

Chapter 2 · Electrochemistry

CBSE Class 12 Chemistry (043) · Physical · Unit 2 = 9 marks (the highest in the paper) · Ultimate Revision Sheet

60-SECOND RECALL

Galvanic cell	Chemical → electrical · anode -ve, cathode +ve · oxidation at anode
Electrolytic cell	Electrical → chemical · anode +ve, cathode -ve
Cell EMF	$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
Nernst	$E = E^\circ - (0.059/n) \log Q$ at 298 K
At equilibrium	$E_{\text{cell}} = 0$ · $E^\circ = (0.059/n) \log K_c$
Thermodynamics	$\Delta G^\circ = -nFE^\circ$ · $F = 96500 \text{ C mol}^{-1}$
Molar conductivity	$\Lambda_m = \kappa \times 1000/M$ · rises on dilution for both types
Faraday	$w = ZIt$ · $w = (M/nF) \times It$

1. The Two Cells

THE COMPARISON — get the signs right

Basis	GALVANIC (voltaic)	ELECTROLYTIC
Conversion	Chemical → electrical	Electrical → chemical
Reaction	Spontaneous , ΔG negative	Non-spontaneous , driven by a battery
Anode	Negative , oxidation	Positive , oxidation
Cathode	Positive , reduction	Negative , reduction

In **BOTH** cells oxidation always happens at the anode and reduction at the cathode. Only the signs swap. That sentence answers the most common trap in this chapter.

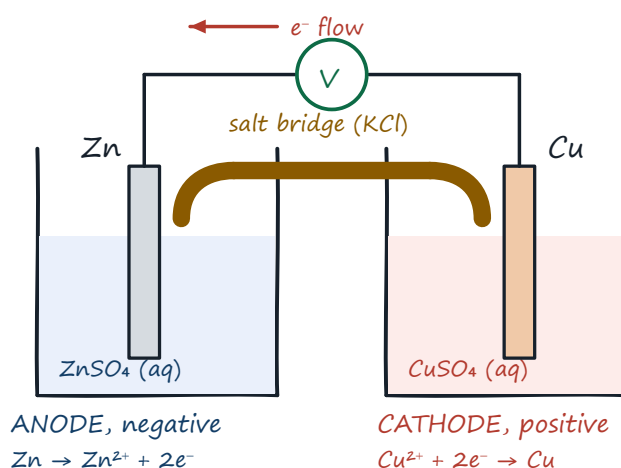
CELL REPRESENTATION



Anode on the **LEFT**, cathode on the right; **||** is the salt bridge.

Salt bridge: completes the circuit, and **maintains electrical neutrality** in the two half-cells by supplying ions. Without it the cell stops almost at once.

Daniell cell



READING THE CELL



Cell notation always puts the **ANODE** on the left. The salt bridge does two jobs: it keeps both solutions electrically neutral, and it completes the circuit.

Oxidation is at the anode in **BOTH** kinds of cell. What flips in an electrolytic cell is only the sign — there the anode is positive. That is the trap this diagram exists to kill.

$\Delta G^\circ = -nFE^\circ$, so a positive E° means a spontaneous cell.

2. Electrode Potential and EMF

FORMULAS

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \text{ (both as reduction potentials)}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \quad E^\circ \text{ positive} \Rightarrow \Delta G^\circ \text{ negative} \Rightarrow \text{spontaneous}$$

SHE (standard hydrogen electrode) is the reference, assigned $E^\circ = 0.00 \text{ V}$ exactly, at 1 bar H_2 , 1 M H^+ , 298 K.

More positive $E^\circ \rightarrow$ stronger **oxidising agent**, more easily reduced (F_2 is highest at +2.87 V).

More negative $E^\circ \rightarrow$ stronger **reducing agent** (Li is lowest at -3.05 V).

3. Nernst Equation

FORMULAS

$$E = E^\circ - \frac{RT}{nF} \ln Q \rightarrow \text{at 298 K: } E = E^\circ - \frac{0.059}{n} \log Q$$

$$\text{For } \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu: } E = E^\circ - \frac{0.059}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

$$\text{At equilibrium } E_{\text{cell}} = 0 \text{ and } Q = K_c, \text{ so } E^\circ = \frac{0.059}{n} \log K_c$$

TRAP Solids and pure liquids never appear in Q — only ion concentrations and gas pressures do.

Increasing the concentration of the **product** ion lowers E ; increasing the **reactant** ion raises it.
When the cell is fully discharged, $E_{\text{cell}} = 0$, not E° .

4. Conductance

THE THREE QUANTITIES

Conductance $G = 1/R$ (siemens, S)

Conductivity $\kappa = G \times (l/A)$ $l/A = \text{cell constant, unit } m^{-1}$

Molar conductivity $\Lambda_m = \kappa \times 1000 / M$ (M in $mol\ L^{-1}$)

ON DILUTION — the graph question Conductivity κ **DECREASES** on dilution — fewer ions per unit volume.

Molar conductivity Λ_m **INCREASES** on dilution — the total volume containing one mole increases.

Strong electrolyte (KCl): Λ_m rises slowly and linearly; Λ_m° is found by **extrapolating** the graph — Debye-Hückel-Onsager: $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$.

Weak electrolyte (CH_3COOH): Λ_m rises steeply near infinite dilution; the graph cannot be extrapolated, so Λ_m° must come from Kohlrausch's law.

KOHLRAUSCH'S LAW The limiting molar conductivity of an electrolyte is the **sum of the individual contributions of its ions**.

$$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) - \Lambda_m^\circ(NaCl)$$

$$\text{Degree of dissociation } \alpha = \Lambda_m / \Lambda_m^\circ$$

5. Electrolysis and Faraday's Laws

FORMULAS

First law: $w \propto Q \rightarrow w = ZIt$ ($Z = \text{electrochemical equivalent}$)

Second law: $w_1/w_2 = E_1/E_2$ (same charge, equivalent masses)

$w = (M \times I \times t) / (n \times 96500)$ — the form to actually use

1 faraday = 96500 C = charge on 1 mole of electrons.

6. Batteries, Fuel Cells and Corrosion

THE FOUR SYSTEMS

System	Key points
Dry cell (primary)	Anode Zn , cathode graphite in $\text{MnO}_2 + \text{NH}_4\text{Cl}$ paste. $\sim 1.5 \text{ V}$. Cannot be recharged.
Lead storage battery (secondary)	Anode Pb , cathode PbO_2 , electrolyte H_2SO_4 . Rechargeable ; used in cars.
Fuel cell	$\text{H}_2\text{-O}_2$ cell with porous carbon electrodes and KOH. Efficiency $\sim 70\%$. Product is only water , so it is pollution-free. Used in Apollo space programme .
Corrosion	An electrochemical process. Iron acts as anode (oxidised to Fe^{2+}), oxygen reduced at cathode; rust is hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

Preventing corrosion: barrier coating (paint, grease) · **galvanisation** (zinc coating) · **cathodic protection** with a sacrificial Mg or Zn block · alloying (stainless steel).

WORKED EXAMPLE For the Daniell cell, $E^\circ_{\text{Cu}} = +0.34 \text{ V}$, $E^\circ_{\text{Zn}} = -0.76 \text{ V}$. Find E°_{cell} and ΔG° .

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

$$n = 2 \text{ (Zn} \rightarrow \text{Zn}^{2+} + 2e^-)$$

$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.10 = -212,300 \text{ J} = -212.3 \text{ kJ mol}^{-1}$$

Negative, so the reaction is **spontaneous** — as it must be for a galvanic cell.

7. Question Triggers which formula the wording wants

If the question says...	Use
"concentrations are not 1 M"	Nernst equation
"calculate the equilibrium constant of a cell reaction"	$E^\circ = (0.059/n) \log K_c$
"is the reaction spontaneous?"	$\Delta G^\circ = -nFE^\circ$; E° positive $\rightarrow$ yes
"mass deposited at an electrode"	$w = MIt/nF$
" Λ°_m of a weak electrolyte"	Kohlrausch's law — cannot extrapolate
"why does κ fall but Λ_m rise on dilution"	Ions per volume vs ions per mole
"cell has stopped working / is dead"	$E_{\text{cell}} = 0$, equilibrium reached
"rust formula"	$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

MOST-ASKED BOARD QUESTIONS

- [3M]** Write the **Nernst equation** and calculate E_{cell} for given concentrations.
- [3M]** Explain how κ and Λ_m vary with dilution for a strong and a weak electrolyte; sketch both graphs.
- [3M]** State **Kohlrausch's law** and use it to find Λ°_m of acetic acid and its degree of dissociation.
- [2M]** Relate ΔG° , E° and K_c .
- [2M]** Describe the **$\text{H}_2\text{-O}_2$ fuel cell** and give two advantages.
- [2M]** Explain **corrosion** as an electrochemical process and give two prevention methods.

7. [1M] What is the function of a salt bridge?

THE HABIT THAT SCORES — Before any Nernst calculation, write $n = ?$ and the balanced half-reactions. Getting n wrong changes every subsequent digit, and it is the single most common error in the highest-weighted chapter of the paper.