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CHAPTER NOTES

# Electrochemistry Class 12 Notes — CBSE Chemistry Chapter 3

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# Electrochemistry Class 12 Notes — CBSE Chemistry Chapter 3

Chapter 3 of Class 12 Chemistry — **Electrochemistry** — connects chemistry with electricity. This chapter explains how chemical reactions can produce electric current (galvanic cells) and how electricity can drive non-spontaneous reactions (electrolytic cells). With **7-8 marks** in Board exams, this is one of the highest-weightage chapters in Chemistry. Master the Nernst equation numericals and you'll ace this!

## Key Concepts

### Electrochemical Cells

| Feature | Galvanic (Voltaic) Cell | Electrolytic Cell |
|---|---|---|
| Energy conversion | Chemical → Electrical | Electrical → Chemical |
| $\Delta G$ | Negative (spontaneous) | Positive (non-spontaneous) |
| E_cell | Positive | Negative (external EMF applied) |
| Anode | Negative terminal | Positive terminal |
| Cathode | Positive terminal | Negative terminal |
| Example | Daniel cell | Electrolysis of NaCl |

**Memory Aid:** In BOTH cells: Oxidation at Anode, Reduction at Cathode (think "An Ox" and "Red Cat"). The sign of the electrode just flips!

### Daniel Cell — The Classic Galvanic Cell

$Zn \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu$

- **Anode (oxidation):** $Zn \rightarrow Zn^{2+} + 2e^-$
- **Cathode (reduction):** $Cu^{2+} + 2e^- \rightarrow Cu$
- **Salt bridge:** Maintains electrical neutrality (usually KCl in agar-agar)
- $E^0\_cell = E^0\_cathode - E^0\_anode = +0.34 - (-0.76) =$ **+1.10 V**

## Standard Electrode Potential ($E^0$)

Measured against the **Standard Hydrogen Electrode (SHE)** which is assigned $E^0 = 0.00$ V.

> **$E^0\_cell = E^0\_cathode - E^0\_anode$**
> If $E^0\_cell > 0$ → reaction is spontaneous
> If $E^0\_cell < 0$ → reaction is non-spontaneous

**Electrochemical Series (selected values):**

| Electrode | $E^0$ (V) | Tendency |
|---|---|---|
| $Li^+/Li$ | –3.05 | Strongest reducing agent |
| $K^+/K$ | –2.93 | Strong reducing agent |
| $Zn^{2+}/Zn$ | –0.76 | Good reducing agent |
| $H^+/H_2$ (SHE) | 0.00 | Reference |
| $Cu^{2+}/Cu$ | +0.34 | Weak oxidising agent |
| $Ag^+/Ag$ | +0.80 | Good oxidising agent |
| $F_2/F^-$ | +2.87 | Strongest oxidising agent |

## Nernst Equation

> **$E\_cell = E^0\_cell - (RT/nF) \ln Q$**
>
> At 298 K: **$E\_cell = E^0\_cell - (0.0591/n) \log Q$**
>
> Where: n = number of electrons transferred, Q = reaction quotient
> At equilibrium: $E\_cell = 0$, so **$E^0\_cell = (0.0591/n) \log K\_c$**

## Relationship Between ΔG and E_cell

> **$\Delta G^0 = -nFE^0\_cell$**
> Where: n = moles of electrons, F = 96485 C/mol (Faraday constant)

If $E^0\_cell > 0 \rightarrow \Delta G^0 < 0 \rightarrow$ spontaneous

If $E^0\_cell < 0 \rightarrow \Delta G^0 > 0 \rightarrow$ non-spontaneous

## Conductance of Electrolytic Solutions

**Conductance (G)** = 1/R (unit: S or $\Omega^{-1}$ or mho)

**Specific conductance (κ)** = 1/ρ = G × (l/A) — unit: S/cm

**Molar conductivity (Λ_m)** = κ × 1000/c — unit: S·cm²/mol

Where c = concentration in mol/L

## Variation of Conductivity with Concentration

- κ (specific conductance) **decreases** with dilution — fewer ions per unit volume
- Λ_m (molar conductivity) **increases** with dilution — more dissociation, less inter-ionic attraction

## Kohlrausch's Law of Independent Migration

$\mathbf{\Lambda^0\_m = v_+\lambda^0_+ + v_-\lambda^0_-}$

Where v = number of ions, $\lambda^0$ = limiting molar conductivity of each ion

Example: $\Lambda^0\_m(NaCl) = \lambda^0(Na^+) + \lambda^0(Cl^-)$

**Applications:**

- Calculate $\Lambda^0\_m$ of weak electrolytes (like $CH_3COOH$) which can't be measured directly
- $\Lambda^0\_m(CH_3COOH) = \Lambda^0\_m(CH_3COONa) + \Lambda^0\_m(HCl) - \Lambda^0\_m(NaCl)$
- Determine degree of dissociation: $\alpha = \Lambda\_m / \Lambda^0\_m$

## Electrolysis — Faraday's Laws

**First Law:** m = ZIt = (M × I × t) / (n × F)

Where: m = mass deposited, Z = electrochemical equivalent, I = current, t = time

**Second Law:** $m_1/m_2 = E_1/E_2$ (equivalent weights)

When same charge passes through different electrolytes

## Batteries

| Battery | Type | Anode | Cathode | E_cell |
|---|---|---|---|---|
| Dry Cell (Leclanché) | Primary | Zn | $MnO_2$ + C | 1.5 V |
| Mercury Cell | Primary | Zn-Hg | HgO | 1.35 V |
| Lead-acid (car) | Secondary | Pb | $PbO_2$ | 2 V/cell |
| Ni-Cd | Secondary | Cd | NiO(OH) | 1.2 V |
| $H_2$-$O_2$ Fuel Cell | Fuel | $H_2$ | $O_2$ | 1.23 V |

## Corrosion

Corrosion is an **electrochemical process.** Rusting of iron:

- **Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (iron dissolves)
- **Cathode:** $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow$ further oxidises to $Fe_2O_3 \cdot xH_2O$ (rust)

**Prevention:** Galvanisation (Zn coating), electroplating, cathodic protection, painting, alloying

## Important Definitions

| Term | Definition |
|---|---|
| Galvanic Cell | Device that converts chemical energy to electrical energy via spontaneous redox reaction |
| Electrolytic Cell | Device that uses electrical energy to drive non-spontaneous chemical reactions |
| Standard Electrode Potential | Potential of an electrode measured against SHE under standard conditions (1M, 1 atm, 25°C) |
| Salt Bridge | U-tube with electrolyte that maintains electrical neutrality in a galvanic cell |
| Molar Conductivity | Conductance of a solution containing 1 mole of electrolyte between electrodes 1 cm apart |
| Faraday Constant | Charge on 1 mole of electrons = 96485 C/mol |
| Corrosion | Electrochemical destruction of metals by reaction with the environment |

## Solved Examples — NCERT Based

### Example 1: EMF of Cell using Nernst Equation

**Q:** Calculate the EMF of the cell: Zn I $Zn^{2+}$(0.001 M) II $Cu^{2+}$(0.1 M) I Cu. Given $E^0(Zn^{2+}/Zn) = -0.76$ V, $E^0(Cu^{2+}/Cu) = +0.34$ V

**Solution:**

$E^0\_cell = 0.34 - (-0.76) = 1.10$ V, n = 2

$Q = [Zn^{2+}]/[Cu^{2+}] = 0.001/0.1 = 0.01$

$E\_cell = 1.10 - (0.0591/2) \times \log(0.01)$

$E\_cell = 1.10 - 0.02955 \times (-2) = 1.10 + 0.0591 =$ **1.159 V**

### Example 2: ΔG from $E^0$_cell

**Q:** Calculate $\Delta G^0$ for the reaction: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$. Given $E^0(Fe^{3+}/Fe^{2+}) = +0.77$ V, $E^0(I_2/I^-) = +0.54$ V

**Solution:**

$E^0\_cell = E^0\_cathode - E^0\_anode = 0.77 - 0.54 = 0.23$ V

n = 2 (2 electrons transferred)

$\Delta G^0 = -nFE^0 = -2 \times 96485 \times 0.23 =$ **−44,383 J = −44.4 kJ**

### Example 3: Faraday's Law — Mass Deposited

**Q:** How much copper is deposited on the cathode if a current of 0.5 A is passed through $CuSO_4$ solution for 2 hours? (M of Cu = 63.5, n = 2)

**Solution:**

$t = 2 \times 3600 = 7200$ s

$m = (M \times I \times t) / (n \times F) = (63.5 \times 0.5 \times 7200) / (2 \times 96485)$

$m = 228600 / 192970 =$ **1.185 g**

### Example 4: Kohlrausch's Law

**Q:** Calculate $\Lambda^0\_m$ of $CH_3COOH$ using: $\Lambda^0\_m(CH_3COONa) = 91.0$, $\Lambda^0\_m(HCl) = 426.2$, $\Lambda^0\_m(NaCl) = 126.5$ (all in S·cm²/mol)

**Solution:**

$\Lambda^0\_m(CH_3COOH) = \Lambda^0\_m(CH_3COONa) + \Lambda^0\_m(HCl) - \Lambda^0\_m(NaCl)$

$= 91.0 + 426.2 - 126.5 =$ **390.7 S·cm²/mol**

## Important Questions for Board Exams

### 1 Mark Questions

1. What is the SI unit of molar conductivity?

2. How does molar conductivity change with dilution?
3. What is the role of salt bridge in a galvanic cell?
4. State Faraday's first law of electrolysis.
5. Why is $E^0$ of SHE taken as zero?

## 2 Mark Questions

1. Differentiate between galvanic and electrolytic cells.
2. Write the Nernst equation and define each term.
3. Explain why $\Lambda_m$ of a weak electrolyte increases sharply at very low concentrations.
4. State Kohlrausch's law. Give one application.

## 3 Mark Questions

1. Describe the construction and working of the Daniel cell with a diagram.
2. How is ΔG related to EMF? Calculate $\Delta G^0$ for a cell with $E^0 = 1.10$ V and n = 2.
3. Explain corrosion of iron as an electrochemical process. How can it be prevented?
4. Calculate the EMF of a cell at 298 K using the Nernst equation given specific conditions.

## 5 Mark Questions

1. What is a fuel cell? Explain the construction and working of the hydrogen-oxygen fuel cell. What are its advantages?
2. State and explain Faraday's laws of electrolysis. Calculate the mass of aluminium deposited when 5 A current is passed through $Al_2O_3$ for 1 hour.

# Quick Revision Points

- Anode = Oxidation, Cathode = Reduction (in ALL cells)
- $E^0_{cell} = E^0_{cathode} - E^0_{anode}$; positive → spontaneous
- Nernst equation at 298K: $E = E^0 - (0.0591/n) \log Q$
- At equilibrium: $E = 0$, $E^0 = (0.0591/n) \log K$
- $\Delta G^0 = -nFE^0$ (link between thermodynamics and electrochemistry)
- κ decreases with dilution; $\Lambda_m$ increases with dilution
- Kohlrausch: $\Lambda^0_m = \nu_+\lambda^0_+ + \nu_-\lambda^0_-$
- Faraday: m = MIt/nF
- Lead-acid: rechargeable, 6 cells × 2V = 12V car battery

- Fuel cells: high efficiency (~70%), clean energy, produce only water
- Corrosion = electrochemical; prevent by galvanisation, cathodic protection

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