

Redox and Electrolysis — AS

01 · OXIDATION AND REDUCTION

Oxidation — loss of electrons, oxidation number rises. **Reduction** — gain of electrons, oxidation number falls. **OIL RIG**.

The **oxidising agent** is itself reduced; the **reducing agent** is itself oxidised. Name the agent, not the process, when asked which is which.

02 · OXIDATION NUMBER RULES

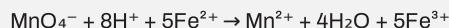
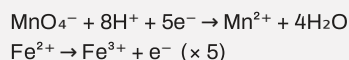
Species	O.N.
uncombined element	0
simple ion	the charge
Group 1 / 2	+1 / +2
H	+1 (–1 in hydrides)
O	–2 (–1 in peroxides, +2 in OF ₂)
F	always –1

Sum = 0 for a neutral compound, = charge for an ion. Roman numerals in a name give the oxidation number: manganate(VII), iron(III).

03 · BUILDING REDOX EQUATIONS

Half-equation method

- balance the main element
- balance O with H₂O
- balance H with H⁺
- balance charge with e[–]
- scale so electrons cancel, then add



04 · DISPROPORTIONATION

One element is simultaneously oxidised and reduced in the same reaction.

Cl₂ + 2NaOH → NaCl + NaClO + H₂O — chlorine goes from 0 to –1 and to +1. Also 2H₂O₂ → 2H₂O + O₂ and Cu⁺ in acid.

05 · ELECTROLYSIS

Cathode (–) attracts cations, which are **reduced**. **Anode (+)** attracts anions, which are **oxidised**. Current flows only when ions are mobile — molten or in solution.

In aqueous solution the water can discharge instead: H₂ at the cathode for reactive metals, O₂ at the anode unless a halide is concentrated.

06 · FARADAY CALCULATIONS

$$Q = It \cdot n(\text{e}^-) = Q \div F$$

$$F = 96\,500 \text{ C mol}^{-1}$$

2.00 A for 30.0 min through CuSO₄(aq).
 $Q = 2.00 \times 1800 = 3600 \text{ C}$
 $n(\text{e}^-) = 3600 \div 96\,500 = 0.0373 \text{ mol}$
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, so $n(\text{Cu}) = 0.0187 \text{ mol}$
 $m = 0.0187 \times 63.5 = \mathbf{1.19 \text{ g}}$

07 · COMMON OXIDISING AND REDUCING AGENTS

Reagent	Becomes	Colour change
MnO ₄ [–] / H ⁺	Mn ²⁺	purple → colourless
Cr ₂ O ₇ ^{2–} / H ⁺	Cr ³⁺	orange → green
I ₂	I [–]	brown → colourless
Fe ²⁺	Fe ³⁺	pale green → yellow
S ₂ O ₃ ^{2–}	S ₄ O ₆ ^{2–}	used in iodine titrations

Manganate(VII) titrations are self-indicating — the first permanent pink is the end point. Use dilute H₂SO₄, never HCl (chloride is oxidised) and never HNO₃ (itself an oxidising agent).

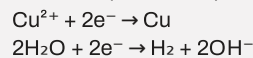
08 · ELECTROLYSIS PRODUCTS IN SOLUTION

Electrolyte	Cathode	Anode
conc. NaCl(aq)	H ₂	Cl ₂
dilute NaCl(aq)	H ₂	O ₂
CuSO ₄ (aq), Pt	Cu	O ₂
molten NaCl	Na	Cl ₂

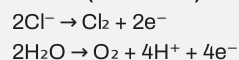
A metal below hydrogen in reactivity is deposited; a more reactive one leaves H₂ instead. With copper electrodes in CuSO₄ the anode dissolves — the basis of electroplating and purification.

09 · ELECTRODE HALF-EQUATIONS

Cathode (reduction)

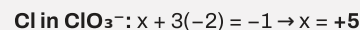
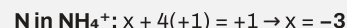
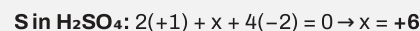
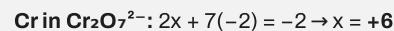


Anode (oxidation)



The same quantity of charge passes through both electrodes, so the mole ratio of products follows the electrons in each half-equation.

10 · WORKED EXAMPLE — OXIDATION NUMBERS



11 · USES OF ELECTROLYSIS

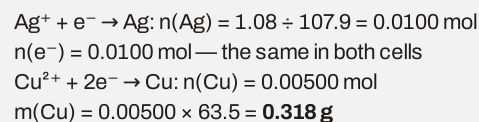
Extraction of aluminium — molten Al₂O₃ in cryolite, which lowers the melting point and cuts the energy cost. Carbon anodes burn away as CO₂ and must be replaced.

Purification of copper — impure Cu anode dissolves, pure Cu deposits on the cathode; the impurities drop as anode sludge.

Electroplating — the object is the cathode and the plating metal the anode, in a solution of that metal's salt.

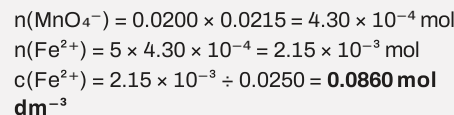
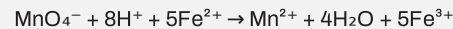
12 · WORKED EXAMPLE — TWO CELLS IN SERIES

The same current passes through AgNO₃(aq) and CuSO₄(aq). 1.08 g of Ag is deposited.



13 · WORKED EXAMPLE — REDOX TITRATION

25.0 cm³ of Fe²⁺ solution needs 21.5 cm³ of 0.0200 mol dm^{–3} KMnO₄ in excess dilute H₂SO₄.



End point: the first permanent pale pink.

MARKS LOST HERE

— Naming the oxidising agent as the species that is oxidised.

— Leaving time in minutes inside $Q = It$.

— Forgetting the electron ratio from the half-equation before converting to mass.

Electrode Potentials — A2

14 · STANDARD CONDITIONS

All solutions 1 mol dm⁻³, gases at 100 kPa, temperature 298 K, measured against the **standard hydrogen electrode** which is defined as 0.00 V.

A platinum electrode is used where no solid metal is involved — it is inert and provides a surface for electron transfer. The salt bridge (KNO₃) completes the circuit and balances charge without mixing the solutions.

15 · READING E° VALUES

Data-booklet half-equations are written as **reductions**. A **more positive E°** means a greater tendency to be reduced, so that species is the better oxidising agent.

A **more negative E°** means the reduced form is the better reducing agent. The more negative half-cell runs backwards and forms the negative electrode.

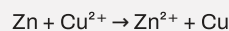
16 · CELL E.M.F.

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{reduced, +ve}) - E^{\circ}(\text{oxidised, -ve})$$

$$\text{Zn}^{2+}/\text{Zn } E^{\circ} = -0.76 \text{ V}, \text{Cu}^{2+}/\text{Cu } E^{\circ} = +0.34 \text{ V}$$

$$E^{\circ}_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V}$$

Zn is oxidised (negative electrode), Cu²⁺ reduced.



Cell diagram: Zn | Zn²⁺ || Cu²⁺ | Cu

Positive E°_{cell} → the reaction is feasible.

Feasible does not mean fast: a large E_a can still make it immeasurably slow.

17 · EFFECT OF CONCENTRATION

Apply Le Chatelier to the half-equation. Raising the concentration of the **oxidised** species drives the reduction forward and makes E° **more positive**; raising the reduced species makes it more negative.

For MnO₄⁻/Mn²⁺, raising [H⁺] makes E more positive — which is why acidified manganate(VII) is the stronger oxidising agent.

18 · ΔG AND E°

$$\Delta G^{\circ} = -n F E^{\circ}_{\text{cell}}$$

n = moles of electrons transferred, F = 96 500 C mol⁻¹. Answer in J mol⁻¹ — divide by 1000 for kJ mol⁻¹. A positive E°_{cell} gives a negative ΔG°, the same feasibility test seen twice.

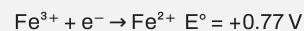
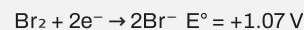
19 · CELLS IN USE

Fuel cell (H₂/O₂, alkaline): anode 2H₂ + 4OH⁻ → 4H₂O + 4e⁻, cathode O₂ + 2H₂O + 4e⁻ → 4OH⁻. Only product is water; efficiency is high, but storing and transporting H₂ is the difficulty.

Rechargeable cells reverse the electrode reactions on charging. Redox potentials also explain corrosion: a metal with a more negative E° protects one with a less negative E° (sacrificial protection of iron by zinc).

20 · PREDICTING REACTIONS FROM E°

Will Br₂ oxidise Fe²⁺?



Br₂ has the more positive E°, so it is reduced and Fe²⁺ oxidised.

$$E^{\circ}_{\text{cell}} = 1.07 - 0.77 = +0.30 \text{ V} \rightarrow \text{feasible.}$$

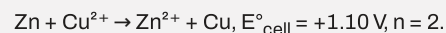
I₂ (E° = +0.54 V) would **not** oxidise Fe²⁺: E°_{cell} = -0.23 V.

21 · HALF-CELL TYPES

Type	Example
metal / metal ion	Zn(s) Zn ²⁺ (aq)
gas / ion, Pt	Pt H ₂ (g) H ⁺ (aq)
two ions, Pt	Pt Fe ²⁺ , Fe ³⁺
ion / solid, Pt	Pt MnO ₄ ⁻ , Mn ²⁺ , H ⁺

In a cell diagram, | is a phase boundary and || the salt bridge; the oxidised form is written next to the bridge on each side.

22 · WORKED EXAMPLE — ΔG° FROM E°



$$\Delta G^{\circ} = -nFE^{\circ}$$

$$\Delta G^{\circ} = -2 \times 96\,500 \times 1.10$$

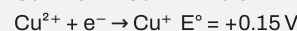
$$\Delta G^{\circ} = -212\,300 \text{ J mol}^{-1}$$

$$\Delta G^{\circ} = -212 \text{ kJ mol}^{-1}$$

Strongly negative, so the reaction is thermodynamically feasible.

23 · DISPROPORTIONATION FROM E° VALUES

A species disproportionates when its own reduction has a **more positive E°** than its own oxidation — the two half-reactions combine to give a positive E°_{cell}.



$$E^{\circ}_{\text{cell}} = 0.52 - 0.15 = +0.37 \text{ V}$$

2Cu⁺ → Cu + Cu²⁺ is feasible, which is why Cu⁺ is unstable in aqueous solution.

24 · E° VALUES WORTH REMEMBERING

Half-cell	E° / V
F ₂ / F ⁻	+2.87
MnO ₄ ⁻ , H ⁺ / Mn ²⁺	+1.52
Cr ₂ O ₇ ²⁻ , H ⁺ / Cr ³⁺	+1.33
Fe ³⁺ / Fe ²⁺	+0.77
Cu ²⁺ / Cu	+0.34
2H ⁺ / H ₂	0.00
Zn ²⁺ / Zn	-0.76

The list is the reactivity series in another form: the most negative metals are the strongest reducing agents, the most positive non-metals the strongest oxidising agents.

25 · CORROSION AND PROTECTION

Rusting is electrochemical: Fe → Fe²⁺ + 2e⁻ at the anodic region, while oxygen is reduced at the cathodic region. Both water and oxygen are needed, and salt speeds it up by carrying the current.

Sacrificial protection — attach a metal with a more negative E° (Zn or Mg) so it corrodes instead. Galvanising does both: the zinc coats the surface and protects sacrificially where it is scratched.

MARKS LOST HERE

— Multiplying E° when scaling a half-equation; E° is intensive and never multiplied.

— Subtracting the wrong way round and reporting a negative E°_{cell} for a feasible cell.

— Treating "feasible" as "will actually happen quickly".

— Forgetting that the quoted values only hold under standard conditions.