# Electrochemistry

## Overall Weightage

JEE Main : 8-12 marks (out of 100)
JEE Advanced: 12-16 marks (out of 120)

Typically comprises 8-12% of the total chemistry section
Most Frequently Tested Concepts
Electrochemical Cells (32%)
Conductance and Conductivity (28%)
Electrolysis (22%)
Batteries and Corrosion (18%)

## 1. Conductors - Basic Classification and Properties

### Metallic Conductors

1. Fundamental Properties:
    - Flow of electricity takes place without the decomposition of the substance
    - Electricity is produced due to the movement of electrons (flow of matter)
    - As temperature increases, electrical conduction decreases due to increase in kernel vibrations
    - Resistance is caused by vibrating kernels
    - Faraday's law is not followed

### Electrolytic Conductors

1. Fundamental Properties:
    - Flow of electricity takes place with the decomposition of the substance
    - Electricity produced due to the movement of ions (flow of matter)
    - As temperature increases, electrolytic conduction increases due to

increase in dissociation
  - Resistance is caused by inter-ionic interactions and viscosity of solvent
  - Faraday's law is followed

## 2. Laws of Electrolysis

### Faraday's First Law

- The mass of substance deposited/liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte
- Mathematical Form: $\boxed{W = Z \times I \times t}$
- Where:
  - $W$ = Mass of substance deposited
  - $Z$ = Electrochemical equivalent
  - $I$ = Current in amperes
  - $t$ = Time in seconds

### Faraday's Second Law

- Mathematical Form:

$$\frac{\text{Weight of X deposited}}{\text{Weight of Y deposited}} = \frac{\text{Equivalent weight of X}}{\text{Equivalent weight of Y}}$$

### Products of Electrolysis

1. For Molten NaCl:
   - At Cathode: Na metal ($Na^+ + e^- \rightarrow Na_{(l)}$)
   - At Anode: $Cl_2$ gas ($Cl^- \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$)

Cathode – Redn (gain of e⁻)
Anode – Oxidation (Loss of e⁻

2. For Aqueous NaCl:
   - At Cathode: $H_2$ gas ($H_2O_{(l)} + e^- \rightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$)
   - At Anode: $Cl_2$ gas ($Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$)
3. For Dilute $H_2SO_4$: ✓
   - At Cathode: $H_2$ gas ($H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$)
   - At Anode: $O_2$ gas ($2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$)
4. For Concentrated $H_2SO_4$: ✓
   - At Cathode: $H_2$ gas ($H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$)

- At Cathode: $H_2$ gas ($H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$)
- At Anode: $SO_2$ gas ($2SO_4^{2-}{}_{(aq)} \rightarrow S_2O_8^{2-}{}_{(aq)} + 2e^-$)

## 3. Conductance Parameters and Their Relationships

### Specific Conductance (κ) → kappa.

1. Definition:
   - Reciprocal of specific resistance of solution of 1 cm length
   - Having 1 cm² area of cross-section
2. Mathematical Form:
   - $\kappa = 1/\rho = l/Ra$
   - Units: $ohm^{-1}\ cm^{-1}$ (or $S\ m^{-1}$ in SI)

### Equivalent Conductance (Λeq)

1. Definition:
   - Conductance of all the ions produced from 1 gram equivalent of electrolyte in a given solution
2. Mathematical Form:
   - $\Lambda_{eq} = \kappa \times V = \kappa \times 1000/\text{Normality}$
   - Units: $ohm^{-1}\ cm^2\ eq^{-1}$

### Molar Conductance (Λm)

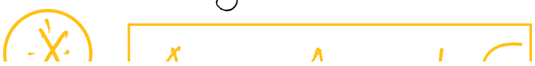
1. Definition:
   - Conductance of all the ions produced by ionization of 1 mole of an electrolyte in a given solution
2. Mathematical Form:
   - $\Lambda_m = \kappa \times V = \kappa \times 1000/\text{Molarity}$
   - Units: $ohm^{-1}\ cm^2\ mol^{-1}$

## 4. Variation of Conductivity with Concentration

Molar conductivity (Λm) is a fundamental concept in electrochemistry that describes how well an electrolyte solution conducts electricity. The behavior of molar conductivity varies significantly between strong and weak electrolytes.

### Strong Electrolytes

Strong electrolytes follow the Debye-Huckel Onsager equation: $\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$



Strong electrolytes follow the Debye-Huckel Onsager equation: $\Lambda m = \Lambda m\infty - b\sqrt{c}$

$\boxed{\Lambda_m = \Lambda_{m_0} - b\sqrt{c}}$

where:

- $\Lambda m\infty$ represents the molar conductivity at infinite dilution (limiting molar conductance)
- b is a constant specific to the electrolyte type
- c is the concentration

Strong electrolytes like KCl show only a small increase in conductance with dilution. This is because they are already completely dissociated into ions at all concentrations, so dilution only reduces the inter-ionic interactions that hinder ion movement.

## Weak Electrolytes

Weak electrolytes, such as $CH_3COOH$ (acetic acid), behave quite differently. They show a dramatic increase in conductance as dilution approaches infinity. This occurs because:

- They dissociate to a much lesser extent than strong electrolytes
- Dilution promotes further dissociation according to Le Chatelier's principle
- The increased dissociation leads to more ions available for conducting electricity

## Kohlrausch's Law and Its Applications

## Fundamental Principle

Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the individual contributions of its constituent ions.

Mathematically: $\Lambda^\circ m = \lambda^\circ + + \lambda^\circ -$

where $\lambda^\circ +$ and $\lambda^\circ -$ are the ionic conductivities of cation and anion at infinite dilution.

## Applications

1. **Calculating Molar Conductivity of Weak Electrolytes** For weak acids like $CH_3COOH$: $\Lambda^\circ m(CH_3COOH) = \lambda^\circ CH_3COO^- + \lambda^\circ H^+$

This can be expanded using known values: $\Lambda^\circ m(CH_3COOH) = \Lambda^\circ$

m(CH3COONa) + Λ°m(HCl) - Λ°m(NaCl)

1. **Determining Degree of Dissociation (α)** α = Λcm/Λ°m This ratio helps quantify how completely an electrolyte dissociates.
2. **Calculating Dissociation Constants** For weak electrolytes: Kc = Cα²/(1-α) where C is concentration and α is the degree of dissociation.

$$K_c = \frac{C\alpha^2}{1-\alpha}.$$

3. **Solubility Calculations** For sparingly soluble salts: Solubility (mol⁻¹) = (κ × 1000)/Λ°m where κ is the specific conductance.

$$\frac{K \times 1000}{\Lambda^\circ_m}$$

## Electrochemical Cells

Electrochemical cells convert between chemical and electrical energy through redox reactions. They come in two main types:

### Galvanic Cells

- Spontaneous conversion of chemical energy to electrical energy
- Anode: Negative terminal, oxidation occurs
- Cathode: Positive terminal, reduction occurs

### Electrolytic Cells

- Non-spontaneous conversion requiring external electrical energy
- Anode: Positive terminal, oxidation occurs
- Cathode: Negative terminal, reduction occurs

$$E^\circ_{cell} = E^\circ_{(ox)} + E^\circ_{red}$$

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

### Nernst Equation and Cell Potential

The Nernst equation relates cell potential to concentration: E = E° - (0.0591/n)log(1/[M(aq)n+])

$$E = E^\circ - \frac{0.0591}{n} \log \left( \frac{1}{M^{n+}_{(aq)}} \right)$$

### Applications include:

1. **Cell Potential Calculations** For a reaction aA + bB → xX + yY: Ecell = E°cell - (0.0591/n)log([X]x[Y]y/[A]a[B]b) at 298K
2. **Equilibrium Constants** At equilibrium (Ecell = 0): E°cell = (0.0591/n)log Kc

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_c.$$

## Electrochemical Series and Predictions

The electrochemical series arranges metals by their oxidation tendency. This arrangement enables several predictions:

1. **Oxidizing and Reducing Agent Strength**

- More positive E° indicates stronger oxidizing agent
- More negative E° indicates stronger reducing agent

### 2. Reaction Feasibility ⊛

- Positive Ecell indicates feasible reaction — Spontaneous.
- Negative Ecell indicates non-feasible reaction — non-Spon.

### 3. Metal Displacement Reactions

- Metals higher in the series can displace lower metals from their salt solutions
- Example: Zinc can displace hydrogen from acids (Zn + H2SO4 → ZnSO4 + H2)

## Types of Cells

### 1. Primary Cells

- Single-use cells where reactions occur only once
- Cannot be recharged after depletion
- Reactions are not reversible

Examples: a) **Dry Cell**

- Anodic Reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- Cathodic Reaction: $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH)(s) + NH_3(g)$
- Used in portable electronics and flashlights

b) **Mercury Cell**

- Anodic Reaction: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$
- Cathodic Reaction: $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$
- Historically used in watches and small electronic devices
- Less common now due to environmental concerns

### 1. Secondary Cells

- Rechargeable cells that can be used multiple times
- Chemical reactions can be reversed by passing current
- More cost-effective for long-term use

Examples: a) **Lead Storage Battery**

- Anodic Reaction: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

- Cathodic Reaction: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
- Commonly used in automobiles
- During charging, these reactions are reversed

b) **Nickel-Cadmium Cell**

- Anodic Reaction: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
- Cathodic Reaction: $NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$
- Used in portable electronics and emergency lighting
- Known for their durability and long cycle life

1. **Fuel Cells**

- Convert chemical energy from fuel directly into electrical energy
- Continuous operation as long as fuel is supplied
- Higher efficiency compared to traditional combustion engines
- Environmentally friendly power source

Example: Hydrogen Fuel Cell

- Anodic Reaction: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
- Cathodic Reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
- Overall Reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- Advantages:
    - Only produces water as a byproduct
    - High energy efficiency (up to 60%)
    - No moving parts, reducing maintenance needs
    - Quick refueling compared to battery charging

Key Differences:

- Primary cells: One-time use, simple construction, affordable
- Secondary cells: Reusable, higher initial cost, more economical long-term
- Fuel cells: Continuous operation, requires fuel supply, highly efficient

## Ionic Mobility and Transport Phenomena

### Ionic Mobility

Ionic mobility represents how fast ions move through a solution under specific conditions. It is defined as the speed of an ion in centimeters per second (cm/s) at infinite dilution when subjected to a potential gradient of 1 volt per centimeter (V/cm). The unit of ionic mobility is expressed as $cm^2\ V^{-1}\ s^{-1}$.

Understanding ionic mobility helps us comprehend several important phenomena:

Size Effects: Smaller ions generally show lower ionic conductivity due to extensive solvation. This might seem counterintuitive at first, but when we consider that smaller ions attract a larger sphere of water molecules (solvation shell), their effective size in solution becomes larger, reducing their mobility.

Special Case of $H^+$ and $OH^-$: These ions exhibit unusually high molar conductivity compared to other ions.

This exceptional behavior occurs through what we call the Grotthuss mechanism, where protons "jump" from one water molecule to another rather than moving through the solution as a whole ion.

### Transport Numbers

The transport number tells us what fraction of the total current is carried by each type of ion. We calculate it using:

$$t_+^\circ = \lambda_+^\circ / (\lambda_+^\circ + \lambda_-^\circ)$$

where:

$t_+^\circ$ is the transport number of the cation

$\lambda_+^\circ$ is the ionic conductivity of the cation at infinite dilution

$\lambda_-^\circ$ is the ionic conductivity of the anion at infinite dilution

### Salt Bridge and Liquid Junction Potential

- A salt bridge serves two crucial functions in electrochemical cells:
- It provides ions with similar conductance to maintain electrical neutrality

- It eliminates the liquid junction potential that naturally occurs due to different ion diffusion rates

- Think of the liquid junction potential like a traffic jam where vehicles (ions) of different sizes try to move through a narrow passage. Without a salt bridge, faster ions would create an uneven charge distribution, affecting our measurements.

Specialized Electrodes and Their Applications

Metal-Metal Ion Electrodes

These electrodes consist of a metal strip immersed in a solution containing its own ions. Common examples include:

$Zn/Zn^{2+}$
$Cu/Cu^{2+}$
$Ag/Ag^{+}$

The electrode potential follows the Nernst equation, allowing us to measure ion concentrations in solution.

Amalgam Electrodes

These electrodes use a mercury amalgam instead of pure metal to enhance activity. For example, the $Zn\text{-}Hg/Zn^{2+}$ electrode provides more stable readings than pure zinc. The amalgamation process:

Improves reproducibility of measurements
Reduces unwanted side reactions
Provides more stable potential readings

Gas Electrodes

These use inert metals (usually platinum) to facilitate gas reactions. Common examples:

$Pt, H_2/H^+$ (hydrogen electrode)
$Pt, Cl_2/Cl^-$ (chlorine electrode)

The platinum serves as a catalyst and electron conductor but doesn't participate in the reaction directly.

Metal-Metal Insoluble Salt-Salt Anion Electrodes

These complex electrodes involve a metal in contact with its sparingly soluble salt and a solution containing the same anion. Examples include:

- Calomel electrode ($Hg\text{-}Hg_2Cl_2(s)\text{-}KCl(aq)$)
- Lead sulfate electrode ($Pb\text{-}PbSO_4(s)\text{-}K_2SO_4(aq)$)
- Silver chloride electrode ($Ag\text{-}AgCl(s)\text{-}KCl(aq)$)

### Redox Electrodes

These electrodes measure electron transfer between different oxidation states of the same element. The classic example is the $Fe^{2+}/Fe^{3+}$ system, where a platinum wire dips into a solution containing both forms of iron.

### Thermodynamic Efficiency of Fuel Cells

The efficiency ($\eta$) is given by:

$\eta = \Delta G/\Delta H = -nFE/\Delta H$ ⊛ $\Delta G = -nFE$

This ratio tells us how much of the total energy change ($\Delta H$) can be converted to useful electrical work ($\Delta G$).

### Concentration Cells

These cells generate potential from concentration differences rather than different chemical species.

For example:

Zinc concentration cell: $Zn \mid Zn^{2+}(C_1) \parallel Zn^{2+}(C_2) \mid Zn$

Gas concentration cell: $Pt(H_2) \mid HCl \mid (H_2)Pt$

The cell potential depends on the concentration ratio:

$E_{cell} = (0.0591/n)\log(C_2/C_1)$ where $C_2 > C_1$

### Overvoltage

When we apply voltage to split water (electrolysis), we need more voltage than thermodynamically predicted. This extra potential, called overvoltage, occurs because:

The oxidation of $H_2O$ is kinetically slow
Additional energy is needed to overcome activation barriers
It can lead to unexpected reactions, such as chloride oxidation occurring before water oxidation at the anode

(JEE Main Online)

To find the standard potential of M3+/M electrode, the following cell is constituted :

Pt|M |M3+ (0.001 mol L^-1) || Ag+(0.01 mol L-1)Ag

The emf of the cell is found to be 0.421 volt at 298 K.

The standard potential of half reaction $M^{3+} + 3e^- \longrightarrow M$ at 298 K will be

(Given : E (Ag+/Ag) = at 298 K =0.80 Volt

(a) 0.32 Volt ✓

(b) 0.66 Volt

(c) 0.38 Volt

(d) 1.28 Volt

$E^0_{M^{3+}/M} = ?$

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[M^{3+}]}{[Ag^+]^3}$$

$$0.421 = E^0_{cell} - \frac{0.059}{3} \log \frac{0.001}{0.01}$$

$$E^0_{cell} = 0.421 + \frac{0.059}{3} \times 3$$

$$E^0_{cell} = \underline{0.480\,V}$$

$$E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{M^{3+}/M}$$

$$0.480 = 0.80 - E_{M^{3+}/M}$$

$$E_{M^{3+}/M} = 0.32\,V$$

Given below are the half-cell reactions : ✓

Mn2++2e - --------> Mn ; E° =- 1.18 V

2(Mn^3++e- ---------> Mn2+); E° = + 1.51 V ✓ ✓

The E° for 3Mn2+ -------> Mn + 2Mn^3+ will be

(a) -0.33 V; the reaction will occur

(b) ✓ -2.69 V; the reaction will not occur

(c) -2.69 V; the reaction will occur

(d) -0.33 V; the reaction will not occur. (JEE Main)

$$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$$

$$E^0_{cell} = -1.18 + (-1.51)$$

$$= -2.69\,V$$

The standard reduction potentials for Zn^2+/Zn, Ni^2+/Ni, and Fe^2+/Fe are -0.76- 0.23 and-0.44V respectively. The reaction X + Y^2+----> x^2+ + Y will be spontaneous

Ni^2+/Ni, and Fe^2+/Fe are -~~0.76~~- 0.23 and-0.44V respectively. The reaction X + Y^2+----> X^2+ + Y will be spontaneous when

$\hookrightarrow E_{cell} = +ve$

(a) X=Ni, Y= Zn (c) X=Zn, Y= Ni

(b) X=Fe, Y=Zn (d) X=Ni, Y=Fe

(IIT JEE)

$$Zn + Ni^{2+} \longrightarrow Zn^{2+} + \underline{Ni}$$

$$E^{\circ} = E^{\circ}_{red} - E^{\circ}_{oxi}$$

✓ ✓

The equivalent conductance of NaCl at concentration C and at infinite dilution are $\lambda_c$ and $\lambda_\infty$, respectively. The correct relationship between $\lambda_c$ and $\lambda_\infty$ is given as (where, the constant B is positive)

(JEE Main)

a) $\lambda_c = \lambda_\infty + (B)\sqrt{C}$

b) $\lambda_c = \lambda_\infty - (B)C$

c) $\lambda_c = \lambda_\infty -$

d)

c) $\lambda_c = \lambda_\infty + (B)C$

✓d) $\lambda_c = \lambda_\infty - B\sqrt{C}$

Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H2 gas at the cathode is ✓

(1 Faraday = 96500 C mol-1)

✓(a) 9.65 x 10^4 sec (c) 28.95 X 10^4 sec

(b) 19.3 x 10^4 sec (d) 38.6 X 10^4 sec

(IIT JEE)

$$Q = It$$

$$Q = 10 \times 10^{-3} \times t$$

$$t = \frac{Q}{10 \times 10^{-3}} \text{ ——— ①}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

$$Q = 2 \times 0.01 \times 96500$$

$$96500 \text{ ——— ②}$$

$Q = 2 \times 0.01 \times 96500$ —— ②

$= 0.02 \times 96500$

$$t = \frac{0.02 \times 96500}{10 \times 10^{-3}} = 19.3 \times 10^{4} \text{ Sec.}$$

The amount of substance deposited by the passage of 1 amp of current for 1 second is equal to

(a) equivalent mass
(b) molecular mass
[✓ (c)] electrochemical equivalent
(d) specific equivalent.

$W = Z \times I \times t$

$I = 1 \quad t = 1$

$\boxed{W = Z}$