Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (2026-27 / New NCERT)

Chapter 2: Electrochemistry

About This Chapter

Electrochemistry studies the interconversion of chemical energy and electrical energy. We begin with redox basics, build up galvanic cells (the Daniel cell as the canonical example), arrive at the Nernst equation and its link to thermodynamics, study how ions conduct electricity in solution (Kohlrausch's law), examine electrolysis (Faraday's laws), and finish with practical devices: batteries, fuel cells, and the corrosion problem. The 12th chapter is among the highest-weightage chapters for both CBSE boards and JEE/NEET.

Contents

Topics covered (NCERT 2026-27):

- Electrochemical cells: galvanic vs. electrolytic
- Galvanic cells, electrode potential, Daniel cell, salt bridge
- Standard hydrogen electrode (SHE) and electrochemical series

- Nernst equation, equilibrium constant, Gibbs energy link
- Conductance of electrolytic solutions; molar conductivity
- Variation of Λ_m with concentration; Kohlrausch’s law
- Electrolysis and Faraday’s laws of electrolysis
- Products of electrolysis; primary and secondary batteries
- Fuel cells; corrosion (electrochemical mechanism and prevention)

1 Redox Reactions and Electrochemical Cells

Every electrochemical phenomenon, from a torch battery to a rusting iron gate, traces back to one idea: **electrons being transferred from one species to another**. When we control the path the electrons take, we can extract electrical work; when we force electrons through a reluctant pathway with an external battery, we drive chemistry in reverse.

1.1 Oxidation, Reduction, and Cell Types

An **oxidation** is loss of electrons; a **reduction** is gain of electrons. The two always occur together (you cannot have one without the other) in a **redox reaction**. The species that loses electrons is the **reducing agent**; the one that gains them is the **oxidising agent**.

OIL RIG and LEO the Lion

OIL RIG: **O**xidation **I**s **L**oss (of electrons); **R**eduction **I**s **G**ain.
LEO the lion goes GER: **L**ose **E**lectrons = **O**xidation; **G**ain **E**lectrons = **R**eduction.

When a metal strip is dipped into a solution of its own ions, two opposing tendencies set up at the interface — the metal tries to dissolve as positive ions, and the ions in solution try to deposit as atoms on the strip. At equilibrium the metal acquires a charge relative to the solution: a potential difference appears across the interface. This is the **electrode potential**. We cannot measure a single electrode potential in isolation; we can only measure a *cell* potential, which is the difference between two such half-cells.

Two Kinds of Electrochemical Cells

Galvanic (voltaic) cell: a spontaneous redox reaction generates electrical energy. $\Delta G < 0$, $E_{\text{cell}} > 0$. Example: Daniel cell.

Electrolytic cell: an external EMF drives a non-spontaneous redox reaction. $\Delta G > 0$ for the chemistry; the external source supplies the energy. Example: electrolysis of molten NaCl.

Galvanic Cell
Spontaneous reaction ⇒ electrical energy out
$\Delta G < 0,\ E_{\text{cell}} > 0$

Chemical → Electrical

Electrolytic Cell
External EMF drives the non-spontaneous reaction
$\Delta G > 0,\ E_{\text{cell, applied}} > 0$

Electrical → Chemical

1.2 Anode and Cathode — a single rule

The names **anode** and **cathode** confuse students because the polarity changes between cell types. The rule that never changes is the chemistry:

Universal Anode/Cathode Definition

Anode: electrode where **oxidation** occurs.
Cathode: electrode where **reduction** occurs.

In a **galvanic cell**: anode is the negative terminal, cathode is the positive terminal.
In an **electrolytic cell**: anode is positive (connected to $+$ of external source), cathode is negative.

Polarity confusion

The cathode is *not always* positive! In a galvanic cell the cathode is the $+$ terminal; in an electrolytic cell the cathode is the $-$ terminal. Always identify by the chemistry first (reduction = cathode), then attach the sign.

2 Galvanic Cells — The Daniel Cell

A galvanic cell is built by physically separating the two half-reactions so that the electrons must travel through an external wire. The classic example is the **Daniel cell**, which couples the Zn/Zn^{2+} half-cell with the Cu/Cu^{2+} half-cell.

2.1 Construction of the Daniel Cell

A zinc rod sits in a beaker of $ZnSO_4$(aq); a copper rod sits in a beaker of $CuSO_4$(aq). The two solutions are connected by a **salt bridge** (typically an inverted U-tube packed with KCl or KNO_3 in agar gel). An external wire with a voltmeter connects the two electrodes.

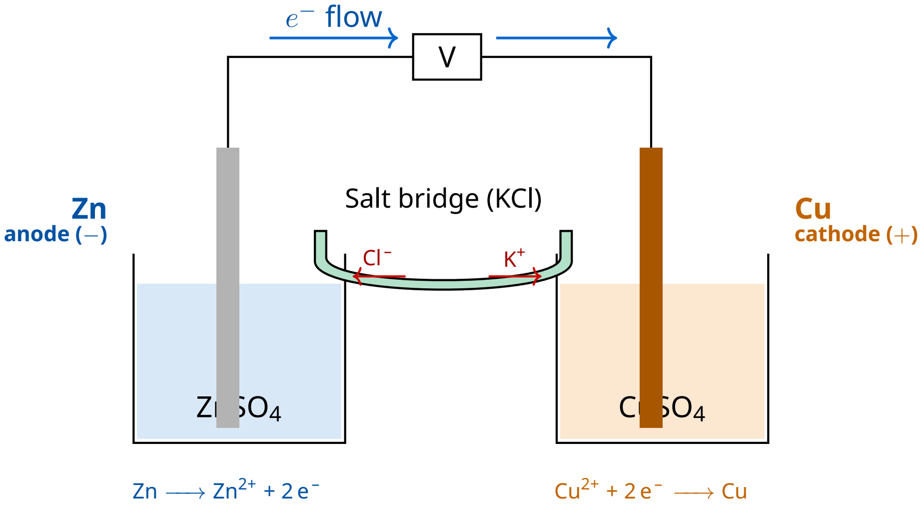

Fig. 2.1 — Daniel cell: Zn anode (left), Cu cathode (right), salt bridge in the middle.

The overall cell rection and the cell notation are:

$$\mathrm{Zn\,(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu\,(s)} \qquad E^\circ_{\text{cell}} = +1.10\ \text{V}$$

$$\boxed{\mathrm{Zn\,(s)\mid Zn^{2+}(aq)\parallel Cu^{2+}(aq)\mid Cu\,(s)}}$$

Cell Notation Rules

- Anode (oxidation) on the **left**, cathode (reduction) on the **right**.
- Single bar | = phase boundary (metal/solution).
- Double bar ‖ = salt bridge.
- Concentrations (or partial pressures, for gases) follow each species.

2.2 Role of the Salt Bridge

As the Daniel cell runs, the left beaker accumulates Zn^{2+} (positive charge piles up) and the right beaker loses Cu^{2+} (becomes net negative). Without a path for ions, this charge build-up would stop the current within milliseconds.

The salt bridge solves three problems at once:

- It **completes the electrical circuit** — positive and negative ions migrate to balance the charge build-up in each half-cell.
- It **prevents mixing** of the two electrolytes (which would short-circuit the cell chemically).
- It **maintains electrical neutrality**: K^+ (cation of the bridge) migrates into the cathode compartment; Cl^- (anion) migrates into the anode compartment.

Why KCl or KNO_3?

The cation K^+ and the anion Cl^- (or $NO_3{}^-$) have nearly equal mobilities. This means both ions diffuse out of the bridge at the same rate, so no extra junction potential develops at either end. NaCl is avoided because Na^+ has lower mobility than Cl^-.

2.3 Cell EMF, Cell Potential, and Sign Convention

The **EMF (electromotive force)** of a cell is the potential difference measured when *no current flows* (i.e., using a high-resistance voltmeter or potentiometer). When current is drawn, internal resistance drops the terminal voltage below the EMF.

Cell Potential

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Both half-cell potentials must be quoted as **reduction potentials** for this formula to apply. A positive E_{cell} means the reaction (as written, anode on left) is spontaneous.

For the Daniel cell at standard conditions:

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = (+0.34) - (-0.76) = +1.10\ \text{V}$$

Sign of the anode potential

When you look up $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76$ V, that is the *reduction* potential. Don't flip the sign when plugging into $E_{\text{cell}} = E_{\text{cath}} - E_{\text{an}}$. The minus sign in the formula already accounts for the reversed direction at the anode.

3 Standard Electrode Potential and the Electrochemical Series

A single electrode potential cannot be measured in isolation; we always need a *reference*. By international agreement, the **Standard Hydrogen Electrode (SHE)** is assigned a potential of exactly zero volts at all temperatures.

3.1 The Standard Hydrogen Electrode (SHE)

The SHE consists of a platinum wire coated with platinum black, dipped in 1 M H^+(aq), with H_2 gas at 1 bar bubbling over the platinum surface. The half-reaction is:

$$2\,\mathrm{H^+(aq, 1\ M)} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2(g, 1\ bar)} \qquad E^\circ \equiv 0.00\ \mathrm{V}$$

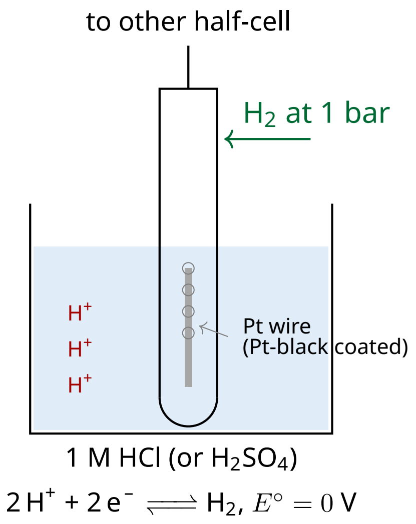

Fig. 2.2 — Standard Hydrogen Electrode (SHE): platinum wire, 1 M H^+, H_2 at 1 bar.

By coupling any half-cell to the SHE and measuring the resulting cell voltage, we obtain the **standard reduction potential** of that half-cell.

3.2 The Electrochemical Series

Arranging half-reactions in order of decreasing E° (reduction potential) gives the **electrochemical series**. The more positive the E°, the stronger the oxidising agent (it accepts electrons readily); the more negative the E°, the stronger the reducing agent.

Half-reaction (reduction)	E° **(V)**	**Comment**
$F_2 + 2e^- \longrightarrow 2F^-$	$+2.87$	Strongest oxidiser
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$+1.51$	Strong oxidiser
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	$+1.36$	Used in bleach
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	$+1.23$	Air, acidic
$Ag^+ + e^- \longrightarrow Ag$	$+0.80$	Noble metal
$Cu^{2+} + 2e^- \longrightarrow Cu$	$+0.34$	Daniel cathode
$2H^+ + 2e^- \longrightarrow H_2$	0.00	Reference (SHE)
$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.13	Borderline
$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.44	Rusting relevant
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76	Daniel anode
$Al^{3+} + 3e^- \longrightarrow Al$	-1.66	
$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37	Strong reducer
$Na^+ + e^- \longrightarrow Na$	-2.71	
$Li^+ + e^- \longrightarrow Li$	-3.04	Strongest reducer

How to use the series

- Any species on the *left* of a given line can oxidise any species on the *right* of a line *below* it. Example: Cu^{2+} oxidises Zn (Cu line is above Zn line).
- A metal can displace another metal from its salt only if the displacing metal lies *below* the other in the table (i.e., has a more negative E°).
- Metals with $E^\circ < 0$ (below SHE) liberate H_2 from dilute acids; metals above SHE do not.

Reactivity series mnemonic

"Please Stop Calling Me A Zebra, I Like Hippos, Cute Spotted Giraffes": Potassium, Sodium, Calcium, Magnesium, Aluminium, Zinc, Iron, Lead, [**H**ydrogen], Copper, Silver, Gold — decreasing tendency to lose electrons (i.e., decreasing reducing strength).

Why are gold and platinum used for jewellery?

Both Au^+/Au ($+1.69$ V) and Pt^{2+}/Pt ($+1.20$ V) sit very high on the series — so high that even oxygen in air ($E^\circ_{O_2/H_2O} = +1.23$ V) struggles to oxidise them. Iron, by contrast, rusts within days. This is the electrochemistry of why gold rings outlast their owners.

4 Nernst Equation and Thermodynamics of Cells

Standard electrode potentials assume 1 M solutions, 1 bar gas pressure, and 298 K. Real cells almost never operate at standard conditions, so we need a way to correct E° for actual concentrations. The **Nernst equation** does exactly that.

4.1 Nernst Equation for a Half-cell

For a general reduction half-reaction $M^{n+} + n\,e^- \longrightarrow M$, the actual electrode potential is:

Nernst Equation (single electrode, 298 K)

$$E_{(\mathrm{M}^{n+}/\mathrm{M})} = E^\circ_{(\mathrm{M}^{n+}/\mathrm{M})} - \frac{RT}{nF}\ln\frac{1}{[\mathrm{M}^{n+}]}$$

Converting natural log to log base 10 and inserting $R = 8.314\ \mathrm{J\,K^{-1}mol^{-1}}$, $T = 298$ K, $F = 96\,500\ \mathrm{C\,mol^{-1}}$:

$$\boxed{E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}^{n+}]}}$$

For a full cell with reaction $aA + bB \longrightarrow cC + dD$ and reaction quotient $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$:

$$\boxed{E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log Q}$$

What the Nernst equation tells us

- If $Q < 1$ (reactants dominate): $\log Q < 0$, so $E_{\text{cell}} > E^\circ_{\text{cell}}$. The cell pushes harder.
- If $Q > 1$ (products dominate): $\log Q > 0$, so $E_{\text{cell}} < E^\circ_{\text{cell}}$. The cell weakens.
- If $Q = K$ (equilibrium): $E_{\text{cell}} = 0$. The cell is "dead" — a discharged battery.

4.2 Worked Example — Nernst Calculation

Problem: For the Daniel cell at 298 K, compute E_{cell} when $[\mathrm{Zn}^{2+}] = 0.10$ M and $[\mathrm{Cu}^{2+}] = 1.0$ M. Take $E^\circ_{\text{cell}} = 1.10$ V.

Solution: The cell reaction is $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$, so $n = 2$ and

$$Q = \frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]} = \frac{0.10}{1.0} = 0.10$$

$$E_{\text{cell}} = 1.10 - \frac{0.0591}{2}\log(0.10) = 1.10 - (0.02955)(-1) = 1.10 + 0.0296 \approx 1.13\ \mathrm{V}$$

Dilute zinc / concentrated copper gives a slightly higher voltage than standard — consistent with Le Chatelier's principle pushing the reaction forward.

4.3 Equilibrium Constant from E°_{cell}

At equilibrium $E_{\text{cell}} = 0$ and $Q = K_c$, so the Nernst equation rearranges to:

Cell EMF ↔ Equilibrium Constant

$$\boxed{\log K_c = \frac{n\,E^\circ_{\text{cell}}}{0.0591}}$$

For the Daniel cell: $\log K_c = \dfrac{2 \times 1.10}{0.0591} = 37.2$, so $K_c \approx 1.6 \times 10^{37}$. Effectively the reaction goes essentially to completion — if you wait long enough, every Zn atom that touches Cu^{2+} converts.

4.4 Gibbs Energy and Cell EMF

The electrical work done by a cell at constant T and P equals the decrease in Gibbs energy of the reaction:

Free Energy and Cell Potential

$$\boxed{\Delta_r G = -nFE_{\text{cell}}}$$

At standard conditions:

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}, \qquad \Delta_r G^\circ = -2.303\,RT \log K$$

- If $E_{\text{cell}} > 0$, then $\Delta_r G < 0$ — spontaneous.
- E° is an **intensive** property; $\Delta_r G^\circ$ is **extensive**. If you double all coefficients, E° stays the same but n doubles, so $\Delta_r G^\circ$ doubles.

Don't multiply E° when balancing

If you multiply a half-reaction by 2 to balance electrons, do *not* multiply its E° value by 2. Potentials are intensive (per electron), not extensive. Only ΔG scales with n.

Nernst sign check

A quick sanity check: if the reactant concentration drops (e.g., Cu^{2+} gets used up), the cell voltage *decreases*. If a product concentration drops, the voltage *increases*. Always verify your Nernst answer matches this trend before circling it.

4.5 Concentration Cells (JEE/NEET extension)

A **concentration cell** is a galvanic cell in which both half-cells have the same electrode and the same ion, but at *different concentrations*. Here $E^\circ_{\text{cell}} = 0$ but $E_{\text{cell}} \neq 0$ because the system seeks to equalise concentrations.

$$\text{Cu}\,(\text{s}) \mid \text{Cu}^{2+}(c_1) \parallel \text{Cu}^{2+}(c_2) \mid \text{Cu}\,(\text{s}), \quad c_2 > c_1$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

The dilute side becomes the anode (Cu dissolves to increase the ion concentration there), and the concentrated side becomes the cathode (Cu^{2+} deposits, lowering its concentration there).

5 Conductance of Electrolytic Solutions

Metals conduct electricity through delocalised electrons. Electrolyte solutions conduct through *ion migration*. The two mechanisms behave quite differently — electrolytic conductance increases with temperature (ions move faster), while metallic conductance decreases.

5.1 Resistance, Conductance, and Cell Constant

For a uniform conductor of length l and area A, the resistance is $R = \rho\,(l/A)$, where ρ is the resistivity. The reciprocals give:

Conductance and Conductivity

$$G = \frac{1}{R}\ \text{(Siemens, S)}, \qquad \kappa = \frac{1}{\rho}\ (\mathrm{S\,m^{-1}})$$

$$\kappa = G \times \frac{l}{A} \quad \Rightarrow \quad \kappa = G \times G^*$$

where $G^* = l/A$ is the **cell constant** (units: $\mathrm{m^{-1}}$).

The cell constant cannot be measured directly because the electrode geometry isn't simple. Instead, we calibrate the cell with a standard solution of known κ (typically KCl of known molarity at 298 K).

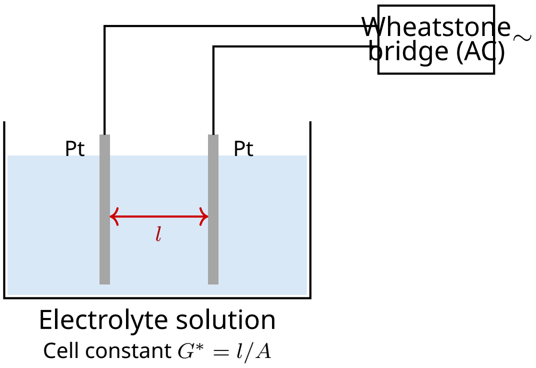

Fig. 2.3 — Conductivity cell with two platinised platinum electrodes of area A separated by distance l. AC source is used so as not to electrolyse the solution.

Why AC and not DC?

A DC source would cause electrolysis at the electrodes, changing the concentration during the measurement and producing junk readings. AC reverses too fast for net deposition — the ions just oscillate.

5.2 Molar and Limiting Molar Conductivity

Conductivity κ depends on the number of ions per unit volume. To compare different electrolytes fairly, normalise to one mole of electrolyte:

Molar Conductivity

$$\boxed{\Lambda_m = \frac{\kappa}{c}}$$

With κ in $\mathrm{S\,m^{-1}}$ and c in $\mathrm{mol\,m^{-3}}$: Λ_m in $\mathrm{S\,m^2\,mol^{-1}}$.

A more practical unit: κ in $\mathrm{S\,cm^{-1}}$, c in $\mathrm{mol\,cm^{-3}}$. NCERT uses $\mathrm{S\,cm^2\,mol^{-1}}$; convert with $1\ \mathrm{S\,m^2 mol^{-1}} = 10^4\ \mathrm{S\,cm^2 mol^{-1}}$.

Variation of Λ_m with concentration:

- For **strong electrolytes** (KCl, NaCl, HCl): Λ_m increases gradually as c decreases, because at lower concentration the ion–ion electrostatic interactions weaken, so each ion drifts more freely. The plot of Λ_m vs. $\sqrt{c}$ is **nearly linear** for strong electrolytes.
- For **weak electrolytes** (CH_3COOH, NH_4OH): Λ_m rises sharply at very low concentrations because the degree of dissociation α shoots up. The curve is steep and non-linear near $c \to 0$.

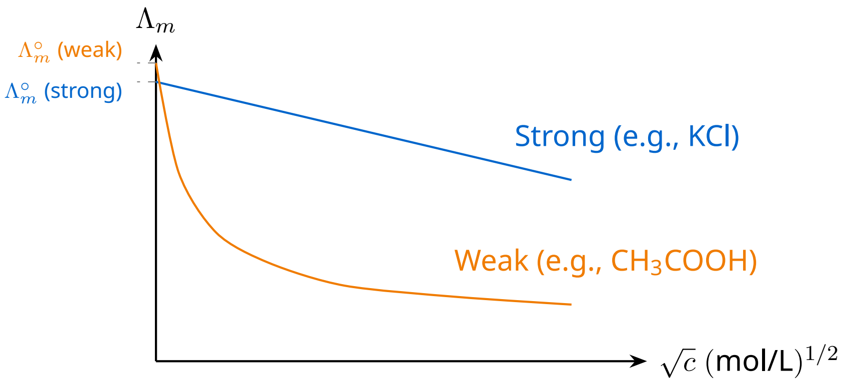

Fig. 2.4 — Variation of molar conductivity with $\sqrt{c}$ for strong (blue) and weak (orange) electrolytes.

The intercept of these curves on the Λ_m axis (i.e., the value at $c \to 0$) is called the **limiting molar conductivity**, Λ_m° — the conductivity when ion–ion interactions vanish.

For strong electrolytes: Debye–Hückel–Onsager equation,

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$$

gives a straight-line extrapolation to find Λ_m°. For weak electrolytes, this extrapolation fails (the curve is too steep at low c), and we must use Kohlrausch's law instead.

5.3 Kohlrausch's Law of Independent Migration of Ions

Kohlrausch's Law

At infinite dilution, every ion contributes a fixed amount to the molar conductivity, independent of the counter-ion present:

$$\boxed{\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ}$$

where ν_+ and ν_- are the stoichiometric coefficients of cation and anion, and $\lambda_\pm^\circ$ are the limiting ionic conductivities.

For example, for $Al_2(SO_4)_3$: $\Lambda_m^\circ = 2\,\lambda_{Al^{3+}}^\circ + 3\,\lambda_{SO_4{}^{2-}}^\circ$.

Application 1 — Λ_m° for a weak electrolyte. You cannot extrapolate Λ_m vs. $\sqrt{c}$ to zero for acetic acid (the curve is too steep). But you can combine three strong-electrolyte values:

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

Each value on the right is measurable by extrapolation. The algebra mirrors a Hess-cycle: ions cancel cleanly.

Application 2 — Degree of dissociation of a weak electrolyte.

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Once α is known, the dissociation constant follows:

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

Why Kohlrausch's law works

At infinite dilution, ions are too far apart to feel each other. Each ion drifts according to its own size, charge and hydration shell — and contributes λ° to the total conductivity. The counter-ion is irrelevant; that's why $\lambda_{Cl^-}^\circ$ is the same whether the cation was Na^+, K^+, or H^+.

Mobility ranking

At 298 K (aqueous): $\lambda_{H^+}^\circ \approx 350$, $\lambda_{OH^-}^\circ \approx 198$, $\lambda_{K^+}^\circ \approx 73.5\,\mathrm{S\,cm^2\,mol^{-1}}$. H^+ and OH^- are far more mobile than other ions because they migrate by the **Grotthuss mechanism** — protons hop along the hydrogen-bonded water network, no need for the bulky hydrated ion to drift physically.

6 Electrolysis and Faraday’s Laws

In an **electrolytic cell**, an external EMF source pushes electrons in the reverse direction — forcing non-spontaneous redox chemistry to happen. This is how we extract reactive metals (Na, Al), refine copper, electroplate, and produce Cl_2/NaOH from brine.

6.1 Basic Electrolytic Setup

Two inert electrodes (or sometimes one reactive electrode) are dipped in a molten salt or electrolyte solution. An external battery is connected with its positive terminal to the anode and its negative terminal to the cathode.

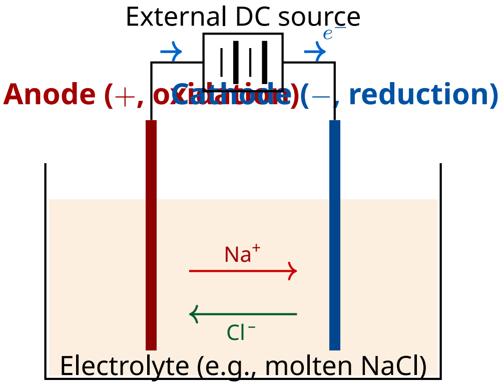

Fig. 2.5 — Electrolytic cell: cations migrate to cathode (reduction), anions migrate to anode (oxidation).

Electrolysis of molten NaCl:

$$\text{Cathode (reduction):}\quad Na^+ + e^- \longrightarrow Na$$

$$\text{Anode (oxidation):}\quad 2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$$

$$\text{Overall:}\quad 2\,NaCl\,(l) \longrightarrow 2\,Na\,(l) + Cl_2(g)$$

This is the industrial **Down’s process** for producing sodium metal.

6.2 Products of Electrolysis — which species discharges?

When the electrolyte is an *aqueous* solution rather than a molten salt, water also competes. At the cathode, the species with the *higher* reduction potential discharges; at the anode, the species with the *lower* reduction potential (i.e., easier to oxidise) discharges.

Selective Discharge Rule

Cathode: among competing cations + water ($2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$, $E^\circ = -0.83$ V at pH 7), the one with the largest reduction potential gets reduced.

Anode: among competing anions + water ($2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$), the one with the smallest reduction potential (easiest to oxidise) gets oxidised — but **overpotential** can shift the order.

Example — electrolysis of aqueous NaCl (brine):

- **Cathode**: Na^+/Na (-2.71 V) vs. H_2O/H_2 (-0.83 V at pH 7). Water wins ⇒ $H_2(g)$ liberated.
- **Anode**: Cl^-/Cl_2 ($+1.36$ V) vs. H_2O/O_2 ($+0.82$ V at pH 7). H_2O should be oxidised first, but the high overpotential for O_2 liberation flips the verdict ⇒ $Cl_2(g)$ is produced instead.
- Net: H_2, Cl_2, and NaOH accumulate — the **chlor-alkali process**.

Overpotential surprise

On purely thermodynamic grounds (Cl^- has the higher $E°$), water should oxidise more easily. But the kinetics of O_2 formation are sluggish at most electrodes — it has an overpotential of about 0.5 V. The slow species loses; Cl^- discharges. Many electrolysis problems fail if you ignore overpotential.

6.3 Faraday's Laws of Electrolysis

Michael Faraday (1834) quantified the relationship between charge passed and mass deposited.

Faraday's First Law

The mass m of substance deposited at an electrode is directly proportional to the quantity of electricity Q passed:

$$\boxed{m = Z\,Q = Z\,I\,t}$$

where Z is the **electrochemical equivalent** (kg C^{-1}), I is current (A), t is time (s).

Faraday's Second Law

When the same quantity of electricity is passed through different electrolytes connected in series, the masses deposited are proportional to their chemical equivalents:

$$\frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{M_1/n_1}{M_2/n_2}$$

where $E = M/n$ is the equivalent weight (M = molar mass, n = number of electrons per ion).

The **Faraday constant** is the charge on one mole of electrons:

$$F = N_A \times e = (6.022 \times 10^{23}) \times (1.602 \times 10^{-19}) \approx 96\,485 \text{ C mol}^{-1}$$

(NCERT rounds this to 96 500 C mol^{-1}.)

Working Formula

For an ion M^{n+} with molar mass M:

$$\boxed{m = \frac{M \times I \times t}{n \times F}}$$

Moles deposited: $n_{\text{mol}} = It/(nF)$. Volume of gas at STP (for H_2, O_2, Cl_2): $V = (It/nF) \times 22\,400$ cm^3.

Worked example. A current of 5.0 A is passed through a $CuSO_4$ solution for 30 minutes. Find the mass of copper deposited. ($M_{\text{Cu}} = 63.5$ g mol^{-1}, $n = 2$, $F = 96\,500$ C mol^{-1}.)

$$Q = It = 5.0 \times 30 \times 60 = 9000 \text{ C}$$

$$m = \frac{M \times Q}{nF} = \frac{63.5 \times 9000}{2 \times 96\,500} = \frac{571\,500}{193\,000} \approx 2.96 \text{ g}$$

1 mole of electrons = 96 500 C

Almost every numerical reduces to “how many moles of electrons did I push?” Compute It/F first — that’s your moles of electrons. Then divide by n (electrons per ion) to get moles of substance. This single workflow handles 90% of Faraday problems.

Electroplating

A silver spoon is electroplated by making the spoon the cathode and a silver bar the anode, dipped in $AgNO_3$ solution. Faraday’s law lets the plater control the deposit thickness to micron precision by setting current and time. Industrial chrome, nickel, and gold plating all run on the same equations.

7 Batteries and Fuel Cells

A **battery** is a self-contained galvanic cell (or stack of cells in series) engineered to be portable. Real batteries are classified by whether they can be recharged.

7.1 Primary Batteries

A primary battery can only be discharged once — the cell reaction is not easily reversible. Once the chemicals are consumed, the battery is dead.

The dry cell (Leclanché cell) is the classic torch / TV-remote battery:

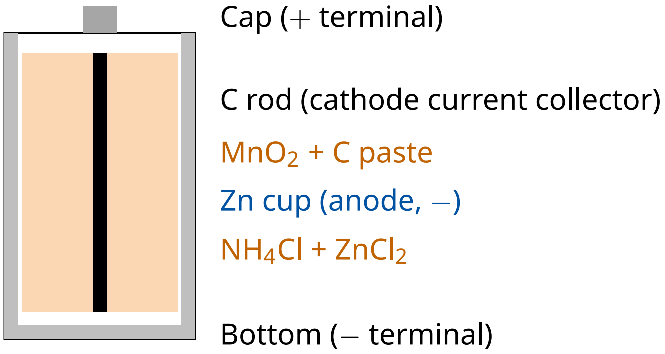

Fig. 2.6 — Dry cell (Leclanché cell): Zn cup anode, central carbon rod cathode in MnO_2/NH_4Cl paste.

The half-reactions are:

$$\text{Anode:}\quad \mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2\,\mathrm{e^-}$$

$$\text{Cathode:}\quad \mathrm{MnO_2} + \mathrm{NH_4}^+ + \mathrm{e^-} \longrightarrow \mathrm{MnO(OH)} + \mathrm{NH_3}$$

EMF ≈ 1.5 V. The voltage drops as the cell is used; once the NH_4Cl paste dries out, the cell is gone.

Mercury cell (used in hearing aids and watches) provides a remarkably constant 1.35 V throughout its life:

$$\text{Anode:}\quad \mathrm{Zn(Hg)} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\,\mathrm{e^-}$$

$$\text{Cathode:}\quad \mathrm{HgO} + \mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Hg} + 2\,\mathrm{OH^-}$$

The overall reaction involves only solids and liquids; ionic concentrations stay constant, so the voltage remains flat throughout the cell's life. Mercury cells are being phased out due to mercury toxicity.

7.2 Secondary Batteries — Lead-acid Storage Battery

A secondary battery can be *recharged*: an external source reverses the cell reaction, regenerating the original reactants. The **lead–acid battery** (in every petrol car) is the classic example.

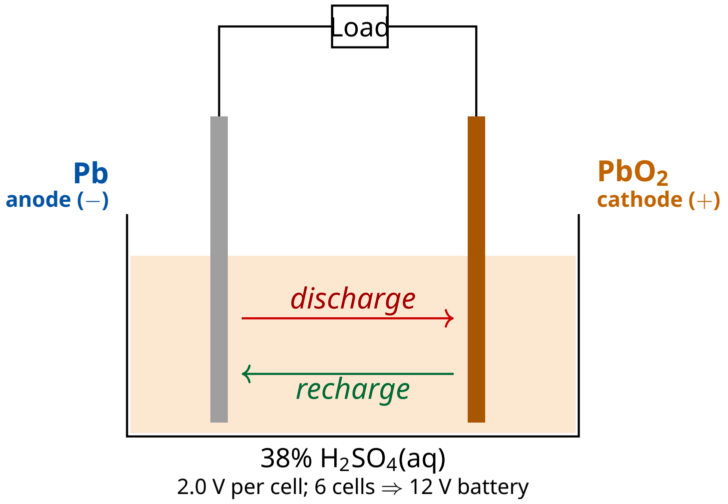

Fig. 2.7 — Lead-acid cell: Pb anode, PbO_2 cathode, dilute H_2SO_4 electrolyte.

Discharge reactions:

$$\text{Anode:}\quad \mathrm{Pb} + \mathrm{SO_4}^{2-} \longrightarrow \mathrm{PbSO_4} + 2\,e^-$$

$$\text{Cathode:}\quad \mathrm{PbO_2} + \mathrm{SO_4}^{2-} + 4\,\mathrm{H}^+ + 2\,e^- \longrightarrow \mathrm{PbSO_4} + 2\,\mathrm{H_2O}$$

$$\text{Overall:}\quad \mathrm{Pb} + \mathrm{PbO_2} + 2\,\mathrm{H_2SO_4} \longrightarrow 2\,\mathrm{PbSO_4} + 2\,\mathrm{H_2O}$$

On recharging, an external source drives the reaction backwards — $PbSO_4$ on both plates reconverts to Pb (cathode) and PbO_2 (anode), and H_2SO_4 regenerates. EMF per cell is ≈ 2.0 V; six cells in series give the familiar 12 V car battery.

Nickel-cadmium cell is another secondary cell, lighter and longer-lasting than lead-acid:

$$\mathrm{Cd} + 2\,\mathrm{Ni(OH)_3} \longrightarrow \mathrm{CdO} + 2\,\mathrm{Ni(OH)_2} + \mathrm{H_2O}$$

Battery dies when H_2SO_4 runs out

In a discharging lead-acid battery, the electrolyte becomes more dilute (water is produced, acid is consumed). Mechanics check battery health using a hydrometer — if specific gravity drops below 1.20, the battery needs charging.

7.3 Fuel Cells

A fuel cell is a galvanic cell that converts the energy of a continuously supplied fuel directly to electricity. Unlike a battery, the reactants are not stored *inside* the cell — they flow in from external tanks.

The **hydrogen-oxygen fuel cell** (used in Apollo spacecraft and modern hydrogen vehicles) has a porous carbon cathode and anode with KOH electrolyte:

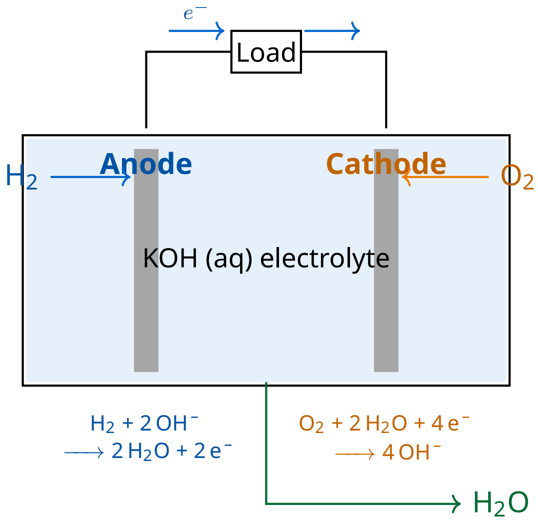

Fig. 2.8 — H_2–O_2 fuel cell: H_2 oxidised at anode, O_2 reduced at cathode, only product is H_2O.

Reactions (alkaline electrolyte):

$$\text{Anode:}\quad 2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

$$\text{Cathode:}\quad O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

$$\text{Overall:}\quad 2H_2 + O_2 \longrightarrow 2H_2O \qquad E^\circ_{\text{cell}} = 1.23\text{ V}$$

Fuel cell advantages

- **High efficiency** ($\sim 70\%$): no Carnot limit applies because the conversion is not heat-based.
- **No pollution**: only product is water.
- **Continuous operation**: runs as long as fuel is supplied.
- **Compact**: high power-to-weight ratio — ideal for spacecraft.

The main drawback is the cost of catalysts (Pt) and the difficulty of storing pure H_2.

Apollo and beyond

NASA's Apollo missions to the Moon used H_2–O_2 fuel cells for onboard power, with the water output drunk by astronauts. Today, Toyota's Mirai and Hyundai's Nexo run on PEM (proton exchange membrane) fuel cells with peak efficiencies near 60%, refilling with H_2 in under 5 minutes.

8 Corrosion

Corrosion is the slow oxidation of a metal by its environment. The most familiar example is the **rusting of iron**, but most metals corrode — copper turns green ($Cu(OH)_2 \cdot CuCO_3$), silver tarnishes black (Ag_2S), and aluminium forms a protective Al_2O_3 skin.

8.1 Electrochemical Mechanism of Rusting

Although rusting looks like a simple chemical reaction, it is actually a **galvanic phenomenon** happening on the surface of the iron itself. A water droplet on iron acts as a tiny electrochemical cell.

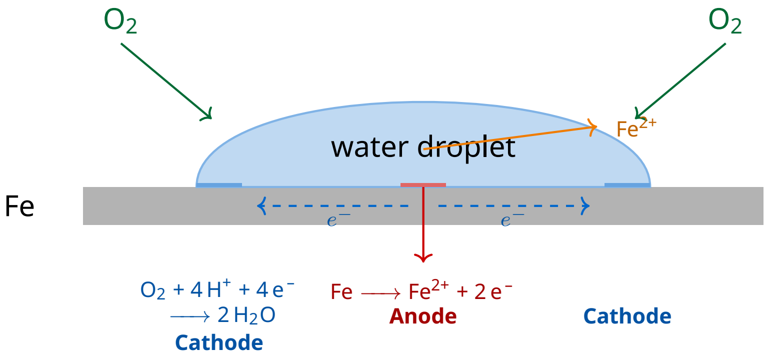

Fig. 2.9 — Mechanism of rusting: Fe oxidises at the centre (anode, low O_2); O_2 reduces at the droplet edge (cathode, high O_2); Fe^{2+} migrates outward and is further oxidised by air to form $Fe_2O_3 \cdot xH_2O$ (rust).

Step-by-step:

1. Beneath the centre of the droplet, oxygen access is poor — this region becomes the **anode**, where iron oxidises:

$$\mathrm{Fe\,(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}, \qquad E^\circ = -0.44\ \mathrm{V}$$

2. At the droplet edge, dissolved oxygen is plentiful — the **cathode** reaction is:

$$\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O\,(l)}, \qquad E^\circ = +1.23\ \mathrm{V}$$

3. Electrons flow through the iron from anode to cathode, while Fe^{2+} ions migrate outward through the water film.
4. In the bulk of the droplet, Fe^{2+} is further oxidised by atmospheric O_2 to Fe^{3+}, which precipitates as hydrated iron(III) oxide — **rust**:

$$4\,\mathrm{Fe^{2+}} + \mathrm{O_2} + 4\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{Fe_2O_3} + 8\,\mathrm{H^+}$$

$$\mathrm{Fe_2O_3} + \mathrm{xH_2O} \longrightarrow \mathrm{Fe_2O_3} \cdot \mathrm{xH_2O}$$

$$E^\circ_{\text{rusting}} = 1.23 - (-0.44) = 1.67\ \mathrm{V}$$

A strongly positive EMF — so rusting is spontaneous wherever moisture, oxygen and iron meet.

Why moisture matters

The water film provides the electrolyte. Dry iron in dry air essentially does not rust. Acidic pollutants (CO_2, SO_2) and salt (NaCl in coastal air or road de-icing) sharply accelerate rusting because they boost ionic conductivity.

8.2 Prevention of Corrosion

Four main strategies:

1. Barrier methods: paint, grease, oil, plastic coating. Blocks water and oxygen from reaching the metal.

2. Galvanisation: coat iron with a thin layer of zinc. Even if the zinc layer is scratched, zinc still corrodes preferentially because $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76$ V $< E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44$ V — zinc is more easily oxidised, so the iron remains protected.

3. Cathodic protection (sacrificial anode): connect a more reactive metal (Mg or Zn block) to the iron object. The reactive metal becomes the anode and corrodes; the iron becomes the cathode and stays intact. Used on ship hulls, underground pipelines, water heater tanks.

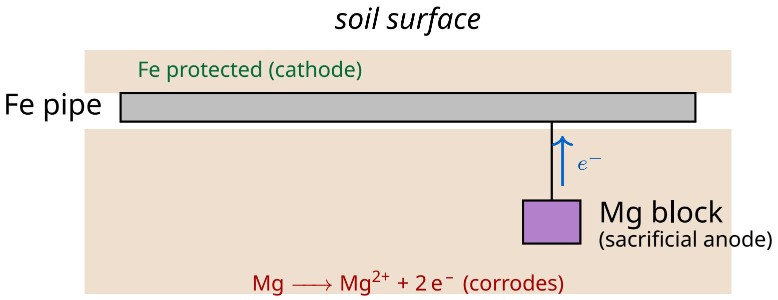

Fig. 2.10 — Cathodic protection: a Mg block (more reactive than Fe) is electrically connected to the iron pipe. Mg corrodes; Fe stays safe.

4. Anti-rust pigments: Pb_3O_4 (red lead) and $ZnCrO_4$ primer paints inhibit corrosion chemically.

The Statue of Liberty

The Statue of Liberty has an inner iron frame and an outer copper skin. The two metals form a giant electrochemical cell — when moisture reached them through deteriorating asbestos insulation, the iron (anode) corroded badly. The 1986 restoration replaced the iron with stainless steel and added PTFE separators to break the galvanic connection.

“Tin-plated” iron is risky

A tin coating ($E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14$ V) protects iron only as long as it’s intact. The

> moment the coating is scratched, iron becomes the anode (Sn is *less* reactive than Fe) and rusts faster than uncoated iron. That's why food cans corrode at scratches but galvanised steel doesn't.

9 Quick Reference Summary

9.1 Master Formula List

Quantity	Formula
Cell EMF (standard)	$E^\circ_{\text{cell}} = E^\circ_{\text{cath}} - E^\circ_{\text{an}}$
Nernst equation (full cell, 298 K)	$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q$
EMF ↔ Eq. constant	$\log K_c = \frac{n\,E^\circ_{\text{cell}}}{0.0591}$
Gibbs energy and EMF	$\Delta_r G = -nFE_{\text{cell}}$
ΔG° and K	$\Delta_r G^\circ = -2.303\,RT \log K$
Conductance	$G = 1/R$ (Siemens)
Conductivity	$\kappa = G\,(l/A) = G\,G^*$
Molar conductivity	$\Lambda_m = \kappa/c$
Variation (strong)	$\Lambda_m = \Lambda^\circ_m - A\sqrt{c}$
Kohlrausch's law	$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$
Degree of dissociation	$\alpha = \Lambda_m/\Lambda^\circ_m$
Ostwald dilution	$K_a = c\alpha^2/(1-\alpha)$
Faraday's first law	$m = Z\,I\,t$
Working form	$m = M\,I\,t/(nF)$
Concentration cell	$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$

9.2 Key Constants

Constant	Value
Faraday constant F	$96\,485 \approx 96\,500$ C mol^{-1}
Gas constant R	8.314 J K^{-1} mol^{-1}
$2.303\,RT/F$ at 298 K	0.0591 V
Avogadro's number N_A	6.022×10^{23} mol^{-1}
Electronic charge e	1.602×10^{-19} C
1 mol of electrons	96 500 C

9.3 Standard Cell Voltages (memorise)

Cell / device	E° (V)
Daniel cell (Zn/Cu)	$+1.10$
Dry cell (Leclanché)	~ 1.5
Mercury cell	1.35 (constant)
Lead-acid (per cell)	~ 2.0
Ni–Cd cell	~ 1.4
H_2/O_2 fuel cell	1.23

9.4 Galvanic vs. Electrolytic — Comparison

Galvanic Cell	Electrolytic Cell
Spontaneous redox reaction	Non-spontaneous; needs external EMF
Chemical $\to$ Electrical energy	Electrical $\to$ Chemical energy
Anode is $-$ (oxidation), cathode is $+$ (reduction)	Anode is $+$, cathode is $-$ (but anode still oxidises, cathode still reduces)
$\Delta G < 0$, $E_{\text{cell}} > 0$	$\Delta G > 0$; needs $E_{\text{applied}} > E_{\text{rev}}$
Two separate electrolytes; salt bridge connects them	Single electrolyte (often a melt or aqueous salt)
Example: Daniel cell, dry cell, fuel cell	Example: electrolysis of NaCl, electroplating

9.5 Final Exam-day Checklist

The 8 facts you must walk in remembering

1. Daniel cell: Zn | Zn^{2+} || Cu^{2+} | Cu, $E^\circ = 1.10$ V.
2. Anode = oxidation; cathode = reduction (always, regardless of cell type).
3. Standard hydrogen electrode: $E^\circ \equiv 0$ V at all T.
4. Nernst at 298 K: $E = E^\circ - (0.0591/n)\log Q$.
5. $\Delta G^\circ = -nFE^\circ$ and $\log K = nE^\circ/0.0591$.
6. Kohlrausch: $\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$.
7. Faraday: 1 mol of $e^- = 96\,500$ C; $m = MIt/(nF)$.
8. Rusting needs water + oxygen + iron; $E^\circ_{\text{rusting}} = 1.67$ V.

How Electrochemistry shows up in exams

- **Boards**: cell diagram + Nernst calculation + Kohlrausch application + one battery description (8–10 marks total).
- **JEE**: numerical with Faraday + simultaneous Nernst + K_c determination from E°; concentration cell calculations.
- **NEET**: concept-driven — order in electrochemical series, products of electrolysis (with overpotential trap), prevention of corrosion.

Drill the Nernst equation till you can write it from memory with sign conventions. About 60% of all electrochemistry questions reduce to a careful Nernst or a careful Faraday calculation.