

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

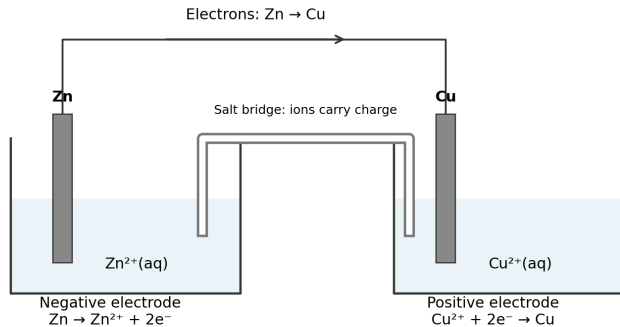
- 1 Track electrons in cells and metal redox cycles.
- 2 Track lone pairs in complexes and organic reactions.
- 3 Use Units 1, 2 and 4 as prerequisites.

Standard means a defined comparison

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

Separate electron and ion paths

Spontaneous zinc-copper cell: schematic



Zinc is oxidised at the negative electrode.

Choose a cell voltage

Your turn

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

- A. $+1.14\text{ V}$
- B. $+0.46\text{ V}$
- C. -0.46 V

Reveal: subtract reductions

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

Feasible does not mean fast

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

Start a redox titre with half-equations

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

Worked titration and uncertainty

- 1 22.40 cm³ of 0.0200 mol dm⁻³ titrant contains 0.000448 mol.
- 2 Fe²⁺ amount = 0.00224 mol; in 25.00 cm³, concentration = 0.0896 mol dm⁻³.
- 3 Two readings at ± 0.05 cm³ give ± 0.10 cm³ worst-case titre uncertainty.

Iodine needs a separate ratio

- 1 $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$.
- 2 Add starch near pale yellow; blue-black disappears at the endpoint.
- 3 Use the oxidant–iodide equation before connecting the original oxidant to the titre.

Fuel-cell media change the half-equations

- 1 Acidic oxygen reduction consumes H^+ ; alkaline oxygen reduction produces OH^- .
- 2 Both hydrogen cells give $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ overall.
- 3 Fuel production and storage matter; methanol operation also produces CO_2 .

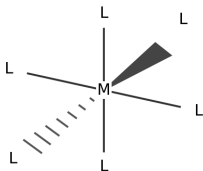
Apply the ion definition

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

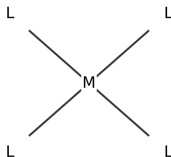
Count donors, then arrange them

Count donor atoms; then distinguish their spatial arrangement

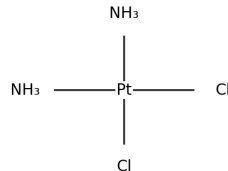
Octahedral: six donors



Square planar: four donors



Cisplatin: adjacent Cl



Coordination number counts donor atoms, not ligand molecules.

Find oxidation state and coordination

Your turn

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ 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 B: chromium is +3 because two chloride ions contribute -2 .
- 2 Four oxygen and two chlorine donor atoms give coordination number six.
- 3 Colour depends on ligand splitting as well as metal oxidation state.

Do not merge the two ammonia stages

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

Some colour changes are not redox

- 1** $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$.
- 2** Chromium stays +6 while yellow changes towards orange.
- 3** In acidic vanadium reductions, V(V), V(IV), V(III), V(II) are yellow, blue, green, violet.

Show the regenerated catalyst

- 1 $\text{V}_2\text{O}_5/\text{V}_2\text{O}_4$ steps sum to $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$.
- 2 $\text{Fe}^{2+}/\text{Fe}^{3+}$ steps cancel in iodide–peroxodisulfate catalysis.
- 3 Mn^{2+} product accelerates the manganate–ethanedioate reaction by autocatalysis.

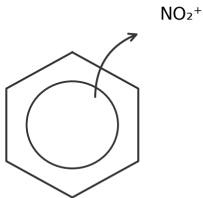
Benzene evidence constrains the model

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

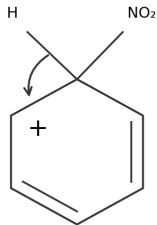
Draw electron-pair movement

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

1 Ring electron pair attacks

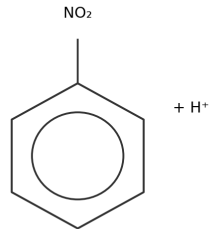


2 Positive intermediate



C-H bond pair restores ring

3 Nitrobenzene + H^+



Generate NO_2^+ using concentrated nitric and sulfuric acids.

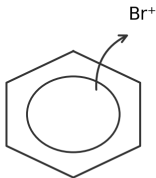
Conditions distinguish aromatic reactions

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

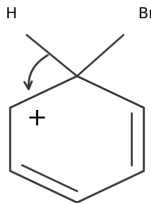
Generate and regenerate the halogen carrier

Bromination: simple electrophile model

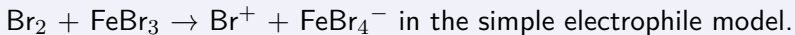
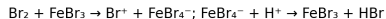
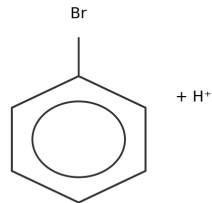
1 Ring pair attacks E^+



2 C-H pair restores ring



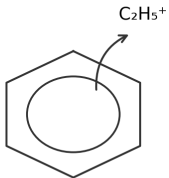
3 Bromobenzene



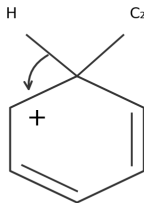
Transfer the aromatic mechanism to alkylation

Alkylation: simple electrophile model

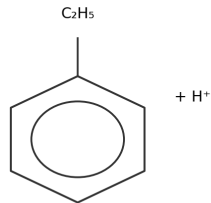
1 Ring pair attacks E^+



2 C-H pair restores ring



3 Ethylbenzene

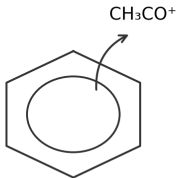


$C_2H_5Cl/AlCl_3$ generates the ethyl electrophile in the simple model.

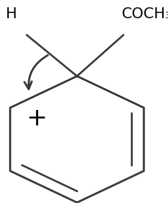
Attach the acyl group through its carbonyl carbon

Acylation: simple electrophile model

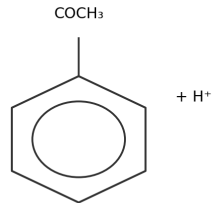
1 Ring pair attacks E^+



2 C-H pair restores ring



3 Phenylethanone



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

Basicity asks about lone-pair availability

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

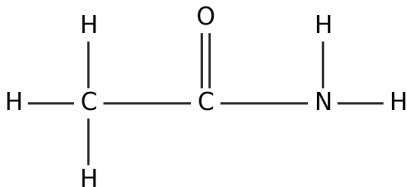
Choose an amine route and work-up

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

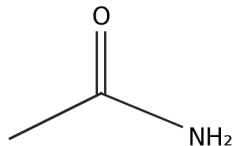
Names distinguish the carbonyl attachment

Ethanamide

Displayed formula



Skeletal formula



Ethanamine has $\text{-CH}_2\text{NH}_2$; ethanamide has -CONH_2 .

Keep diazotisation and coupling separate

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

Choose the amino-acid form

Your turn

Which glycine form predominates in strongly alkaline solution?

- A. $^+\text{H}_3\text{NCH}_2\text{COOH}$
- B. $^+\text{H}_3\text{NCH}_2\text{COO}^-$
- C. $\text{H}_2\text{NCH}_2\text{COO}^-$

Reveal: track protons and net charge

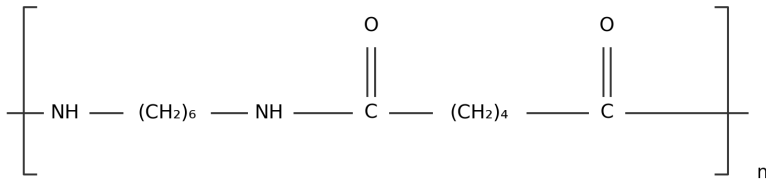
- 1 C: $\text{H}_2\text{NCH}_2\text{COO}^-$, with net charge -1 .
- 2 The zwitterion has NH_3^+ and COO^- , net zero.
- 3 Glycine is achiral because its central carbon has two H atoms.

Measure optical activity under matched conditions

- 1** Zero the polarimeter with solvent; use monochromatic plane-polarised light.
- 2** Match concentration, path length, temperature and wavelength.
- 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 Ethylmagnesium bromide plus ethanal then acid gives butan-2-ol.
- 2 With methanal it gives propan-1-ol; with CO_2 then acid it gives propanoic acid.
- 3 Water added early destroys the reagent and forms ethane.

Use every analytical constraint

- 1 $\text{C}_3\text{H}_6\text{O}$ with a carbonyl, aldehyde H and positive Tollens' test fits propanal.
- 2 Propanone fits formula and carbonyl but fails the aldehyde evidence.
- 3 Check predicted carbon-13 and proton environments against the remaining data.

Reaction, isolation and purity are different

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

Plan unknown tests and control the measurement

- 1 Use separate samples for metal-ion and organic tests with positive controls.
- 2 For melting range, dry the solid and heat slowly near the expected temperature.
- 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 B: $2.76/138 = 0.0200$ mol; theoretical mass = 3.60 g.
- 2 Yield = $2.52/3.60 \times 100 = 70.0\%$.
- 3 Wet crystals raise apparent mass without increasing aspirin amount.