CHAPTER 2

Electrochemistry

CBSE Class 12 · Chemistry · Chapter 2

CBSE · Chemistry · Class 12

WHAT THIS CHAPTER DOES

Boards prep that builds confidence, not anxiety.

TODAY'S MISSION

Today's mission

WHY THIS MATTERS

Why this chapter matters

TOPIC

A

Galvanic vs Electrolytic Cells

THEOREM · LOAD-BEARING RESULT

Two types of electrochemical cells

> *Electrochemical cells convert between chemical and electrical energy. There are two fundamental types — GALVANIC (chemical → electrical, spontaneous) and ELECTROLYTIC (electrical → chemical, non-spontaneous).*

STATEMENT

GALVANIC CELL: a spontaneous redox reaction ($\Delta G < 0$, $E°\_cell > 0$) drives external current — the cell PRODUCES electrical energy from chemical energy. Example: Daniell cell (Zn-Cu), every battery, fuel cells. ELECTROLYTIC CELL: an

WHY THIS MATTERS

- The galvanic-electrolytic distinction is the conceptual organising principle of electrochemistry
- All batteries are galvanic
- all electroplating/refining is electrolytic

WATCH OUT FOR

NOTE In galvanic cells, anode is NEGATIVE (loses electrons → e^- flow out) and cathode is POSITIVE (gains electrons). In electrolytic cells, the polarities REVERSE relative to the external source: anode is POSITIVE (connected to + terminal of battery), cathode is NEGATIVE. The chemistry definition is consistent (anode = oxidation, cathode =

TOPIC

Anatomy of a galvanic cell — Daniell cell example

ANODE HALF-CELL

Zn(s) immersed in $ZnSO_4$ solution. Zn is OXIDISED: $Zn \rightarrow Zn^{2+} + 2e^-$. Electrons flow OUT of the Zn electrode through the external circuit. The Zn electrode acts as the NEGATIVE terminal (electrons accumulate, leave through wire). Zn^{2+} ions enter the solution, raising its concentration.

CATHODE HALF-CELL

Cu(s) immersed in $CuSO_4$ solution. Cu^{2+} is REDUCED: $Cu^{2+} + 2e^- \rightarrow Cu$. Electrons flow INTO the Cu electrode from the external wire. The Cu electrode acts as the POSITIVE terminal. Cu metal plates onto the electrode; $[Cu^{2+}]$ in solution decreases.

SALT BRIDGE

A U-tube filled with KNO_3 or KCl gel, connecting the two half-cells. Function: completes the electrical circuit AND maintains electrical neutrality. Cations (K^+) migrate toward the cathode half-cell (replacing Cu^{2+} being consumed); anions (NO_3^-) migrate toward the anode half-cell (balancing the Zn^{2+} being produced). Without salt

CELL NOTATION + EMF

$Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s)$. The $\parallel$ represents the salt bridge. $E^\circ_{Zn^{2+}/Zn} = -0.76V$; $E^\circ_{Cu^{2+}/Cu} = +0.34V$. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-0.76) = +1.10V$. Positive E° confirms galvanic (spontaneous) direction. This is the most-tested example in CBSE.

TOPIC

B

Standard Electrode Potentials + SHE

THEOREM · LOAD-BEARING RESULT

Standard Hydrogen Electrode (SHE) — the universal reference

> *The Standard Hydrogen Electrode (SHE) is the half-cell used as the international reference point for measuring all electrode potentials. By CONVENTION, the standard reduction potential of SHE is defined as E° = 0.00 V at 298 K.*

STATEMENT

SHE construction: a platinum electrode coated with platinum-black (high surface area) immersed in 1 M H^+ solution, with H_2 gas bubbled in at 1 atm pressure. Symbol: Pt(s) | H_2(g, 1 atm) | H^+(aq, 1M). Half-reaction:

WHY THIS MATTERS

- Electrode potentials cannot be measured absolutely (only differences are physically meaningful)
- The SHE convention provides a shared zero point against which all other potentials are measured
- The resulting table of standard electrode potentials (electrochemical series) lets us predict the direction of

WATCH OUT FOR

NOTE Don't claim SHE = 0V is an 'absolute zero' like 0 K. It is a chosen reference. Real SHE measurements have an uncertainty of ~10 mV; the 0.00V value is a definition, not a measurement. CBSE explicitly tests this 'convention vs absolute' distinction in 2-mark questions.

TOPIC

C

Nernst Equation

THEOREM · LOAD-BEARING RESULT

Nernst Equation — predicting EMF at non-standard concentrations

> *The Nernst equation gives the electrode potential (or cell EMF) at any concentration / temperature, by adjusting the standard value E° for non-standard conditions.*

STATEMENT

General Nernst equation: E = E° – (RT/nF) ln Q, where Q is the reaction quotient (concentration of products / concentration of reactants, with stoichiometric powers). At T = 298 K, the constants combine to give the

WHY THIS MATTERS

- Real cells rarely operate at standard 1 M concentrations
- As a galvanic cell runs, reactant concentrations decrease and product concentrations increase, so Q grows and E_cell drops over time
- The Nernst equation is the quantitative tool for tracking this

WATCH OUT FOR

NOTE Common errors: (1) using ln when the formula needs log (or vice versa), (2) writing Q wrong (reverse of products/ reactants), (3) wrong sign on (0.0591/n). Memorise the room-temperature form: 'E = E° MINUS (0.0591/n) log Q'. At standard state, Q = 1, log 1 = 0, so E = E° (consistency check).

TOPIC

D

Faraday's Laws of Electrolysis

TOPIC

Two laws governing electrolysis

FIRST LAW

Mass of substance deposited / liberated at an electrode is PROPORTIONAL to the QUANTITY OF CHARGE passed through the electrolyte. Mathematically: $m = Z \times Q = Z \times I \times t$, where Z is the ELECTROCHEMICAL EQUIVALENT (units g/C). Z = equivalent weight / F = (atomic weight/n) / 96500

SECOND LAW

When the SAME quantity of charge passes through different electrolytes in series, the masses of substances deposited are PROPORTIONAL to their EQUIVALENT WEIGHTS. $m_1/m_2 = E_1/E_2$. Example: same Q through Cu^{2+} and Ag^+ solutions: m_Cu / m_Ag = (63.5/2) / (108/1) = 31.75/108 ≈ 0.294. If 1 g of Cu deposits, ~3.4 g of Ag

CHARGE FROM MOLES OF ELECTRONS

$Q = n \times F$ where n is moles of electrons. Example: depositing 1 mole of Cu (which is $Cu^{2+} + 2e^- \rightarrow Cu$) requires 2 × 96500 = 193,000 C. Depositing 1 mole of Ag ($Ag^+ + e^- \rightarrow Ag$) requires 96,500 C. Standard CBSE numerical step.

EQUIVALENT WEIGHT DEFINITION

Equivalent weight = molecular weight / number of electrons transferred in the half-reaction. Example: $Cu^{2+} + 2e^- \rightarrow Cu$: equivalent weight of Cu = 63.5/2 = 31.75 g/eq. $Al^{3+} + 3e^- \rightarrow Al$: equivalent weight of Al = 27/3 = 9 g/eq. CBSE numericals often require computing equivalent weight first.

TOPIC

E

Conductance of Electrolytic Solutions

TOPIC

Conductivity + molar conductivity + Kohlrausch's law

CONDUCTIVITY Κ (KAPPA)

Conductivity κ is the conductance of a unit cube of solution ($1\ cm^3$). Units: $S \cdot cm^{-1}$ or $S \cdot m^{-1}$. Depends on number of ions, ion mobility, charge. κ DECREASES with dilution (fewer ions per unit volume). For pure water, $\kappa \approx 6 \times 10^{-8}\ S \cdot cm^{-1}$ (very poor conductor).

MOLAR CONDUCTIVITY Λ_M

Molar conductivity $\Lambda_m = \kappa \times 1000/c$ (units: $S \cdot cm^2 \cdot mol^{-1}$, where c is in mol/L). Captures conductivity per mole of electrolyte, isolating the per-ion contribution. Λ_m INCREASES with dilution (counter-intuitive!) — at infinite dilution, ions move freely without interionic interference.

KOHLRAUSCH'S LAW

At INFINITE DILUTION, the molar conductivity Λ°_m of an electrolyte is the SUM of the contributions of its constituent ions: $\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$. Each ion contributes independently. Used to find Λ°_m of weak electrolytes (which cannot be measured directly because they don't fully dissociate).

APPLICATION — WEAK ELECTROLYTE FROM STRONG

Kohlrausch's law lets us find Λ°_m of weak electrolyte CH_3COOH from data on strong electrolytes: $\Lambda^\circ_m(CH_3COOH) = \Lambda^\circ_m(CH_3COONa) + \Lambda^\circ_m(HCl) - \Lambda^\circ_m(NaCl)$. The ions are added/subtracted to give the desired combination. CBSE 3-mark numericals test this combinatorial logic.

TOPIC

F

Batteries + Fuel Cells + Corrosion

TOPIC

Practical electrochemical cells

PRIMARY (NON-RECHARGEABLE) CELLS

Reaction is non-reversible. Once the reactants are consumed, the cell is dead — must be discarded. Examples: Dry cell (Zn-MnO_2, ~1.5V), Mercury cell (Zn-HgO, ~1.35V, stable voltage, used in watches/hearing aids). Cheap to manufacture, limited energy density.

SECONDARY (RECHARGEABLE) CELLS

Reaction is reversible — can be recharged by applying reverse voltage. Examples: Lead-acid (Pb-PbO_2, 2.05V/cell × 6 for 12V car battery), Lithium-ion (Li intercalation, 3.6V, phones/EVs/laptops). Higher cost but reusable hundreds-thousands of cycles.

FUEL CELLS

Continuous flow of reactants from external supply — never 'runs out' as long as fuel is supplied. Example: H_2-O_2 fuel cell used on Apollo spacecraft and in modern hydrogen-fuel-cell vehicles. Reactions: anode $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$; cathode $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. By-product: pure water. Efficiency 70%+ vs

CORROSION OF IRON

Iron rusting is an ELECTROCHEMICAL process. Requires THREE: (1) oxygen, (2) water, (3) electrolyte (CO_2 dissolved as carbonic acid suffices). Iron acts as anode: $Fe \rightarrow Fe^{2+} + 2e^-$; O_2 at cathode is reduced: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. $Fe^{2+} + O_2 + H_2O \rightarrow Fe_2O_3{\cdot}xH_2O$ (rust). Prevention: galvanisation (Zn coating — Zn is more

PYQ PATTERNS

Top 5 PYQ patterns

MARKS DISTRIBUTION

Marks distribution

TOPIC

Anode vs cathode — sign in galvanic vs electrolytic cell

TRAP → TRUTH

✗ **MISTAKE** Anode is always positive and cathode is always negative.

✓ **CORRECT** In a GALVANIC cell (spontaneous): anode is NEGATIVE (loses electrons → e^- flow out), cathode is POSITIVE (gains electrons). In an ELECTROLYTIC cell (non-spontaneous, driven by external source): anode is POSITIVE (connected to + terminal of source), cathode is NEGATIVE. The OPERATIONAL definition is consistent: anode = oxidation, cathode = reduction. But the SIGN reverses between cell types. CBSE 1-mark MCQ explicitly tests this.

TOPIC

Standard Hydrogen Electrode value

TRAP → TRUTH

× **MISTAKE** Standard Hydrogen Electrode potential is the absolute zero — like 0 K for temperature.

✓ **CORRECT** SHE potential = 0.00V is a CONVENTION, not an absolute zero. By international agreement, the reduction potential of the SHE half-cell (Pt | H_2(1 atm) | H^+(1M, 298K)) is DEFINED as 0.00V, and all other electrode potentials are MEASURED relative to it. There is no 'absolute' electrode potential — only relative values. CBSE explicitly tests this 'convention vs absolute' distinction.

TOPIC

Nernst equation — when is it applicable?

TRAP → TRUTH

× **MISTAKE** The Nernst equation only applies to standard conditions (1M, 25°C, 1 atm).

✓ **CORRECT** Nernst equation applies at NON-STANDARD conditions. The STANDARD electrode potential E° is what you get at the standard state. The Nernst equation tells you how E shifts when you move AWAY from standard state: $E = E° - (RT/nF) \ln Q$ where Q is the reaction quotient. At standard conditions $Q = 1$, $\ln Q = 0$, so $E = E°$ (consistency). CBSE asks 'what does Nernst predict at standard conditions?' Answer: $E = E°$.

TOPIC

Galvanic vs electrolytic — driver of process

TRAP → TRUTH

× **MISTAKE** Galvanic and electrolytic cells are essentially the same — both involve electron flow.

✓ **CORRECT** Galvanic (Voltaic) cells are SPONTANEOUS: a spontaneous redox reaction ($\Delta G < 0$) drives current externally — they PRODUCE energy. Electrolytic cells are NON-SPONTANEOUS: external electrical source (battery) drives a non-spontaneous reaction ($\Delta G > 0$) — they CONSUME energy. The reaction direction is OPPOSITE in the two types. CBSE 3-mark distinguish-questions test this explicitly.

TOPIC

Faraday's law — units of equivalent weight

TRAP → TRUTH

× **MISTAKE** Equivalent weight in Faraday's second law equals the molecular weight.

✓ **CORRECT** Equivalent weight = atomic/molecular weight / n (where n = number of electrons transferred in the half-reaction). Example: $Cu^{2+} + 2e^- \rightarrow Cu$ has n = 2, so equivalent weight of Cu = 63.5/2 = 31.75 g/eq. For $Ag^+ + e^- \rightarrow Ag$, n = 1, equivalent weight = 108 g/eq. Faraday's second law compares equivalent weights, NOT molecular weights. CBSE numericals test this distinction.

TOPIC

Molar conductivity behaviour with concentration

TRAP → TRUTH

× **MISTAKE** Molar conductivity always increases with concentration because there are more ions.

✓ **CORRECT** Molar conductivity Λ_m DECREASES with increasing concentration — counter-intuitive but true. Reason: at higher concentration, ion-ion interactions (interionic attraction) slow down ion mobility; effectively, ions interfere with each other. At INFINITE DILUTION, interactions vanish and Λ_m reaches its maximum value Λ°_m. Conductivity κ (per unit volume) does increase with concentration; molar conductivity $\Lambda_m = \kappa \times 1000/c$ does not.

TOPIC

Corrosion of iron — what drives it?

TRAP → TRUTH

× **MISTAKE** Iron rusts because of pure oxygen contact alone.

✓ **CORRECT** Corrosion of iron is an ELECTROCHEMICAL process requiring (1) oxygen AND (2) moisture (water) AND (3) usually some electrolyte (CO_2 dissolved in water creates carbonic acid). Iron acts as ANODE (oxidised to Fe^{2+}), oxygen at cathode is reduced. Without water + electrolyte, oxygen alone cannot rust iron at room temperature in reasonable time. This is why galvanisation (Zn barrier) + cathodic protection (sacrificial Zn) prevent rusting. CBSE 3-mark questions test the three requirements.

TOPPER TEMPLATE · MARK-BY-MARK

5-mark question: Derive Nernst equation for a half-cell + apply at non-standard concentrations

1	**START FROM THERMODYNAMIC RELATIONSHIP**	1 m	$\Delta G = \Delta G^\circ + RT\,\mathrm{In}\,Q$ (general result for any reaction at non-standard state). For electrochemical reaction, the work done is electrical: $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$. Substitute: $-nFE = -nFE^\circ + RT\,\mathrm{In}\,Q$.
2	**SOLVE FOR E**	1 m	Divide both sides by $-nF$: $E = E^\circ - (RT/nF)\,\mathrm{In}\,Q$. This is the NERNST EQUATION in its general form. T = absolute temperature in Kelvin; F = Faraday constant = 96485 C/mol; R = 8.314 J/(mol·K); n = number of electrons transferred.
3	**SUBSTITUTE ROOM-TEMPERATURE CONSTANTS**	1 m	At T = 298 K (25°C), the constants combine: $RT/F \times \ln(10) = (8.314 \times 298 / 96485) \times 2.303 \approx 0.0591$ V. Substituting: $E = E^\circ - (0.0591/n) \log Q$. This is the room-temperature working form examiners expect in numerical questions.
4	**APPLY TO A SPECIFIC CELL**	1 m	For $Cu^{2+} + 2e^- \rightarrow Cu$ at 0.1 M $[Cu^{2+}]$: $Q = 1/[Cu^{2+}] = 1/0.1 = 10$. $E = 0.34 - (0.0591/2) \times \log(10) = 0.34 - 0.02955 \approx 0.31$ V. So reducing $[Cu^{2+}]$ from 1M to 0.1M lowers the half-cell potential by ~30mV.
5	**APPLICATION — CELL EMF AT NON-STANDARD STATE**	1 m	For a complete cell, E_cell = E°_cell − (0.0591/n) log Q where Q is the cell reaction quotient. EMF DROPS as the reaction proceeds (products build, reactants deplete, Q increases). When E_cell = 0, the cell has reached equilibrium — no more useful work. This is the basis of all battery design + Nernst-equation calculations CBSE tests.

TOPPER TEMPLATE · MARK-BY-MARK

4-mark question: Galvanic cell EMF computation from E° values + cell notation

1 IDENTIFY CATHODE (HIGHER E°) AND ANODE (LOWER E°)

1 m

Given two half-cells, both written as REDUCTION potentials. The half-cell with HIGHER E° (more positive reduction potential) acts as CATHODE — gets reduced. The LOWER E° half-cell acts as ANODE — gets oxidised. Example: Zn^{2+}/Zn ($E^\circ = -0.76V$) and Cu^{2+}/Cu ($E^\circ = +0.34V$). Cu is cathode; Zn is anode.

2 COMPUTE CELL EMF

1 m

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ (both as REDUCTION potentials). Example: $E^\circ_{cell} = 0.34 - (-0.76) = +1.10$ V. Positive E°_{cell} confirms the spontaneous direction. If E°_{cell} is negative, you've got the cathode/anode wrong — swap them.

3 WRITE CELL NOTATION

1 m

Convention: ANODE | anode-ion (concentration) || cathode-ion (concentration) | CATHODE. The | separates phases; the || represents the salt bridge. Example: $Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s)$. The double-bar emphasises that the salt bridge eliminates liquid junction potential.

4 IDENTIFY ELECTRON FLOW AND ION MIGRATION

1 m

Electrons flow from anode (Zn) to cathode (Cu) in the external circuit. In the salt bridge, cations migrate toward the cathode half-cell; anions migrate toward the anode half-cell — completing the circuit and maintaining electrical neutrality. CBSE rewards explicit mention of both directions in 5-mark long-answers.

TOPPER TEMPLATE · MARK-BY-MARK

4-mark numerical: Faraday's laws — mass deposited / moles of gas evolved

	Step	Marks	Working
1	**COMPUTE TOTAL CHARGE Q PASSED**	1 m	$Q = I \times t$ (current in amperes × time in seconds). Example: $I = 2$ A, $t = 30$ min $= 1800$ s. $Q = 2 \times 1800 = 3600$ C.
2	**COMPUTE MOLES OF ELECTRONS (OR USE FARADAY'S LAW)**	1 m	Moles of electrons = Q/F where F = 96500 C/mol. Example: 3600/96500 = 0.0373 mol of electrons. Alternative direct route via Faraday's first law: $m = (Z \times I \times t)$ where Z = equivalent weight / 96500 (electrochemical equivalent).
3	**APPLY TO HALF-REACTION TO FIND PRODUCT**	1 m	Identify half-reaction. Example: $Cu^{2+} + 2e^- \rightarrow Cu$ means 2 moles of electrons produce 1 mole of Cu. So 0.0373 mol electrons → 0.0373/2 = 0.0187 mol Cu = 0.0187 × 63.5 g = 1.18 g Cu deposited at the cathode.
4	**QUOTE FINAL ANSWER WITH UNITS + VERIFY**	1 m	1.18 g of Cu deposited. Verify: Cu equivalent weight = 63.5/2 = 31.75 g/eq. Mass = (3600/96500) × 31.75 = 1.18 g ✓. Always quote units (g for mass, L or mol for gas) — CBSE deducts 0.5 mark for missing units.

PYQ PATTERNS

Top PYQ patterns to drill

#1	Nernst equation derivation + calculation at non-standard concentration (5 marks)	90%
#2	Galvanic cell EMF from E° values (4 marks)	90%
#3	Faraday's laws application (4 marks)	80%
#4	Molar conductivity at infinite dilution (Kohlrausch's law) (3 marks)	70%
#5	Standard hydrogen electrode (SHE) and reference (3 marks)	60%

MARKS DISTRIBUTION

10-year marks distribution

10-YEAR PYQ MARKS DISTRIBUTION

Nernst equation derivation + calculations	**25%**
Galvanic cell + EMF + cell notation	**20%**
Standard electrode potentials + activity/EMF series	**15%**
Molar conductivity + Kohlrausch's law	**15%**
Electrolysis + Faraday's laws	**15%**
Batteries (primary, secondary, fuel cells) + corrosion	**10%**

RECAP · MEMORISE THESE

5-line revision

1 Galvanic vs Electrolytic — Galvanic = spontaneous (battery, $\Delta G<0$, $E°>0$). Electrolytic = non-spontaneous (needs external source, $\Delta G>0$). Anode = oxidation, cathode = reduction in both.

2 SHE — Pt | H_2(1atm) | H^+(1M). E° = 0.00V BY CONVENTION (not absolute). All other E° measured against SHE.

3 Cell EMF + Nernst — E°_cell = E°_cathode – E°_anode. Nernst (298K): E = E° – (0.0591/n) log Q. At equilibrium, E_cell = 0.

4 Faraday's laws — First: m = Z·I·t. Second: m_1/m_2

5 Kohlrausch + Corrosion — $\Lambda°\_m = v_+\lambda°_+ + v_-\lambda°_-$

WHAT'S NEXT

Coming up next

- → Chapter 3 — Chemical Kinetics (rate of redox + other reactions; activation energy + Arrhenius).
- → Quick check: can you derive Nernst equation + state Faraday's two laws in under 5 minutes?

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