

5 • Transition Metals and Organic Nitrogen Chemistry

Pearson Edexcel • International A-Level • Chemistry

From a battery to a medicine

A battery transfers electrons through a wire. A metal catalyst changes a reaction pathway. An organic synthesis joins chosen carbon groups. In each case, success depends on identifying the particles and the conditions. This unit connects redox measurements, metal complexes and organic routes.

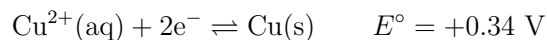
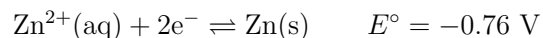
Prerequisites: oxidation numbers, half-equations, equilibrium, entropy, organic functional groups and Unit 4 analytical methods. This reference covers Pearson Topics 16–20 and the theory of core practicals 12–16. Separate practical Unit 6 requires practical-source preparation. Laboratory work needs the approved supervised procedure and its risk assessment.

Electrode potentials: compare reductions under the same conditions

A **half-cell** contains an oxidised/reduced pair in contact with a conducting electrode. A metal electrode can be the reacting solid. An inert platinum electrode carries electrons when the pair contains only solutions or a gas and solution. A **salt bridge** allows ions to move and completes the circuit without directly mixing the main solutions. Electrons flow through the wire, not the bridge.

An individual electrode potential cannot be measured alone. Connect it to a reference. The **standard hydrogen electrode** has hydrogen gas at 100 kPa, aqueous H^+ at 1.00 mol dm^{-3} and platinum, at 298 K. Its standard potential is defined as zero. The **standard electrode potential** of another couple is its potential relative to that reference under standard conditions. Other solutes have concentration 1.00 mol dm^{-3} ; pure solids and liquids are in their standard states.

Write table entries as reductions. For example:



The more positive reduction is favoured at the positive electrode of the spontaneous cell. Zinc is oxidised at the negative electrode; Cu^{2+} is reduced at the positive electrode. The net equation is $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$. Cancel equal electron amounts after multiplying half-equations, but **never multiply an electrode potential** by a coefficient.

$$E_{\text{cell}}^\circ = E_{\text{right}}^\circ - E_{\text{left}}^\circ = +0.34 - (-0.76) = +1.10 \text{ V}$$

The cell diagram is $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})$. A single line represents a phase boundary; the double line represents the salt bridge. State concentrations and conditions alongside the diagram. For an $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution half-cell, include $\text{Pt}(\text{s})$ as the inert contact. Species in one aqueous phase are separated by a comma, not an extra phase boundary.

In core practical 12, clean the metal surfaces and use a high-resistance voltmeter. Check electrode identity, solution concentration, temperature and good electrical contacts. Do not assume a smaller measured voltage disproves the table: actual conditions, oxide films and internal resistance affect measurements.

■ Feasibility has limits

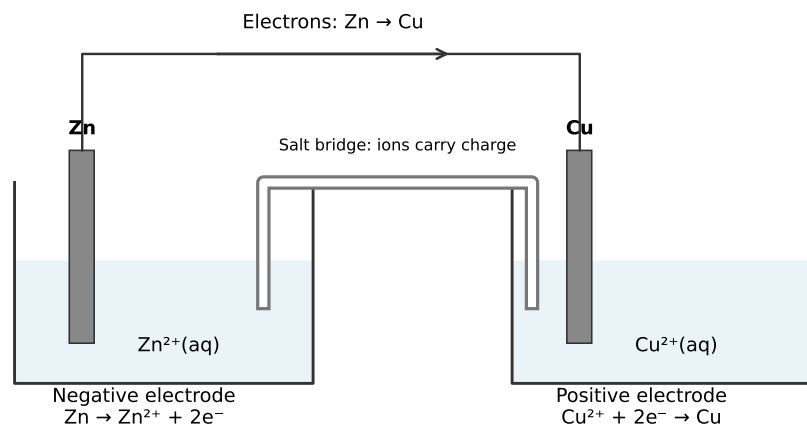
A positive standard cell potential predicts thermodynamic feasibility for the stated overall reaction under standard conditions. It does not predict a visible reaction rate. A high activation barrier can prevent an observable change. Non-standard concentrations can change the electrode potentials and even the predicted direction. Compare the same conditions; do not treat a standard table as a concentration-independent rule.

For a defined cell reaction, E_{cell}° is proportional to its standard total entropy change. It is also related to $\ln K$, with electron number and temperature included in the proportionality. Thus positive E° corresponds to positive total entropy and $K > 1$. Reversing the reaction changes the sign of E° and inverts K . Changing the balanced equation's scale changes the entropy change and electron number, but not the voltage.

A **reducing agent** donates electrons and is oxidised. The reduced form of a very negative-potential couple is usually a strong reducing agent. An **oxidising agent** accepts electrons and is reduced. The oxidised form of a very positive-potential couple is usually a strong oxidising agent. Name the actual species, not just “the half-cell”.

A **disproportionation** reaction oxidises and reduces the same element from one starting oxidation state. To test it, use the reductions leading to the starting state and away from it. If the reduction of the starting species is more positive than reduction into that state, the proposed disproportionation has positive E° . For illustrative $\text{A}^{3+}/\text{A}^{2+} = +0.80 \text{ V}$ and $\text{A}^{2+}/\text{A} = -0.20 \text{ V}$, disproportionation of A^{2+} to A^{3+} and A gives $-0.20 - 0.80 = -1.00 \text{ V}$. It is not feasible under those standard conditions. This example concerns hypothetical A , not measured values for a named metal.

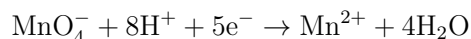
Spontaneous zinc-copper cell: schematic



Electron flow and separate ion conduction in a zinc-copper cell.

Redox titrations: use the electrons before the volume

Acidified manganate(VII) is reduced from purple MnO_4^- to nearly colourless Mn^{2+} :



Iron(II) loses one electron: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. Therefore one mole MnO_4^- reacts with five moles Fe^{2+} . Use dilute sulfuric acid. Hydrochloric acid can be oxidised; nitric acid can oxidise Fe^{2+} before titration. Near the endpoint add manganate(VII) dropwise while swirling. The first persistent faint pink shows a slight excess. No separate indicator is needed.

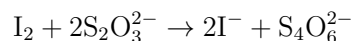
A 25.00 cm^3 Fe^{2+} sample requires 20.00 cm^3 of $0.0200 \text{ mol dm}^{-3}$ MnO_4^- :

$$n(\text{MnO}_4^-) = 0.0200 \text{ mol dm}^{-3} \times \frac{20.00}{1000} \text{ dm}^3 = 4.00 \times 10^{-4} \text{ mol}$$

$$n(\text{Fe}^{2+}) = 5(4.00 \times 10^{-4}) = 2.00 \times 10^{-3} \text{ mol}$$

$$c(\text{Fe}^{2+}) = \frac{2.00 \times 10^{-3} \text{ mol}}{0.02500 \text{ dm}^3} = 0.0800 \text{ mol dm}^{-3}$$

For iodine and thiosulfate:



Add starch when the iodine solution becomes pale yellow. Adding it to concentrated iodine can make a strongly bound complex and an indistinct endpoint. The final blue-black colour disappears. If another oxidant liberates iodine from excess iodide, first use its equation to connect oxidant to iodine, then use the 1:2 iodine/thiosulfate ratio. These are different stoichiometric steps.

Core practicals 13a and 13b use redox titration to determine concentrations. Rinse a burette with its titrant and a pipette with the sampled solution. Water remaining in a conical flask does not change the moles transferred by the pipette. A burette reading uncertainty of $\pm 0.05 \text{ cm}^3$ at each end gives a worst-case titre uncertainty of $\pm 0.10 \text{ cm}^3$. For 20.00 cm^3 , percentage uncertainty is $(0.10/20.00)100 = 0.50\%$. Include dilution and other apparatus uncertainties when the question requires the final concentration uncertainty. Repeat concordant titres reduce random variation; they do not remove a systematic concentration error.

Fuel cells require a continuing supply

A **fuel cell** produces electricity while fuel and oxidant enter from outside. For hydrogen and oxygen, the overall reaction is $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.

Medium	Oxidation half-equation	Reduction half-equation
Acidic	$2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
Alkaline	$2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

Cancel H^+ or OH^- only after matching electrons. Both media give the same overall equation. Hydrogen-cell operation produces water, but hydrogen production, storage and transport have environmental costs. Methanol is easier to store as a liquid but produces CO_2 . Its overall oxygen-cell equation is $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$. Compare total production pathways and energy efficiency, not just the cell's exhaust.

Transition metals: distinguish atoms, ions and complexes

A **transition element** forms at least one stable ion with an incomplete d subshell. Scandium forms Sc^{3+} , which is d^0 , and zinc forms Zn^{2+} , which is d^{10} . They do not meet this definition. Copper qualifies because Cu^{2+} is d^9 , even though Cu^+ is d^{10} .

For Sc to Zn, the neutral atom configurations after [Ar] are: Sc $3d^1 4s^2$; Ti $3d^2 4s^2$; V $3d^3 4s^2$; Cr $3d^5 4s^1$; Mn $3d^5 4s^2$; Fe $3d^6 4s^2$; Co $3d^7 4s^2$; Ni $3d^8 4s^2$; Cu $3d^{10} 4s^1$; Zn $3d^{10} 4s^2$. Chromium and copper are exceptions to the simple filling pattern. When these atoms form positive ions, remove 4s electrons before 3d electrons. Fe^{2+} is $[\text{Ar}]3d^6$, not $[\text{Ar}]3d^4 4s^2$. Similar 3d and 4s energies help explain variable oxidation states.

A **ligand** donates a lone pair to a metal ion, forming a coordinate bond. A **complex ion** contains a central metal ion surrounded by ligands. The **coordination number** counts donor atoms directly bonded to the metal, not the number of ligand molecules. Six water ligands give $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, coordination

number six. Three bidentate ethanedioate ligands also give coordination number six. Water, OH^- , NH_3 and Cl^- are monodentate. Ethane-1,2-diamine, often written en, is bidentate. EDTA^{4-} can be hexadentate. Neutral ligands do not change the ion's charge; each anionic ligand contributes its charge. In $[\text{Fe}(\text{CN})_6]^{3-}$, six CN^- contribute -6 , so iron is $+3$.

Six ligand electron-pair regions repel and arrange around the metal with the greatest available separation. This gives an octahedral arrangement for the six-coordinate complexes here. Larger chloride ligands favour four-coordinate complexes such as tetrahedral $[\text{CoCl}_4]^{2-}$. Some four-coordinate complexes are square planar. Cisplatin has two NH_3 and two Cl ligands around platinum in a square plane. The two chloride ligands are adjacent in the cis form; opposite positions define the trans form. Cisplatin is used in cancer treatment as the single cis isomer, not a mixture with the trans form. A four-coordinate formula alone does not prove tetrahedral geometry.

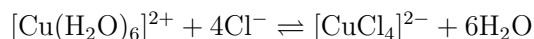
■ Colour and ligand exchange

Ligands split the d orbitals into different energy levels. Absorbing visible light can promote a d electron between these levels. The remaining transmitted/reflected light produces the observed colour. Changing the metal oxidation state, ligand or coordination number can change the energy gap and colour. A d^0 or d^{10} ion has no suitable d–d transition; this explains many colourless complexes, but does not claim every colour in chemistry is a d–d transition.

A **ligand exchange** replaces one ligand with another. Excess ammonia changes the pale blue copper(II) aqueous complex into a deep blue solution:



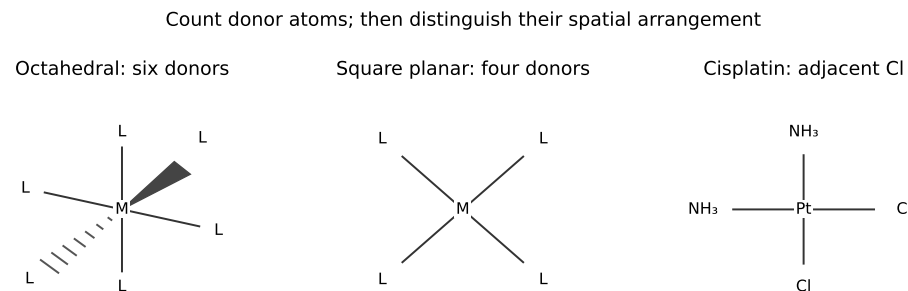
Initially, a small amount of NH_3 acts as a base and makes a pale blue hydroxide precipitate. In excess NH_3 , that precipitate dissolves as the ammine complex forms. Do not describe both stages as one precipitate colour change. Excess concentrated chloride gives yellow $[\text{CuCl}_4]^{2-}$, often through an observed green mixture:



For cobalt, pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ exchanges with chloride to form blue $[\text{CoCl}_4]^{2-}$. Adding water shifts towards pink; increasing chloride concentration favours blue. State whether water or chloride concentration changed before explaining the equilibrium.

Replacing six water ligands with three bidentate ligands releases six free water molecules while using three free ligand molecules. The increase in freely moving particles often favours the chelate complex through entropy. It is not simply “more coordinate bonds”: both complexes can have six metal–donor bonds. In haemoglobin, Fe^{2+} is held by a polydentate ligand and binds oxygen reversibly. Carbon

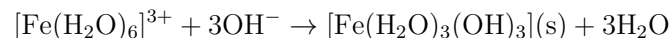
monoxide competes strongly for binding and prevents normal oxygen transport. The detailed haem structure is not required here.



Six-coordinate octahedral and four-coordinate square-planar arrangements.

Metal-ion tests and redox changes

Hydroxide removes protons from coordinated water, producing a hydrated hydroxide precipitate. A simplified equation is $\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3(\text{s})$. A hydrated-complex equation is:



Ammonia first accepts protons from coordinated water; write NH_4^+ as a product. For copper:



The following table distinguishes initial precipitates from the solution in excess reagent. Observations refer to fresh aqueous tests. Air oxidation and slow ligand substitution can change colours during standing; record those conditions rather than silently combining stages.

Ion	Initial hydroxide precipitate	Excess NaOH	Excess NH_3
Cr^{3+}	Green/grey-green	Dissolves, green solution	Does not dissolve in the usual room-temperature test
Mn^{2+}	Off-white, darkens in air	Remains	Remains
Fe^{2+}	Green, turns brown in air	Remains	Remains

Ion	Initial hydroxide precipitate	Excess NaOH	Excess NH ₃
Fe ³⁺	Red-brown	Remains	Remains
Co ²⁺	Blue initially; may change on standing	Remains	Can dissolve to a straw-coloured ammine solution; air oxidation changes it
Ni ²⁺	Green	Remains	Dissolves to a blue/violet ammine solution
Cu ²⁺	Pale blue	Remains	Dissolves to deep blue solution
Zn ²⁺	White	Dissolves, colourless solution	Dissolves, colourless solution

The initial precipitate column applies to small additions of either hydroxide or ammonia in these tests. For a divalent metal M, the simplified equations are $M^{2+} + 2OH^- \rightarrow M(OH)_2(s)$ and $M^{2+} + 2NH_3 + 2H_2O \rightarrow M(OH)_2(s) + 2NH_4^+$. Here M can be Mn, Fe, Co, Ni, Cu or Zn. For Cr³⁺ and Fe³⁺, replace the coefficients 2 with 3 and use M(OH)₃. These formulae describe the same proton-removal chemistry as the hydrated-complex equations.

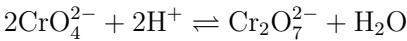
For the excess-ammonia stage, Co(OH)₂ or Ni(OH)₂ can form $[M(NH_3)_6]^{2+}$ with six NH₃, releasing two OH[−]. Zinc forms $[Zn(NH_3)_4]^{2+}$ with four NH₃, releasing two OH[−]. For copper, $Cu(OH)_2 + 4NH_3 + 2H_2O \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$. These equilibria account for dissolution in sufficient ammonia; the observed extent and subsequent cobalt oxidation depend on conditions. Chromium, manganese and iron precipitates do not dissolve in the usual excess-ammonia test. Do not use the deep-blue copper colour for every ammine complex.

The **amphoteric** Cr(OH)₃ and Zn(OH)₂ react with excess hydroxide. For example $Zn(OH)_2(s) + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$. Zinc also forms $[Zn(NH_3)_4]^{2+}$ in excess ammonia. “Dissolves in both” does not mean both ligands produce the same complex. Chromium(III) may be represented as $[Cr(OH)_6]^{3-}$ in excess hydroxide; follow the species convention supplied in the question.

Vanadium shows several oxidation states in acidic solution: V(V), yellow VO₂⁺; V(IV), blue VO²⁺; V(III), green V³⁺; V(II), violet V²⁺. Zinc in acid reduces through these stages. Yellow and blue mixed during a change can look green; this alone is not proof of pure V³⁺. Combine colour with the reaction conditions and electrode data.

Acidified orange dichromate(VI) is reduced to green Cr³⁺. Zinc in acid can reduce it further to blue Cr²⁺; air readily oxidises Cr²⁺ back. In alkaline solution, hydrogen peroxide can oxidise Cr(III) to yellow chromate(VI). Subsequent acidification favours

orange dichromate:

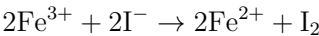
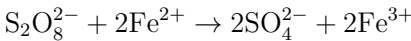


Chromium stays +6 in this equilibrium. It is an acid–base equilibrium, not a redox change. Check oxidation numbers before assuming every colour change transfers electrons.

■ **Catalysts can change oxidation state**

In the Contact process, V₂O₅ catalyses SO₂ oxidation. A useful cycle is V₂O₅ + SO₂ → V₂O₄ + SO₃, then 2V₂O₄ + O₂ → 2V₂O₅. Add the steps to cancel the catalyst and recover 2SO₂ + O₂ → 2SO₃. On catalytic-converter surfaces, reactants adsorb, react through a lower-energy pathway and desorb. For example 2CO + 2NO → 2CO₂ + N₂. Surface blockage reduces the available sites.

For the aqueous iodide/peroxodisulfate reaction, Fe²⁺/Fe³⁺ provides a homogeneous cycle:



Adding cancels iron ions. For acidified manganate(VII) and ethanedioate, Mn²⁺ product acts as an autocatalyst. The reaction can start slowly, accelerate as Mn²⁺ builds up, then slow as reactants are used. Core practical 14 prepares a transition-metal complex: calculate limiting amount and theoretical yield, isolate and dry crystals, and distinguish product loss from impurities that falsely raise mass.

Arenes: substitution preserves the delocalised ring

Benzene is an **arene**. Its six p orbitals overlap into a delocalised electron system above and below the carbon plane. The carbon–carbon bonds have equal lengths, between typical single and double bonds. X-ray evidence supports equal bond lengths. Its infrared spectrum has aromatic ring vibrations and aromatic C–H absorption above 3000 cm^{−1}. Use supplied reference data to compare its bands with a localised-alkene prediction; IR alone does not count three ordinary isolated double bonds. Together with its lower-than-expected hydrogenation enthalpy, the evidence disagrees with the three-isolated-bond model.

If one isolated double bond gives hydrogenation enthalpy −120 kJ mol^{−1}, three would predict −360. An illustrative measured benzene value of −208 is 152 kJ mol^{−1} less exothermic. Benzene starts at lower enthalpy than that localised model. This comparison uses a hypothetical reference; benzene does not rapidly switch between three fixed double bonds.

Benzene usually resists addition because it would destroy ring delocalisation. It does not decolourise bromine water like an alkene under the usual test conditions. It burns with a smoky flame when combustion is incomplete because of its high carbon proportion. Substitution replaces H while restoring the delocalised ring.

An **electrophilic substitution** reaction has three essential stages: generate the electrophile, use a ring electron pair to form a C–E bond, then lose H^+ to restore delocalisation. The intermediate has a positive charge and a ring carbon bonded to both H and E. Draw a curly arrow from the ring electron system to E^+ , then from the C–H bond back into the ring. An arrow starting at H^+ is not electron flow.

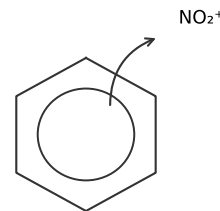
Reaction	Reagents and conditions	Product/change
Bromination	Br_2 with FeBr_3 or AlBr_3 catalyst	Bromobenzene + HBr
Nitration	Concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$, warm controlled conditions	Nitrobenzene + H_2O
Sulfonation	Fuming sulfuric acid	Benzenesulfonic acid
Friedel–Crafts alkylation	Halogenoalkane with anhydrous AlCl_3	Alkylbenzene
Friedel–Crafts acylation	Acyl chloride with anhydrous AlCl_3	Aryl ketone

For nitration, $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$ generates the nitronium ion. Ring substitution gives nitrobenzene and releases H^+ , regenerating the acid catalyst. For Friedel–Crafts acylation, $\text{RCOCl} + \text{AlCl}_3 \rightarrow \text{RCO}^+ + \text{AlCl}_4^-$; substitution then forms HCl and regenerates AlCl_3 . For bromination, the simple electrophile model is $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$. FeBr_4^- accepts the released H^+ to form HBr and regenerate FeBr_3 . For alkylation, $\text{RCl} + \text{AlCl}_3 \rightarrow \text{R}^+ + \text{AlCl}_4^-$; AlCl_4^- accepts H^+ to form HCl and regenerate AlCl_3 . In each case the ring-attack and ring-restoration electron-pair arrows follow the nitration pattern. These are simplified mechanism models of catalyst-assisted electrophile generation; free ions are not assumed to exist in the original reagent bottle. Sulfonation conditions and products are required here; its detailed mechanism is outside this specification statement.

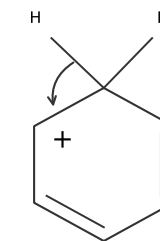
Phenol reacts much more easily with bromine water, giving a white precipitate of 2,4,6-tribromophenol and decolourisation without a halogen carrier. Oxygen's lone pair increases ring electron density by interaction with the ring. This makes attack by an electrophile easier. Do not transfer benzene's catalyst requirement to phenol.

Nitration mechanism after NO_2^+ generation; curly arrows show electron pairs

1 Ring electron pair attacks

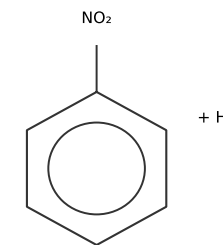


2 Positive intermediate



C–H bond pair restores ring

3 Nitrobenzene + H^+



Electron-pair arrows for benzene nitration after electrophile generation.

Amines and amides: the nitrogen lone pair matters

An **amine** derives from ammonia by replacing H with carbon groups. Butan-1-amine is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; phenylamine is $\text{C}_6\text{H}_5\text{NH}_2$. Nitrogen's lone pair accepts H^+ , making amines bases and nucleophiles. $\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ + \text{OH}^-$, and $\text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_3^+\text{Cl}^-$. Small amines dissolve in water through hydrogen bonding. Solubility generally falls as the non-polar carbon group grows.

Aliphatic amines are generally stronger bases than ammonia in the comparisons required here. Alkyl groups increase electron density at nitrogen. Phenylamine is a weaker base because its lone pair interacts with the aromatic ring and is less available to bind H^+ . Basicity is not decided by counting N–H bonds. Hydrogen bonding also raises boiling points compared with similar-sized hydrocarbons.

Excess ethanolic ammonia with a halogenoalkane, heated in a sealed apparatus under the approved procedure, forms a primary amine. Excess ammonia reduces further substitution but does not make it impossible. The amine product can attack more halogenoalkane, giving secondary/tertiary amines and eventually a quaternary ammonium salt. Butylamine can also act as a ligand towards Cu^{2+} through its lone pair.

Reducing a nitrile with LiAlH_4 in dry ether followed by suitable aqueous work-up gives a primary amine. $\text{R}-\text{C}\equiv\text{N}$ becomes $\text{R}-\text{CH}_2\text{NH}_2$. The nitrile carbon remains in the chain. Making a nitrile from a halogenoalkane using ethanolic cyanide then reducing it increases the carbon chain by one overall.

Reduce nitrobenzene using tin and concentrated HCl under reflux. The acidic mixture initially contains the phenylammonium salt. Add alkali during work-up to liberate phenylamine. Writing free phenylamine as the only species in the strongly acidic reaction mixture misses this stage.

An **amide** has nitrogen bonded to a carbonyl carbon. Ethanoyl chloride re-

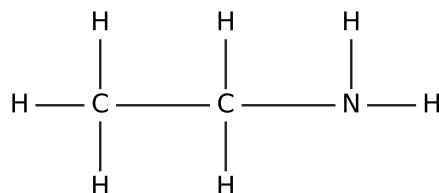
acts with a primary amine to form a substituted amide. $\text{CH}_3\text{COCl} + 2\text{C}_4\text{H}_9\text{NH}_2 \rightarrow \text{CH}_3\text{CONHC}_4\text{H}_9 + \text{C}_4\text{H}_9\text{NH}_3^+\text{Cl}^-$. One amine molecule forms the amide; another neutralises HCl. The amide lone pair interacts with the carbonyl system, so amides are much less basic than amines. Do not name CH_3CONH_2 as an amine or confuse its $\text{C}=\text{O}$ with a ketone.

Names and complete structures

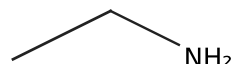
Use –amine for the amine, –amide for the amide and an amino– prefix with the carboxylic-acid parent for an amino acid. Ethanamine is $\text{CH}_3\text{CH}_2\text{NH}_2$; ethanamide is CH_3CONH_2 ; alanine is 2-aminopropanoic acid. A displayed formula includes every atom and bond. A skeletal formula omits carbon labels and their attached hydrogens, but retains nitrogen, oxygen and their attached hydrogens.

Ethanamine (ethylamine)

Displayed formula

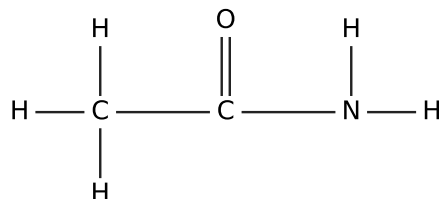


Skeletal formula

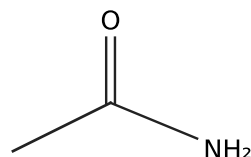


Ethanamide

Displayed formula



Skeletal formula



Diazotisation and colour

Cold nitrous acid, made from NaNO_2 and dilute acid, reacts with phenylamine below about 10°C to form a diazonium salt. Keep the mixture cold because these salts are unstable when warmed. Coupling with phenol in alkaline solution produces an azo compound containing $-\text{N}=\text{N}-$ between aromatic systems. The extended delocalised system absorbs visible light, producing colour. Distinguish making the

diazonium ion from the separate coupling step.

Amino acids, proteins and polymers

An **amino acid** contains both amine and carboxylic acid groups. A typical α -amino acid is $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COOH}$. Most have a chiral central carbon, but glycine has two H atoms and is achiral. In the solid and much aqueous solution, proton transfer gives a **zwitterion**, $^+\text{H}_3\text{N}-\text{CH}(\text{R})-\text{COO}^-$. Its net charge is zero, but it contains two charged groups. It is not an uncharged $\text{H}_2\text{N}/\text{COOH}$ molecule.

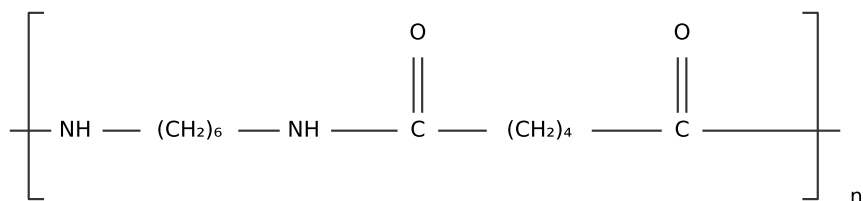
In acid the principal form is $^+\text{H}_3\text{N}-\text{CH}(\text{R})-\text{COOH}$. In alkali it is $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COO}^-$. Explain changes by adding/removing protons at the correct group. To investigate acid/base behaviour, add acid and alkali separately to measured amino-acid samples and follow pH with a calibrated meter. To investigate optical activity, zero a polarimeter with the solvent, then measure a clear solution with plane-polarised monochromatic light. Control concentration, path length, temperature and wavelength when comparing rotations. Pure opposite enantiomers rotate equally in opposite directions under matched conditions. A racemic mixture has zero net rotation; glycine is also inactive, so zero alone does not prove a racemate.

Linking an amino group and carboxyl group produces an amide or **peptide bond**, $-\text{C}(=\text{O})-\text{NH}-$, with loss of water. Two different amino acids can give two ordered dipeptides; reversing their order changes the molecule.

A **polyamide** forms by condensation between suitable diamines and dicarboxylic acids or their acyl chlorides. Nylon-6,6 uses $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ and $\text{HOOC}(\text{CH}_2)_4\text{COOH}$. Its repeat is $[-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-]$ with continuing bonds at both ends. Protein chains are polyamides formed from amino acids. Their N–H and C=O groups form hydrogen bonds between chains, affecting strength and melting behaviour.

Poly(propenamide), $[-\text{CH}_2-\text{CH}(\text{CONH}_2)-]$, is an addition polymer. The side group contains an amide, but the backbone forms by opening the $\text{C}=\text{C}$ bond without elimination of a small molecule. Poly(ethenol), $[-\text{CH}_2-\text{CH}(\text{OH})-]$, has many hydroxyl groups that hydrogen-bond to water. Its water solubility allows suitable laundry bags or liquid-detergent capsules to dissolve during washing. Distinguish water-soluble polymers from polymers that merely absorb water; formulation and conditions matter.

Condensation polymer repeat unit

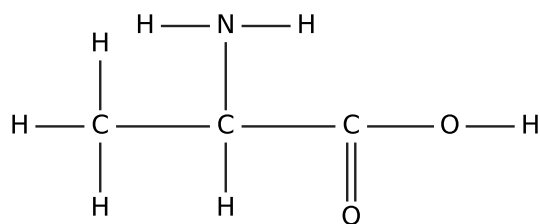


Nylon-6,6: open bonds continue through the brackets; amide links lie in the backbone.

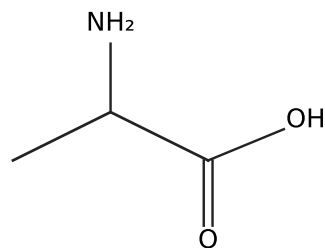
Completed nylon-6,6 repeat with backbone amide links and open bonds.

2-aminopropanoic acid (alanine; uncharged form)

Displayed formula



Skeletal formula



Plan a synthesis, then choose the purification

A **Grignard reagent** is made by reacting a halogenoalkane with magnesium in dry ether: $\text{RX} + \text{Mg} \rightarrow \text{RMgX}$. Water destroys it, forming RH . Dry glassware and solvent matter because this reaction consumes the intended reagent before it can build the carbon chain.

With CO_2 followed by acidic work-up, RMgX forms RCOOH , adding one carbon. With methanal, it forms a primary alcohol; with another aldehyde, a secondary alcohol; with a ketone, a tertiary alcohol. The carbon group R bonds to the former carbonyl carbon. Oxygen becomes OH during the separate acidic work-up. Count every carbon from both starting fragments.

For example ethylmagnesium bromide plus ethanal gives $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ after work-up: butan-2-ol. Using methanal instead gives propan-1-ol. Adding acid before the carbonyl consumes the Grignard reagent, so the order cannot be reversed.

When a task specifies four synthetic conversions, one valid route is bromoethane $\rightarrow$ ethanol (aqueous OH^- , heat) $\rightarrow$ ethanal (controlled oxidation and distillation) $\rightarrow$ butan-2-ol (ethylmagnesium bromide, dry ether, then acidic work-up) $\rightarrow$ butan-2-one

(oxidation). Each arrow changes the main organic compound. The Grignard reagent is prepared separately. Check functional group, carbon count and conditions at every arrow.

■ Evidence can constrain an unfamiliar product

Use combustion data to determine the empirical formula; combine it with molar mass for the molecular formula. Element tests identify elements, not a unique structure. IR constrains functional groups; mass spectra constrain molecular mass and fragments. Carbon-13 NMR counts distinct carbon environments; proton NMR adds chemical shifts, integration and splitting. Several structures may fit one spectrum. Seek one structure fitting **all** the observations.

An unknown has formula $\text{C}_3\text{H}_6\text{O}$, a strong $\text{C}=\text{O}$ absorption, a proton signal near 9–10 ppm, and a positive Tollens' test. Propanal fits the aldehyde proton and oxidation test. Propanone fits the formula and $\text{C}=\text{O}$ but lacks an aldehyde H and normally gives a negative Tollens' test. Predict propanal's three carbon environments and its aldehyde/ CH_2 / CH_3 proton environments as a further check. Core practical 15 identifies both inorganic and organic unknowns through a planned sequence of small-scale tests, with positive controls and separate samples. Use metal-ion precipitation/excess-reagent tests for appropriate inorganic samples. Avoid adding every reagent to one tube: later changes may come from previous reagents rather than the original unknown.

■ Isolation is not the same as reaction

Reflux heats a mixture without losing volatile reactants: vapour condenses and returns. Distillation collects a volatile component separately. Never seal a heated reflux apparatus. During extraction, a separating funnel divides immiscible layers. Identify which layer contains the product from solvent density and solubility; the organic layer is not always uppermost. Vent the funnel away from people.

Water washes remove water-soluble impurities. Sodium carbonate washes remove acidic impurities but release CO_2 , so vent carefully. A suitable anhydrous drying agent removes residual water from an organic liquid; filter or decant before distillation. Steam distillation carries a suitable water-insoluble volatile compound over with steam at a lower temperature than its normal boiling point.

Recrystallisation dissolves an impure solid in a minimum amount of hot solvent. Cool to crystallise; filter, wash with a little cold solvent and dry. Too much solvent lowers recovery. Insoluble impurities can be removed by hot filtration, while soluble impurities remain mainly in the mother liquor. A narrow melting range near the expected value supports purity; a lower, broader range suggests impurities. For melting temperature, use a dry finely powdered sample in a capillary and heat slowly near the expected range. Record the first melting and completion temperatures. For a liquid boiling temperature, place the thermometer bulb at the side-arm entrance so vapour reaching the condenser passes it. Record the pressure and a steady boiling

temperature; compare reference values at matching pressure. Mixtures can boil over a range. Neither melting point nor percentage yield alone proves identity.

Core practical 16 prepares aspirin by acylating salicylic acid with ethanoic anhydride under the approved method, then purifying the solid. Calculate theoretical yield from the limiting reagent using the 1:1 salicylic acid/aspirin ratio. If 1.38 g salicylic acid ($M = 138 \text{ g mol}^{-1}$) is limiting, $n = 1.38/138 = 0.0100 \text{ mol}$ and theoretical aspirin mass is $0.0100 \times 180 = 1.80 \text{ g}$. A dry yield of 1.26 g gives $(1.26/1.80)100 = 70.0\%$. Wet crystals can give an artificially high yield and a misleading melting range.

Independent transfer checks

1. A cell uses reduction couples $+0.54 \text{ V}$ and -0.25 V . Give the positive electrode, E°_{cell} , and one reason a predicted reaction may not be seen.
2. A 25.00 cm^3 aliquot liberates iodine requiring 18.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ thio-sulfate. Calculate iodine moles. State what extra equation is needed to find the original oxidant concentration.
3. A four-coordinate complex is blue. Explain why these facts alone do not establish its geometry or the metal oxidation state.
4. Methanal reacts with propylmagnesium bromide, then acid. Identify the alcohol and explain the effect of adding water too early.
5. A polymer has $-\text{CONH}_2$ side groups and a carbon-only backbone. Decide whether the presence of amide groups proves condensation polymerisation.

Answers: 1. The $+0.54 \text{ V}$ reduction is at the positive electrode; $E^\circ_{\text{cell}} = 0.79 \text{ V}$. A high activation barrier can make the reaction too slow. Non-standard conditions also limit the standard prediction. 2. Thiosulfate amount $= 0.100 \times 0.01800 = 0.00180 \text{ mol}$; iodine $= 0.000900 \text{ mol}$. The oxidant/iodide equation gives the separate mole ratio. 3. Four-coordinate complexes may be tetrahedral or square planar; colour also depends on ligand and coordination, so further evidence is needed. 4. Butan-1-ol; water consumes the Grignard reagent and forms propane. 5. No: poly(propenamide) forms by addition across $\text{C}=\text{C}$ while retaining amide side groups.