MEGA LECTURE

IB DP CHEMISTRY

Reactivity 3: What Are the Mechanisms of Chemical Change?

Reactivity 3.2 Electron Transfer Reactions

Revision Notes · Standard and Higher Level

Fahad H. Ahmad

+92 323 509 4443 | Megalecture.com

Original notes prepared for the IB Diploma Programme Chemistry course (2025 syllabus)

What the syllabus requires

Reactivity 3.2 is about reactions in which electrons are transferred from one species to another. It runs from simple oxidation-number bookkeeping (SL) all the way to quantitative electrochemistry (HL). Use this checklist as a final map of the skills examiners expect.

Understanding	You should be able to...
Redox as electron transfer	Define oxidation and reduction in terms of electrons, oxygen, hydrogen and oxidation number (OIL RIG).
Oxidation states	Assign oxidation numbers using the standard rules; name compounds with Stock notation.
Oxidising / reducing agents	Identify the species oxidised, the species reduced, and the two agents in any redox change.
Half-equations	Balance half-equations for atoms, oxygen, hydrogen and charge, and combine them into a full ionic equation.
Reactivity series	Predict metal displacement and metal-acid reactions from an activity series.
Electrochemical series (HL)	Use standard electrode potentials E° to rank oxidising and reducing strength and predict spontaneity.
Voltaic cells	Describe construction, identify electrodes and electron flow, write cell notation and (HL) calculate E°_{cell}.
Electrolytic cells	Predict electrode products for molten and (HL) aqueous electrolytes; (HL) apply $Q = It$ in Faraday calculations.
Applications	Explain rusting and its prevention, electroplating and metal extraction in redox terms.

> **Exam note:** Everything up to the electrochemical series is common SL/HL. Standard electrode potentials, spontaneity predictions, electrolysis of aqueous solutions and quantitative electrolysis (Faraday) are HL only and are flagged (HL) throughout these notes.

1. Oxidation and reduction: the electron-transfer picture

A **redox reaction** is one in which electrons are transferred between species. Every redox change is really two changes happening at once: one species loses electrons while another gains them. The two cannot be separated — there is no oxidation without a matching reduction.

The definitions have grown over time, from oxygen to hydrogen to the modern electron definition. All three are still examined.

	Oxidation is...	Reduction is...
Electrons	loss of electrons	gain of electrons
Oxidation number	an increase in oxidation number	a decrease in oxidation number
Oxygen	gain of oxygen	loss of oxygen

	Oxidation is...	Reduction is...
Hydrogen	loss of hydrogen	gain of hydrogen

- **OIL RIG** is the memory hook: **O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain — of electrons.

For example, when magnesium burns in oxygen:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

each magnesium atom loses two electrons ($Mg \rightarrow Mg^{2+} + 2e^-$) and is oxidised, while each oxygen atom gains two electrons ($O + 2e^- \rightarrow O^{2-}$) and is reduced. The oxygen definition and the electron definition agree: magnesium gains oxygen *and* loses electrons.

Oxidising agents and reducing agents

The two reactants play opposite roles, and the naming trips up many students because each agent does the *opposite* of what its own name suggests.

Species	What it does	What happens to it	Contains / becomes
Oxidising agent	oxidises the other species (takes its electrons)	is itself reduced	gains electrons; ox. number falls
Reducing agent	reduces the other species (gives it electrons)	is itself oxidised	loses electrons; ox. number rises

In $2Mg + O_2 \rightarrow 2MgO$, magnesium is the reducing agent (it is oxidised) and oxygen is the oxidising agent (it is reduced). Common laboratory oxidising agents include acidified MnO_4^-, $Cr_2O_7^{2-}$, Cl_2 and concentrated HNO_3; common reducing agents include reactive metals, H_2, C, and ions such as Fe^{2+} and I^-.

> **Exam trap:** The oxidising agent is the species that is *reduced*; the reducing agent is the species that is *oxidised*. Write the two half-changes first, then read off which is which — do not guess from the name.

2. Oxidation states (oxidation numbers)

The **oxidation state** of an atom is the charge it *would* carry if every bond were treated as fully ionic — that is, if the shared electrons were given entirely to the more electronegative atom. It is a piece of bookkeeping, not a real charge, but it lets us track electron transfer even in covalent species.

Rules for assigning oxidation numbers

Apply the rules in order; the higher a rule sits in the list, the higher its priority when two rules conflict.

Rule	Oxidation number
Free element (uncombined), e.g. Na, O_2, P_4	0
Monatomic ion, e.g. Na^+, S^{2-}	equal to the ionic charge (+1, −2)
Group 1 metals / Group 2 metals in compounds	+1 / +2
Fluorine in compounds	−1 (always)
Hydrogen in compounds	+1 (but −1 in metal hydrides, e.g. NaH)

Rule	Oxidation number
Oxygen in compounds	−2 (but −1 in peroxides, +2 in OF_2)
Sum over a neutral compound	0
Sum over a polyatomic ion	equal to the charge on the ion

Stock notation

When an element can take more than one oxidation state, the state is shown as a Roman numeral in brackets after the element name — this is **Stock notation**. It removes ambiguity: iron(II) chloride is $FeCl_2$, iron(III) chloride is $FeCl_3$; copper(I) oxide is Cu_2O, copper(II) oxide is CuO. In oxoanions the numeral refers to the central atom, so sulfate(VI) is SO_4^{2-} and sulfate(IV) (sulfite) is SO_3^{2-}.

Worked example 1 — assigning oxidation numbers

Find the oxidation number of the underlined atom in each species.

(a) S in $H_2\underline{S}O_4$: 2(+1) + S + 4(−2) = 0, so S = +6.

(b) Cr in $\underline{Cr}_2O_7^{2-}$: 2Cr + 7(−2) = −2, so 2Cr = +12 and Cr = **+6**.

(c) N in $N\underline{H}_4^+$: N + 4(+1) = +1, so N = **−3**.

(d) O in $H_2\underline{O}_2$ (a peroxide): the O−O bond makes each O = **−1**, overriding the usual −2.

(e) Fe in $\underline{Fe}_3O_4$: 3Fe + 4(−2) = 0, so Fe = **+8/3** — a fractional average, because the solid is really $FeO{\cdot}Fe_2O_3$ (a mix of +2 and +3 iron).

Using oxidation-number changes to identify redox

Assign oxidation numbers to every atom on both sides of an equation. If any atom changes its oxidation number, the reaction is redox. The atom whose number **rises** is oxidised; the atom whose number **falls** is reduced. If no number changes (as in most acid-base or precipitation reactions), the reaction is not redox.

Worked example 2 — is it redox, and what is oxidised?

Classify each reaction; if redox, name the species oxidised and reduced.

(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Zn: 0 → +2 (oxidised); Cu: +2 → 0 (reduced). **Redox.** Zn is the reducing agent, Cu^{2+} the oxidising agent.

(b) $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Every atom keeps its oxidation number (Ag +1, Cl −1, Na +1, N +5, O −2). **Not redox** — it is a precipitation reaction.

(c) $Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$

Chlorine goes 0 → −1 (in NaCl) *and* 0 → +1 (in NaClO). One element is both oxidised and reduced: this is **disproportionation**.

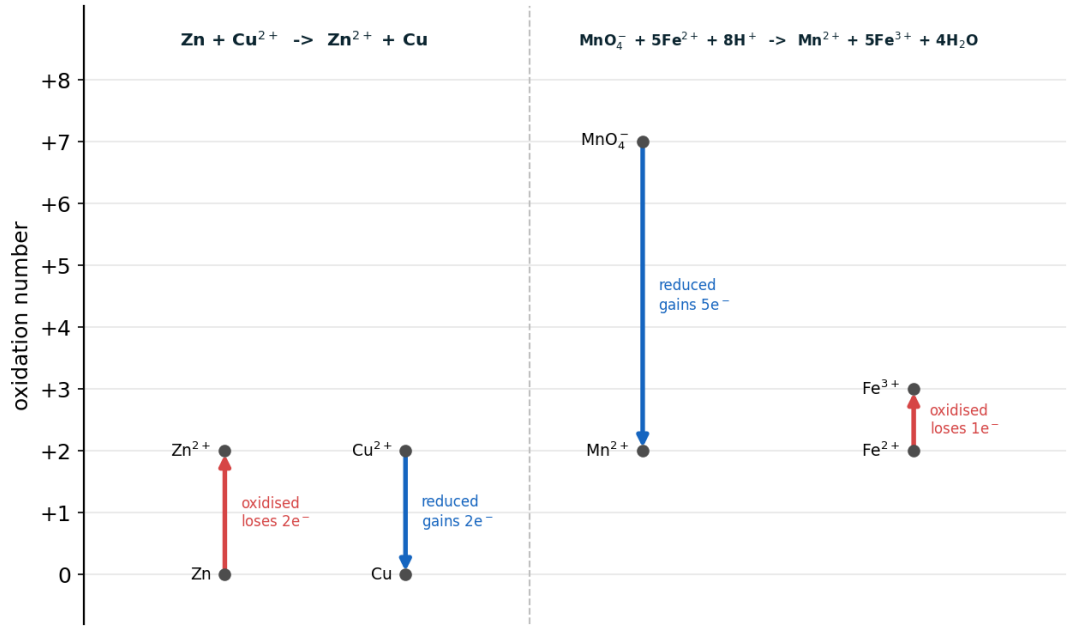

Figure 2.1. Tracking oxidation numbers. In Zn + Cu^{2+}, Zn rises 0 → +2 (oxidised, loses $2e^-$) while Cu falls +2 → 0 (reduced, gains $2e^-$). For MnO_4^- + Fe^{2+}, Mn falls +7 → +2 (gains $5e^-$) and five Fe^{2+} each rise +2 → +3, balancing the 5 electrons.

3. Balancing redox equations by half-equations

A **half-equation** shows one half of a redox process, with the electrons written explicitly. Reduction half-equations have electrons on the left (gained); oxidation half-equations have electrons on the right (lost).

The five-step method (acidic solution)

1. Write the species that change, and balance all atoms except O and H. 2. Balance O by adding H_2O. 3. Balance H by adding H^+. 4. Balance charge by adding electrons (e^-) to the more positive side. 5. Check: atoms balance and the total charge is equal on both sides.

Worked example 3 — a half-equation in acid

Balance the reduction of the manganate(VII) ion, MnO_4^-, to Mn^{2+} in acidic solution.

Step 1 (Mn balanced): $MnO_4^- \rightarrow Mn^{2+}$

Step 2 (O with H_2O): $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

Step 3 (H with H^+): $8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

Step 4 (charge): left = 8(+1) + (−1) = +7; right = +2. Add $5e^-$ to the left:

$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (charge +2 both sides).

Combining half-equations

To build a full ionic equation, multiply each half-equation so that the electrons lost equal the electrons gained, then add the two and cancel the electrons (and any species appearing identically on both sides).

Worked example 4 — combining half-equations

Manganate(VII) oxidises iron(II) in acid. Combine the two half-equations.

Reduction: $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (gains $5e^-$)

Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (loses $1e^-$)

Multiply the iron half-equation by 5 so both involve $5e^-$, then add and cancel electrons:

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Check charge: left = (−1) + 8 + 5(+2) = +17; right = (+2) + 5(+3) = +17. Balanced.

Balancing in basic solution (HL)

In alkaline conditions H^+ cannot appear in the final equation. Balance first *as if acidic*, then neutralise every H^+ by adding the same number of OH^- to **both** sides. The H^+ and OH^- on one side combine to water; cancel any water that then appears on both sides.

Worked example 5 (HL) — a half-equation in base

Balance the reduction of MnO_4^- to MnO_2(s) in basic solution.

Acidic form first: $4H^+ + MnO_4^- + 3e^- \rightarrow MnO_2 + 2H_2O$

Add $4OH^-$ to both sides; the $4H^+ + 4OH^-$ on the left become $4H_2O$:

$4H_2O + MnO_4^- + 3e^- \rightarrow MnO_2 + 2H_2O + 4OH^-$

Cancel $2H_2O$ from each side:

$2H_2O + MnO_4^- + 3e^- \rightarrow MnO_2 + 4OH^-$ (charge −4 both sides).

> **Checkpoint:** A correctly balanced half- or full equation must balance for *both* atoms and charge. Always finish by adding up the charge on each side — it is the fastest way to catch a slip with electrons or H^+.

4. The reactivity series and displacement reactions

Metals differ in how readily they give up electrons to form positive ions. Ranking them by this tendency gives the **reactivity (activity) series**. A more reactive metal is a stronger reducing agent and will displace a less reactive metal from a solution of its ions.

Metal (most → least reactive)	Reaction with water / acid	Tendency to lose e^-
K, Na, Ca	react with cold water; violent with acids	greatest (strongest reducing agents)
Mg, Al, Zn, Fe	slow / no reaction with water; react with dilute acid → H_2	high
Pb, (H), Cu	Pb slowly, Cu not at all, with dilute acid	low
Ag, Au, Pt	unreactive; found native	least (very weak reducing agents)

Metal displacement

If a strip of zinc is placed in blue copper(II) sulfate solution, the blue colour fades and a red-brown deposit of copper forms on the zinc:

$$\mathbf{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

Zinc is above copper in the series, so zinc atoms hand electrons to copper ions: zinc is oxidised, copper(II) is reduced. The reverse experiment — copper in zinc sulfate — does **not** occur, because copper is the weaker reducing agent. This is how the series lets you predict whether a reaction will happen.

Metal-acid reactions

Any metal above hydrogen in the series reduces H^+ from a dilute acid, releasing hydrogen gas:

$$\mathbf{Mg(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2(g)}$$

The rate of effervescence mirrors the ranking: magnesium fizzes vigorously, zinc steadily, iron slowly; copper (below hydrogen) does not react with dilute HCl or H_2SO_4 at all. Metals below hydrogen dissolve only in oxidising acids that attack them by a different route.

Worked example 6 — predicting a displacement

Will a reaction occur when (a) iron is added to silver nitrate solution, (b) silver is added to iron(II) sulfate solution?

(a) Iron is above silver, so iron displaces silver. Reaction occurs:

$Fe(s) + 2Ag^{+}(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$.

(b) Silver is below iron and is a weaker reducing agent, so it cannot displace iron. **No reaction.**

5. The electrochemical series and standard electrode potentials (HL)

The reactivity series is qualitative. Electrochemistry makes the same ordering quantitative through **standard electrode potentials**, E°, measured in volts. Each E° is the potential of a half-cell, written as a reduction, relative to a common reference.

The standard hydrogen electrode (SHE)

Absolute electrode potentials cannot be measured, so all values are quoted against the **standard hydrogen electrode**, defined as exactly 0.00 V. The SHE consists of H_2 gas at 100 kPa bubbled over a platinum electrode dipping in 1 mol dm^{-3} $H^{+}(aq)$ at 298 K:

$$\mathbf{2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g)} \quad \mathbf{E^{\circ} = 0.00\ V}$$

Standard conditions are 298 K, 100 kPa for gases, and 1 mol dm^{-3} for solutions. Under these conditions the measured cell voltage against the SHE gives the E° of the other half-cell.

Reading the electrochemical series

Half-equations are listed as reductions in order of E°. A **more positive** E° means the species on the left is more easily reduced — a stronger oxidising agent. A **more negative** E° means the species on the right is more easily oxidised — a stronger reducing agent.

Reduction half-equation	E° / V	Note
$F_2 + 2e^{-} \rightleftharpoons 2F^{-}$	+2.87	strongest oxidising agent (top)
$Cl_2 + 2e^{-} \rightleftharpoons 2Cl^{-}$	+1.36	strong oxidising agent
$Ag^{+} + e^{-} \rightleftharpoons Ag$	+0.80	
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.34	
$2H^{+} + 2e^{-} \rightleftharpoons H_2$	0.00	reference (SHE)
$Fe^{2+} + 2e^{-} \rightleftharpoons Fe$	−0.44	
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$	−0.76	
$Na^{+} + e^{-} \rightleftharpoons Na$	−2.71	strong reducing agent (Na)
$Li^{+} + e^{-} \rightleftharpoons Li$	−3.04	strongest reducing agent (bottom)

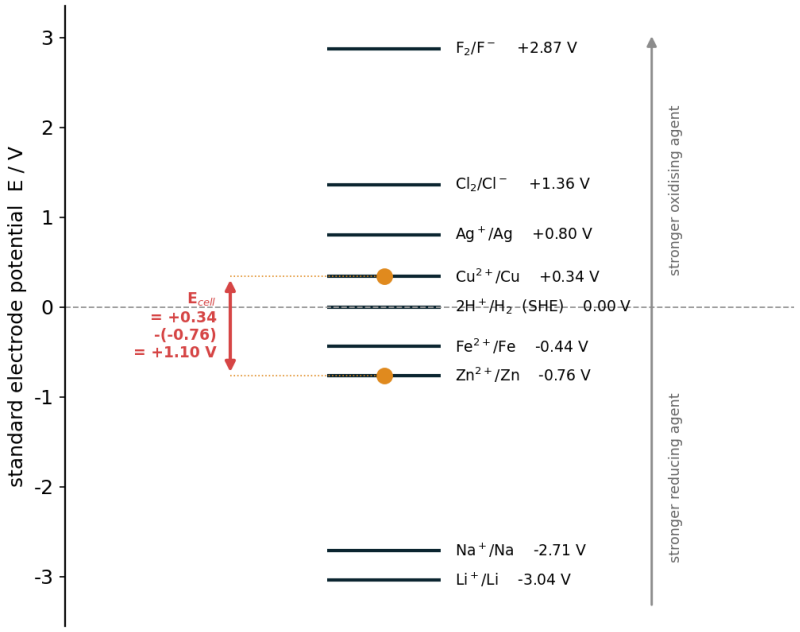

Figure 5.1. Standard electrode potentials E° measured against the SHE (0.00 V); a more positive E° marks a stronger oxidising agent. Pairing Cu (+0.34 V, cathode) with Zn (−0.76 V, anode) gives $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ = (+0.34) − (−0.76) = +1.10 V.

Predicting spontaneity from E°

Combine two half-cells into a full cell. The half-cell with the more positive E° runs as the **reduction** (cathode); the other reverses and runs as the **oxidation** (anode). The standard cell potential is

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

If E°_{cell} is **positive**, the reaction as written is spontaneous under standard conditions (and °G° is negative). If E°_{cell} is negative, the reaction is not spontaneous — the reverse reaction is. A larger positive E°_{cell} means a stronger thermodynamic driving force.

> **Key rule:** A spontaneous redox reaction pairs the stronger oxidising agent (higher E°, reduced) with the stronger reducing agent (lower E°, oxidised). Positive E°_{cell} → it goes.

Worked example 7 (HL) — spontaneity from E°

Use $E^\circ(Cu^{2+}/Cu)$ = +0.34 V and $E^\circ(Zn^{2+}/Zn)$ = −0.76 V to decide whether Zn(s) reacts with $Cu^{2+}(aq)$.

Cu^{2+}/Cu is more positive, so it is the cathode (reduction); Zn^{2+}/Zn is the anode (oxidation), i.e. Zn is oxidised.

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ = (+0.34) − (−0.76) = **+1.10 V**.

Positive, so the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ is **spontaneous** — confirming the displacement of Section 4.

6. Voltaic (galvanic) cells

A **voltaic cell** converts the free energy of a spontaneous redox reaction into electrical energy. It works by physically separating the two half-reactions so that the electrons have to travel through an external wire, where they can do useful work.

Construction

- Two **half-cells**, each a metal electrode dipping in a solution of its own ions (e.g. Zn in $ZnSO_4$, Cu in $CuSO_4$).
- An external **wire** (often through a voltmeter) connecting the electrodes, carrying the electrons.
- A **salt bridge** (e.g. KNO_3 in agar) that completes the circuit by letting ions migrate, keeping each solution electrically neutral.

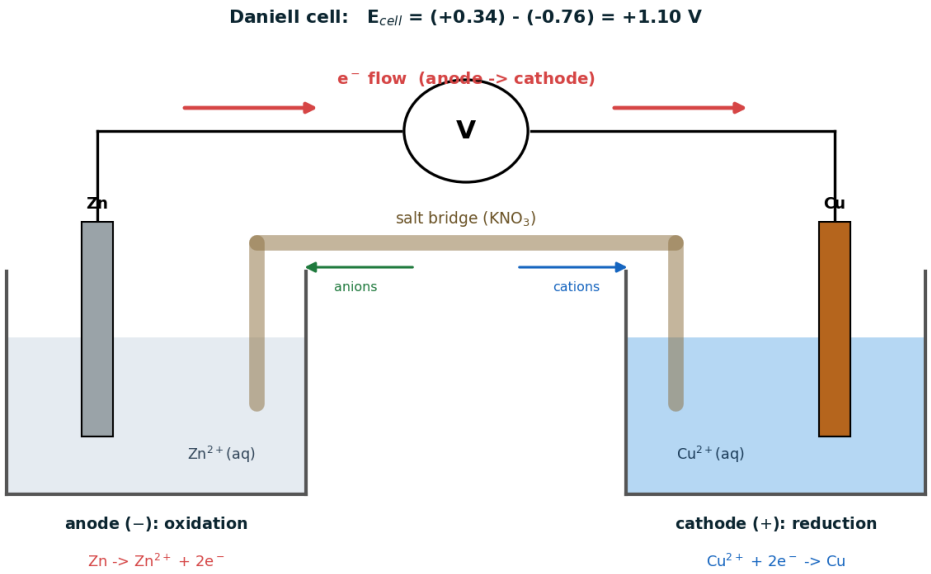

Figure 6.1. The Zn−Cu (Daniell) voltaic cell. Zinc is the anode (−, oxidation) and copper the cathode (+, reduction); electrons flow through the external wire from anode to cathode while ions migrate through the salt bridge. Standard cell potential E°_{cell} = +1.10 V.

Electrode roles and electron flow

Oxidation always happens at the **anode** and reduction at the **cathode** (mnemonic: **AN OX** and **RED CAT**). In a voltaic cell the anode is the **negative** terminal (electrons are released there) and the cathode is the **positive** terminal. Electrons flow through the external wire from anode (−) to cathode (+); in the salt bridge, anions move toward the anode and cations toward the cathode.

	Anode	Cathode
Process	oxidation (loss of e^-)	reduction (gain of e^-)
Sign (voltaic)	negative (−)	positive (+)
Zn/Cu example	$Zn \rightarrow Zn^{2+} + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
Electrode mass	decreases (dissolves)	increases (metal deposits)

Cell diagram (notation)

The cell is summarised by a **cell diagram**: anode on the left, cathode on the right, a single vertical line for a phase boundary and a double line for the salt bridge:

$$\mathbf{Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)}$$

The measured potential difference across the terminals is the **cell potential** (EMF). For the Daniell (Zn/Cu) cell it is +1.10 V under standard conditions.

Worked example 8 (HL) — cell notation and EMF

A voltaic cell is built from Mg^{2+}/Mg ($E^\circ = -2.37$ V) and Ag^{+}/Ag ($E^\circ = +0.80$ V). Give the cell diagram and E°_{cell}.

Ag^{+}/Ag is more positive → cathode (reduction); Mg^{2+}/Mg → anode (oxidation).

$E^\circ_{cell} = (+0.80) - (-2.37) =$ **+3.17 V**.

Cell diagram: **$Mg(s) \mid Mg^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$**. The overall reaction is $Mg + 2Ag^{+} \rightarrow Mg^{2+} + 2Ag$.

Note: although two Ag^{+} are reduced, E° is an intensive property and is **not** multiplied by the coefficient.

7. Electrolytic cells

An **electrolytic cell** does the opposite of a voltaic cell: it uses an external power supply to drive a **non-spontaneous** redox reaction. Electrical energy is converted into chemical energy — for example, decomposing a stable compound into its elements.

The battery pushes electrons onto the **cathode**, making it the **negative** electrode, where cations are reduced; it draws electrons from the **anode**, making it the **positive** electrode, where anions are oxidised. Oxidation is still at the anode and reduction still at the cathode — only the signs are swapped relative to a voltaic cell.

Electrolysis of molten salts

A molten binary ionic compound gives its two elements: the metal at the cathode and the non-metal at the anode. For molten lead(II) bromide:

$$\mathbf{Cathode\ (-):\ Pb^{2+} + 2e^{-} \rightarrow Pb(l)\quad Anode\ (+):\ 2Br^{-} \rightarrow Br_2(g) + 2e^{-}}$$

Electrolysis of aqueous solutions (HL)

In water there is competition, because water itself can be oxidised or reduced. Which ion is discharged (**selective discharge**) depends on the electrode potentials, the concentration of the solution, and the nature of the electrode.

Electrode	Species competing	General outcome
Cathode (−)	metal cation vs H_2O/H^{+}	less reactive metals (below H, e.g. Cu, Ag) deposit; very reactive metals (K, Na, Ca, Al) stay in solution and H_2 is released

Electrode	Species competing	General outcome
Anode (+)	anion vs H_2O/OH^-	with inert electrodes: concentrated halides give the halogen; dilute or oxoanion solutions (SO_4^{2-}, NO_3^-) give O_2

So dilute sulfuric acid (or Na_2SO_4) gives H_2 at the cathode and O_2 at the anode — the net electrolysis of water. Concentrated NaCl (brine) gives H_2 at the cathode and Cl_2 at the anode, leaving NaOH in solution.

Inert vs active electrodes

Inert electrodes (graphite, platinum) only carry current. **Active** electrodes take part: in copper refining with copper electrodes, the anode dissolves ($Cu \rightarrow Cu^{2+} + 2e^-$) and pure copper plates onto the cathode. Choosing an active electrode can change the anode product entirely.

Voltaic vs electrolytic — a comparison

Feature	Voltaic (galvanic) cell	Electrolytic cell
Energy change	chemical → electrical	electrical → chemical
Reaction	spontaneous ($E^\circ_{cell} > 0$)	non-spontaneous (driven by supply)
Anode sign	negative (−)	positive (+)
Cathode sign	positive (+)	negative (−)
Anode process	oxidation	oxidation
Cathode process	reduction	reduction
Electrolyte	two half-cells + salt bridge	single molten/aqueous electrolyte

> **Exam trap:** In *both* cells the anode is where oxidation happens and the cathode is where reduction happens — that never changes. What flips is the *sign*: the anode is − in a voltaic cell but + in an electrolytic cell.

Quantitative electrolysis — Faraday's laws (HL)

The amount of product is proportional to the charge passed. Charge is

$$Q = It \text{ (charge / C = current / A} \times \text{time / s)}$$

One mole of electrons carries the **Faraday constant**, $F \approx 96500$ C mol^{-1}. So the moles of electrons passed = Q / F. Combine this with the electrode half-equation, which gives the mole ratio of electrons to product.

$$\text{moles of } e^- = It / F$$

Worked example 9 (HL) — a Faraday calculation

A current of 1.50 A flows for 45.0 minutes through molten $CuCl_2$. What mass of copper is deposited at the cathode? (F = 96500 C mol^{-1}; A_r Cu = 63.5)

Charge: $Q = It = 1.50 \times (45.0 \times 60) = 1.50 \times 2700 = 4050$ C.

Moles of electrons = $Q/F = 4050 / 96500 = 0.0420$ mol.

Cathode half-equation: $Cu^{2+} + 2e^- \rightarrow Cu$, so moles of Cu = 0.0420 / 2 = 0.0210 mol.

Mass = 0.0210 × 63.5 = **1.33 g of copper**.

Worked example 10 (HL) — gas volume at an electrode

In the same cell, what volume of chlorine (at STP, molar volume 22.7 dm^3 mol^{-1}) is produced at the anode over the 45.0 minutes?

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$. Moles of e^- = 0.0420 mol (same charge), so moles of Cl_2 = 0.0210 mol.

Volume = 0.0210 × 22.7 = **0.477 dm^3** (about 477 cm^3).

8. Applications of electron transfer

Rusting of iron

Rusting is the electrochemical corrosion of iron: it needs both oxygen and water. Part of the iron surface acts as an anode where iron is oxidised, and another part acts as a cathode where oxygen is reduced:

$$\textbf{Anode: } Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad \textbf{Cathode: } O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The Fe^{2+} is further oxidised by oxygen to hydrated iron(III) oxide, $Fe_2O_3 \cdot xH_2O$ — the flaky brown solid we call rust. Salt speeds corrosion by raising the conductivity of the solution.

Preventing rust: sacrificial protection

- **Barrier methods** (paint, oil, plastic, galvanising with zinc) keep out oxygen and water.
- **Sacrificial protection**: attach a more reactive metal such as zinc or magnesium. Being the stronger reducing agent, it is oxidised in preference to the iron, so the iron is protected even if the coating is scratched. Blocks of zinc bolted to ship hulls and underground pipelines work this way.
- **Galvanising** combines both ideas: the zinc layer is a barrier *and* a sacrificial anode.

Electroplating

Electroplating uses electrolysis to coat an object with a thin layer of metal for protection or appearance. The object to be plated is the **cathode**; the plating metal is the anode; the electrolyte contains ions of that metal. To silver-plate a spoon, the spoon is the cathode in silver nitrate solution with a silver anode:

$$\textbf{Cathode: } Ag^+(aq) + e^- \rightarrow Ag(s) \quad \textbf{Anode: } Ag(s) \rightarrow Ag^+(aq) + e^-$$

Metal extraction

The position of a metal in the reactivity series decides how it is extracted. Very reactive metals (K, Na, Ca, Mg, Al) hold their ions too strongly to be reduced by carbon, so they are obtained by **electrolysis** of a molten compound — aluminium from molten Al_2O_3, sodium from molten NaCl. Less reactive metals such as iron and zinc are reduced from their ores by carbon (a cheaper chemical reducing agent) in a furnace, while the least reactive metals (Au, Ag, Pt) occur native or need only gentle treatment.

9. Common pitfalls

- Forgetting the exceptions to the oxygen and hydrogen rules: O is -1 in peroxides and +2 in OF_2; H is -1 in metal hydrides.
- Mixing up the agents: the **oxidising** agent is the species **reduced**, and the **reducing** agent is the species **oxidised**.
- Balancing charge before atoms, or forgetting to check total charge at the end of a half-equation.
- Assuming the anode is always negative. It is − in a voltaic cell but + in an electrolytic cell; only "oxidation at the anode" is constant.
- Multiplying E° by the stoichiometric coefficient when combining half-cells. E° is intensive and is never scaled.
- Using minutes instead of seconds in $Q = It$, or forgetting to divide by the number of electrons in the electrode half-equation.
- Predicting aqueous electrolysis products without checking concentration — concentrated NaCl gives Cl_2, but very dilute NaCl gives O_2.

10. Quick reference

Idea	Statement
OIL RIG	Oxidation Is Loss, Reduction Is Gain (of electrons).
Oxidising agent	is reduced (gains e^-); reducing agent is oxidised (loses e^-).
Half-equation balancing	atoms; O with H_2O; H with H^+; charge with e^- (then OH^- for base, HL).
Displacement	a more reactive metal displaces a less reactive metal from solution.
Spontaneity (HL)	$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$; positive → spontaneous.
Electrode processes	AN OX (oxidation at anode); RED CAT (reduction at cathode) — in both cell types.
Cell signs	voltaic: anode −, cathode +. electrolytic: anode +, cathode −.
Cell notation	anode | anode ion || cathode ion | cathode.
Faraday (HL)	$Q = It$; moles $e^- = Q/F$; $F \approx 96500$ C mol^{-1}.

11. Test yourself

Attempt all ten without notes, then check against the full answers that follow.

1. Find the oxidation number of chlorine in (a) Cl_2, (b) NaCl, (c) ClO_3^-, (d) ClO_4^-.

2. In the reaction $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$, identify the species oxidised, the species reduced, the oxidising agent and the reducing agent.

3. Balance in acid: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (a reduction half-equation).

4. Combine the half-equations $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ and $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ into a full ionic equation.

5. Using the series in Section 5, will Cu(s) react with dilute HCl? Explain with E° values.

6. (HL) A cell is made from Ni^{2+}/Ni ($E^\circ = -0.26$ V) and Ag^+/Ag ($E^\circ = +0.80$ V). Give the cell diagram, state the electron flow direction, and calculate E°_{cell}.

7. Predict the products of electrolysing molten KBr, giving both electrode half-equations.

8. (HL) Predict the products of electrolysing dilute aqueous Na_2SO_4 with inert electrodes, and name the overall change.

9. (HL) A current of 2.00 A is passed through molten Al_2O_3 for 1.00 hour. Find the mass of aluminium deposited. (A_r Al = 27.0; F = 96500 C mol^{-1})

10. Explain, with half-equations, why bolting blocks of magnesium to a steel ship's hull protects it from rusting.

Answers

1. (a) 0 (free element); (b) −1; (c) in ClO_3^-: Cl + 3(−2) = −1, so Cl = **+5**; (d) in ClO_4^-: Cl + 4(−2) = −1, so Cl = **+7**.

2. Al: 0 → +3, oxidised (the reducing agent). Cu: +2 → 0, reduced. Cu^{2+} is the oxidising agent; Al is the reducing agent.

3. Balance Cr (2), O with $7H_2O$, H with $14H^+$, charge with $6e^-$: **$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$** (charge +6 both sides).

4. Balance electrons: ×2 the MnO_4^- half ($10e^-$) and ×5 the $C_2O_4^{2-}$ half ($10e^-$), add and cancel: **$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$.**

5. No. Copper ($E^\circ = +0.34$ V) lies below hydrogen (0.00 V), so H^+ cannot oxidise Cu; E°_{cell} for Cu + $2H^+$ would be 0.00 − 0.34 = −0.34 V (negative, non-spontaneous).

6. Ag^+/Ag is more positive → cathode; Ni is the anode (oxidised). Electrons flow through the wire from Ni to Ag. E°_{cell} = (+0.80) − (−0.26) = **+1.06 V**. Diagram: **Ni(s) | Ni^{2+}(aq) || Ag^+(aq) | Ag(s)**.

7. Cathode: $K^+ + e^- \rightarrow K(l)$; Anode: $2Br^- \rightarrow Br_2(g) + 2e^-$. Products: potassium metal and bromine.

8. Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (Na^+ too reactive to discharge); Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (SO_4^{2-} not discharged). Overall this is the **electrolysis of water** — H_2 and O_2 in a 2:1 ratio.

9. $Q = It = 2.00 \times 3600 = 7200$ C; moles e^- = 7200/96500 = 0.0746 mol. $Al^{3+} + 3e^- \rightarrow Al$, so moles Al = 0.0746/3 = 0.0249 mol; mass = 0.0249 × 27.0 = **0.671 g**.

10. Magnesium is above iron in the series (stronger reducing agent), so it is oxidised in preference: $Mg \rightarrow Mg^{2+} + 2e^-$. The electrons it releases flow into the steel, keeping the iron reduced, so $Fe \rightarrow Fe^{2+}$ is suppressed. The magnesium is the **sacrificial anode** and corrodes instead of the hull.