Unit 2: Electrochemistry

Engineering Chemistry — DI01000071

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April 2, 2026

Unit 2 — Overview

Syllabus Topics

2.1 Oxidation & Reduction (Redox)
2.2 Electrochemical Cells
2.3 Standard Electrode Potential & EMF
2.4 Nernst Equation
2.5 Conductance & Kohlrausch's Law
2.6 Faraday's Laws of Electrolysis
2.7 Applications of Electrolysis

Weightage: $\approx 14\%$

Teaching Hrs: ≈ 7 hrs

Section 2.1
Oxidation & Reduction

Oxidation · Reduction · Redox Reactions · Oxidation Numbers

OIL RIG: Oxidation Is Loss, Reduction Is Gain

Oxidation & Reduction — Electronic Concept

Oxidation

Loss of electrons

Increase in oxidation state

Example:
$Zn \rightarrow Zn^{2+} + 2e^{-}$

Oxidation = **O**-**I**-**L**

Reduction

Gain of electrons

Decrease in oxidation state

Example:
$Cu^{2+} + 2e^{-} \rightarrow Cu$

Reduction = **R**-**I**-**G**

OIL RIG Mnemonic

Oxidation **I**s **L**oss **R**eduction **I**s **G**ain — always occur simultaneously

Redox Reactions

Definition

Reactions involving **simultaneous oxidation and reduction**. The substance that loses electrons is the **reducing agent**; the substance that gains electrons is the **oxidizing agent**.

Example: $Zn + CuSO_4$ (PYQ – Su'23)

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

$Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation; Zn = reducing agent)

$Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction; Cu^{2+} = oxidizing agent)

Oxidation Numbers — Rules

Rules for Assigning Oxidation Number

R1	Free element: ON $= 0$ (e.g., Fe, O_2, Cl_2)
R2	Monoatomic ion: ON $=$ charge ($Na^+ = +1$, $Cl^- = -1$)
R3	Oxygen: ON $= -2$ (except peroxides: -1; OF_2: $+2$)
R4	Hydrogen: ON $= +1$ (except metal hydrides: -1)
R5	Sum of ON in compound $= 0$; in ion $=$ ion charge

Example: $K_2Cr_2O_7$

$$2(+1) + 2x + 7(-2) = 0 \Rightarrow x = +6$$

Cr has oxidation number **+6**

Section 2.2
Electrochemical Cells

Galvanic Cell (Daniel Cell) · Electrolytic Cell
Salt Bridge · Cell Notation · EMF

Galvanic Cell — Daniel Cell (PYQ – W'23, Su'24)

Construction

Anode (−): Zn rod in $ZnSO_4$ solution

Cathode (+): Cu rod in $CuSO_4$ solution

Connected by **salt bridge** and external wire

Reactions

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

Overall: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Cell notation: $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$

EMF

$E_{cell} = E_{cathode} - E_{anode} = 0.34 - (-0.76) = \mathbf{1.10\,V}$

Salt Bridge — Functions & Composition

What is a Salt Bridge?

A U-shaped tube filled with concentrated **KCl or NH_4NO_3 in agar-agar** gel, connecting the two half-cells.

Functions

1. Completes the internal circuit by allowing ion flow
2. Maintains **electrical neutrality** in both half-cells
3. Prevents direct mixing of the two electrolyte solutions
4. Minimises liquid junction potential

Without Salt Bridge

Cell reaction stops quickly due to charge build-up; no sustained current flow.

Electrolytic Cell

Definition

A cell in which **electrical energy drives a non-spontaneous** chemical (redox) reaction. Requires external power supply.

Anode (+)

Connected to positive terminal of battery

Oxidation occurs

Anions discharge here

Cathode (−)

Connected to negative terminal of battery

Reduction occurs

Cations discharge here

Applications

Electroplating, electro-refining, electrometallurgy, electrolysis of water/NaCl

Galvanic vs Electrolytic Cell

Feature	Galvanic Cell	Electrolytic Cell
Energy conversion	Chemical $\rightarrow$ Electrical	Electrical $\rightarrow$ Chemical
Reaction	Spontaneous ($\Delta G < 0$)	Non-spontaneous ($\Delta G > 0$)
External supply	Not required	Required
Anode polarity	Negative ($-$)	Positive ($+$)
Cathode polarity	Positive ($+$)	Negative ($-$)
Example	Daniel cell, battery	Electroplating, electrolysis

Standard Electrode Potential & Electrochemical Series

Definition

Potential of a half-cell measured relative to **Standard Hydrogen Electrode (SHE)** at 298 K, 1 atm, 1 M concentration.

Selected Reduction Potentials (E°/V)

Half-reaction	E° (V)
$Li^+ + e^- \rightarrow Li$	-3.04
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$2H^+ + 2e^- \rightarrow H_2$	0.00 (SHE)
$Cu^{2+} + 2e^- \rightarrow Cu$	$+0.34$
$Ag^+ + e^- \rightarrow Ag$	$+0.80$

Standard Hydrogen Electrode (SHE)

Construction

- Platinum electrode coated with platinum black
- Immersed in 1 M HCl ($H^+ = 1\,M$)
- H_2 gas bubbled at 1 atm, 298 K
- Standard potential = **0.00 V** (reference)

Half-Cell Reaction

$$\text{Oxidation: } H_2 \rightarrow 2H^+ + 2e^- \quad (E^\circ = 0.00\,V)$$

$$\text{Reduction: } 2H^+ + 2e^- \rightarrow H_2 \quad (E^\circ = 0.00\,V)$$

Nernst Equation (PYQ – W'24, Su'25)

Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q \quad \text{(at 298K)}$$

Terms

E°_{cell}	Standard EMF (V)
R	Gas constant (8.314 J/mol K)
T	Temperature (K)
n	No. of electrons transferred
F	Faraday's constant (96485 C/mol)
Q	Reaction quotient

Nernst Equation — Solved Example (PYQ – W'24)

Problem

Calculate E_{cell} for Daniel cell at 298 K when $[Zn^{2+}] = 0.1\,\text{M}$ and $[Cu^{2+}] = 0.01\,\text{M}$.
$E^\circ(Zn^{2+}/Zn) = -0.76\,\text{V}; \quad E^\circ(Cu^{2+}/Cu) = +0.34\,\text{V}$

Solution

$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10\,\text{V}; \quad n = 2$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01} = 10$$

$$E = 1.10 - \frac{0.0592}{2}\log 10 = 1.10 - 0.0296 = \mathbf{1.07\,V}$$

Section 2.5
Conductance of Electrolytic Solutions

Resistance · Conductance · Conductivity

Molar Conductance · Kohlrausch's Law

Resistance, Conductance & Conductivity

Quantity	Definition	Formula	Unit
Resistance (R)	Opposition to current flow	$R = \rho\, l/A$	Ω
Conductance (G)	Reciprocal of resistance	$G = 1/R$	S (siemen)
Resistivity (ρ)	Resistance per unit cross-section	$\rho = R\,A/l$	Ω·cm
Conductivity (κ)	Conductance per unit length	$\kappa = 1/\rho$	S/cm

Key

κ increases with concentration (more ions). But molar conductance *decreases* with concentration due to interionic attraction.

Molar Conductance (Λ_m)

Definition & Formula

Conductance of a solution containing **1 mole of electrolyte** placed between electrodes 1 cm apart

$$\Lambda_m = \frac{\kappa \times 1000}{C} \quad (\mathrm{S\,cm^2/mol})$$

where C is concentration in mol/L

Strong Electrolyte

Λ_m increases slowly
on dilution (Kohlrausch)

Weak Electrolyte

Λ_m rises sharply
at high dilution (ionization)

Kohlrausch's Law of Independent Migration

Statement (PYQ – W'25)

"At infinite dilution, each ion migrates **independently** and contributes a definite amount to the molar conductance."

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

Application: CH_3COOH (PYQ – Su'24)

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

Used to find Λ_m° of **weak electrolytes** (cannot be measured directly)

Applications of Conductance Measurements

Application	**Principle**
Degree of ionization	$\alpha = \Lambda_m / \Lambda_m^\circ$
Ionization constant (K_a)	$K_a = C\alpha^2/(1-\alpha)$
Solubility of sparingly sol. salt	From conductivity of saturated soln.
Conductometric titration	Endpoint = minimum conductance
Water purity testing	Pure water: very low conductivity

Conductometric Titration

Strong acid + strong base: conductance drops to minimum at equivalence point, then rises with excess base.

Section 2.6

Faraday's Laws of Electrolysis

First Law ($m \propto Q$) · Second Law ($m \propto E_w$)

Faraday's Constant $F = 96485\,\mathrm{C/mol} \approx 96500\,\mathrm{C/mol}$

Faraday's First Law of Electrolysis

Statement

"The mass of substance deposited/liberated at an electrode is **directly proportional to the quantity of charge** passed."

$$m = Z \cdot Q = Z \cdot I \cdot t$$

Terms

m	Mass deposited (g)
Z	Electrochemical equivalent (g/C)
Q	Charge $= I \times t$ (coulombs)
I	Current (A); $t =$ time (s)
Z	$= E_w/F = M_w/(n \cdot F)$

Faraday's Second Law of Electrolysis

Statement

"When the same quantity of charge is passed through different electrolytic solutions, the masses deposited are **proportional to their equivalent weights**."

$$\frac{m_1}{m_2} = \frac{E_{w1}}{E_{w2}}$$

Example (PYQ – Su'23)

Same charge through $CuSO_4$ & $AgNO_3$ in series:

$$\frac{m_{Cu}}{m_{Ag}} = \frac{E_w(Cu)}{E_w(Ag)} = \frac{31.75}{108} = 0.294$$

If 1.08 g Ag deposited $\Rightarrow$ 0.318 g Cu deposited

Faraday's Law Numericals (PYQ – W'25, Su'25)

Problem 1

Find mass of Cu deposited by 2 A for 1 hr from $CuSO_4$.

$Q = 2 \times 3600 = 7200\,\text{C}; \quad E_w(\text{Cu}) = 31.75$

$$m = \frac{E_w \times Q}{96500} = \frac{31.75 \times 7200}{96500} = \mathbf{2.37\,g}$$

Problem 2

Find time to deposit 1 g Ag by 0.5 A from $AgNO_3$.

$$m = ZQ \Rightarrow t = \frac{m \times 96500}{E_w \times I} = \frac{1 \times 96500}{108 \times 0.5} = \mathbf{1787\,s}$$

Electrolysis of Water

Setup

Dilute H_2SO_4 or NaOH used to increase conductivity. Pt electrodes.

Reactions

Cathode (−): $4H^+ + 4e^- \rightarrow 2H_2 \uparrow$ (reduction)

Anode (+): $2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-$ (oxidation)

Overall: $2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$

Volume Ratio

$H_2 : O_2 = \mathbf{2 : 1}$ (by volume). H_2 collected at cathode; O_2 at anode.

Electro-Refining (PYQ – W'23, Su'24)

Principle

Purification of metals using electrolysis. **Impure metal = anode**; **pure metal = cathode**; electrolyte = salt of same metal.

Copper Refining

Anode: Impure Cu $\rightarrow Cu^{2+} + 2e^-$ (dissolves)

Cathode: $Cu^{2+} + 2e^- \rightarrow$ Cu (pure, deposits)

Anode mud: Ag, Au, Pt settle below anode (valuable by-product)

Electrolyte: $CuSO_4 + H_2SO_4$

Other Metals

Ag, Au, Ni, Pb, Zn are also refined by same principle.

Electroplating (PYQ – Su'23, W'24)

Principle

Depositing a thin layer of metal on another object to improve **appearance, corrosion resistance, or surface hardness**. Object to be plated = **cathode**; plating metal = **anode**.

Silver Plating Example

Component	Detail
Cathode	Object to be plated (e.g., Cu spoon)
Anode	Pure silver rod
Electrolyte	AgCN in KCN solution
Reaction (cathode)	$Ag^+ + e^- \rightarrow Ag$
Reaction (anode)	$Ag \rightarrow Ag^+ + e^-$

Electrometallurgy

Definition

Extraction of metals from their ores using electrolysis. Used for highly electropositive metals (cannot be reduced by carbon/H_2).

Important Examples

Metal	Ore/Source	Process
Al	Alumina (Al_2O_3)	Hall-Héroult (molten cryolite)
Na	NaCl (molten)	Down's cell
Mg	$MgCl_2$ (molten)	Electrolysis of molten salt
Cu	$CuSO_4$ (aq.)	Electrolytic deposition

Electrolysis of Aqueous NaCl (Brine)

Reactions (PYQ – Su'24)

Cathode: $2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$

Anode: $2Cl^- \rightarrow Cl_2 \uparrow + 2e^-$

Overall (Chlor-alkali process):
$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$

Products & Uses

Cl_2: PVC, bleaching powder, disinfectants

H_2: Fuel, NH_3 synthesis, hydrogenation

NaOH: Soap, paper, textiles, alumina processing

Unit 2 — Mid-Point Summary (Frames 1–30)

Topic	Key Point
Oxidation/Reduction	OIL RIG; simultaneous
Daniel cell	$E = 1.10\,\text{V}$; Zn anode, Cu cathode
Salt bridge	Maintains neutrality
SHE	Reference; $E^\circ = 0.00\,\text{V}$
Nernst equation	$E = E^\circ - (0.0592/n)\log Q$
Conductance	$G = 1/R$; $\kappa = 1/\rho$
Kohlrausch's law	$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$
Faraday's 1st law	$m = ZIt$
Faraday's 2nd law	$m_1/m_2 = E_{w1}/E_{w2}$
Electro-refining	Impure anode $\rightarrow$ pure cathode

EMF & Gibbs Free Energy

Relationship

$\Delta G = -nFE_{\text{cell}}$ (at standard conditions: $\Delta G^\circ = -nFE^\circ_{\text{cell}}$)

Symbol	Meaning
n	number of electrons transferred
F	Faraday constant $= 96500\,\text{C mol}^{-1}$
E_{cell}	cell EMF (V)
ΔG	Gibbs free energy (J)

Spontaneity

$E > 0$	$\Delta G < 0$ (spontaneous)
$E = 0$	$\Delta G = 0$ (equilibrium)
$E < 0$	$\Delta G > 0$ (non-spont.)

Equilibrium Link

$$\Delta G^\circ = -RT \ln K$$

$$\Rightarrow E^\circ = \frac{RT}{nF} \ln K$$

At 298 K: $E^\circ = \dfrac{0.0592}{n} \log K$

Electrochemical Series — Applications

Standard Reduction Potential Order

$Li^+ < K^+ < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Ni^{2+} < H^+ < Cu^{2+} < Ag^+ < Au^{3+}$

Application	Rule
Displacement reactions	Higher activity metal displaces lower (Zn displaces Cu from $CuSO_4$)
Predicting cell reaction	More –ve E° = anode; more +ve = cathode
Electroplating order	Use cathode as base metal, anode as coating metal
Corrosion tendency	Metals above H in series dissolve more readily

Example: Can Zn displace Cu?

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

$E^\circ_{cell} = 0.34 - (-0.76) = +1.10\,V > 0$ **Yes, spontaneous.**

Concentration Cells

Definition

A cell in which **both electrodes are identical** but immersed in solutions of **different concentrations**. EMF arises due to concentration difference (not chemical difference).

Cell Notation

$\mathrm{Cu}|c_1||\mathrm{Cu}^{2+}|c_2|\mathrm{Cu}$

Anode: lower conc. (c_1)

Cathode: higher conc. (c_2)

Nernst for Conc. Cell

$$E = \frac{0.0592}{n} \log \frac{c_2}{c_1}$$

$E^\circ = 0$ (same electrodes)

Example: Cu–Cu cell, $c_1 = 0.01\,\mathrm{M}$, $c_2 = 0.1\,\mathrm{M}$

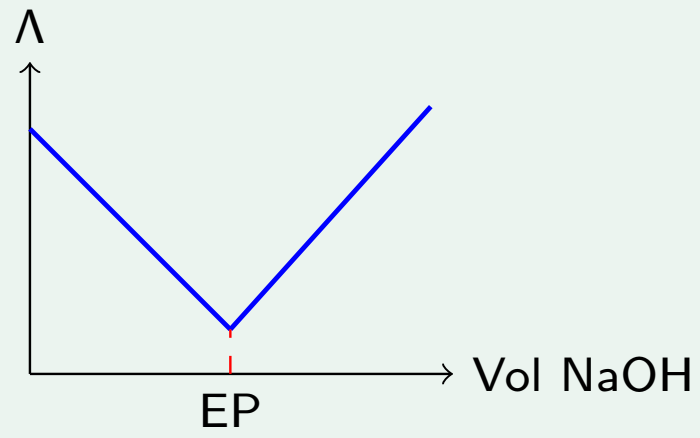
$$E = \frac{0.0592}{2} \log \frac{0.1}{0.01} = 0.0296 \times 1 = \mathbf{0.0296}\,\mathrm{V}$$

Conductometric Titration

Principle

Conductance of a solution changes as titrant is added. End point determined from **change in slope** of conductance vs. volume graph — no indicator needed.

Strong Acid–Strong Base



Graph Shape

Titration	**Shape**
Strong acid–strong base	V-shaped
Weak acid–strong base	Falling, then rise
Salt soln–precipitation	V-shaped

Advantages: Suitable for coloured/turbid solutions; applicable to very dilute solutions; precise end point detection.

Chromium & Nickel Electroplating

Chromium Plating

Electrolyte	CrO_3 in H_2SO_4
Anode	Lead (Pb)
Cathode	Object to plate
Thickness	0.25 μm (decor)
	25 μm (hard chrome)

Uses: Auto parts, tools, shafts (hard/wear-resistant)

Nickel Plating

Electrolyte	$NiSO_4$ + $NiCl_2$ (Watts bat
Anode	Nickel metal
Cathode	Object to plate
pH	3.5–4.5

Uses: Base coat under chrome; sanitary fittings; corrosion protection

Key Reactions — Chromium

Cathode: $Cr_2O_7^{2-} + 14H^+ + 12e^- \rightarrow 2Cr + 7H_2O$

Zinc Electroplating & Galvanizing

Zinc Electroplating

Item	Material	Role
Electrolyte	$ZnSO_4$ solution	Zn^{2+} source
Anode	Zinc metal	Dissolves
Cathode	Iron/steel	Coated

Anode: $Zn - 2e^- \rightarrow Zn^{2+}$

Cathode rxn: $Zn^{2+} + 2e^- \rightarrow Zn$

Hot-Dip Galvanizing

Steel dipped in molten Zn (450 °C). Zinc–iron alloy layer forms. Better adhesion; thicker coat. **Used for**: roofing sheets, pipes, buckets, nails.

Why Zinc Protects

Zn is more active than Fe. Acts as **sacrificial anode** — even if coating is scratched, Zn corrodes preferentially, protecting Fe.

Anodizing of Aluminium

What is Anodizing?

An **electrochemical process** that thickens the natural Al_2O_3 oxide layer on aluminium surface. Unlike electroplating, the metal is the **anode**.

Process

Electrolyte	H_2SO_4 (15–20%)
Anode	Aluminium object
Cathode	Lead / Al
Reaction	$2Al + 3H_2O \rightarrow Al_2O_3 + 6H$

Advantages

- Hard, corrosion-resistant surface
- Porous $\rightarrow$ can be dyed (coloured finishes)
- Better paint adhesion
- Electrical insulation

Applications: Aircraft parts, window frames, cookware, consumer electronics (iPhone body)

Corrosion — Electrochemical Nature (Preview)

Definition

Corrosion is the **gradual deterioration** of metals by electrochemical reaction with environment (moisture, O_2, acids).

Rusting of Iron

Anode (Fe, oxidation):

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Cathode (O_2, reduction):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$$\rightarrow Fe_2O_3 \cdot xH_2O \text{ (rust)}$$

Electrochemical Cell in Rust

Different regions of same metal act as micro-anode and micro-cathode due to:

- Stress differences
- Concentration differences
- Grain boundary effects

(Detail in Unit 3)

Electrochemical Equivalent Values

Electrochemical Equivalent $Z = M/(nF)$ (g C^{-1})

Element	M (g/mol)	n	Z $\times 10^{-4}$	Reaction
Silver (Ag)	107.87	1	11.18	$Ag^{+} + e^{-} \rightarrow Ag$
Copper (Cu)	63.55	2	3.29	$Cu^{2+} + 2e^{-} \rightarrow Cu$
Gold (Au)	197.0	3	6.81	$Au^{3+} + 3e^{-} \rightarrow Au$
Nickel (Ni)	58.69	2	3.04	$Ni^{2+} + 2e^{-} \rightarrow Ni$
Zinc (Zn)	65.38	2	3.39	$Zn^{2+} + 2e^{-} \rightarrow Zn$
Aluminium (Al)	26.98	3	0.93	$Al^{3+} + 3e^{-} \rightarrow Al$
Hydrogen (H)	1.008	1	0.104	$H^{+} + e^{-} \rightarrow \frac{1}{2}H_2$

Use in Faraday's First Law

$m = ZIt = Z \times Q$ where $Q = It$ (charge in coulombs)

Solved EMF & ΔG Numerical

Problem (PYQ W'24 type)

Calculate E°_{cell} and ΔG° for: $\text{Zn}\,|\,\text{Zn}^{2+}(1\text{M})\,||\,\text{Cu}^{2+}(1\text{M})\,|\,\text{Cu}$
Given: $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\,\text{V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34\,\text{V}$

Solution

Step 1: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = +1.10\,\text{V}$

Step 2: $n = 2$, $F = 96500\,\text{C mol}^{-1}$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.10$

$$\boxed{\Delta G^\circ = -212300\,\text{J mol}^{-1} = -212.3\,\text{kJ mol}^{-1}}$$

$\Delta G^\circ < 0$ confirms the reaction is **spontaneous**.

Conductance Numericals (PYQ)

Q1 (PYQ Su'24): Molar Conductance

Conductivity of 0.02 M KCl $= 2.768 \times 10^{-3}$ S cm^{-1}. Find Λ_m.

$$\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{2.768 \times 10^{-3} \times 1000}{0.02}$$

$$\boxed{\Lambda_m = 138.4 \text{ S cm}^2\text{mol}^{-1}}$$

Q2 (PYQ W'25): Kohlrausch's Law

$$\Lambda_m^\infty(CH_3COOH) = \Lambda_{H^+}^\infty + \Lambda_{CH_3COO^-}^\infty$$
$$= 349.6 + 40.9 = 390.5 \text{ S cm}^2\text{mol}^{-1}$$

If Λ_m at 0.05 M $= 7.36$, degree of dissociation:

$$\alpha = \frac{7.36}{390.5} = \mathbf{0.0188} \ (1.88\%)$$

Applications of Electrolysis — Summary

Application	Electrolyte	Cathode	Anode
Electroplating (Cu)	$CuSO_4 + H_2SO_4$	Object (coated)	Pure Cu
Electro-refining	Crude metal salt	Pure metal	Crude metal
Electroplating (Ag)	$KAg(CN)_2$	Object	Pure Ag
Electroplating (Cr)	$CrO_3 + H_2SO_4$	Object	Pb (inert)
Anodizing (Al)	H_2SO_4	Pb/Al	Al object
Chlor-alkali	NaCl brine	Fe ($H_2\uparrow$)	C ($Cl_2\uparrow$)
Water splitting	Dil. H_2SO_4	Pt ($H_2\uparrow$)	Pt ($O_2\uparrow$)
Electroforming	Metal salt	Mandrel	Metal

Remember: Cathode = reduction = deposition; Anode = oxidation = dissolution (active) or gas evolution (inert)

PYQ 7-Mark Questions — Electrochemistry

Frequently Asked Long Questions

Question	Papers
Describe Daniel cell with reactions and cell notation	W'23, Su'24
Explain electroplating of copper with neat diagram	Su'23, W'24
State and explain Faraday's laws with numericals	W'25, Su'25
Explain electrolysis of NaCl brine (chlor-alkali)	Su'24, W'23
Explain electro-refining of copper; what is anode mud?	W'23, Su'24
Write Nernst equation; derive and solve numerical	W'24, Su'25
Explain Kohlrausch's law and its applications	W'25, Su'24

Strategy

7-mark answers need: Definition + Diagram + Reactions/Formula + Example/Numerical + Conclusion

Unit 2 PYQ Pattern Analysis

Topic	Su'23	W'23	Su'24	W'24	Su'25 / W'25
Daniel cell	2	7	7	2	2
Nernst equation	—	2	2	7	7
Faraday's laws	7	2	2	2	7
Electroplating	7	7	2	7	2
Electrolysis NaCl	2	7	7	2	2
Conductance	2	2	7	2	7
Kohlrausch's law	—	—	7	2	7
Oxidation no.	2	2	2	2	2
Electro-refining	2	7	7	2	2

Top 3 to master: Faraday's laws + Nernst + Electroplating — appear in every paper as 7-mark

Unit 2 — Key Formulas Summary

Formula	Variables
$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$	standard or actual EMF
$E = E^\circ - \dfrac{0.0592}{n} \log Q$	Nernst (298 K)
$\Delta G^\circ = -nFE^\circ$	n=electrons, F=96500
$m = ZIt = \dfrac{M}{nF} \cdot It$	Faraday 1st law
$\dfrac{m_1}{m_2} = \dfrac{E_1}{E_2}$	Faraday 2nd law
$\Lambda_m = \dfrac{\kappa \times 1000}{C}$	molar conductance
$\Lambda_m^\infty = \sum \nu_+ \lambda_+ + \sum \nu_- \lambda_-$	Kohlrausch's law
$\alpha = \dfrac{\Lambda_m}{\Lambda_m^\infty}$	degree of dissociation
$E^\circ = \dfrac{0.0592}{n} \log K_c$	equilibrium link

Faraday's Law — Numerical Variations (PYQ)

Q1 (PYQ W'25): Find time

How long must 2 A current pass to deposit 1.27 g of copper? ($Z_{Cu} = 3.29 \times 10^{-4}$ g/C)

$$t = \frac{m}{Z \cdot I} = \frac{1.27}{3.29 \times 10^{-4} \times 2}$$

$$\boxed{t = 1930\,\text{s} \approx 32.2\,\text{min}}$$

Q2 (PYQ Su'25): Find current

What current deposits 5.4 g Ag in 1 hour? ($M_{Ag} = 108$, $n = 1$)

$$I = \frac{m \cdot n \cdot F}{M \cdot t} = \frac{5.4 \times 1 \times 96500}{108 \times 3600}$$

$$\boxed{I = 1.34\,\text{A}}$$

Selective Electrode Reactions in Electrolysis

Why Some Ions Discharge First?

When several ions are present, the **ease of discharge** follows electrochemical series:

- At cathode: ion with **higher reduction potential** discharges first
- At anode: ion requiring **least energy** to oxidize discharges first

Example: Electrolysis of $CuSO_4$ with Pt electrodes

Cathode: Cu^{2+} ($+0.34$ V) discharges before H^+ (0.00 V)
$Cu^{2+} + 2e^- \rightarrow Cu$ (deposits)

Anode: OH^- discharges before SO_4^{2-} (very stable)
$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Batteries — Primary vs Secondary

Primary Battery

Non-rechargeable. Reactions irreversible.

Type	**EMF**
Dry cell	1.5 V
Alkaline	1.5 V
Mercury	1.35 V
Zinc-air	1.4 V

Secondary Battery

Rechargeable. Reactions reversible.

Type	**EMF**
Lead-acid	2 V/cell
Ni-Cd	1.25 V
Ni-MH	1.2 V
Li-ion	3.6 V

Lead-acid (car battery) $= 6$ cells $\times$ 2 V $=$ 12 V

Lead-Acid Battery (Secondary Battery)

Construction

Anode: spongy Pb Cathode: PbO_2 Electrolyte: H_2SO_4 ($d = 1.28$ g/mL)

Discharge Reactions

Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
Overall: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Recharging

Reverse reactions occur. $PbSO_4 \rightarrow Pb$ and PbO_2. Acid density increases on charging (H_2SO_4 regenerated).

Fuel Cells

Definition

A device that **continuously converts chemical energy** of a fuel directly to electrical energy as long as fuel and oxidant are supplied. Efficiency $\approx 70\%$ vs thermal 30–40%.

H_2–O_2 Fuel Cell

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall: $2H_2 + O_2 \rightarrow 2H_2O$

Advantages

- No pollution (product: H_2O)
- High efficiency
- No moving parts
- Continuous operation
- Used in space vehicles

Galvanic vs Electrolytic Cell — Detailed Comparison

Feature	Galvanic Cell	Electrolytic Cell
Energy conversion	Chemical→Electrical	Electrical→Chemical
Spontaneity	Spontaneous	Non-spontaneous
Anode sign	Negative $(-)$	Positive $(+)$
Cathode sign	Positive $(+)$	Negative $(-)$
External supply needed?	No (generates EMF)	Yes
Salt bridge	Required	Not required
Container setup	Two half-cells	Single container
Examples	Daniel cell, batteries	Plating, refining
ΔG	Negative	Positive

Key trick: Anode = oxidation in *both* types; only the charge sign flips.

Nernst Equation — Extended Numerical (PYQ Su'25)

Problem

Calculate EMF of: $\mathrm{Zn}\,|\,\mathrm{Zn^{2+}}(0.001\ \mathrm{M})\,||\,\mathrm{Cu^{2+}}(0.1\ \mathrm{M})\,|\,\mathrm{Cu}$

$E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76\,\mathrm{V}, \quad E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.34\,\mathrm{V}$

Solution

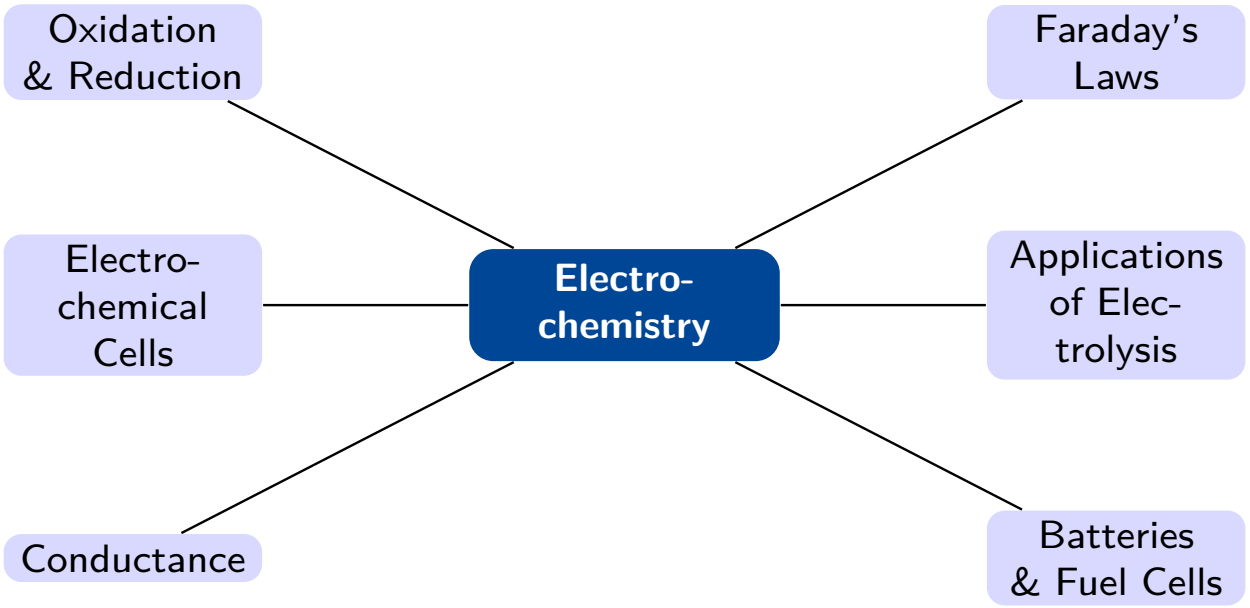
Step 1: $E^\circ_{\mathrm{cell}} = 0.34 - (-0.76) = 1.10\,\mathrm{V}$

Step 2: $Q = \dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]} = \dfrac{0.001}{0.1} = 0.01; \quad n = 2$

Step 3: $E = 1.10 - \dfrac{0.0592}{2}\log(0.01) = 1.10 - 0.0296 \times (-2)$

$$\boxed{E = 1.10 + 0.059 = 1.159\,\mathrm{V}}$$

Unit 2 — Electrochemistry Mind Map



OIL RIG | Nernst | Daniel cell | SHE | Kohlrausch | $m = ZIt$ | Electroplating | Lead-acid

Exam Tips — Unit 2 Electrochemistry

Do's

- Write full half-reactions for both electrodes
- State Faraday's laws in words before formula
- Show units at every step in numericals
- Draw neat Daniel cell / electrolytic cell diagram
- Use OIL RIG for oxidation/reduction definition

Don'ts

- Don't confuse anode charge sign (galvanic vs electrolytic)
- Don't mix log and ln in Nernst
- Don't forget n in $Z = M/(nF)$
- Don't skip salt bridge explanation
- Don't say cathode = oxidation site (it's reduction!)

Quick recall: $m = ZIt$ | $E = E^\circ - \frac{0.0592}{n} \log Q$ | $\Delta G = -nFE^\circ$

PYQ Short-Answer Practice — 2 Marks

Frequently Asked 2-Mark Questions

#	Question
1	Define oxidation number. Find O.N. of Cr in $K_2Cr_2O_7$.
2	What is SHE? What is its electrode potential?
3	State Faraday's second law with formula.
4	Distinguish between specific and molar conductance.
5	What is electrochemical equivalent? Give its unit.
6	Define degree of dissociation and give formula.
7	What is salt bridge? State its two functions.
8	Explain OIL RIG with one example.
9	Write Nernst equation; define each term.
10	What are concentration cells? Give one example.

Specific & Molar Conductance Numerical (PYQ W'24)

Problem

Resistance of conductance cell filled with 0.1 M KCl = 100 Ω. Cell constant = $0.88\,\text{cm}^{-1}$.
Find (a) specific conductance and (b) molar conductance.

Solution

(a) $\kappa = \dfrac{\text{Cell constant}}{R} = \dfrac{0.88}{100} = 8.8 \times 10^{-3}\,\text{S cm}^{-1}$

(b) $\Lambda_m = \dfrac{\kappa \times 1000}{C} = \dfrac{8.8 \times 10^{-3} \times 1000}{0.1}$

$$\boxed{\Lambda_m = 88\,\text{S cm}^2\text{mol}^{-1}}$$

Units: κ in S/cm; C in mol/L; Λ_m in S·cm^2/mol

Galvanic Corrosion (Bridge to Unit 3)

Galvanic Corrosion

When two **dissimilar metals** are in electrical contact in an electrolyte, the more active metal (lower E°) becomes the anode and corrodes faster.

Fe–Cu Couple in Seawater

Anode: Fe (-0.44 V) oxidizes
Cathode: Cu ($+0.34$ V) protected

$\Rightarrow$ Iron rusts faster at junction

Prevention

- Use metals close in series
- Use insulating spacers
- Apply protective coatings
- Cathodic protection (Unit 3)

Unit 2 Revision Flash Points

Must Know Facts

- SHE potential $= 0.00$ V (by convention)
- 1 Faraday $= 96500$ C $=$ charge of 1 mol e^-
- Daniel cell: Zn anode, Cu cathode, $E^\circ = 1.10$ V
- Salt bridge: KCl/NH_4NO_3 in agar-agar
- Plating time $\propto$ mass; $\propto 1/\text{current}$
- Λ_m increases with dilution (weak electrolytes)

Common Exam Errors

- Writing anode as +ve in galvanic cell ✗
- Forgetting n in $Z = M/(nF)$
- Confusing κ (S/cm) with Λ_m
- Wrong Q in Nernst equation
- Saying cathode $=$ oxidation site ✗

Overpotential & Decomposition Potential

Decomposition Potential

The **minimum voltage** required to cause continuous electrolysis.
Water: theoretical = 1.23 V, actual $\approx$ 1.7 V (due to overpotential).

Overpotential

Extra voltage beyond the theoretical value due to:

- Electrode surface effects (especially for H_2 and O_2 evolution)
- Ohmic resistance of electrolyte
- Concentration polarization

Overpotential = Actual applied potential − Theoretical potential

H_2 overpotential is highest on smooth Pt, lowest on platinized Pt. Hence spongy/platinized electrodes are preferred.

Unit 2 Complete — Bridge to Unit 3: Corrosion

Unit 2 Summary

Topic	Core Outcome
Redox	OIL RIG; O.N. rules; cell reactions
Electrochemical cells	Daniel cell; Nernst; E°; SHE
Conductance	κ, Λ_m, Kohlrausch's law
Faraday's Laws	$m = ZIt$; 2nd law; numericals
Electrolysis	Plating, refining, brine, galvanizing
EMF & ΔG	$\Delta G = -nFE$; spontaneity
Batteries	Lead-acid; fuel cells; primary/secondary

Coming Next — Unit 3: Corrosion

Corrosion is **electrochemistry in action** on metal surfaces. Unit 3: dry vs wet corrosion, rusting mechanism, factors affecting corrosion, prevention by galvanizing, cathodic protection, inhibitors, and coatings.