Unit 5: Transition metals and organic nitrogen chemistry

Topics 16–20 and theory of core practicals 12–16; source-backed authoring in progress, no full acceptance claimed.

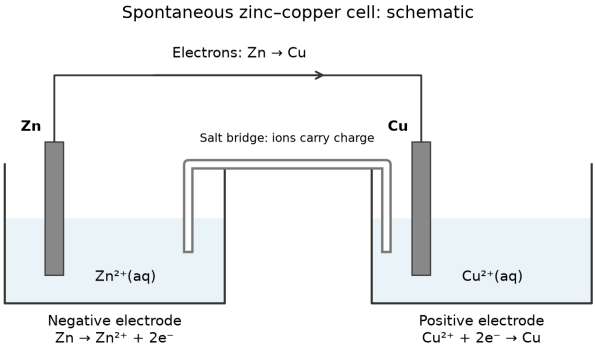
Particles and conditions connect the unit

1. **1** Track electrons in cells and metal redox cycles.
2. **2** Track lone pairs in complexes and organic reactions.
3. **3** Use Units 1, 2 and 4 as prerequisites.

Standard means a defined comparison

1. **1** 298 K, 100 kPa gas pressure and 1.00 mol dm^{-3} solutions.
2. **2** The **standard hydrogen electrode** defines zero.
3. **3** Use inert platinum when the redox pair has no suitable solid electrode.

Separate electron and ion paths



Zinc is oxidised at the negative electrode.

Choose a cell voltage

Your turn

Reduction potentials are $+0.80$ V and $+0.34$ V. What is spontaneous E°_{cell}?

A. $+1.14$ V
B. $+0.46$ V
C. -0.46 V

Reveal: subtract reductions

1. **1** B: $+0.80 - (+0.34) = +0.46$ V.
2. **2** The more positive couple is reduced.
3. **3** Do not multiply a voltage when balancing electron numbers.

Feasible does not mean fast

1. **1** Positive standard E predicts standard thermodynamic feasibility.
2. **2** A large activation barrier can make the reaction too slow to see.
3. **3** Non-standard concentrations can change potentials and direction.

Start a redox titre with half-equations

1. **1** MnO_4^- gains five electrons in acid; Fe^{2+} loses one.
2. **2** One mole manganate(VII) reacts with five moles Fe^{2+}.
3. **3** Use sulfuric acid; the endpoint is persistent faint pink.

Worked titration and uncertainty

1. **1** 22.40 cm^3 of 0.0200 mol dm^{-3} titrant contains 0.000448 mol.
2. **2** Fe^{2+} amount $=$ 0.00224 mol; in 25.00 cm^3, concentration $=$ 0.0896 mol dm^{-3}.
3. **3** Two readings at $\pm$0.05 cm^3 give $\pm$0.10 cm^3 worst-case titre uncertainty.

Iodine needs a separate ratio

1. **1** $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.
2. **2** Add starch near pale yellow; blue-black disappears at the endpoint.
3. **3** Use the oxidant–iodide equation before connecting the original oxidant to the titre.

Fuel-cell media change the half-equations

1. **1** Acidic oxygen reduction consumes H^+; alkaline oxygen reduction produces OH^-.
2. **2** Both hydrogen cells give $2H_2 + O_2 \rightarrow 2H_2O$ overall.
3. **3** Fuel production and storage matter; methanol operation also produces CO_2.

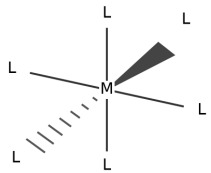
Apply the ion definition

1. **1** Transition elements form a stable ion with an incomplete d subshell.
2. **2** Sc^{3+} is d^0 and Zn^{2+} is d^{10}; Cu^{2+} is d^9.
3. **3** Remove 4s electrons before 3d in positive-ion formation.

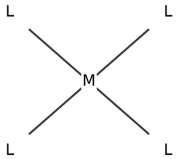
Count donors, then arrange them

Count donor atoms; then distinguish their spatial arrangement

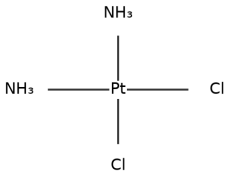
Octahedral: six donors



Square planar: four donors



Cisplatin: adjacent Cl



Coordination number counts donor atoms, not **ligand** molecules.

Find oxidation state and coordination

Your turn

$[Cr(H_2O)_4Cl_2]^+$ has which chromium state and coordination number?

A. $+1$ and 4

B. $+3$ and 6

C. $+3$ and 2

Reveal: charge and donor count differ

1. **1** B: chromium is $+3$ because two chloride ions contribute -2.
2. **2** Four oxygen and two chlorine donor atoms give **coordination number** six.
3. **3** Colour depends on **ligand** splitting as well as metal oxidation state.

Do not merge the two ammonia stages

1. **1** Small NH_3 gives copper hydroxide precipitate through proton transfer.
2. **2** Excess NH_3 gives deep blue dissolved ammine complex through **ligand exchange**.
3. **3** Zinc hydroxide also dissolves in excess OH^- because it is **amphoteric**.

Some colour changes are not redox

1. **1** $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.
2. **2** Chromium stays $+6$ while yellow changes towards orange.
3. **3** In acidic vanadium reductions, V(V), V(IV), V(III), V(II) are yellow, blue, green, violet.

Show the regenerated catalyst

1. **1** V_2O_5/V_2O_4 steps sum to $2SO_2 + O_2 \rightarrow 2SO_3$.
2. **2** Fe^{2+}/Fe^{3+} steps cancel in iodide–peroxodisulfate catalysis.
3. **3** Mn^{2+} product accelerates the manganate–ethanedioate reaction by autocatalysis.

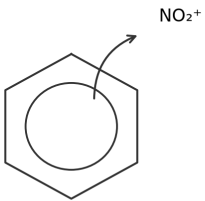
Benzene evidence constrains the model

1. **1** Equal intermediate C–C lengths support delocalisation.
2. **2** Hydrogenation is less exothermic than three isolated C=C bonds predict.
3. **3** Substitution restores the **delocalised** ring; ordinary addition loses it.

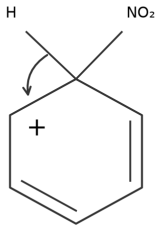
Draw electron-pair movement

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

1 Ring electron pair attacks

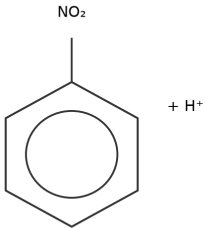


2 Positive intermediate



C–H bond pair restores ring

3 Nitrobenzene + H^+



Generate NO_2^+ using concentrated nitric and sulfuric acids.

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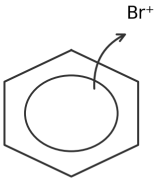
Conditions distinguish aromatic reactions

1. **1** Benzene bromination uses a halogen carrier; phenol needs none in bromine water.
2. **2** Friedel–Crafts alkylation uses a halogenoalkane/$AlCl_3$.
3. **3** Acylation uses an acyl chloride/$AlCl_3$; sulfonation uses fuming sulfuric acid.

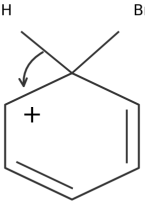
Generate and regenerate the halogen carrier

Bromination: simple electrophile model

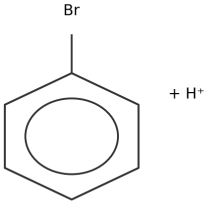
1 Ring pair attacks E^+



2 C–H pair restores ring



3 Bromobenzene



$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$; $FeBr_4^- + H^+ \rightarrow FeBr_3 + HBr$

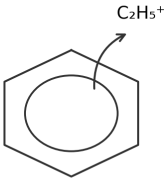
$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$ in the simple electrophile model.

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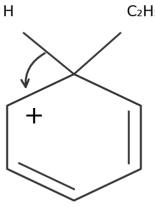
Transfer the aromatic mechanism to alkylation

Alkylation: simple electrophile model

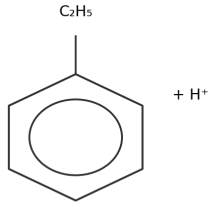
1 Ring pair attacks E^+



2 C–H pair restores ring



3 Ethylbenzene



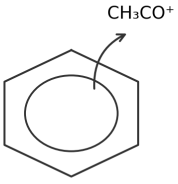
$C_2H_5Cl + AlCl_3 \rightarrow C_2H_5^+ + AlCl_4^-$; $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

$C_2H_5Cl/AlCl_3$ generates the ethyl electrophile in the simple model.

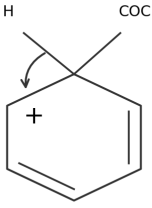
Attach the acyl group through its carbonyl carbon

Acylation: simple electrophile model

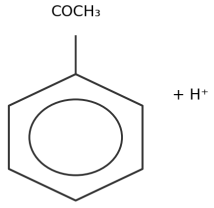
1 Ring pair attacks E^+



2 C–H pair restores ring



3 Phenylethanone



$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$; $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

CH_3CO^+ bonds to the ring through its carbonyl carbon.

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Basicity asks about lone-pair availability

1. **1** Alkyl groups generally increase **amine** basicity relative to ammonia.
2. **2** Phenylamine's lone pair interacts with the ring, reducing basicity.
3. **3** Amides have nitrogen bonded to a carbonyl and are much less basic.

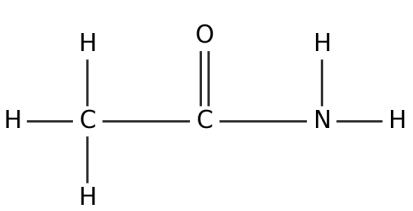
Choose an amine route and work-up

1. **1** Halogenoalkane with excess ethanolic ammonia gives a primary **amine** with further-substitution limits.
2. **2** Nitrile reduction retains the nitrile carbon.
3. **3** Sn/HCl reduces nitrobenzene; alkali liberates free phenylamine from the salt.

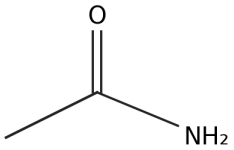
Names distinguish the carbonyl attachment

Ethanamide

Displayed formula



Skeletal formula



Ethanamine has $-CH_2NH_2$; ethanamide has $-CONH_2$.

Keep diazotisation and coupling separate

1. **1** Cold nitrous acid makes the **diazonium** salt.
2. **2** Alkaline phenol then couples to form an **azo** linkage.
3. **3** Extended delocalisation allows visible-light absorption.

Choose the amino-acid form

Your turn

Which glycine form predominates in strongly alkaline solution?

A. $^{+}H_3NCH_2COOH$

B. $^{+}H_3NCH_2COO^{-}$

C. $H_2NCH_2COO^{-}$

Reveal: track protons and net charge

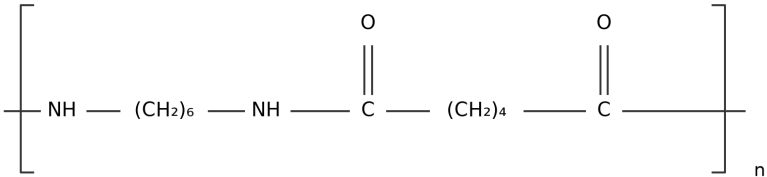
1. **1** C: $H_2NCH_2COO^-$, with net charge -1.
2. **2** The **zwitterion** has NH_3^+ and COO^-, net zero.
3. **3** Glycine is achiral because its central carbon has two H atoms.

Measure optical activity under matched conditions

1. **1** Zero the polarimeter with solvent; use monochromatic plane-polarised light.
2. **2** Match concentration, path length, temperature and wavelength.
3. **3** Opposite pure alanine enantiomers rotate equally oppositely; glycine and a racemate can both give zero.

Backbone links decide polymer class

Condensation polymer repeat unit



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

Nylon-6,6 forms by condensation with backbone **amide** links.

Count carbons before naming the product

1. **1** Ethylmagnesium bromide plus ethanal then acid gives butan-2-ol.
2. **2** With methanal it gives propan-1-ol; with CO_2 then acid it gives propanoic acid.
3. **3** Water added early destroys the reagent and forms ethane.

Use every analytical constraint

1. **1** C_3H_6O with a carbonyl, aldehyde H and positive Tollens' test fits propanal.
2. **2** Propanone fits formula and carbonyl but fails the aldehyde evidence.
3. **3** Check predicted carbon-13 and proton environments against the remaining data.

Reaction, isolation and purity are different

1. **1 Reflux** retains vapour; distillation collects a volatile product.
2. **2 Extraction** separates layers; carbonate washes remove acid and release CO_2.
3. **3** Recrystallise from minimum hot solvent, wash cold and dry before yield/melting range.

Plan unknown tests and control the measurement

1. **1** Use separate samples for metal-ion and organic tests with positive controls.
2. **2** For melting range, dry the solid and heat slowly near the expected temperature.
3. **3** For boiling temperature, place the bulb at the side arm and record pressure.

Aspirin transfer calculation

Your turn

2.76 g salicylic acid, M=138, gives aspirin M=180 in 1:1 ratio. Dry mass is 2.52 g. What is yield?

A. 50.0%
B. 70.0%
C. 91.3%

Check yourself

1. **1** B: $2.76/138 = 0.0200$ mol; theoretical mass $= 3.60$ g.
2. **2** Yield $= 2.52/3.60 \times 100 = 70.0\%$.
3. **3** Wet crystals raise apparent mass without increasing aspirin amount.