FREE NOTES · NCERT + JEE/NEET LEVEL

Electrochemistry

Galvanic cells, electrode potential and the electrochemical series, Nernst equation, Gibbs energy, conductance and Kohlrausch's law, electrolysis and Faraday's laws, batteries, fuel cells and corrosion.

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02 Electrode potential & SHE
03 Electrochemical series
04 Nernst equation & Gibbs energy
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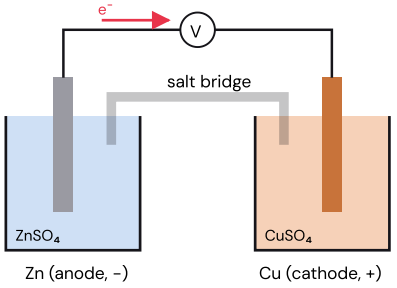
01 Galvanic (voltaic) cell

A galvanic cell turns the chemical energy of a **spontaneous redox reaction** into electrical energy. Example: the **Daniell cell**.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s),\ E^{\circ}_{cell} = 1.1\ V$$

- **Anode** = oxidation = negative (in a galvanic cell).
- **Cathode** = reduction = positive.
- Electrons flow anode → cathode in the outer wire.
- **Salt bridge** (KCl/KNO_3 in agar) completes the circuit and keeps both solutions neutral.

Cell notation: $Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$ (anode on the left).



Daniell cell: electrons go from Zn to Cu

MEMORY TRICK

AN OX and **RED CAT**: anode-oxidation, reduction-cathode. True for every cell; only the signs flip in an electrolytic cell.

02 Electrode potential & SHE

The potential difference between a metal and its ion solution is the **electrode potential**. We can't measure one alone, so we compare with the **standard hydrogen electrode (SHE)**: Pt in 1 M H^+ with H_2 gas at 1 bar, E° = 0.00 V.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{right} - E^{\circ}_{left}$$

Use **standard reduction potentials** for both. $E^{\circ}_{cell} > 0 \Rightarrow$ the reaction is spontaneous.

03 Electrochemical series

Half reaction	E° (V)
$F_2 + 2e^- \rightarrow 2F^-$	+2.87 (strongest oxidising agent)
$Au^{3+} + 3e^- \rightarrow Au$	+1.40
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Li^+ + e^- \rightarrow Li$	-3.05 (strongest reducing agent)

HOW TO USE IT

- Higher E° ⇒ more easily reduced ⇒ better oxidising agent.
- Lower E° ⇒ better reducing agent; a metal with E° < 0 displaces H_2 from dilute acid.
- A metal displaces any metal below it (higher E°) from its salt solution: Zn displaces Cu.

04 Nernst equation & Gibbs energy

For the reaction aA + bB → cC + dD with n electrons:

$$E_{cell} = E^\circ_{cell} - (0.059/n)\log Q \ \ (\text{at } 298\ K)$$

$Q = [C]^c[D]^d/[A]^a[B]^b$ (solids and pure liquids = 1)

Single electrode $M^{n+} + ne^- \rightarrow M$: $E = E^\circ - (0.059/n)\log(1/[M^{n+}])$

EQUILIBRIUM AND GIBBS ENERGY

At equilibrium $E_{cell} = 0 \Rightarrow E^\circ_{cell} = (0.059/n)\log K_c$

$$\Delta G^\circ = -nFE^\circ_{cell} = -2.303\ RT\log K_c$$

F = 96487 ≈ 96500 C/mol. $E^\circ > 0 \Rightarrow \Delta G^\circ < 0 \Rightarrow$ spontaneous and $K > 1$.

05 Conductance of electrolytic solutions

Quantity	Formula	Unit
Resistance	$R = \rho\, l/A$	Ω
Conductance	$G = 1/R$	S (siemens)
Conductivity κ	$\kappa = 1/\rho = G \times (l/A)$	S m^{-1} (or S cm^{-1})
Cell constant G*	$G^* = l/A = R\,\kappa$	m^{-1}
Molar conductivity	$\Lambda_m = \kappa \times 1000 / M$ (κ in S cm^{-1})	S cm^2 mol^{-1}

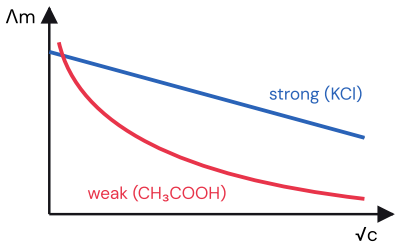
EFFECT OF DILUTION

On dilution **κ decreases** (fewer ions per cm^3) but **Λ_m increases** (each mole of electrolyte is spread over more volume, and weak electrolytes dissociate more). Conductivity is measured with AC (a Wheatstone bridge) to avoid electrolysis.

06 Kohlrausch's law

Strong electrolytes: $\Lambda_m = \Lambda^\circ_m - A\sqrt{c}$ (Debye-Hückel-Onsager). Straight line; extrapolate to c = 0 to get Λ°_m.

Weak electrolytes: Λ_m rises steeply at low c, so Λ°_m can't be found by extrapolation. Use Kohlrausch's law.



Λm vs √c: straight for strong, steep curve for weak electrolyte

LAW OF INDEPENDENT MIGRATION OF IONS

$$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$$

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

$$\alpha = \Lambda_m/\Lambda^\circ_m,\ K_a = c\alpha^2/(1-\alpha)$$

07 Electrolysis & Faraday's laws

In an **electrolytic cell** electrical energy drives a non-spontaneous reaction. Anode is **positive**, cathode is **negative**; still oxidation at anode, reduction at cathode.

First law: $w = Z\,I\,t = (M/nF) \times I\,t$

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

1 F = charge on 1 mol electrons = 96500 C.

Electrolysis of	Cathode	Anode
Molten NaCl	Na	Cl_2
Aqueous NaCl (brine)	H_2 (water reduced, not Na^+)	Cl_2 (overpotential of O_2)
Aqueous $CuSO_4$, Pt electrodes	Cu	O_2
Aqueous $CuSO_4$, Cu electrodes	Cu	Cu dissolves (refining)
Dilute H_2SO_4	H_2	O_2 (conc. acid gives $S_2O_8^{2-}$)

08 Batteries, fuel cell & corrosion

Cell	Anode / Cathode	Notes
Dry (Leclanché) cell	Zn / MnO_2 + C	Primary, ~1.5 V, NH_4Cl + $ZnCl_2$ paste
Mercury cell	Zn-Hg / HgO + C	Primary, 1.35 V constant (watches, hearing aids)
Lead storage	Pb / PbO_2, 38% H_2SO_4	Secondary (rechargeable), car battery; $PbSO_4$ forms on discharge
Ni-Cd	Cd / NiO(OH)	Secondary, longer life
H_2-O_2 fuel cell	H_2 / O_2, KOH, porous C	~70% efficient, pollution-free, used in Apollo; product water

CORROSION (RUSTING)

An electrochemical process. Anode: $Fe \rightarrow Fe^{2+} + 2e^-$. Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. Fe^{2+} is oxidised further to rust $Fe_2O_3 \cdot xH_2O$. Salt water and acid speed it up. Prevention: paint, oil, **galvanisation** (Zn coating), **sacrificial anode** (Mg/Zn block), tin plating.

09 JEE Extra + Tricks

JEE LEVEL

- Nernst: $E = E^\circ - (0.059/n) \log Q$ at 298 K. At equilibrium $E = 0 \Rightarrow \log K = nE^\circ/0.059$.
- $\Delta G^\circ = -nFE^\circ$. Concentration cell: $E = (0.059/n) \log(C_2/C_1)$ ($E^\circ = 0$).
- Kohlrausch law: $\Lambda^\circ_m(CH_3COOH) = \Lambda^\circ(CH_3COONa) + \Lambda^\circ(HCl) - \Lambda^\circ(NaCl)$; degree of dissociation $\alpha = \Lambda_m/\Lambda^\circ_m$.
- Faraday: $m = ZIt = (M/nF)\cdot Q$; same charge deposits masses in ratio of equivalent weights.
- Electrolysis products: aqueous NaCl $\Rightarrow$ H_2 at cathode, Cl_2 at anode (overpotential of O_2); dilute $H_2SO_4 \Rightarrow O_2$ at anode.
- Higher E°(reduction) $\Rightarrow$ stronger oxidising agent (F_2 strongest); lower $E^\circ \Rightarrow$ stronger reducing agent (Li strongest in water).

10 Solved numericals

Q1. $E°(Zn^{2+}/Zn) = -0.76$ V, $E°(Cu^{2+}/Cu) = +0.34$ V. Find $E°_{cell}$ and $\Delta G°$.

$E° = 0.34 - (-0.76) = 1.10$ V; $\Delta G° = -2 \times 96500 \times 1.10 = -212300$ J = **−212.3 kJ/mol**.

Q2. Find E for $Zn|Zn^{2+}(0.1\ M)||Cu^{2+}(0.01\ M)|Cu$ at 298 K.

$Q = [Zn^{2+}]/[Cu^{2+}] = 10 \Rightarrow E = 1.10 - (0.059/2) \log 10 = 1.10 - 0.0295 =$ **1.0705 V**.

Q3. 2 A is passed through $CuSO_4$ for 965 s. Mass of Cu deposited? (Cu = 63.5)

$Q = 1930$ C = 0.02 F; Cu^{2+} needs 2F per mol ⇒ 0.01 mol ⇒ **0.635 g**.

Q4. κ of 0.02 M KCl = 0.0025 S cm^{-1}. Find Λ_m.

$\Lambda_m = 0.0025 \times 1000/0.02 =$ **125 S cm^2 mol^{-1}**.

11 Mistakes, formula sheet & practice

- Writing $E°_{cell} = E°_{anode} - E°_{cathode}$. It's cathode minus anode.
- Multiplying E° by the coefficients when balancing. E° is intensive and never multiplied.
- Thinking κ and Λ_m both decrease on dilution.
- In brine electrolysis, writing Na at the cathode.

Cell emf	$E° = E°_c - E°_a$
Nernst	$E = E° - (0.059/n) \log Q$
Gibbs / K	$\Delta G° = -nFE°;\ E° = (0.059/n) \log K$
Molar conductivity	$\Lambda_m = 1000\kappa/M$
Weak electrolyte	$\alpha = \Lambda_m/\Lambda°_m$
Faraday	$w = MIt/(nF)$

1. Why is a salt bridge needed?
2. Can we store $CuSO_4$ solution in a zinc pot?
3. Which is used to find Λ° of a weak electrolyte?
4. Charge needed to reduce 1 mol Al^{3+} to Al?

ANSWERS

1) Completes the circuit and keeps solutions neutral · 2) No, Zn displaces Cu (Zn has lower E°) · 3) Kohlrausch's law · 4) 3F = 289500 C

12 Quick revision: 5 minutes before the exam

CELLS

- AN OX, RED CAT.
- Galvanic: anode −; electrolytic: anode +.
- $Zn|Zn^{2+}||Cu^{2+}|Cu$, E° = 1.1 V.

EQUATIONS

- E = E° − (0.059/n) log Q.
- $\Delta G^\circ = -nFE^\circ$.
- F = 96500 C.

CONDUCTANCE

- Dilution: κ ↓, Λ_m ↑.
- $\Lambda_m = 1000\kappa/M$.
- Kohlrausch for weak Λ°.

APPLICATIONS

- Lead battery: rechargeable.
- Fuel cell: $H_2 + O_2 \rightarrow$ water.
- Rust prevention: Zn coating.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.