FREE EDITION · NOTES + 3 SAMPLE MCQS

CUET · CHEMISTRY · CLASS XII · CODE 306

Electrochemistry

CUET unit: Electrochemistry

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Establishes the bridge between thermodynamics and electricity: a spontaneous redox reaction in a galvanic (Daniell) cell yields an emf, while an external voltage can drive a non-spontaneous reaction in an electrolytic cell.
- Sets up the quantitative toolkit examiners love: Nernst equation, $\Delta G^\circ = -nFE^\circ$, $\log K = nE^\circ/0.0591$, conductivity κ, molar conductivity Λm, Kohlrausch's law and Faraday's two laws.
- Couples the abstract relations with concrete devices — SHE, dry cell, mercury cell, lead storage battery, Ni–Cd cell, H2–O2 fuel cell — and a real-world electrochemical problem (corrosion of iron).
- CUET routinely tests this unit through (i) Nernst/EMF numericals, (ii) Faraday's law mass-deposition numericals, (iii) interpretation of standard electrode potential tables and (iv) one-liners on cell construction, salt bridge, SHE convention.

📖 Detailed Notes

2.1 Core concepts

- An electrochemical cell has two electrodes dipped in electrolyte(s); a galvanic/voltaic cell converts the chemical energy of a spontaneous redox reaction into electrical energy while an electrolytic cell uses electrical energy to drive a non-spontaneous reaction (NCERT §2.1, p. 32).
- The Daniell cell (Zn|ZnSO4 || CuSO4|Cu) is built on Zn(s) + Cu2+(aq) → Zn2+(aq) + Cu(s) and delivers 1.1 V when [Zn2+] = [Cu2+] = 1 mol dm–3; if an opposing external voltage of exactly 1.1 V is applied the current is zero, below 1.1 V it works as a galvanic cell, above 1.1 V it functions as an electrolytic cell with reversed reaction (NCERT §2.1, Fig. 2.2, p. 32).
- A galvanic cell is built from two half-cells (redox couples); each half-cell has a metal electrode in its electrolyte and the two electrolytes are linked internally by a salt bridge and externally by a wire and voltmeter (NCERT §2.2, p. 33).
- IUPAC convention: anode on the left, cathode on the right, single vertical bar between metal and electrolyte, double vertical bar for the salt bridge; Ecell = Eright – Eleft and is positive for a spontaneous cell (NCERT §2.2, p. 34).

- The potential of a single electrode cannot be measured; the standard hydrogen electrode (SHE), Pt(s)|H2(g, 1 bar)|H+(aq, 1 M), is assigned zero potential at all temperatures and serves as the reference (NCERT §2.2.1, p. 34, Fig. 2.3).
- IUPAC standard electrode potentials are reduction potentials measured at unit activity; a positive E° indicates the species is reduced more easily than H+, a negative E° indicates the reverse — so F2/F– (+2.87 V) is the strongest oxidising agent and Li+/Li (–3.05 V) places Li as the strongest reducing agent in aqueous solution (NCERT §2.2.1, Table 2.1, p. 37).
- Nernst equation for a half-cell Mn+ + ne– → M is E = E° – (RT/nF) ln(1/[Mn+]); for a general cell aA + bB → cC + dD, Ecell = E°cell – (RT/nF) ln Q, which at 298 K becomes Ecell = E°cell – (0.059/n) log Q (NCERT §2.3, eqns 2.8–2.13, pp. 36–38).
- At equilibrium Ecell = 0 and Q = Kc, giving E°cell = (0.059/n) log Kc at 298 K; for the Daniell cell E°cell = 1.1 V yields log Kc = 37.288, Kc ≈ 2 × 1037 (NCERT §2.3.1, p. 39).
- The Gibbs energy change of a cell reaction is ΔrG = –nFEcell and at standard state ΔrG° = –nFE°cell; ΔrG° is extensive (depends on n), Ecell is intensive (NCERT §2.3.2, eqns 2.15–2.16, p. 40).
- Resistance R = ρ(l/A); the reciprocal ρ–1 is conductivity κ (S m–1), measured in S m–1 or S cm–1 (1 S cm–1 = 100 S m–1); conductivity of metals depends on the metal and decreases with temperature, whereas electrolytic (ionic) conductance depends on the electrolyte, ion size and solvation, solvent viscosity, concentration and increases with temperature (NCERT §2.4, eqns 2.17–2.18, pp. 41–43).
- Cell constant G = l/A is determined by measuring R for a KCl solution of known κ; conductivity of an unknown solution is then κ = G/R; resistance is measured on a Wheatstone bridge with an AC source to avoid electrolysis (NCERT §2.4.1, eqns 2.18–2.20, pp. 43–44, Fig. 2.5).
- Molar conductivity Λm = κ/c (S m2 mol–1 if c is in mol m–3); 1 S m2 mol–1 = 104 S cm2 mol–1 (NCERT §2.4.1, eqn 2.21, pp. 44–45).
- Conductivity κ always decreases on dilution; molar conductivity Λm always increases on dilution; for a strong electrolyte Λm rises slowly per Λm = Λ°m – Ac1/2, while for a weak electrolyte Λm rises steeply near infinite dilution as α increases (NCERT §2.4.2, eqn 2.23, Fig. 2.6, pp. 46–47).
- Kohlrausch's law of independent migration of ions: Λ°m = ν+λ°+ + ν–λ°–; this lets us compute Λ°m for weak electrolytes (e.g. Λ°m(HAc) = Λ°m(HCl) + Λ°m(NaAc) – Λ°m(NaCl)) and from there α = Λm/Λ°m and Ka = cα2/(1 – α) (NCERT §2.4.2, eqns 2.24–2.27, pp. 49–50).
- In an electrolytic cell the cation discharging at the cathode and the species oxidised at the anode are decided by E° values (modified by overpotentials and Nernst effects); e.g. molten NaCl gives Na and Cl2 whereas aqueous NaCl gives H2 (at cathode, from H+/H2O) and Cl2 (at anode, due to O2 overpotential) (NCERT §2.5/2.5.1, eqns 2.28–2.39, pp. 51–54).

- Faraday's first law: amount of substance produced at an electrode ∝ quantity of electricity passed ($Q = It$); second law: amounts of different substances produced by the same Q are in the ratio of their chemical equivalent weights; one Faraday $F = N_A \cdot e = 96487\ C\ mol^{-1}$ ($\approx 96500\ C\ mol^{-1}$) is the charge per mole of electrons (NCERT §2.5, pp. 51–52).
- Primary batteries (one-shot): Leclanche dry cell uses Zn anode, MnO_2 + C cathode, NH_4Cl + $ZnCl_2$ paste electrolyte, ~1.5 V; mercury cell uses Zn–Hg amalgam anode, HgO + C cathode, KOH/ZnO paste, ~1.35 V constant during life (NCERT §2.6.1, pp. 54–55).
- Secondary batteries (rechargeable): lead storage cell (Pb anode, PbO_2-on-Pb-grid cathode, 38% H_2SO_4 electrolyte; discharge: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$); Ni–Cd cell (longer life but more expensive; discharge: $Cd + 2Ni(OH)_3 \rightarrow CdO + 2Ni(OH)_2 + H_2O$) (NCERT §2.6.2, pp. 55–56).
- A fuel cell converts the combustion energy of a fuel (H_2, CH_4, CH_3OH, etc.) directly into electricity; the H_2–O_2 cell used in the Apollo programme has porous carbon electrodes (Pt/Pd catalysts) in conc. NaOH, with cathode $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ and anode $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$, giving $2H_2 + O_2 \rightarrow 2H_2O$ at ~70% efficiency, pollution-free (NCERT §2.7, p. 56).
- Corrosion of iron (rusting) is an electrochemical phenomenon: at the anodic spot $Fe \rightarrow Fe^{2+} + 2e^-$ ($E^\circ = -0.44$ V) and at the cathodic spot $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E^\circ = 1.23$ V), overall $E^\circ_{cell} = 1.67$ V; Fe^{2+} is further oxidised by atmospheric O_2 to hydrated $Fe_2O_3 \cdot xH_2O$ (rust); prevention: painting/coating, electroplating with Sn or Zn, or using a sacrificial electrode of Mg/Zn (NCERT §2.8, Fig. 2.13, p. 57).

2.2 Definitions to memorise

Term	Definition	Page
Galvanic/voltaic cell	Electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy	32
Electrolytic cell	Cell that uses external electrical energy to drive a non-spontaneous redox reaction	32
Electrode potential	Potential difference that develops at the electrode-electrolyte interface due to separation of charges	33
Standard electrode potential	Electrode potential measured when all species in the half-cell are at unit activity/concentration; IUPAC takes it as the reduction potential	33
SHE	Pt(s)	H_2(g, 1 bar)
Cell emf	Potential difference between the two electrodes when no current is drawn: $E_{cell} = E_{right} - E_{left}$	34
	$E_{cell} = E^\circ_{cell} - (0.059/n) \log Q$	38

Term	Definition	Page
Nernst equation (298 K)		
ΔrG° relation	$\Delta rG^\circ = -nFE^\circ cell$	40
K from emf	$E^\circ cell = (0.059/n) \log Kc$ at 298 K	39
Resistivity ρ	Resistance of a sample 1 m long and 1 m2 in cross-section; SI unit Ω m	41
Conductivity κ	Inverse of resistivity; SI unit S m−1 (1 S cm−1 = 100 S m−1)	41
Cell constant G*	I/A for a conductivity cell; $G^* = R\cdot\kappa$	44
Molar conductivity Λm	κ/c; conductance of the volume of solution containing 1 mole of electrolyte	45
Limiting molar conductivity $\Lambda^\circ m$	Value of Λm extrapolated to zero concentration (infinite dilution)	47
Kohlrausch's law	$\Lambda^\circ m = \nu+\lambda^\circ+ + \nu-\lambda^\circ-$ (limiting molar conductivities of independent ions add up)	49
Faraday's 1st law	Mass deposited ∝ quantity of electricity (Q = It)	51
Faraday's 2nd law	Masses deposited by the same Q are in the ratio of equivalent weights	51
Faraday constant F	Charge per mole of electrons = 96487 C mol−1 (≈ 96500)	52
Fuel cell	Galvanic cell in which fuel and oxidant are fed continuously; converts combustion energy directly into electricity	56
Corrosion	Electrochemical oxidation of a metal in presence of moisture and atmospheric gases, forming oxides/salts	57

2.3 Diagrams / processes to remember

- Fig. 2.1 (p. 32): Daniell cell — Zn rod in ZnSO4, Cu rod in CuSO4, salt bridge linking the two beakers, voltmeter showing 1.1 V.
- Fig. 2.2 (p. 32): three modes when an external Eext is applied to a Daniell cell — Eext < 1.1 V (galvanic, current flows Cu→Zn outside), Eext = 1.1 V (no current, no reaction), Eext > 1.1 V (electrolytic, reaction reversed).
- Fig. 2.3 (p. 34): SHE — Pt black electrode in 1 M HCl with H2 at 1 bar bubbled over it; reference half-cell with E° = 0.
- Table 2.1 (p. 37): standard electrode potentials at 298 K from F2/F– (+2.87 V) down to Li+/Li (–3.05 V); oxidising power decreases and reducing power increases top to bottom.
- Fig. 2.5 (p. 44): Wheatstone-bridge setup for measuring resistance of an electrolytic solution with an AC oscillator and detector.

- Fig. 2.6 (p. 47): Λ_m vs $c^{1/2}$ — straight line for KCl (strong electrolyte) with intercept Λ°_m, steep rise near zero concentration for acetic acid (weak electrolyte).
- Fig. 2.8 (p. 54): commercial Leclanche dry cell — Zn container (anode), central graphite rod (cathode) packed in MnO_2 + C, with moist NH_4Cl + $ZnCl_2$ paste.
- Fig. 2.9 (p. 55): mercury cell with Zn–Hg amalgam anode and HgO + C cathode in KOH/ZnO paste.
- Fig. 2.10 (p. 55): lead storage battery — alternating Pb plates and PbO_2-on-Pb grids immersed in 38% H_2SO_4.
- Fig. 2.12 (p. 56): H_2–O_2 fuel cell with porous carbon electrodes in concentrated NaOH, H_2 fed to anode and O_2 to cathode.
- Fig. 2.13 (p. 57): corrosion of iron — anodic and cathodic spots on the same iron surface, water film acting as the electrolyte, with the overall rust formation reaction.

2.4 Common confusions / NTA trap points

- Sign of Ecell vs $\Delta_r G$: spontaneous cell has $E_{cell} > 0$ AND $\Delta_r G < 0$ (because $\Delta_r G = -nFE_{cell}$). NTA loves to flip the sign convention or quote "negative emf ⇒ spontaneous".
- Standard electrode potentials in Table 2.1 are reduction potentials. For an oxidation half-reaction the sign is reversed — but Ecell is still computed as $E^\circ_{cathode} - E^\circ_{anode}$ using reduction potentials of both, never adding oxidation and reduction potentials.
- Daniell cell at E_{ext} = 1.1 V gives I = 0 (no current and no reaction); only when E_{ext} > 1.1 V does the cell run as an electrolytic cell with reversed reaction.
- Conductivity κ decreases on dilution but molar conductivity Λ_m increases on dilution — students often invert the two.
- For a weak electrolyte Λ°_m cannot be obtained by extrapolating Λ_m vs $c^{1/2}$ (the curve is too steep near zero); it must be calculated from Kohlrausch's law using strong-electrolyte data.
- In aqueous NaCl electrolysis the anode product is Cl_2 (not O_2) despite O_2 having a lower E° — because of the overpotential of oxygen. A favourite distractor.
- The Faraday constant 96487 C mol^{-1} is the charge per mole of electrons, not per mole of any ion; for $Al^{3+} \rightarrow Al$ you need 3F per mole of Al, for $Cu^{2+} \rightarrow Cu$ you need 2F.

🎯 Practice MCQs

Q1. In a Daniell cell operating spontaneously with $[Zn^{2+}] = [Cu^{2+}] = 1$ M at 298 K, the standard cell potential is:

- **A.** 0.34 V
- **B.** 0.76 V
- **C.** 1.10 V
- **D.** 2.20 V

Q2. The reaction in a Daniell cell on which an external voltage E_{ext} greater than 1.1 V is applied:

- **A.** continues in the original direction with a higher current
- **B.** stops altogether and no current flows
- **C.** reverses, so the cell now functions as an electrolytic cell
- **D.** the cell now produces 2.2 V on its own

Q3. According to IUPAC convention, the standard hydrogen electrode is represented as $Pt(s)|H_2(g, 1\ bar)|H^+(aq, 1\ M)$ and is assigned:

- **A.** +0.76 V at 298 K
- **B.** zero potential at all temperatures
- **C.** zero potential only at 298 K
- **D.** +0.34 V at all temperatures

📊 PYQ Alignment

> Electrochemistry is one of the heaviest-weighted physical-chemistry units in CUET (UG) — typically 3–5 of the 35 questions in the Chemistry paper come from this chapter every year (2023–25). NTA prefers Nernst-equation EMF calculations at non-standard

concentrations, Faraday's-law mass/charge numericals, interpretation of the standard electrode potential table (predicting spontaneity of a redox combination), one-line distinctions between dry/mercury/lead-storage/Ni–Cd/fuel cells, and the κ-vs-Λm conceptual trap; expect at least one assertion-reason on Kohlrausch's law or one case-based item on corrosion.

CUET 2025 — Actual PYQs from this chapter

Q.6 (CUET 2025) The unit of E°cell is:

- A) $V\ m^{-1}$ B) $S\ cm^{-1}$ C) V D) $S\ cm^2\ mol^{-1}$

Tests: Electrochemistry Answer: Not in extracted key

Q.7 (CUET 2025) Match Property with Unit. Property Unit (A) Cell constant (i) Ω cm (B) Molar conductance (ii) $\Omega^{-1}\ cm^2\ mol^{-1}$ (C) Specific conductance (iii) $\Omega^{-1}\ cm^{-1}$ (D) Conductance (iv) Ω^{-1} Options given.

- A) — B) — C) — D) —

Tests: Electrochemistry Answer: Not in extracted key

Q.8 (CUET 2025) The following statements describe properties of a Mercury cell. (A) Converts energy of combustion into electrical energy (B) It is rechargeable (C) Reaction: Zn + HgO → ZnO + Hg (D) It is a low current device used in hearing aids Choose correct option.

- A) — B) — C) — D) —

Tests: Electrochemistry Answer: Not in extracted key

Q.9 (CUET 2025) Which cell is used in automobiles and inverters?

- A) Mercury cell B) Dry cell C) Lead storage cell D) Fuel cell

Tests: Electrochemistry Answer: Not in extracted key

Q.10 (CUET 2025) A galvanic cell behaves as an electrolytic cell when:

- A) Ecell = Eext B) Ecell = 0 C) Eext > Ecell D) Ecell > Eext

Tests: Electrochemistry Answer: Not in extracted key

CUET 2024 — Actual PYQs from this chapter

Q.33 (CUET 2024) Number of moles of electrons produced in oxidation of 67.2 L H_2 at STP:

- A) 2 mol B) 4 mol C) 1 mol D) 6 mol

Tests: Electrochemistry Answer: Not in extracted key

Q.34 (CUET 2024) Quantity of electricity produced in oxidation of 67.2 L H_2 is:

- A) 96500 C B) 579000 C C) 193000 C D) 48250 C

Tests: Electrochemistry Answer: Not in extracted key

Q.35 (CUET 2024) If the current produced is used to deposit Ag from Ag^+ solution, the amount of silver deposited is:

- A) 324 g B) 648 g C) 108 g D) 216 g

Tests: Electrochemistry Answer: Not in extracted key

Q.36 (CUET 2024) Which of the following statements about fuel cells is correct?

- A) Energy efficiency is lower than combustion engines B) Produces electricity directly from fuel oxidation C) Requires intermediate mechanical energy conversion D) Produces large amounts of pollutants

Tests: Electrochemistry Answer: Not in extracted key

Q.37 (CUET 2024) Which of the following does not occur at cathode in electrochemical cells?

- A) Reduction B) Gain of electrons C) Oxidation D) Positive electrode in galvanic cell

Tests: Electrochemistry Answer: Not in extracted key

Q.38 (CUET 2024) The standard electrode potential of a half-cell depends on:

- A) Temperature B) Nature of electrode C) Concentration of ions D) All of these

Tests: Electrochemistry Answer: Not in extracted key

Q.39 (CUET 2024) In electrolysis, Faraday's first law states that:

- A) Mass deposited $\propto$ current B) Mass deposited $\propto$ time C) Mass deposited $\propto$ charge passed D) Mass deposited independent of charge

Tests: Electrochemistry Answer: Not in extracted key

Q.40 (CUET 2024) The relationship between Gibbs free energy and cell potential is:

- A) $\Delta G = nFE^\circ$ B) $\Delta G = -nFE^\circ$ C) $\Delta G = -F/E^\circ$ D) $\Delta G = nF/E^\circ$

Tests: Electrochemistry Answer: Not in extracted key

Q.44 (CUET 2024) For a weak electrolyte, molar conductivity:

- A) decreases with dilution B) increases with dilution C) remains constant D) first increases then decreases

Tests: Electrochemistry Answer: Not in extracted key

Q.45 (CUET 2024) Kohlrausch's law helps determine:

- A) Degree of dissociation B) Limiting molar conductivity C) Solubility of sparingly soluble salts D) All of these

Tests: Electrochemistry Answer: Not in extracted key

Q.47 (CUET 2024) The unit of molar conductivity is:

- A) $S\ cm^2\ mol^{-1}$ B) $\Omega\ cm$ C) $S\ cm^{-1}$ D) $\Omega^{-1}\ cm$

Tests: Electrochemistry Answer: Not in extracted key

Q.46 (CUET 2024) The conductance of a solution depends on:

- A) Distance between electrodes B) Area of electrodes C) Nature of electrolyte D) All of these

Tests: Conductance — factors affecting Answer: Not in extracted key

CUET 2023 — Actual PYQs from this chapter

Q.2 (CUET 2023) The standard reduction potentials of Sn^{4+}/Sn^{2+} is +0.15 V and Cr^{3+}/Cr is –0.74 V. These two half cells are connected to make a galvanic cell. The galvanic cell can be represented as:

- A) $Sn^{2+}(aq)|Sn^{4+}(aq)||Cr^{3+}(aq)|Cr(s)$ B) $Sn^{4+}(aq)|Sn^{2+}(aq)||Cr^{3+}(aq)|Cr(s)$ C) $Cr(s)|Cr^{3+}(aq)||Sn^{4+}(aq)|Sn^{2+}(aq)$ D) $Cr(s)|Cr^{3+}(aq)||Sn^{2+}(aq)|Sn^{4+}(aq)$

Tests: Electrochemistry Answer: Not in extracted key

Q.6 (CUET 2023) The quantity of charge required to obtain 2 mol of Mn^{2+} from MnO_4^- is:

- A) 2 F B) 10 F C) 5 F D) 1 F

Tests: Electrochemistry Answer: Not in extracted key

Q.36 (CUET 2023) The cell reaction occurring at anode in the electrolysis of aqueous NaCl solution is:

- A) (H^+(aq) + e^- → \frac{1}{2}H_2(g)) B) (Cl^-(aq) → \frac{1}{2}Cl_2(g) + e^-) C) (Na^+(aq) + e^- → Na(s)) D) (2H_2O(l) → O_2(g) + 4H^+(aq) + 4e^-)

Tests: Electrochemistry Answer: Not in extracted key

Q.39 (CUET 2023) Match List-I with List-II. List-I List-II (A) Fuel Cell (I) Rechargeable (B) Mercury Cell (II) Reaction at anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (C) Leclanche Cell (III) Cell reaction: $2H_2 + O_2 \rightarrow 2H_2O$ (D) Ni-Cd Cell (IV) Gives steady potential Options:

- A) A-I, B-IV, C-III, D-II B) A-III, B-I, C-IV, D-II C) A-III, B-IV, C-II, D-I D) A-IV, B-I, C-II, D-III

Tests: Electrochemistry Answer: Not in extracted key