very slowly with cold water but burns in steam: $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2$.

Oxides and chlorides

Oxide	Bonding/structure	Nature	Key reaction
Na ₂ O	Giant ionic	Basic	Na ₂ O + H ₂ O → 2NaOH (pH about 13 to 14)
MgO	Giant ionic	Basic	Slightly soluble, pH about 9; MgO + 2HCl → MgCl ₂ + H ₂ O
Al ₂ O ₃	Giant ionic (some covalent character)	Amphoteric	Insoluble in water; reacts with acids and with NaOH: Al ₂ O ₃ + 2NaOH + 3H ₂ O → 2NaAl(OH) ₄
SiO ₂	Giant covalent	Acidic	Insoluble in water; reacts with hot concentrated NaOH: SiO ₂ + 2NaOH → Na ₂ SiO ₃ + H ₂ O
P ₄ O ₁₀	Simple molecular	Acidic	P ₄ O ₁₀ + 6H ₂ O → 4H ₃ PO ₄ (pH about 2)
SO ₂ , SO ₃	Simple molecular	Acidic	SO ₂ + H ₂ O → H ₂ SO ₃ ; SO ₃ + H ₂ O → H ₂ SO ₄

Chloride	Bonding/structure	With water
NaCl	Giant ionic	Dissolves; pH 7
MgCl ₂	Giant ionic	Dissolves; slightly acidic, pH about 6.5
AlCl ₃	Covalent (Al ₂ Cl ₆ dimer)	Hydrolysis; acidic, pH about 3; white fumes of HCl with little water
SiCl ₄	Simple molecular	Hydrolysis: SiCl ₄ + 2H ₂ O → SiO ₂ + 4HCl; pH about 2
PCl ₅	Simple molecular	Hydrolysis: PCl ₅ + 4H ₂ O → H ₃ PO ₄ + 5HCl; pH about 2

- The highest oxidation number in oxides and chlorides equals the number of outer electrons (Na +1 up to S +6 in SO₃ and Cl +7 in Cl₂O₇).
- Pattern: across the period, oxides change from basic ionic to acidic covalent, matching the increase in electronegativity of the element.
- Deducing an unknown element: use clues such as melting point, conductivity, acid-base nature of its oxide and pH of its chloride solution.

10. Group 2

- Atomic radius increases down the group; first ionisation energy decreases; the metals become more reactive (they lose two electrons more easily).
- With oxygen: 2M + O₂ → 2MO (white solids).
- With water: M + 2H₂O → M(OH)₂ + H₂. Reactivity increases from Mg (very slow with cold water) to Ba (vigorous). Mg with steam gives MgO + H₂.
- With dilute acids: M + 2HCl → MCl₂ + H₂. With sulfuric acid, Ca, Sr and Ba soon stop reacting because an insoluble sulfate layer coats the metal.
- Oxides and hydroxides are basic: MO + H₂O → M(OH)₂; MO + 2HCl → MCl₂ + H₂O.
- Carbonates react with acids: MCO₃ + 2HCl → MCl₂ + H₂O + CO₂.

Property	Trend down the group (Mg to Ba)
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Solubility of hydroxides	Increases ($\text{Mg}(\text{OH})_2$ sparingly soluble; $\text{Ba}(\text{OH})_2$ fairly soluble); so the pH of a saturated solution increases
Solubility of sulfates	Decreases (MgSO_4 soluble; BaSO_4 insoluble)
Thermal stability of carbonates and nitrates	Increases (they need a higher temperature to decompose)

- Thermal decomposition: $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$; $2\text{M}(\text{NO}_3)_2 \rightarrow 2\text{MO} + 4\text{NO}_2 + \text{O}_2$ (brown gas).
- Explanation: down the group the cation is larger with the same 2+ charge, so it has a lower charge density and polarises (distorts) the electron cloud of the large carbonate or nitrate anion less. The anion is less destabilised, so more heat is needed to decompose it.
- Uses: $\text{Ca}(\text{OH})_2$ (slaked lime) and CaO (lime) neutralise acidic soils; CaCO_3 (limestone) is used in building and in making cement; $\text{Mg}(\text{OH})_2$ is an antacid; BaSO_4 is used in barium meals because it is insoluble.
- Test for sulfate: add acidified $\text{BaCl}_2(\text{aq})$; a white precipitate of BaSO_4 forms.

Worked example: Group 2 calculation

Calculate the mass of calcium oxide formed when 5.00 g of calcium carbonate is completely decomposed. (A_r : Ca 40.1, C 12.0, O 16.0.)

$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$. $n(\text{CaCO}_3) = 5.00 / 100.1 = 0.04995 \text{ mol}$.

$n(\text{CaO}) = 0.04995 \text{ mol}$; $M(\text{CaO}) = 56.1 \text{ g mol}^{-1}$; mass = $0.04995 \times 56.1 = 2.80 \text{ g}$.

Heating to constant mass shows when decomposition is complete.

- Flame colours (useful for identifying Group 2 compounds): calcium brick-red, strontium red (crimson), barium apple-green; magnesium compounds give no characteristic colour.

11. Group 17: the halogens

Physical properties

- Colours: chlorine pale yellow-green gas; bromine red-brown liquid (orange-brown vapour); iodine grey-black solid (purple vapour).
- Volatility decreases down the group: boiling point increases because the molecules have more electrons, so instantaneous dipole-induced dipole forces are stronger.
- Bond strength of X-X : $\text{Cl-Cl} > \text{Br-Br} > \text{I-I}$ (longer bonds down the group). F-F is unexpectedly weak because of repulsion between lone pairs on the small atoms. Use the Data Booklet values.

Chemical properties

- Halogens are oxidising agents; oxidising power decreases down the group ($\text{Cl}_2 > \text{Br}_2 > \text{I}_2$). Down the group the atoms are larger and the incoming electron is further from the nucleus and more shielded, so it is attracted less.
- Displacement: a halogen oxidises halide ions below it. $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$ (solution turns orange); $\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2$ (brown); $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$. Shaking with cyclohexane gives orange (Br_2) or purple (I_2) organic layers.

- With hydrogen: $H_2 + X_2 \rightarrow 2HX$. Reactivity decreases down the group (fluorine explosive; iodine slow and reversible).
- Thermal stability of HX decreases down the group because the H–X bond gets weaker (longer). HI decomposes into H_2 and purple I_2 on heating with a hot wire.
- Halide ions are reducing agents; reducing power increases down the group ($I^- > Br^- > Cl^-$).

Reactions of halide ions

Halide	With $AgNO_3(aq)$ (after dilute HNO_3)	Then dilute NH_3	Then concentrated NH_3
Cl^-	White precipitate $AgCl$	Dissolves	Dissolves
Br^-	Cream precipitate $AgBr$	Does not dissolve	Dissolves
I^-	Yellow precipitate AgI	Does not dissolve	Does not dissolve

- With concentrated sulfuric acid:
 - $NaCl$: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (steamy white fumes). No redox: Cl^- is too weak a reducing agent.
 - $NaBr$: HBr forms, then some is oxidised: $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$ (orange-brown fumes).
 - NaI : HI forms and is oxidised strongly; products include I_2 (purple fumes, black solid), SO_2 , S (yellow) and H_2S (rotten egg smell). Sulfur is reduced from +6 as far as –2.

Chlorine with water and alkali

- $Cl_2 + H_2O \rightleftharpoons HCl + HClO$ (disproportionation). $HClO$ (chloric(I) acid) kills bacteria; this is why chlorine is used to treat water. Benefits must be weighed against the toxicity of chlorine and possible formation of chlorinated organic compounds.
- Cold dilute $NaOH$ (about 15 °C): $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$. Chlorine: 0 → –1 and +1. $NaClO$ is household bleach.
- Hot concentrated $NaOH$ (about 70 °C): $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$. Chlorine: 0 → –1 and +5.

12. Nitrogen and sulfur

Nitrogen and ammonia

- N_2 is very unreactive because the $N \equiv N$ triple bond is very strong (high bond energy) and the molecule is non-polar.
- Ammonia is a base: $NH_3 + H^+ \rightarrow NH_4^+$. The lone pair on nitrogen accepts a proton, forming a dative bond. NH_3 is trigonal pyramidal (107°); NH_4^+ is tetrahedral (109.5°).
- Ammonium salts react with bases on warming to release ammonia: $NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$. Ammonia turns damp red litmus blue; this is the test for NH_4^+ .
- Ammonia is made by the Haber process (Topic 7) and is used to make fertilisers (ammonium

nitrate, ammonium sulfate) and nitric acid.

Oxides of nitrogen and the environment

- In a car engine, the high temperature allows nitrogen and oxygen from the air to react: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$. In air, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.
- Catalytic converters remove NO and CO: $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$. Unburnt hydrocarbons are also oxidised to CO_2 and H_2O .
- NO_2 catalyses the oxidation of SO_2 in the atmosphere: $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$, then $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$. The NO_2 is regenerated, so it acts as a catalyst. SO_3 dissolves in rain to form sulfuric acid (acid rain).
- NO and NO_2 react with unburnt hydrocarbons in sunlight to form photochemical smog, which contains peroxyacetyl nitrate (PAN), an eye and lung irritant.
- Nitrates from fertilisers can leach into rivers and cause eutrophication: algal growth, then decay by bacteria uses up dissolved oxygen, so fish die.

Sulfur

- SO_2 is produced when fossil fuels containing sulfur are burned; it causes acid rain, which damages buildings (limestone and marble), lakes and trees.
- Sulfuric acid is made by the Contact process (Topic 7): $\text{S} \rightarrow \text{SO}_2 \rightarrow \text{SO}_3$, then SO_3 is absorbed in concentrated sulfuric acid.
- Sulfur dioxide is used as a food preservative because it is an antioxidant and kills bacteria.

13. Introduction to organic chemistry

Formulae and naming

- Types of formula: empirical (CH_2 for ethene); molecular (C_2H_4); structural ($\text{CH}_2=\text{CH}_2$); displayed (all atoms and bonds shown); skeletal (carbon chain as zig-zag lines, with H atoms on carbon left out).
- A homologous series is a family of compounds with the same functional group and general formula; each member differs by CH_2 ; they have similar chemical properties and a gradual trend in physical properties.
- A functional group is the group of atoms responsible for the characteristic reactions of a compound.
- Stems: meth (1 C), eth (2), prop (3), but (4), pent (5), hex (6). Number the chain to give the functional group the lowest number.
- Carbon atoms are classed as primary, secondary or tertiary by the number of other carbon atoms joined to the carbon carrying the functional group (one, two or three).

Homologous series	Functional group	Example
Alkane	C–C only	Propane
Alkene	C=C	But-2-ene

Halogenoalkane	C–X	2-bromopropane
Alcohol	–OH	Propan-1-ol
Aldehyde	–CHO	Ethanal
Ketone	C=O between two carbons	Propanone
Carboxylic acid	–COOH	Ethanoic acid
Ester	–COO–	Ethyl ethanoate
Amine	–NH ₂	Ethylamine
Nitrile	–C≡N	Propanenitrile

Reaction types and mechanisms

Nucleophile: a species that donates a pair of electrons to form a new covalent bond (for example OH[–], CN[–], NH₃).

Electrophile: a species that accepts a pair of electrons to form a new covalent bond (for example H⁺, Br^{δ+}, NO₂⁺).

Homolytic fission: a covalent bond breaks so that each atom takes one electron, forming two free radicals.

Heterolytic fission: a covalent bond breaks so that one atom takes both electrons, forming a cation and an anion.

- Reaction types: addition, substitution, elimination, hydrolysis, condensation, oxidation, reduction.
- In mechanisms, a curly arrow shows the movement of a pair of electrons. It starts from a lone pair or a bond and ends where the new bond forms.
- [O] and [H] can be used for the oxidising and reducing agent in balanced organic equations.

Isomerism

Structural isomers have the same molecular formula but different structural formulae.

Stereoisomers have the same structural formula but a different arrangement of atoms in space.

- Structural isomerism: chain (different carbon skeleton), positional (functional group in a different position), functional group (different functional group, such as propanal and propanone).
- Geometrical (cis/trans) isomerism: needs a C=C (no rotation about the π bond) and two different groups on each carbon of the double bond. Cis: same groups on the same side; trans: on opposite sides.
- Optical isomerism: a chiral centre is a carbon atom attached to four different atoms or groups. The two isomers are non-superimposable mirror images (enantiomers). They rotate plane-polarised light in opposite directions. Draw them as 3D tetrahedral mirror images.

Worked example: counting isomers of C₄H₈ (alkenes only)

Structural isomers: but-1-ene (CH₂=CHCH₂CH₃), but-2-ene (CH₃CH=CHCH₃) and methylpropene ((CH₃)₂C=CH₂).

Only but-2-ene has two different groups (H and CH₃) on each carbon of the C=C, so it exists as cis and trans isomers.

Total: four alkene isomers. (Cyclobutane and methylcyclopropane are also C₄H₈, but they are not alkenes.)

- To spot a chiral centre quickly: look for a carbon with one H, and three different other groups, for example the central carbon of butan-2-ol, CH₃CH(OH)CH₂CH₃ (groups: H, OH, CH₃, C₂H₅).
- Carbon atoms in CH₃ or CH₂ groups, or in C=C or C=O, can never be chiral centres.

14. Hydrocarbons

Alkanes

- General formula C_nH_{2n+2}. Saturated, sp³ carbons, bond angles about 109.5°.
- Generally unreactive: C–C and C–H bonds are strong and almost non-polar.
- Obtained from crude oil by fractional distillation; cracking breaks long alkanes into shorter alkanes and alkenes, which are more useful (for example C₁₀H₂₂ → C₈H₁₈ + C₂H₄). Cracking uses heat and a catalyst such as Al₂O₃ or a zeolite.
- Complete combustion gives CO₂ and H₂O; incomplete combustion gives toxic CO and soot (C). Pollutants from engines: CO, NO_x, unburnt hydrocarbons; CO₂ is a greenhouse gas.

Free-radical substitution: CH₄ + Cl₂ → CH₃Cl + HCl (UV light)

Initiation: Cl₂ → 2Cl• (homolytic fission by UV light)

Propagation: CH₄ + Cl• → •CH₃ + HCl, then •CH₃ + Cl₂ → CH₃Cl + Cl•

Termination: Cl• + Cl• → Cl₂; •CH₃ + Cl• → CH₃Cl; •CH₃ + •CH₃ → C₂H₆

Further substitution gives CH₂Cl₂, CHCl₃ and CCl₄, so the method gives a mixture of products.

Alkenes

- General formula C_nH_{2n}. Unsaturated; the C=C is a σ bond plus a π bond; trigonal planar, 120°.
- The π bond is an area of high electron density above and below the plane, so it attracts electrophiles. It is weaker than the σ bond, so alkenes are more reactive than alkanes.
- Preparation: dehydration of alcohols (Topic 16), elimination from halogenoalkanes (Topic 15), cracking.

Reagent	Conditions	Product (from ethene)
H ₂	Nickel catalyst, about 150 °C (or Pt at room temperature)	Ethane

H ₂ O (steam)	H ₃ PO ₄ catalyst, high temperature and pressure	Ethanol
HBr(g)	Room temperature	Bromoethane
Br ₂ (aq or in organic solvent)	Room temperature	1,2-dibromoethane; bromine water decolourises (orange to colourless): the test for C=C
Cold dilute acidified KMnO ₄	Room temperature	Ethane-1,2-diol; purple to colourless
Hot concentrated acidified KMnO ₄	Heat	C=C splits; fragments are oxidised to ketones, carboxylic acids or CO ₂ depending on the groups on each carbon

- With hot concentrated KMnO₄: a =CH₂ end gives CO₂; a =CHR end gives RCOOH; a =CR₂ end gives a ketone R₂C=O. This helps locate the double bond in an unknown alkene.

Electrophilic addition: ethene + HBr

1. The π electrons of C=C attack the δ^+ H of H-Br (curly arrow from the double bond to H); the H-Br bond breaks heterolytically (curly arrow from the bond to Br).
2. A carbocation (CH₃CH₂⁺) and Br⁻ form.
3. The lone pair on Br⁻ attacks the positive carbon (curly arrow from lone pair to C⁺), giving CH₃CH₂Br.

With Br₂, the π electrons induce a dipole in Br-Br; Br ^{δ^+} is attacked and the same steps follow.

- Markovnikov addition to unsymmetrical alkenes: the major product comes from the more stable carbocation. Stability: tertiary > secondary > primary, because alkyl groups are electron-donating (positive inductive effect) and spread the positive charge. So propene + HBr gives mainly 2-bromopropane.
- Addition polymerisation of alkenes: see Topic 20.

15. Halogen compounds

- Preparation of halogenoalkanes: free-radical substitution of alkanes (X₂, UV); electrophilic addition of HX or X₂ to alkenes; substitution of alcohols with HX, PCl₃ and heat, PCl₅ at room temperature, or SOCl₂.
- The C-X bond is polar (C ^{δ^+}), so the carbon is attacked by nucleophiles.
- Reactivity order: R-I > R-Br > R-Cl. The C-I bond is the weakest, so it breaks most easily. Bond strength matters more than bond polarity.

Reagent and conditions	Reaction type	Product
NaOH(aq), heat under reflux	Nucleophilic substitution (hydrolysis)	Alcohol: RBr + OH ⁻ → ROH + Br ⁻

KCN in ethanol, heat under reflux	Nucleophilic substitution	Nitrile: $\text{RBr} + \text{CN}^- \rightarrow \text{RCN} + \text{Br}^-$ (chain lengthened by one carbon)
Excess NH_3 in ethanol, heated in a sealed tube under pressure	Nucleophilic substitution	Primary amine: $\text{RBr} + 2\text{NH}_3 \rightarrow \text{RNH}_2 + \text{NH}_4\text{Br}$
NaOH in ethanol, heat	Elimination	Alkene + H_2O + NaBr
$\text{AgNO}_3(\text{aq})$ in ethanol, warm	Hydrolysis (test)	Precipitate of AgX ; the rate of appearance shows C–X reactivity (iodo fastest, yellow)

S_N2 mechanism (primary halogenoalkanes)

The OH^- lone pair attacks the δ^+ carbon from the side opposite the halogen; at the same time the C–Br bond breaks heterolytically. A five-coordinate transition state forms (shown in square brackets with a negative charge). One step; rate depends on both halogenoalkane and OH^- .

S_N1 mechanism (tertiary halogenoalkanes)

Step 1 (slow): the C–Br bond breaks heterolytically to give a tertiary carbocation and Br^- . Step 2 (fast): OH^- attacks the carbocation. Rate depends only on the halogenoalkane. Tertiary carbocations are stabilised by three electron-donating alkyl groups, and the crowded carbon blocks back-side attack.

Secondary halogenoalkanes can react by both mechanisms.

- Uses and problems: CFCs are unreactive and non-toxic, so were used as refrigerants and aerosol propellants. In the stratosphere UV breaks C–Cl bonds to release $\text{Cl}\cdot$ radicals, which catalyse the breakdown of ozone: $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{ClO}\cdot + \text{O}_2$; $\text{ClO}\cdot + \text{O}_3 \rightarrow \text{Cl}\cdot + 2\text{O}_2$.

16. Hydroxy compounds: alcohols

- Alcohols have higher boiling points than alkanes of similar M_r because of hydrogen bonding; short-chain alcohols are soluble in water because they hydrogen bond with water.
- Preparation: steam + alkene (H_3PO_4 catalyst); $\text{NaOH}(\text{aq})$ + halogenoalkane; reduction of aldehydes or ketones with NaBH_4 ; reduction of carboxylic acids with LiAlH_4 ; hydrolysis of esters; fermentation of sugars for ethanol.

Reaction	Reagent and conditions	Product
Combustion	Oxygen	$\text{CO}_2 + \text{H}_2\text{O}$
Substitution to halogenoalkane	HX (for example $\text{KBr} + \text{H}_2\text{SO}_4$), PCl_3 + heat, PCl_5 , or SOCl_2	RX
With sodium	Na metal, room temperature	Sodium alkoxide + H_2 (fizzing): $2\text{C}_2\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{ONa} + \text{H}_2$
Oxidation of primary alcohol	$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$; distil off as it forms	Aldehyde
Oxidation of primary alcohol	Excess $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, heat under reflux	Carboxylic acid

Oxidation of secondary alcohol	$K_2Cr_2O_7/H_2SO_4$, heat	Ketone
Dehydration	Heated Al_2O_3 , or concentrated H_2SO_4 or H_3PO_4 and heat	Alkene + H_2O
Esterification	Carboxylic acid, concentrated H_2SO_4 catalyst, heat	Ester + water

- With acidified dichromate, the colour changes from orange ($Cr_2O_7^{2-}$) to green (Cr^{3+}) for primary and secondary alcohols. Tertiary alcohols are not oxidised: the solution stays orange.
- Acidified $KMnO_4$ can also be used (purple to colourless).
- Esters are named from the alcohol part then the acid part: ethanol + ethanoic acid $\rightarrow$ ethyl ethanoate. Esters have fruity smells and are used as solvents and flavourings.
- Hydrolysis of esters: with dilute acid and heat (reversible) gives the acid and alcohol; with $NaOH(aq)$ and heat (goes to completion) gives the carboxylate salt and alcohol.
- Triiodomethane (iodoform) test: alkaline aqueous iodine, warm. A pale yellow precipitate of CHI_3 forms with alcohols containing $CH_3CH(OH)-$ (ethanol and secondary methyl alcohols such as propan-2-ol) and with carbonyl compounds containing CH_3CO- .
- Acidity: alcohols are weaker acids than water; they react with Na but not with NaOH or carbonates.

17. Carbonyl compounds: aldehydes and ketones

- Aldehydes ($RCHO$) come from oxidation of primary alcohols; ketones ($RCOR'$) from oxidation of secondary alcohols.
- Reduction with $NaBH_4$ (in water or methanol) or $LiAlH_4$ (in dry ether): aldehyde $\rightarrow$ primary alcohol; ketone $\rightarrow$ secondary alcohol. For example $CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$.
- The $C=O$ bond is polar ($C^{\delta+}$), so carbonyls are attacked by nucleophiles. They undergo nucleophilic **addition** (not electrophilic addition, unlike $C=C$).

Nucleophilic addition: HCN to a carbonyl (HCN with a KCN catalyst)

1. The lone pair on CN^- attacks the $\delta+$ carbon of $C=O$; the π bond breaks and the electrons move onto oxygen (curly arrow from $C=O$ to O).
2. An intermediate with O^- forms.
3. O^- takes H^+ from HCN (or water), regenerating CN^- . Product: a 2-hydroxynitrile, for example $CH_3CHO \rightarrow CH_3CH(OH)CN$ (2-hydroxypropanenitrile).

The planar $C=O$ can be attacked from either side, so with aldehydes (other than methanal) and unsymmetrical ketones a racemic mixture of optical isomers forms.

Tests for carbonyl compounds

Test	Aldehyde	Ketone
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2,4-dinitrophenylhydrazine (2,4-DNPH)	Orange/yellow precipitate	Orange/yellow precipitate
Tollens' reagent (ammoniacal silver nitrate), warm	Silver mirror (Ag^+ reduced to Ag)	No change
Fehling's solution, warm	Blue solution gives a red-brown precipitate (Cu_2O)	Stays blue
Acidified $\text{K}_2\text{Cr}_2\text{O}_7$, warm	Orange to green	Stays orange
Alkaline iodine (triiodomethane test)	Yellow precipitate only for ethanal (CH_3CHO)	Yellow precipitate for methyl ketones ($\text{CH}_3\text{CO}-$)

- The melting point of the purified 2,4-DNPH derivative can be compared with data to identify the specific carbonyl compound.

18. Carboxylic acids and derivatives

- Preparation: oxidation of primary alcohols or aldehydes (acidified dichromate, reflux); hydrolysis of nitriles by heating with dilute acid ($\text{RCN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{RCOOH} + \text{NH}_4^+$); hydrolysis of esters.
- They are weak acids: $\text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{H}^+$.
- Reactions as acids:
 - With reactive metals: $2\text{CH}_3\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{COO})_2\text{Mg} + \text{H}_2$
 - With alkalis: $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
 - With carbonates: $2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$ (fizzing; distinguishes acids from alcohols)
- Esterification with alcohols (concentrated H_2SO_4 , heat, reversible).
- Reduction with LiAlH_4 in dry ether gives a primary alcohol. (NaBH_4 is not strong enough.)
- Boiling points are high because carboxylic acids form hydrogen-bonded dimers.

19. Nitrogen compounds

- Primary amines are made from halogenoalkanes and excess ammonia in ethanol, heated in a sealed tube (Topic 15). Excess ammonia reduces further substitution to secondary and tertiary amines.
- Nitriles are made from halogenoalkanes and KCN in ethanol (Topic 15); hydroxynitriles from aldehydes and ketones with HCN and KCN (Topic 17).
- Nitriles and hydroxynitriles are hydrolysed to carboxylic acids by heating with dilute acid. These reactions are useful because they add one carbon atom to the chain.

20. Polymerisation

- Addition polymerisation: many alkene monomers join; the $\text{C}=\text{C}$ opens and no other product forms. The polymer has the same empirical formula as the monomer.

- To draw a repeat unit: take the two carbons of the C=C, draw them with single bonds, keep the substituents, and add extension bonds on each side. Example: chloroethene $\text{CH}_2=\text{CHCl}$ gives poly(chloroethene), PVC, with repeat unit $-\text{CH}_2-\text{CHCl}-$.
- To find the monomer from a polymer chain: pick a two-carbon repeat unit and put a double bond between the carbons.
- Examples: poly(ethene) from ethene (bags, bottles); poly(propene) from propene (crates, ropes); PVC (pipes, window frames, cable insulation).
- Poly(alkenes) are chemically inert because they are saturated with strong, non-polar C–C and C–H bonds. They are non-biodegradable, so they persist in landfill and the environment.
- Disposal: burning releases energy but produces CO_2 , and burning PVC also releases toxic HCl (and other harmful chlorinated compounds). Recycling and reduction in use are preferred.

21. Organic synthesis

- Plan multi-step routes by linking reactions: alkane $\rightarrow$ halogenoalkane $\rightarrow$ alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid $\rightarrow$ ester; alkene $\rightarrow$ alcohol or halogenoalkane; halogenoalkane $\rightarrow$ nitrile $\rightarrow$ carboxylic acid (one more carbon).
- For each step, state the reagent, conditions and type of reaction. Identify functional groups in a complex molecule and predict how each will react with a given reagent.
- Useful techniques: heating under reflux (heats for a long time without loss of volatile liquids); distillation (separates a volatile product as it forms, such as an aldehyde); using a separating funnel to wash an organic layer; drying with anhydrous CaCl_2 or MgSO_4 .

Worked example: a two-step route

Convert bromoethane into propanoic acid.

Step 1: KCN in ethanol, heat under reflux (nucleophilic substitution): $\text{CH}_3\text{CH}_2\text{Br} + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{Br}^-$

Step 2: heat under reflux with dilute HCl (hydrolysis): $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$

22. Analytical techniques

Infrared (IR) spectroscopy

- Covalent bonds absorb infrared radiation at characteristic frequencies, which makes them vibrate (stretch and bend) more. The spectrum plots transmittance against wavenumber (cm^{-1}); absorptions appear as downward troughs.
- Use the Data Booklet table to identify bonds. The approximate ranges most used are below.

Bond	Found in	Approximate wavenumber / cm^{-1}
O–H (hydrogen bonded)	Alcohols	3200 to 3600, broad
O–H (hydrogen bonded)	Carboxylic acids	2500 to 3000, very broad

N–H	Amines	3300 to 3500
C–H	Most organic compounds	2850 to 2950
C≡N	Nitriles	2200 to 2250
C=O	Aldehydes, ketones, acids, esters	1670 to 1740, strong and sharp
C=C	Alkenes	1500 to 1680
C–O	Alcohols, esters, acids	1040 to 1300

- Typical deductions: alcohol (broad O–H, no C=O); carboxylic acid (very broad O–H plus C=O); aldehyde or ketone (C=O, no O–H); ester (C=O plus C–O, no O–H).
- The region below about 1500 cm⁻¹ (the fingerprint region) is unique to each compound and can be matched with a database.
- IR is used in breathalysers (ethanol C–H absorption) and to monitor atmospheric gases that absorb IR (greenhouse gases).

Mass spectrometry

- The molecular ion peak, M⁺, is the peak at the highest m/e value (apart from small isotope peaks); its m/e gives the M_r.
- The M+1 peak is caused by molecules containing one ¹³C atom (natural abundance about 1.1%). Number of carbon atoms: $n = (100 \times \text{height of } M+1) / (1.1 \times \text{height of } M^+)$.
- Chlorine: M⁺ and M+2 peaks in a ratio of about 3 : 1 (³⁵Cl and ³⁷Cl). Bromine: M⁺ and M+2 in a ratio of about 1 : 1 (⁷⁹Br and ⁸¹Br).
- Fragmentation: the molecular ion breaks into a positive fragment (detected) and a neutral radical (not detected). Common fragments: m/e 15 CH₃⁺; 29 C₂H₅⁺ or CHO⁺; 43 C₃H₇⁺ or CH₃CO⁺; 45 COOH⁺; 31 CH₂OH⁺.
- Mass spectra of elements give isotopic abundances, from which A_r is calculated (Topic 2).

Common exam mistakes to avoid

- Writing "an atom of carbon-12" without "1/12 of the mass of" in the relative atomic mass definition.
- Leaving out "gaseous" in ionisation energy definitions, or writing "one mole of electrons from one atom".
- Saying intermolecular forces are broken when a covalent substance boils, but then also saying covalent bonds break. Boiling a simple molecular substance overcomes intermolecular forces only.
- Forgetting the sign of ΔH in calorimetry, or dividing q by the wrong number of moles (use the limiting reagent).
- Stating that a catalyst "moves the equilibrium to the right". It does not change the position of equilibrium.
- Drawing Boltzmann curves that touch the energy axis, or that start above the origin, or changing the area under the curve when temperature changes.

- Confusing electrophilic addition (alkenes) with nucleophilic addition (carbonyl compounds), and nucleophilic substitution (halogenoalkanes) with free-radical substitution (alkanes).
- Curly arrows that start from an atom instead of a lone pair or a bond, or that point the wrong way.
- Writing that tertiary alcohols are oxidised to ketones. Tertiary alcohols are not oxidised by acidified dichromate.
- Giving the repeat unit of an addition polymer with a double bond still present, or without extension bonds.
- In IR questions, quoting only a wavenumber without naming the bond and the functional group it shows.

Key terms table

Term	Meaning
Isotopes	Atoms of the same element with the same number of protons but different numbers of neutrons
Orbital	A region of space around the nucleus that can hold up to two electrons with opposite spins
First ionisation energy	Energy to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous 1+ ions
Relative atomic mass	Weighted mean mass of an atom of an element compared with 1/12 of the mass of an atom of carbon-12
Mole	Amount of substance containing 6.02×10^{23} particles
Empirical formula	Simplest whole-number ratio of atoms of each element in a compound
Electronegativity	Power of an atom to attract electrons to itself in a covalent bond
Dative covalent bond	A covalent bond in which both shared electrons come from one atom
Hydrogen bond	Attraction between a δ^+ H bonded to N, O or F and a lone pair on N, O or F of another molecule
Ideal gas	A gas whose molecules have negligible volume and no intermolecular forces, with elastic collisions
Enthalpy change of formation	Enthalpy change when one mole of a compound forms from its elements in their standard states under standard conditions
Hess's law	The total enthalpy change is independent of the route taken
Bond energy	Energy needed to break one mole of a given covalent bond in the gaseous state (an average value)
Oxidising agent	A species that accepts electrons and is reduced
Disproportionation	A reaction in which the same element is both oxidised and reduced
Dynamic equilibrium	Forward and reverse rates are equal in a closed system, so concentrations stay constant

Le Chatelier's principle	The position of equilibrium moves to minimise any change made to the system
Brønsted-Lowry acid	A proton donor
Activation energy	Minimum energy colliding particles need in order to react
Catalyst	Increases the rate by providing a route of lower activation energy; chemically unchanged at the end
Amphoteric	Reacts with both acids and bases (for example Al_2O_3)
Homologous series	Compounds with the same functional group and general formula, each differing by CH_2
Nucleophile	Electron pair donor that attacks a $\delta+$ carbon
Electrophile	Electron pair acceptor that attacks a region of high electron density
Free radical	A species with one or more unpaired electrons
Chiral centre	A carbon atom attached to four different atoms or groups
Stereoisomers	Same structural formula, different arrangement of atoms in space
Addition polymer	A polymer formed when many alkene monomers join, with no other product
Molecular ion	The ion formed when a molecule loses one electron; its m/e gives the M_r

Quick check

Use A_r : H 1.0, C 12.0, O 16.0, Ca 40.1. Molar gas volume at room conditions = $24.0 \text{ dm}^3 \text{ mol}^{-1}$.
 $c(\text{water}) = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

- Write the full electronic configurations of (a) a chromium atom and (b) a sulfide ion, S^{2-} . [2]
- Define first ionisation energy and explain why the first ionisation energy of sulfur is lower than that of phosphorus. [4]
- 2.50 g of calcium carbonate reacts with excess dilute hydrochloric acid. Calculate the volume of carbon dioxide produced at room conditions, in cm^3 . [3]
- (a) State the shape and bond angle of NCl_3 and of BCl_3 . Explain why BCl_3 is non-polar even though its bonds are polar. [4]
 (b) Explain why water has a much higher boiling point than hydrogen sulfide. [3]
- Use these average bond energies (kJ mol^{-1}) to calculate the enthalpy change of combustion of methane, assuming all species are gaseous: C–H 410, O=O 496, C=O 805, O–H 460. Suggest why the answer differs from the data-book value of ΔH_c . [4]
- 50.0 cm^3 of 1.00 mol dm^{-3} HCl is mixed with 50.0 cm^3 of 1.00 mol dm^{-3} NaOH. The temperature rises by 6.7°C . Calculate the enthalpy change of neutralisation. [3]
- Hydrogen peroxide oxidises iodide ions in acid solution. Construct the two half-equations and the overall ionic equation, and identify the oxidising agent. [3]
- For $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, ΔH is negative.
 (a) Write an expression for K_c and give its units. [2]
 (b) State and explain the effect of raising the temperature on the yield of SO_3 and on the value of K_c .

[2]

9. For $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, at equilibrium the total pressure is 100 kPa and the mole fraction of NO_2 is 0.40. Calculate K_p . [3]

10. Use the Boltzmann distribution to explain why a small rise in temperature causes a large increase in the rate of a reaction. [3]

11. (a) Write equations for the reactions of aluminium oxide with hydrochloric acid and with aqueous sodium hydroxide. What do these show? [3]

(b) Explain why the thermal stability of the Group 2 carbonates increases down the group. [3]

12. Describe tests, with observations, to distinguish aqueous sodium chloride from aqueous sodium bromide using silver nitrate and ammonia. Write an equation for the reaction of solid sodium bromide with concentrated sulfuric acid that produces bromine. [4]

13. 2-bromo-2-methylpropane reacts with $\text{NaOH}(\text{aq})$ and, separately, with NaOH in ethanol.

(a) Name the type of reaction and the organic product in each case. [4]

(b) Describe the mechanism of the reaction with $\text{NaOH}(\text{aq})$. [3]

14. Alcohol X, $\text{C}_3\text{H}_8\text{O}$, turns hot acidified potassium dichromate(VI) from orange to green when distilled, giving Y. Y gives a silver mirror with Tollens' reagent. X gives no precipitate with alkaline aqueous iodine.

(a) Identify X and Y. [2]

(b) Y reacts with HCN in the presence of KCN . Name the mechanism, give the structure of the product and explain why the product is not optically active. [4]

15. Compound Z, $\text{C}_3\text{H}_6\text{O}_2$, has an IR spectrum with a very broad absorption at 2500 to 3000 cm^{-1} and a strong absorption at about 1710 cm^{-1} . Its mass spectrum has a molecular ion peak at $m/e = 74$ of height 40.0 and an $M+1$ peak of height 1.32, and fragment peaks at $m/e = 29$ and 45.

(a) Show that Z has three carbon atoms. [1]

(b) Identify Z, explaining each piece of evidence. [4]

(c) Z can be made from chloroethane in two steps. State the reagents and conditions. [2]

1. (a) Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ (one 4s electron is placed in 3d to give a half-filled, more stable d sub-shell).

(b) S^{2-} has $16 + 2 = 18$ electrons: $1s^2 2s^2 2p^6 3s^2 3p^6$.

2. First ionisation energy: the energy required to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous $1+$ ions.

P is $[\text{Ne}] 3s^2 3p^3$: three unpaired 3p electrons in separate orbitals. S is $[\text{Ne}] 3s^2 3p^4$: one 3p orbital holds a pair of electrons. The repulsion between the paired electrons makes one of them easier to remove, which outweighs the extra nuclear charge of sulfur. Both electrons are removed from the same 3p sub-shell with similar shielding.

3. $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$.

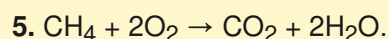
$M_r(\text{CaCO}_3) = 40.1 + 12.0 + 48.0 = 100.1$. $n = 2.50 / 100.1 = 0.02498$ mol.

$n(\text{CO}_2) = 0.02498$ mol (1 : 1). $V = 0.02498 \times 24.0 = 0.599 \text{ dm}^3 = 599 \text{ cm}^3$ (about 600 cm^3).

4. (a) NCl_3 : three bonding pairs and one lone pair on N, so trigonal pyramidal, about 107° . BCl_3 : three bonding pairs, no lone pairs on B, so trigonal planar, 120° . In BCl_3 the three B–Cl dipoles are equal and arranged symmetrically at 120° , so they cancel and there is no overall dipole.

(b) Water molecules form hydrogen bonds with each other (H bonded to the very electronegative

O, which has lone pairs). H_2S has only weaker permanent dipole and instantaneous dipole-induced dipole forces, because S is much less electronegative. More energy is needed to overcome the hydrogen bonds in water, so its boiling point is much higher even though H_2S has more electrons.



Bonds broken: $4 \text{ C-H} + 2 \text{ O=O} = 4(410) + 2(496) = 1640 + 992 = 2632 \text{ kJ}$.

Bonds made: $2 \text{ C=O} + 4 \text{ O-H} = 2(805) + 4(460) = 1610 + 1840 = 3450 \text{ kJ}$.

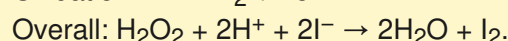
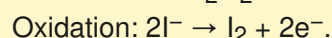
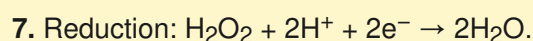
$$\Delta H = 2632 - 3450 = -818 \text{ kJ mol}^{-1}.$$

It differs because bond energies are average values from many compounds, not the exact values in these molecules, and because the calculation treats water as a gas, whereas under standard conditions water is a liquid; condensing water releases extra energy, so the data-book value is more exothermic.

6. Mass of solution $\approx 100 \text{ g}$ (assume density 1.00 g cm^{-3}). $q = mc\Delta T = 100 \times 4.18 \times 6.7 = 2800 \text{ J} = 2.80 \text{ kJ}$.

$$n(\text{H}_2\text{O}) = n(\text{HCl}) = 1.00 \times 50.0/1000 = 0.0500 \text{ mol}.$$

$$\Delta H_{\text{neut}} = -2.80 / 0.0500 = -56 \text{ kJ mol}^{-1} \text{ (negative because the temperature rose: exothermic).}$$



H_2O_2 is the oxidising agent (oxygen goes from -1 to -2 ; it accepts electrons).

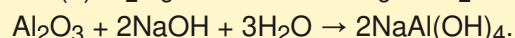
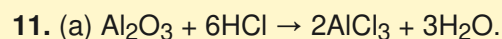
8. (a) $K_c = [\text{SO}_3]^2 / ([\text{SO}_2]^2[\text{O}_2])$. Units: $(\text{mol dm}^{-3})^2 / (\text{mol dm}^{-3})^3 = \text{mol}^{-1} \text{ dm}^3$.

(b) The forward reaction is exothermic, so raising the temperature moves the equilibrium to the left (endothermic direction) to absorb the added heat. The yield of SO_3 falls and K_c decreases.

9. $p(\text{NO}_2) = 0.40 \times 100 = 40 \text{ kPa}$. Mole fraction of $\text{N}_2\text{O}_4 = 1 - 0.40 = 0.60$, so $p(\text{N}_2\text{O}_4) = 60 \text{ kPa}$.

$$K_p = p(\text{NO}_2)^2 / p(\text{N}_2\text{O}_4) = 40^2 / 60 = 1600 / 60 = 27 \text{ kPa} \text{ (26.7 kPa)}.$$

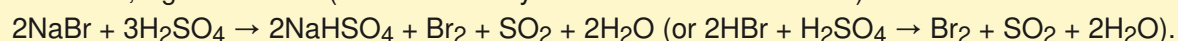
10. At a higher temperature the Boltzmann distribution curve flattens and shifts to the right (the area stays the same). The activation energy is unchanged, but a much larger proportion of molecules now have energy equal to or greater than E_a (the area under the curve beyond E_a increases greatly). So the frequency of successful collisions rises sharply; the small increase in total collision frequency is much less important.



It reacts with both an acid and a base, so aluminium oxide is amphoteric.

(b) Down the group the M^{2+} ions are larger with the same charge, so their charge density decreases. Smaller, high charge density ions (Mg^{2+}) polarise the large carbonate ion strongly, weakening its C–O bonds and making it decompose to the oxide and CO_2 more easily. Larger cations polarise the carbonate ion less, so more heat is needed to decompose it.

12. Acidify each with dilute nitric acid, then add aqueous silver nitrate. NaCl gives a white precipitate (AgCl); NaBr gives a cream precipitate (AgBr). Add dilute aqueous ammonia: AgCl dissolves; AgBr does not (it dissolves only in concentrated ammonia).



13. (a) NaOH(aq) , heat: nucleophilic substitution (hydrolysis), giving 2-methylpropan-2-ol, $(\text{CH}_3)_3\text{COH}$. NaOH in ethanol, heat: elimination, giving methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$.

(b) S_N1 , because the halogenoalkane is tertiary. Step 1 (slow): the C–Br bond breaks heterolytically, forming the tertiary carbocation $(CH_3)_3C^+$ and Br^- (curly arrow from the C–Br bond to Br). Step 2 (fast): the lone pair of OH^- attacks the positive carbon (curly arrow from the lone pair on O to C^+), forming the alcohol. The tertiary carbocation is stabilised by three electron-donating methyl groups.

14. (a) X is oxidised to an aldehyde (Y gives a silver mirror), so X is a primary alcohol: propan-1-ol, $CH_3CH_2CH_2OH$ (consistent with no triiodomethane precipitate, as it has no $CH_3CH(OH)-$ group). Y is propanal, CH_3CH_2CHO .

(b) Nucleophilic addition. Product: 2-hydroxybutanenitrile, $CH_3CH_2CH(OH)CN$. It has a chiral carbon (bonded to H, OH, CN and C_2H_5), but the $C=O$ group in propanal is planar, so CN^- attacks equally from either side. Equal amounts of both enantiomers form (a racemic mixture), and their rotations of plane-polarised light cancel.

15. (a) $n = (100 \times 1.32) / (1.1 \times 40.0) = 132 / 44.0 = 3.0$, so three carbon atoms.

(b) Very broad absorption at 2500 to 3000 cm^{-1} : O–H of a carboxylic acid. 1710 cm^{-1} : C=O. M^+ at 74 matches $C_3H_6O_2$ ($36 + 6 + 32 = 74$). Fragment at 45 is $COOH^+$ and at 29 is $C_2H_5^+$, from breaking the C–C bond next to $COOH$. Z is propanoic acid, CH_3CH_2COOH .

(c) Step 1: KCN in ethanol, heat under reflux, giving propanenitrile, CH_3CH_2CN . Step 2: heat under reflux with dilute acid (for example $HCl(aq)$) to hydrolyse the nitrile to propanoic acid.