Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 2: Electrochemistry

About this Chapter

This chapter studies **electrochemistry**: the interconversion of chemical and electrical energy. We learn how a **galvanic cell** (Daniell cell) converts a spontaneous redox reaction into electricity, how the cell EMF is split into electrode potentials measured against the **Standard Hydrogen Electrode**, and how the **Nernst equation** corrects E°_{cell} for non-standard concentrations. We then study ionic conduction: conductivity κ, molar conductivity Λ_m, **Kohlrausch's law** and how it gives Λ°_m for weak electrolytes. Finally, **Faraday's laws of electrolysis** relate charge to the mass of substance deposited, and we predict products of electrolysis using overpotential and electrode reactions.

Topics covered: Galvanic cells • Standard electrode potential • Nernst equation • EMF and $\Delta_r G^\circ$ • Equilibrium constant • Conductivity & molar conductivity • Kohlrausch's law • Faraday's laws of electrolysis • Products of electrolysis • Batteries and corrosion

Quick Formula Sheet

Cell EMF:

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Nernst equation:

$E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n} \log Q$ (at 298 K)

Gibbs energy:

$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$

Equilibrium constant:

$\log K = \dfrac{nE^\circ_{\text{cell}}}{0.0591}$

Conductivity: $\kappa = \dfrac{1}{\rho} = G \cdot \dfrac{l}{A}$

Molar conductivity:

$\Lambda_m = \dfrac{\kappa \times 1000}{c}$ ($\mathrm{S\,cm^2\,mol^{-1}}$)

Kohlrausch's law:

$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$

Degree of dissociation:

$\alpha = \Lambda_m/\Lambda^\circ_m$

Faraday's first law: $w = Z \cdot I \cdot t$

Charge per mole: $Q = nF$, $F = 96\,500\ \mathrm{C/mol}$

Chapter 2 Exercises

Q 2.1 **Arrange the following metals in the order in which they displace each other from the solution of their salts: Al, Cu, Fe, Mg and Zn.**

SOLUTION

Concept used. A more **reactive metal** (one with a more negative standard reduction potential $E°$) displaces a less reactive metal from the aqueous solution of the latter's salt. This is because the more reactive metal is the stronger reducing agent: it loses electrons more readily and pushes them onto the cations of the less reactive metal, which are then reduced to the free metal. The relevant **electrochemical series** positions (values from NCERT Table 2.1) are

$$\mathrm{Mg^{2+}/Mg}: \ -2.37\,\mathrm{V}; \quad \mathrm{Al^{3+}/Al}: \ -1.66\,\mathrm{V}; \quad \mathrm{Zn^{2+}/Zn}: \ -0.76\,\mathrm{V};$$

$$\mathrm{Fe^{2+}/Fe}: \ -0.44\,\mathrm{V}; \quad \mathrm{Cu^{2+}/Cu}: \ +0.34\,\mathrm{V}.$$

☞ Displacement rule

The metal that sits higher in the activity series (more negative $E°$) displaces the metal that sits lower. So Mg can displace Al, Zn, Fe, Cu from their salt solutions, but Cu cannot displace any of them.

Step 1. List the standard reduction potentials in increasing (less negative to more positive) order:

$$\mathrm{Mg^{2+}/Mg}\ (-2.37) < \mathrm{Al^{3+}/Al}\ (-1.66) < \mathrm{Zn^{2+}/Zn}\ (-0.76)$$

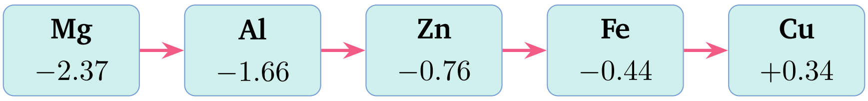
$$< \mathrm{Fe^{2+}/Fe}\ (-0.44) < \mathrm{Cu^{2+}/Cu}\ (+0.34).$$

Step 2. Reading from most negative to most positive, the metal at the left is the strongest reducing agent. So the order in which one displaces the next from solution is

$$\mathrm{Mg} \rightarrow \mathrm{Al} \rightarrow \mathrm{Zn} \rightarrow \mathrm{Fe} \rightarrow \mathrm{Cu}.$$

Step 3. Read across left-to-right: Mg displaces Al from $AlCl_3$ solution; Al displaces Zn from $ZnSO_4$; Zn displaces Fe from $FeSO_4$; Fe displaces Cu from $CuSO_4$. Each metal can displace any metal to its right.

Decreasing reducing power, increasing $E°$



Each metal displaces every metal to its right from its salt solution.

Final Answer: Order of displacement: $\mathrm{Mg} > \mathrm{Al} > \mathrm{Zn} > \mathrm{Fe} > \mathrm{Cu}$.

EXPERT'S SOLUTION : *Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. A metal A displaces a metal B from B's salt solution if and only if A is the stronger reducing agent — equivalently, if $E^\circ(A^{n+}/A) < E^\circ(B^{m+}/B)$. The more negative E° sits to the left of the **electrochemical series**.

Alternative approach: thermodynamic check. For a displacement $A + B^{m+} \to A^{n+} + B$, compute $E^\circ_{\text{cell}} = E^\circ(B^{m+}/B) - E^\circ(A^{n+}/A)$. For $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$: $E^\circ_{\text{cell}} = 0.34 - (-2.37) = +2.71$ V, hugely positive so $\Delta_r G^\circ = -nFE^\circ_{\text{cell}} \ll 0$. The reverse, $\text{Cu} + \text{Mg}^{2+}$, gives -2.71 V and is impossible.

Step 1. **Rank by E°.** Mg^{2+}/Mg (-2.37) is the most negative, so Mg is the strongest reducer; Cu^{2+}/Cu $(+0.34)$ the most positive, so Cu the weakest reducer.

Step 2. **Apply pairwise.**

$$3\,\text{Mg}\,(s) + 2\,\text{AlCl}_3(aq) \longrightarrow 3\,\text{MgCl}_2(aq) + 2\,\text{Al}\,(s),$$

$$2\,\text{Al}\,(s) + 3\,\text{ZnSO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\,\text{Zn}\,(s),$$

$$\text{Zn}\,(s) + \text{FeSO}_4(aq) \longrightarrow \text{ZnSO}_4(aq) + \text{Fe}\,(s),$$

$$\text{Fe}\,(s) + \text{CuSO}_4(aq) \longrightarrow \text{FeSO}_4(aq) + \text{Cu}\,(s).$$

Step 3. **No reverse reactions.** Cu cannot displace any of the other four; their E° values are all more negative than $+0.34$ V.

Step 4. **Concept linkage.** The same ranking decides which Daniell-type galvanic cells are spontaneous: anode = more negative-E° metal; cathode = more positive-E° metal. A $\text{Mg}\,|\,\text{Mg}^{2+}\,\|\,\text{Cu}^{2+}\,|\,\text{Cu}$ cell delivers $E^\circ_{\text{cell}} = +2.71$ V — nearly twice the Daniell cell.

JEE/NEET relevance. Activity-series ordering recurs every year: "which metals displace copper from CuSO_4?" The reliable answer: every metal above Cu in the series. The same series predicts which metals corrode in acidic rainwater (those above hydrogen) and which can be extracted by carbon reduction (those below carbon).

> **Final Answer:** $\text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Cu}$ in decreasing reducing power; Mg displaces all four, Cu displaces none.

☞ Five-metal mnemonic

"**M**y **A**unt **Z**arna **F**eeds **C**urd" captures $\text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Cu}$ of decreasing reducing power. Couple it with: "most negative E° first."

♥ Why activity ordering matters in metallurgy

Reactive metals (Na, Mg, Al) cannot be extracted by carbon reduction; only *electrolytic* reduction of the molten salt works (Hall-Héroult for Al, Downs cell for Na). Less reactive metals (Fe, Cu) are won from their ores by smelting. The crossover sits at **carbon** in the activity series.

Q 2.2 **Given the standard electrode potentials,**
$\mathrm{K^+/K} = -2.93$ **V,** $\mathrm{Ag^+/Ag} = 0.80$ **V,**
$\mathrm{Hg^{2+}/Hg} = 0.79$ **V,** $\mathrm{Mg^{2+}/Mg} = -2.37$ **V,** $\mathrm{Cr^{3+}/Cr} = -0.74$ **V.**
Arrange these metals in their increasing order of reducing power.

SOLUTION

Concept used. The **reducing power** of a metal is its tendency to donate electrons (to be oxidised). For the reduction half-reaction $M^{n+} + ne^- \to M$, a *lower* (more negative) standard electrode potential E° means the forward reduction is unfavourable, so the *reverse* oxidation $M \to M^{n+} + ne^-$ is favoured. Hence

$$\text{lower } E^\circ \iff \text{stronger reducing agent.}$$

To rank metals in *increasing* reducing power, we order their E° values from *most positive to most negative*.

Step 1. Tabulate the five given E° values, from most positive to most negative:

$$E^\circ(\mathrm{Ag^+/Ag}) = +0.80\,\mathrm{V}$$

$$E^\circ(\mathrm{Hg^{2+}/Hg}) = +0.79\,\mathrm{V}$$

$$E^\circ(\mathrm{Cr^{3+}/Cr}) = -0.74\,\mathrm{V}$$

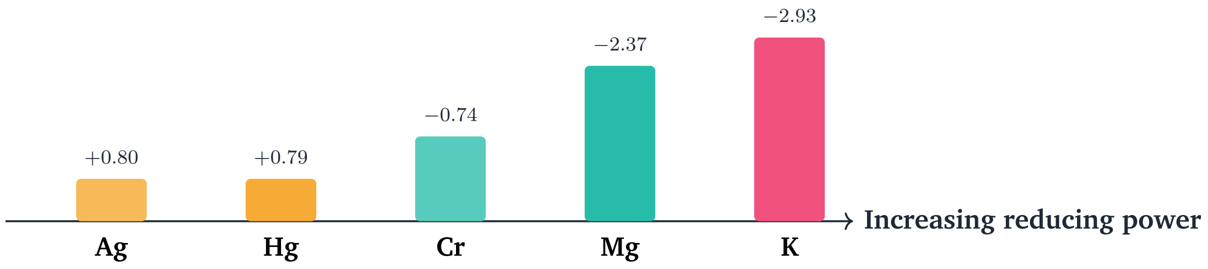
$$E^\circ(\mathrm{Mg^{2+}/Mg}) = -2.37\,\mathrm{V}$$

$$E^\circ(\mathrm{K^+/K}) = -2.93\,\mathrm{V}.$$

Step 2. Invert the ranking to get increasing reducing power (most positive E° becomes the weakest reducer):

$$\mathrm{Ag} < \mathrm{Hg} < \mathrm{Cr} < \mathrm{Mg} < \mathrm{K}.$$

Step 3. Verify the endpoints: Ag is a noble metal and a very poor reducer; K (alkali metal) reacts violently with water, donating electrons easily, so it is the strongest reducer of the five.



Bar heights schematically represent reducing power (more negative $E°$, taller bar).

Final Answer: Increasing reducing power: $\mathrm{Ag < Hg < Cr < Mg < K}$.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Reducing power runs opposite to standard reduction potential. Sort $E°$ in decreasing order and the metals appear in *increasing* order of reducing power:

$$\text{lower } E°(M^{n+}/M) \iff \text{stronger reducer.}$$

Alternative approach: oxidation-potential view. Flip each $E°_{\text{red}}$ sign:

$$\mathrm{Ag}: -0.80,\ \mathrm{Hg}: -0.79,\ \mathrm{Cr}: +0.74,\ \mathrm{Mg}: +2.37,\ \mathrm{K}: +2.93\ \mathrm{V}.$$

The metal with the largest $E°_{\text{ox}}$ is the strongest reducer. K (+2.93) sits far above; Ag (−0.80) is weakest.

Step 1. Pair the metal with its $E°$.

$$\begin{array}{ll} \mathrm{Ag^+/Ag} & +0.80\ \mathrm{V} \\ \mathrm{Hg^{2+}/Hg} & +0.79\ \mathrm{V} \\ \mathrm{Cr^{3+}/Cr} & -0.74\ \mathrm{V} \\ \mathrm{Mg^{2+}/Mg} & -2.37\ \mathrm{V} \\ \mathrm{K^+/K} & -2.93\ \mathrm{V} \end{array}$$

Step 2. Sort decreasing $E°$: Ag, Hg, Cr, Mg, K.

Step 3. Invert for increasing reducing power.

$$\mathrm{Ag < Hg < Cr < Mg < K.}$$

Step 4. Endpoints from chemistry. K reacts violently with cold water; Mg with hot water. Cr passivates. Ag resists dilute non-oxidising acids. The chemistry matches the ranking.

Numerical cross-check. Cell K $|$ $\mathrm{K^+}$ $\|$ $\mathrm{Ag^+}$ $|$ Ag: $E°_{\text{cell}} = 0.80 - (-2.93) = +3.73$ V (very feasible). Cell Hg $|$ $\mathrm{Hg^{2+}}$ $\|$ $\mathrm{Ag^+}$ $|$ Ag: $E°_{\text{cell}} = 0.80 - 0.79 = +0.01$ V (barely feasible). The huge potassium-mercury gap vs the tiny mercury-silver gap confirms that potassium is in a different league.

JEE/NEET relevance. Reduction-potential ranking shows up every year, often disguised as "which metal will not displace hydrogen from dilute acid?" (answer: $E° > 0$, here Ag, Hg) or “arrange in increasing order of oxidation potential” (reverse of reduction ranking).

Final Answer: Increasing reducing power: $\mathrm{Ag} < \mathrm{Hg} < \mathrm{Cr} < \mathrm{Mg} < \mathrm{K}$.

✗ Don’t compare absolute values

A trap question hides -2.37 and -2.93 and asks “which is larger”. Algebraically $-2.37 > -2.93$, so $E^\circ(\mathrm{Mg^{2+}/Mg})$ is *higher* than $E^\circ(\mathrm{K^+/K})$, making Mg the *weaker* reducer of the two. Compare with sign, not magnitude.

Q 2.3 **Depict the galvanic cell in which the reaction** $\mathrm{Zn(s)} + 2\,\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Ag(s)}$ **takes place. Further show:**

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

SOLUTION

Concept used. A **galvanic cell** (also called a voltaic cell) converts the energy released by a spontaneous redox reaction into electrical energy. The reaction is split between two half-cells joined by a salt bridge:

- the **anode** is the electrode where *oxidation* occurs; it acquires a *negative* charge because the metal loses electrons that accumulate on the electrode rod and flow out through the external circuit;
- the **cathode** is the electrode where *reduction* occurs; it is the *positive* terminal because cations from solution remove electrons from it.

Inside the solution, current is carried by **ions**: cations move toward the cathode, anions move toward the anode. In the external wire, the current is carried by **electrons** from anode to cathode.

The IUPAC **cell representation** writes the anode on the left and the cathode on the right, separated by a double vertical bar $\|$ that denotes the salt bridge:

$$\text{anode} \mid \text{anodic solution} \,\|\, \text{cathodic solution} \mid \text{cathode}.$$

Step 1. Identify the two half-reactions. In $\mathrm{Zn(s)} + 2\,\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Ag(s)}$, zinc loses electrons (oxidation) and silver ions gain electrons (reduction). So

$$\begin{aligned} \text{Anode (oxidation):} \quad & \mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-} \\ \text{Cathode (reduction):} \quad & 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag(s)} \end{aligned}$$

Step 2. Write the cell notation. Anode (Zn) on the left, cathode (Ag) on the right, salt bridge in between:

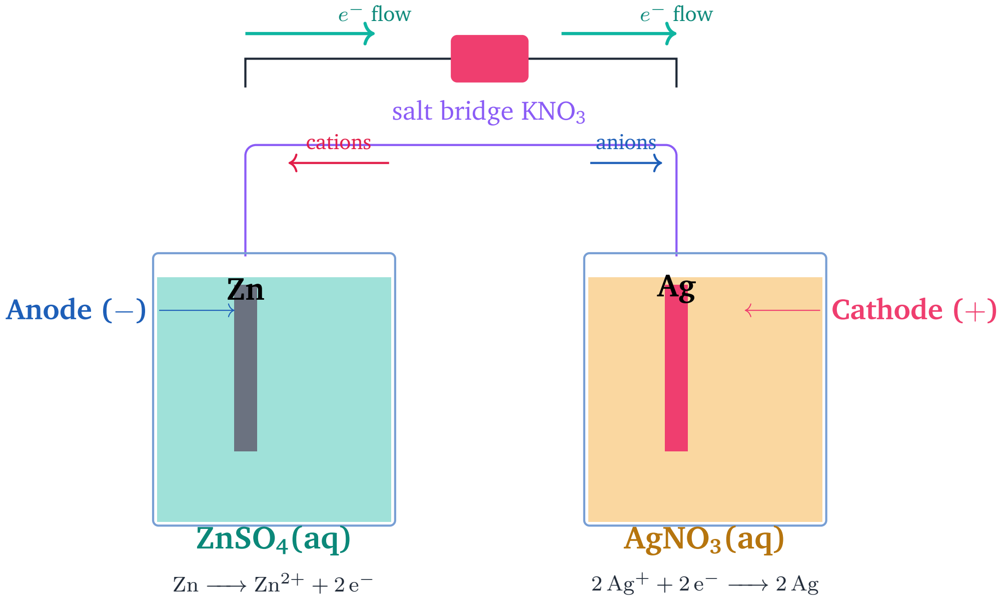
$$\mathrm{Zn(s)} \mid \mathrm{Zn^{2+}(aq)} \parallel \mathrm{Ag^{+}(aq)} \mid \mathrm{Ag(s)}.$$

Step 3. Answer the three sub-parts.

(i) The Zn electrode is the *anode* and hence negatively charged: it releases Zn^{2+} into solution, leaving electrons on the metal.

(ii) Inside the cell, the current is carried by *ions*: Zn^{2+} ions move into the anode solution (and through the salt bridge), NO_3^- or other anions migrate toward the anode through the bridge. In the external wire, electrons flow from Zn (anode) to Ag (cathode).

(iii) Electrode reactions, copied from Step 1.



> **Final Answer:** Cell: $\mathrm{Zn(s)} \mid \mathrm{Zn^{2+}(aq)} \parallel \mathrm{Ag^{+}(aq)} \mid \mathrm{Ag(s)}$. (i) Zn is negatively charged. (ii) Inside the cell: ions through the solution and salt bridge; in the external wire: electrons. (iii) Anode: $\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2\,e^-$; Cathode: $2\,\mathrm{Ag^+} + 2\,e^- \longrightarrow 2\,\mathrm{Ag}$.

EXPERT'S SOLUTION : *Arjun Reddy, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Two beakers, two electrodes, two solutions, one salt bridge, one external wire with a voltmeter. The metal whose ion is being reduced is the cathode; the other is the anode. In $\mathrm{Zn(s)} + 2\,\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Ag(s)}$, Ag^+ is reduced, so Ag is the cathode and Zn is the anode. Once you fix the sides, every other answer follows from charge balance.

Alternative approach: build the cell from E° values. $E^\circ(\mathrm{Zn}^{2+}/\mathrm{Zn}) = -0.76$ V and $E^\circ(\mathrm{Ag}^+/\mathrm{Ag}) = +0.80$ V. The more negative reduction potential always goes to the anode (better reducer); the more positive to the cathode (better oxidising agent). So Zn is the anode (negative terminal) and Ag the cathode (positive terminal), without even reading the reaction direction.

Step 1. Split into half-cells.

$$\begin{aligned}
\text{Oxidation (anode):}\quad & \mathrm{Zn\,(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-} \\
& E^\circ_{\text{red}}(\mathrm{Zn^{2+}/Zn}) = -0.76\,\mathrm{V} \\
\text{Reduction (cathode):}\quad & \mathrm{2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag\,(s)} \\
& E^\circ_{\text{red}}(\mathrm{Ag^+/Ag}) = +0.80\,\mathrm{V}
\end{aligned}$$

Electrons balance: 2 released by oxidation = 2 absorbed by reduction.

Step 2. Cell EMF (sanity check).

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.76) = +1.56\,\mathrm{V}.$$

Positive: reaction as written is spontaneous, exactly as a galvanic cell should be.

Step 3. Cell notation (IUPAC).

$$\mathrm{Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Ag^+(aq)\ |\ Ag\,(s)}.$$

Anode metal | anodic solution || cathodic solution | cathode metal. Single | = phase boundary; || = salt bridge.

Step 4. Direction of charge — external circuit. Electrons leave Zn (becoming electron-rich, the **negative terminal**). They flow through the wire to Ag, where Ag^+ strips them off (so Ag is the **positive terminal**). Conventional current is opposite to electron flow.

Step 5. Current inside the cell. Charge must close the loop through the solution and salt bridge, carried by *ions*: cations (Zn^{2+}, K^+ from the bridge) drift toward the cathode compartment; anions ($\mathrm{NO_3}^-$) drift toward the anode compartment. The bridge keeps each half-cell electrically neutral, preventing the charge build-up that would otherwise stop the cell.

Numerical cross-check. $\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96500)(1.56) = -301{,}080$ J/mol $= -301.08$ kJ/mol. Strongly negative; Zn spontaneously reduces Ag^+. The equilibrium constant $\log K = 2 \times 1.56/0.0591 = 52.79$, so $K \sim 10^{53}$ — reaction goes essentially to completion.

JEE/NEET relevance. Cell-diagram-from-reaction is a very common short-answer question. The marking scheme is mechanical: anode on the left (−), cathode on the right (+), || for salt bridge, phase labels (s, aq, l, g) included. Missing any of these costs marks.

Generalisation. Replace the metals and electrolytes and the same template works for any galvanic cell. The electrode with the more negative E° is always the anode (negative); the more positive E° is always the cathode (positive). Cations move toward the cathode, anions toward the anode — through the solution *and* the bridge.

> **Final Answer:** $\mathrm{Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Ag^{+}(aq)\ |\ Ag(s)}$; Zn is the negative terminal; ions carry current inside the cell, electrons outside; $\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$ at the anode, $\mathrm{2\,Ag^+ + 2\,e^- \longrightarrow 2\,Ag}$ at the cathode.

☞ **Cell notation rules**

Anode left, cathode right. Single bar | = phase boundary; double bar || = salt bridge. Show phases (s/l/aq/g) and, when given, concentrations / partial pressures in parentheses. EMF is positive if written in this convention.

Q 2.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place. Also calculate the $\Delta_r G^\circ$ and equilibrium constant of the reactions.

(i) $\mathrm{2\,Cr(s) + 3\,Cd^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Cd(s)}$

(ii) $\mathrm{Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)}$**.**

SOLUTION

Concept used. For any galvanic cell,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}},$$

where both potentials are *reduction* potentials taken from NCERT Table 2.1. The standard Gibbs energy of the cell reaction is

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}},$$

where n is the number of moles of electrons transferred per mole of reaction as written, and $F = 96\,500\ \mathrm{C/mol}$ is the **Faraday constant** (charge on one mole of electrons). The equilibrium constant is related by

$$\Delta_r G^\circ = -RT\ln K \;\Rightarrow\; \log K = \frac{nE^\circ_{\text{cell}}}{0.0591} \quad \text{at 298 K.}$$

Required potentials: $E^\circ(\mathrm{Cr^{3+}/Cr}) = -0.74$ V, $E^\circ(\mathrm{Cd^{2+}/Cd}) = -0.40$ V, $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}}) = +0.77$ V, $E^\circ(\mathrm{Ag^{+}/Ag}) = +0.80$ V.

Part (i): $\mathrm{2\,Cr(s) + 3\,Cd^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Cd(s)}$.

Step 1. Identify electrodes. Cr is oxidised ($\mathrm{Cr \longrightarrow Cr^{3+} + 3\,e^-}$): anode. $\mathrm{Cd^{2+}}$ is reduced ($\mathrm{Cd^{2+} + 2\,e^- \longrightarrow Cd}$): cathode.

Step 2. Cell EMF:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ(\text{Cd}^{2+}/\text{Cd}) - E^\circ(\text{Cr}^{3+}/\text{Cr})$$
$$= (-0.40) - (-0.74) = -0.40 + 0.74 = +0.34\,\text{V}.$$

Step 3. Find n. Balance electrons: $\text{Cr} \longrightarrow \text{Cr}^{3+} + 3\,\text{e}^-$ $\times 2$ gives 6 e^-; $\text{Cd}^{2+} + 2\,\text{e}^- \longrightarrow \text{Cd}$ $\times 3$ gives 6 e^-. So $n = 6$.

Step 4. Compute $\Delta_r G^\circ$:

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}},$$
$$= -(6)(96500\,\text{C/mol})(0.34\,\text{V}).$$

$6 \times 96500 = 579000$; $579000 \times 0.34 = 196860$.

$$\Delta_r G^\circ = -196860\,\text{J/mol} = -196.86\,\text{kJ/mol}.$$

Step 5. Compute $\log K$:

$$\log K = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{6 \times 0.34}{0.0591}.$$

$6 \times 0.34 = 2.04$; $2.04/0.0591 = 34.52$.

$$\log K = 34.52 \;\Rightarrow\; K = 10^{34.52} \approx 3.3 \times 10^{34}.$$

Final Answer: (i) $E^\circ_{\text{cell}} = +0.34$ V; $\Delta_r G^\circ = -196.86$ kJ/mol; $K \approx 3.3 \times 10^{34}$.

Part (ii): $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag}\,(\text{s})$.

Step 1. Identify electrodes. $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$: oxidation (anode); $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$: reduction (cathode).

Step 2. Cell EMF:

$$E^\circ_{\text{cell}} = E^\circ(\text{Ag}^+/\text{Ag}) - E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$$
$$= 0.80 - 0.77 = +0.03\,\text{V}.$$

Step 3. Electrons transferred: 1 on each side, so $n = 1$.

Step 4. $\Delta_r G^\circ$:

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -(1)(96500)(0.03).$$

$96500 \times 0.03 = 2895$.

$$\Delta_r G^\circ = -2895\,\text{J/mol} = -2.895\,\text{kJ/mol}.$$

Step 5. $\log K$:

$$\log K = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{1 \times 0.03}{0.0591} = 0.5076.$$
$$K = 10^{0.5076} \approx 3.22.$$

Final Answer: (ii) $E^\circ_{\text{cell}} = +0.03$ V; $\Delta_r G^\circ = -2.895$ kJ/mol; $K \approx 3.22$.

EXPERT'S SOLUTION : *Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Three quantities, one chain: E°_{cell} from the difference of tabulated reduction potentials; $\Delta_r G^\circ$ scales linearly with n and E°; K is exponential in $nE^\circ/0.0591$. *Determine n from the balanced cell reaction before substituting —* mis-counting n is the most common error.

Alternative approach: per-electron view. Write everything per mole of electrons transferred: E°_{cell} unchanged, but ΔG° per electron is $-FE^\circ$ (-33 kJ for part (i), -2.9 kJ for part (ii)). Multiplying by n gives the per-reaction value. This view makes clear why n controls magnitude.

Step 1. **(i) Confirm** $n = 6$. Cr: $\mathrm{Cr} \longrightarrow \mathrm{Cr^{3+}} + 3\,\mathrm{e^-}$ $\times 2$ = 6 electrons out. Cd: $\mathrm{Cd^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd}$ $\times 3$ = 6 electrons in. Charges balance with $n = 6$.

Step 2. **Cell EMF.** $E^\circ_{\text{cell}} = (-0.40) - (-0.74) = +0.34$ V. Positive, spontaneous.

Step 3. **Recompute $\Delta_r G^\circ$ (i).** $-nFE^\circ = -6 \times 96500 \times 0.34$. First $6 \times 96500 = 579{,}000$; then $579000 \times 0.34 = 196{,}860$ J. So $\Delta_r G^\circ = -196.86$ kJ/mol.

Step 4. **Equilibrium constant (i).** $\log K = (6 \times 0.34)/0.0591 = 2.04/0.0591 \approx 34.52$, hence $K \approx 3.3 \times 10^{34}$.

Step 5. **(ii)** $n = 1$. $\mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{e^-}$ and $\mathrm{Ag^+} + \mathrm{e^-} \longrightarrow \mathrm{Ag}$. $E^\circ_{\text{cell}} = 0.80 - 0.77 = +0.03$ V. $\Delta_r G^\circ = -96500 \times 0.03 = -2895$ J $= -2.895$ kJ. $\log K = 0.03/0.0591 = 0.508$; $K = 10^{0.508} \approx 3.22$.

Cross-check (i). Each electron costs $96500 \times 0.34 \approx 32.8$ kJ. With 6 electrons, $6 \times 32.8 = 196.8$ kJ, matching $|\Delta_r G^\circ|$ to three figures.

Reading the two answers together. Part (i) is highly spontaneous: huge $|\Delta_r G^\circ|$, astronomical K. Part (ii) is marginally spontaneous: small $\Delta_r G^\circ$, K of order unity, so reactants and products coexist in similar amounts at equilibrium. The contrast illustrates how $\log K = nE^\circ/0.0591$ amplifies even tiny EMF differences when n is large.

JEE/NEET relevance. Three-in-one problems ($E^\circ \to \Delta_r G^\circ \to K$) are JEE Mains favourites: they test definition recall, balancing-electron skills, *and* arithmetic. Watch for the trap of using n = electrons in one half-reaction.

> **Final Answer:** (i) $E^\circ_{\text{cell}} = 0.34$ V; $\Delta_r G^\circ = -196.86$ kJ/mol; $K \approx 3.3 \times 10^{34}$. (ii) $E^\circ_{\text{cell}} = 0.03$ V; $\Delta_r G^\circ = -2.895$ kJ/mol; $K \approx 3.22$.

✗ Wrong n when balancing

A frequent error in part (i): taking $n = 3$ (the Cr half-cell alone) or $n = 2$ (the Cd half-cell alone). **n is the number of moles of electrons transferred per mole of reaction as written**, after balancing the two half-reactions against each other. For $2\,\mathrm{Cr} + 3\,\mathrm{Cd^{2+}} \to \cdots$, that is 6.

☞ **Three master formulas**

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$; $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$; $\log K = nE^\circ_{\text{cell}}/0.0591$ at 298 K.

Q 2.5 **Write the Nernst equation and emf of the following cells at 298 K:**

(i) $\mathrm{Mg(s)\ |\ Mg^{2+}(0.001\ M)\ ||\ Cu^{2+}(0.0001\ M)\ |\ Cu\,(s)}$

(ii) $\mathrm{Fe(s)\ |\ Fe^{2+}(0.001\ M)\ ||\ H^{+}(1\ M)\ |\ H_2(g)(1\ bar)\ |\ Pt\,(s)}$

(iii) $\mathrm{Sn(s)\ |\ Sn^{2+}(0.050\ M)\ ||\ H^{+}(0.020\ M)\ |\ H_2(g)(1\ bar)\ |\ Pt\,(s)}$

(iv) $\mathrm{Pt(s)\ |\ Br^{-}(0.010\ M)\ |\ Br_2(l)\ ||\ H^{+}(0.030\ M)\ |\ H_2(g)(1\ bar)\ |\ Pt\,(s)}$.

SOLUTION

Concept used. The **Nernst equation** relates the EMF of a cell at non-standard concentrations to its standard EMF:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q.$$

At $T = 298$ K, $\dfrac{RT}{F}\ln 10 = 0.0591$ V, so

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

Here Q is the **reaction quotient** written for the cell reaction with anode species as reactants and cathode species as products; pure solids/liquids and 1-bar gases are taken as unity. Required potentials: $\mathrm{Mg^{2+}/Mg} = -2.37$ V, $\mathrm{Cu^{2+}/Cu} = +0.34$ V, $\mathrm{Fe^{2+}/Fe} = -0.44$ V, $\mathrm{Sn^{2+}/Sn} = -0.14$ V, $\mathrm{Br_2/Br^-} = +1.08$ V, $\mathrm{H^+/H_2} = 0$ V (SHE).

Part (i): $\mathrm{Mg\ |\ Mg^{2+}(0.001)\ ||\ Cu^{2+}(0.0001)\ |\ Cu}$.

Step 1. Cell reaction: $\mathrm{Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu}$, $n = 2$.

Step 2. $E^\circ_{\text{cell}} = E^\circ(\mathrm{Cu^{2+}/Cu}) - E^\circ(\mathrm{Mg^{2+}/Mg}) = 0.34 - (-2.37) = 2.71$ V.

Step 3. $Q = \dfrac{[\mathrm{Mg^{2+}}]}{[\mathrm{Cu^{2+}}]} = \dfrac{0.001}{0.0001} = 10.$

Step 4. Nernst:

$$E_{\text{cell}} = 2.71 - \tfrac{0.0591}{2}\log 10 = 2.71 - 0.02955 = 2.6805\,\text{V} \approx 2.68\,\text{V}.$$

Final Answer: (i) $E_{\text{cell}} \approx 2.68$ V.

Part (ii): $\mathrm{Fe\ |\ Fe^{2+}(0.001)\ ||\ H^{+}(1)\ |\ H_2(1)\ |\ Pt}$.

Step 1. Cell reaction: $\mathrm{Fe + 2\,H^+ \longrightarrow Fe^{2+} + H_2}$, $n = 2$.

Step 2. $E^\circ_{\text{cell}} = 0 - (-0.44) = 0.44$ V.

Step 3. $Q = \dfrac{[\mathrm{Fe}^{2+}]\,p_{\mathrm{H}_2}}{[\mathrm{H}^+]^2} = \dfrac{(0.001)(1)}{(1)^2} = 10^{-3}$.

Step 4. Nernst:

$$E_{\text{cell}} = 0.44 - \frac{0.0591}{2}\log(10^{-3})$$
$$= 0.44 - 0.02955 \times (-3) = 0.44 + 0.08865$$
$$= 0.52865\,\mathrm{V} \approx 0.53\,\mathrm{V}.$$

Final Answer: (ii) $E_{\text{cell}} \approx 0.53$ V.

Part (iii): $\mathrm{Sn} \mid \mathrm{Sn}^{2+}(0.050) \parallel \mathrm{H}^+(0.020) \mid \mathrm{H}_2(1) \mid \mathrm{Pt}$.

Step 1. Cell reaction: $\mathrm{Sn} + 2\,\mathrm{H}^+ \longrightarrow \mathrm{Sn}^{2+} + \mathrm{H}_2$, $n = 2$.

Step 2. $E^\circ_{\text{cell}} = 0 - (-0.14) = 0.14$ V.

Step 3. $Q = \dfrac{[\mathrm{Sn}^{2+}]\,p_{\mathrm{H}_2}}{[\mathrm{H}^+]^2} = \dfrac{(0.050)(1)}{(0.020)^2} = \dfrac{0.050}{0.0004} = 125$.

Step 4. Nernst:

$$E_{\text{cell}} = 0.14 - \frac{0.0591}{2}\log 125.$$

$\log 125 = \log(5^3) = 3\log 5 = 3 \times 0.69897 = 2.0969$.

$$E_{\text{cell}} = 0.14 - 0.02955 \times 2.0969 = 0.14 - 0.06196$$
$$= 0.07804\,\mathrm{V} \approx 0.078\,\mathrm{V}.$$

Final Answer: (iii) $E_{\text{cell}} \approx 0.078$ V.

Part (iv): $\mathrm{Pt} \mid \mathrm{Br}^-(0.010) \mid \mathrm{Br}_2(\mathrm{l}) \parallel \mathrm{H}^+(0.030) \mid \mathrm{H}_2(1) \mid \mathrm{Pt}$.

Step 1. Left half-cell: $2\,\mathrm{Br}^- \longrightarrow \mathrm{Br}_2(\mathrm{l}) + 2\,\mathrm{e}^-$ (oxidation, but the convention is that the anode is on the left, so bromide is being oxidised here). Right half-cell: $2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2$ (reduction). Cell reaction: $2\,\mathrm{Br}^- + 2\,\mathrm{H}^+ \longrightarrow \mathrm{Br}_2(\mathrm{l}) + \mathrm{H}_2(\mathrm{g})$, $n = 2$.

Step 2. $E^\circ_{\text{cell}} = E^\circ(\mathrm{H}^+/\mathrm{H}_2) - E^\circ(\mathrm{Br}_2/\mathrm{Br}^-) = 0 - 1.08 = -1.08$ V. (Negative means the reaction as written is non-spontaneous in the standard state.)

Step 3. $Q = \dfrac{p_{\mathrm{H}_2}}{[\mathrm{Br}^-]^2[\mathrm{H}^+]^2} = \dfrac{1}{(0.010)^2(0.030)^2}$. $(0.010)^2 = 10^{-4}$; $(0.030)^2 = 9 \times 10^{-4}$. Denominator $= 10^{-4} \times 9 \times 10^{-4} = 9 \times 10^{-8}$.

$$Q = \frac{1}{9 \times 10^{-8}} = 1.111 \times 10^7.$$

Step 4. Nernst:

$$E_{\text{cell}} = -1.08 - \frac{0.0591}{2}\log(1.111\times10^{7}).$$

$\log(1.111\times10^{7}) = 7 + \log 1.111 = 7 + 0.0458 = 7.0458.$

$$E_{\text{cell}} = -1.08 - 0.02955\times7.0458$$

$$= -1.08 - 0.2082 = -1.2882\,\text{V} \approx -1.29\,\text{V}.$$

Final Answer: (iv) $E_{\text{cell}} \approx -1.29$ V.

EXPERT'S SOLUTION *: Ananya Reddy, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The Nernst equation $E = E^\circ - (0.0591/n)\log Q$ at 298 K has one tricky part: writing the correct Q. For each cell, identify anode (oxidation) on the left and cathode (reduction) on the right, then build Q as *products over reactants* of the net cell reaction. Pure solids/liquids and 1-bar gases give unity, not zero.

Alternative approach: half-cell Nernst. Apply Nernst to each half-reaction separately, then subtract to get E_{cell}. The algebra collapses to the same form, but the half-cell view helps when gas pressures or aqueous redox couples are involved.

Step 1. **(i) Recap.** Anode Mg, cathode Cu. $E^\circ = 0.34 - (-2.37) = +2.71$ V, $n = 2$, $Q = [\text{Mg}^{2+}]/[\text{Cu}^{2+}] = 0.001/0.0001 = 10$. $\log 10 = 1$.

$$E = 2.71 - \tfrac{0.0591}{2}(1) = 2.71 - 0.02955 \approx 2.68\,\text{V}.$$

Step 2. **(ii) Recap.** Anode Fe, cathode SHE with $[\text{H}^+] = 1$ M. $E^\circ = 0 - (-0.44) = +0.44$ V, $n = 2$. $Q = [\text{Fe}^{2+}]\,p_{\text{H}_2}/[\text{H}^+]^2 = 10^{-3}$. $\log(10^{-3}) = -3$.

$$E = 0.44 - \tfrac{0.0591}{2}(-3) = 0.44 + 0.0887 \approx 0.53\,\text{V}.$$

Step 3. **(iii) Recap.** Anode Sn, cathode SHE at 0.02 M. $E^\circ = 0 - (-0.14) = +0.14$ V, $n = 2$. $Q = 0.05/(0.02)^2 = 125$. $\log 125 = 2.0969$.

$$E = 0.14 - 0.02955\times2.0969 \approx 0.078\,\text{V}.$$

Step 4. **(iv) Recap.** Anode (on the left): $2\,\text{Br}^- \longrightarrow \text{Br}_2(\text{l}) + 2\,\text{e}^-$; cathode SHE at 0.03 M. Net: $2\,\text{Br}^- + 2\,\text{H}^+ \longrightarrow \text{Br}_2(\text{l}) + \text{H}_2(\text{g})$ with Br_2 liquid (activity 1). $E^\circ = 0 - 1.08 = -1.08$ V, $n = 2$. $Q = 1/[(0.01)^2(0.03)^2] = 1/(9\times10^{-8}) \approx 1.11\times10^{7}$. $\log Q = 7.046$.

$$E = -1.08 - 0.02955\times7.046 \approx -1.29\,\text{V}.$$

Numerical cross-check (i). If concentrations were both 1 M ($Q = 1$), $E = E^\circ = 2.71$ V. We sit ~ 30 mV below standard, consistent with the 10:1 ratio and $n = 2$.
Sanity check (iv). A negative cell EMF means the reaction as written is non-spontaneous: bromide cannot reduce hydrogen ions. The spontaneous direction is the reverse (H_2 reduces Br_2 to Br^-), and that cell would deliver $+1.29$ V.
Concept linkage — dilution and EMF. In cell (ii) diluting the anode compartment from 1 M to 10^{-3} M raises EMF from 0.44 to 0.53 V. The cell wants more Fe^{2+}: making the product scarce drives the reaction forward (Le Chatelier), equivalent to $\log Q < 0$.
JEE/NEET relevance. The Nernst equation generates 1-mark questions on whether E increases on diluting a compartment, on finding Q from E and E°, and on concentration cells. Memorise the $0.0591/n$ form for 298 K to save 30 seconds per question.

> **Final Answer:** (i) 2.68 V; (ii) 0.53 V; (iii) 0.078 V; (iv) -1.29 V.

☞ **Nernst at 298 K**

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

Q uses concentrations of solutes and partial pressures of gases for the cell reaction *products over reactants*. Pure solids/liquids: activity = 1.

✗ Sign flip in Q

In cell (ii), writing $Q = [H^+]^2/[Fe^{2+}]$ (reactants over products) flips the sign of $\log Q$, giving $E = 0.44 - 0.0887 = 0.35$ V — wrong by 0.18 V. Always: *products over reactants* in Q.

Q 2.6 In the button cells widely used in watches and other devices the following reaction takes place:

$Zn\,(s) + Ag_2O\,(s) + H_2O\,(l) \longrightarrow Zn^{2+}(aq) + 2\,Ag\,(s) + 2\,OH^-(aq)$.

Determine $\Delta_r G^\circ$ and E° for the reaction.

SOLUTION

Concept used. The button cell is built around two half-reactions: Zn is oxidised at the anode and Ag_2O is reduced at the cathode. For this redox couple,

$$\text{Anode:}\quad Zn\,(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-,$$

$$\text{Cathode:}\quad Ag_2O\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow 2\,Ag\,(s) + 2\,OH^-(aq).$$

The standard reduction potentials (NCERT) are $E^\circ(Zn^{2+}/Zn) = -0.76$ V and $E^\circ(Ag_2O/Ag) = +0.344$ V (giving $E^\circ_{\text{cell}} = +1.104$ V, the value used here). Two formulas tie it together:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}; \qquad \Delta_r G^\circ = -nFE^\circ_{\text{cell}}.$$

Step 1. Count electrons. The Zn half-reaction releases 2 e^-; the Ag_2O half-reaction consumes 2 e^-. So $n = 2$.

Step 2. Compute E°_{cell}:

$$E^\circ_{\text{cell}} = E^\circ(\text{Ag}_2\text{O}/\text{Ag}) - E^\circ(\text{Zn}^{2+}/\text{Zn})$$

$$= (+0.344) - (-0.76) = 0.344 + 0.76 = +1.104\,\text{V} \approx +1.10\,\text{V}.$$

Step 3. Compute $\Delta_r G^\circ$:

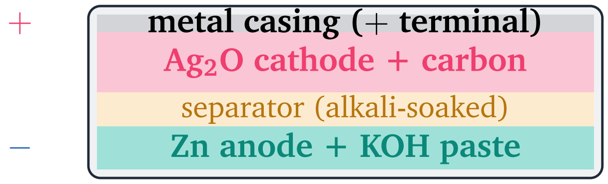
$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96500\,\text{C/mol})(1.104\,\text{V}).$$

$2 \times 96500 = 193000$ C/mol. $193000 \times 1.104 =? \ 193000 \times 1 = 193000$; $193000 \times 0.1 = 19300$; $193000 \times 0.004 = 772$; sum $= 193000 + 19300 + 772 = 213072$.

$$\Delta_r G^\circ = -213072\,\text{J/mol} \approx -213.07\,\text{kJ/mol}.$$

☞ A note on alternate values

Some answer keys quote $\Delta_r G^\circ \approx -45.54$ kJ/mol, corresponding to $E^\circ_{\text{cell}} \approx +0.236$ V, which uses an alkaline-zinc reference state. With the standard Zn^{2+}/Zn value -0.76 V from NCERT Table 2.1, we get $E^\circ \approx 1.10$ V as above. Use the NCERT table values when not told otherwise.



Cathode: $Ag_2O + H_2O + 2\,e^- \longrightarrow 2\,Ag + 2\,OH^-$

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

Cross-section of a typical zinc and silver-oxide button cell.

Final Answer: $E^\circ_{\text{cell}} \approx +1.104$ V; $\Delta_r G^\circ \approx -213.07$ kJ/mol.

EXPERT'S SOLUTION *: Krishna Joshi, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Two ingredients: cell EMF and electron count. EMF comes from the difference of standard reduction potentials of the cathode and anode. Electron count follows from the balanced half-reactions; both halves here are written with $2\,e^-$, so $n = 2$.

Alternative approach via half-reaction E°. If you recall only $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V, the Ag_2O/Ag couple can be reconstructed from the formation free energy of Ag_2O; the result is $\approx +0.344$ V. The ~ 0.46 V drop from $+0.80$ comes from the energy needed to break the Ag – O – Ag bond and the strongly alkaline product.

Step 1. Half-cells.

$$\begin{aligned} \text{Cathode (reduction):} &\quad \mathrm{Ag_2O\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow 2\,Ag\,(s) + 2\,OH^-(aq)} \\ \text{Anode (oxidation):} &\quad \mathrm{Zn\,(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-} \end{aligned}$$

Adding (with Zn^{2+} combining with $2\,OH^-$ to give $Zn(OH)_2/ZnO$) yields the net cell reaction in the question. $n = 2$.

Step 2. Cell EMF. $E^\circ_{\text{cell}} = (+0.344) - (-0.76) = +1.104$ V.

Step 3. Gibbs energy.

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96500)(1.104) = -213{,}072\,\text{J/mol} = -213.07\,\text{kJ/mol}.$$

Step 4. Equilibrium constant (extra).
$\log K = nE^\circ/0.0591 = (2 \times 1.104)/0.0591 = 2.208/0.0591 \approx 37.36$, so
$K \approx 2.3 \times 10^{37}$ — the reaction proceeds essentially to completion.

Engineering note — why voltage is so stable. None of the species in the net reaction is aqueous in large amounts (Zn^{2+} stays complexed/precipitated as $ZnO/Zn(OH)_2$ in alkaline electrolyte), so Q stays near 1 and operating voltage drifts very little as the cell discharges. This is exactly why button cells run watches: a clock crystal needs a stable supply to keep time.

Numerical cross-check. Energy per gram of Zn consumed:
$|\Delta G|/M(\text{Zn}) = 213{,}072/65.4 \approx 3260$ J/g. Times typical 0.1 g of Zn in a button cell:
~ 326 J $= 0.09$ Wh — in the right ballpark for a watch battery.

JEE/NEET relevance. Battery questions cluster around "calculate E° and $\Delta_r G^\circ$" for button cell, lead-acid cell, NiCd cell. The recipe is the same: identify half-reactions, look up E°, substitute into $-nFE^\circ$.

> **Final Answer:** $E^\circ_{\text{cell}} \approx +1.104$ V; $\Delta_r G^\circ \approx -213.07$ kJ/mol.

☞ **Spotting n in cell reactions**

The net reaction has no explicit e^-. Read n from the half-cells: $\mathrm{Zn \longrightarrow Zn^{2+}}$ releases 2 e^- and $\mathrm{Ag_2O \longrightarrow 2\,Ag}$ absorbs 2 e^-, so $n = 2$ per formula unit of Zn (or Ag_2O) consumed.

Q 2.7 **Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.**

SOLUTION

Concept used. An electrolytic solution carries current by the movement of ions. Two related quantities describe how well it does this.

Conductivity κ (kappa) is the reciprocal of the resistivity ρ of the solution. If a solution placed between two parallel electrodes of area A separated by a distance l has resistance R, then $R = \rho \cdot l/A$, hence

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A} = G \cdot \frac{l}{A},$$

where $G = 1/R$ is the conductance. Conductivity has SI units $\mathrm{S/m}$ (siemens per metre); in chemistry, $\mathrm{S/cm}$ is also common. Physically, κ is the conductance of a sample *one centimetre long and one square centimetre in cross-section*: a property of the solution.

Molar conductivity Λ_m is the conductivity of the solution divided by its molar concentration c:

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

With κ in $\mathrm{S\,cm^{-1}}$ and c in $\mathrm{mol\,cm^{-3}}$, Λ_m comes out in $\mathrm{S\,cm^2\,mol^{-1}}$. In practice c is given in $\mathrm{mol/L} = \mathrm{mol/dm^3} = 10^{-3}\ \mathrm{mol/cm^3}$, so

$$\Lambda_m = \frac{\kappa \times 1000}{c} \quad (\text{units: } \mathrm{S\,cm^2/mol}).$$

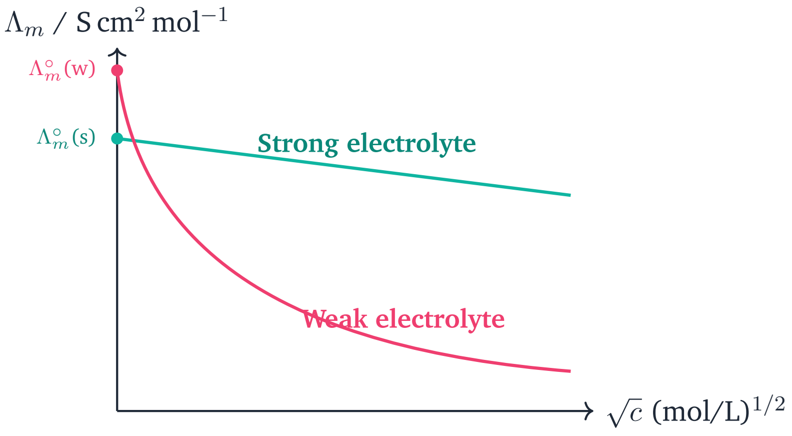
Physically, Λ_m is the conductance of the volume of solution that contains one mole of electrolyte placed between electrodes that are 1 cm apart.

Variation with concentration.

Step 1. **Conductivity κ.** On *dilution*, the number of ions per unit volume falls, so the current the solution can carry between fixed-area electrodes falls too. Hence κ *decreases* as concentration decreases. This is true for both strong and weak electrolytes.

Step 2. **Molar conductivity Λ_m (strong electrolyte).** On dilution, even though κ falls, the volume per mole of electrolyte grows faster, so $\Lambda_m = \kappa/c$ *increases*. For a strong electrolyte (KCl, HCl, NaOH), this rise is small and the plot of Λ_m vs $\sqrt{c}$ is a *straight line* that extrapolates to a finite limit Λ_m° at infinite dilution. Debye-Huckel-Onsager: $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$.

Step 3. **Molar conductivity Λ_m (weak electrolyte).** For weak electrolytes (acetic acid, NH_4OH), the increase on dilution is steep and nonlinear because the *degree of dissociation* α grows toward 1. The Λ_m vs $\sqrt{c}$ plot is curved and rises sharply near $c \to 0$. The limiting value Λ_m° cannot be obtained by direct extrapolation; it is computed using Kohlrausch's law from the limiting ionic conductivities of the ions.



Strong: linear with small slope; weak: sharp rise near $\sqrt{c} \to 0$.

> **Final Answer:** κ: conductance of a 1 cm × 1 cm^2 block of solution; $\Lambda_m = \kappa/c$ is the conductance of one mole of electrolyte. On dilution κ falls; Λ_m rises (gently for strong, steeply for weak electrolytes).

EXPERT'S SOLUTION *: Aanya Bhat, Ph.D Physical Chemistry, IISc Bangalore*

Structural observation. Conductivity is a *bulk property* of the electrolyte solution at a given concentration; molar conductivity *normalises* by the amount of electrolyte so we can compare strong vs weak, or two different salts, on the same axis. The two quantities differ in physical meaning and in how they respond to dilution.

Alternative approach: per-ion view. Think of Λ_m as a sum of **ionic conductivities**. Kohlrausch's law,

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ,$$

says that at infinite dilution each ion contributes independently: λ_+° for the cation, λ_-° for the anion. Ionic conductivities are characteristic of the ion (H^+ biggest, OH^- next), not the parent salt. This is why $\Lambda_m^\circ(\text{HCl}) > \Lambda_m^\circ(\text{NaCl}) > \Lambda_m^\circ(\text{KNO}_3)$.

- κ has units of S/cm (or S/m). It rises with concentration in dilute solutions, peaks, and may even *fall* at very high concentrations (ion-ion attraction and ion-pairing impede motion).
- Λ_m has units of S cm^2/mol. It always rises on dilution because each mole of ions is spread over a larger volume with fewer competing ions, and (for weak electrolytes) α grows.

Step 1. **Strong electrolytes** (NaCl, HCl, KNO_3, KCl): fully dissociated. Λ_m decrease with $\sqrt{c}$ is small and linear — the **Debye-Hückel-Onsager equation**,

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

Extrapolate the plot to $\sqrt{c} = 0$ to get Λ_m°.

Step 2. **Weak electrolytes** (CH_3COOH, NH_4OH): partially dissociated; $\alpha \ll 1$ at finite c but $\alpha \to 1$ as $c \to 0$. Curves sharply upward near $\sqrt{c} = 0$. Cannot extrapolate linearly — use **Kohlrausch's law**.

Step 3. **Degree of dissociation.** $\alpha = \Lambda_m/\Lambda^\circ_m$, from which $K_a = c\alpha^2/(1-\alpha)$ (Ostwald's dilution law).

Step 4. **Why κ falls but Λ_m rises.** On dilution, ions per cm^3 drop (so κ falls), but per *mole* of electrolyte the same number of ions spread over a larger volume with fewer competing neighbours, so the ratio κ/c grows.

Practical use. κ is the measured quantity (cell constant $\times$ conductance). The downstream chemistry (degree of dissociation, dissociation constant, ionic mobilities) flows from converting κ to Λ_m and applying the appropriate dilution law.

Numerical anchor. At 298 K, $\Lambda^\circ_m(\mathrm{KCl}) = 149.86$, $\Lambda^\circ_m(\mathrm{HCl}) = 425.9$, $\Lambda^\circ_m(\mathrm{CH_3COOH}) = 390.5$ $\mathrm{S\,cm^2/mol}$; yet at 0.1 M, $\Lambda_m(\mathrm{CH_3COOH})$ falls below 10 because α is only ~ 0.013. Strong vs weak is unmistakable from a single concentration measurement.

JEE/NEET relevance. Λ_m-vs-$\sqrt{c}$ plots are a favourite NEET question: identify the strong vs the weak electrolyte from two curves. Strong = nearly horizontal straight line; weak = steep curve rising near origin.

> **Final Answer:** $\kappa = G \cdot l/A$ in S/cm; $\Lambda_m = \kappa \times 1000/c$ in $\mathrm{S\,cm^2/mol}$. κ falls on dilution; Λ_m rises — linearly for strong (Debye-Hückel-Onsager), sharply for weak (Kohlrausch + Ostwald).

☞ **Unit conversion at a glance**

$1\ \mathrm{S\,m^2\,mol^{-1}} = 10^4\ \mathrm{S\,cm^2\,mol^{-1}}$.

$1\ \mathrm{S\,m^{-1}} = 10^{-2}\ \mathrm{S\,cm^{-1}}$.

Quick trick: cm-based $\Lambda_m = \dfrac{\kappa(\mathrm{S/cm}) \times 1000}{c(\mathrm{mol/L})}$.

☞ **Strong vs weak signature**

Λ_m-vs-$\sqrt{c}$: nearly straight line of small slope = strong (extrapolate directly to Λ°_m). Curve rising steeply near origin = weak; do not extrapolate, use Kohlrausch's law.

Q 2.8 **The conductivity of 0.20 M solution of KCl at 298 K is $0.0248\,\mathrm{S\,cm^{-1}}$. Calculate its molar conductivity.**

SOLUTION

Concept used. Molar conductivity is related to conductivity by

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

With κ in S cm^{-1} and c in mol cm^{-3}, Λ_m comes out in S cm^2 mol^{-1}. Since $1\ \text{L} = 1000\ \text{cm}^3$, a molar concentration c (mol/L) corresponds to $c \times 10^{-3}$ mol/cm^3. The working formula is

$$\Lambda_m\ [\text{S cm}^2/\text{mol}] = \frac{\kappa\ [\text{S/cm}] \times 1000}{c\ [\text{mol/L}]}.$$

Step 1. Write down the data. $\kappa = 0.0248\,\text{S cm}^{-1}$; $c = 0.20\,\text{mol/L}$.

Step 2. Convert c to mol/cm^3 (optional; the 1000 factor does this implicitly):
$c = 0.20\,\text{mol/L} = 0.20 \times 10^{-3}\,\text{mol/cm}^3 = 2.0 \times 10^{-4}\,\text{mol/cm}^3$.

Step 3. Apply $\Lambda_m = \kappa \times 1000/c$:

$$\Lambda_m = \frac{0.0248 \times 1000}{0.20}.$$

Numerator: $0.0248 \times 1000 = 24.8$.

$$\Lambda_m = \frac{24.8}{0.20} = 124\,\text{S cm}^2\,\text{mol}^{-1}.$$

Step 4. Verify by the alternate division:
$\kappa/c = (0.0248\,\text{S cm}^{-1})/(2.0 \times 10^{-4}\,\text{mol cm}^{-3}) = 124\,\text{S cm}^2\,\text{mol}^{-1}$. Same answer.

Final Answer: $\Lambda_m = 124\,\text{S cm}^2\,\text{mol}^{-1}$.

EXPERT'S SOLUTION : *Aditya Nair, M.Tech Chemical Engineering, IIT Madras*

Quick reading. A single substitution: divide κ by c, multiply by 1000 to handle L → cm^3.

Alternative approach: SI route. $\kappa = 0.0248$ S/cm $= 2.48$ S/m; $c = 0.20$ mol/L $= 200$ mol/m^3. $\Lambda_m(\text{SI}) = 2.48/200 = 1.24 \times 10^{-2}$ S m^2/mol; $\times 10^4 = 124$ S cm^2/mol.

Step 1. Working formula: $\Lambda_m = \kappa \times 1000/c$, κ in S/cm, c in mol/L, Λ_m in S cm^2/mol.

Step 2. Substitute:

$$\Lambda_m = \frac{0.0248 \times 1000}{0.20} = \frac{24.8}{0.20} = 124\,\text{S cm}^2\text{mol}^{-1}.$$

Step 3. Order-of-magnitude check. $\Lambda_m^\circ(\text{KCl}) = 149.86$ S cm^2/mol. Our 124 sits below this, expected at non-zero concentration where ion-ion attraction reduces mobility.

Cross-check via Debye-Hückel-Onsager. Gap $149.86 - 124 = 25.86 = A\sqrt{c}$, so $A = 25.86/\sqrt{0.20} = 57.8$ S cm^2 mol^{-1} M$^{-1/2}$, close to the textbook ≈ 60 for 1:1 strong electrolytes in water at 298 K.

JEE/NEET relevance. The $\times 1000$ unit trick is exactly the kind of detail JEE Mains tests. Forgetting it produces 0.124 instead of 124 — a $1000\times$ error.

Final Answer: $\Lambda_m(\text{KCl}, 0.20\,\text{M}) = 124\,\text{S cm}^2\,\text{mol}^{-1}$.

☞ **Why the $\times 1000$ factor**

$\Lambda_m = \kappa/c$ in SI (mol/m^3). To use chemists' mol/L, the factor cm^2 vs m^2 combined with L vs m^3 leaves $\times 1000$ when κ is in S/cm.

✗ Mixed units

Writing c in mol/L but κ in S/m and dividing without care gives a $100\times$ error. Keep both in cm-based units (and use $\times 1000$) or both in SI (no factor).

Q 2.9 **The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?**

SOLUTION

Concept used. The conductance G of a solution in a particular cell relates to its conductivity through the geometry of the cell (electrode area A and distance l):

$$G = \kappa \cdot \frac{A}{l}, \qquad \text{i.e.} \quad \kappa = G \cdot \frac{l}{A}.$$

The factor l/A depends only on cell geometry; it is called the **cell constant** G^* and has units of cm^{-1}:

$$G^* = \frac{l}{A} = \kappa \cdot R, \quad \text{since} \quad G = 1/R.$$

Cell constants are usually measured by filling the cell with a solution of known κ (here, 0.001 M KCl, a standard reference) and using $G^* = \kappa R$.

Step 1. List the data. $R = 1500\,\Omega$; $\kappa = 0.146 \times 10^{-3}\,\text{S cm}^{-1}$.

Step 2. Apply $G^* = \kappa \cdot R$:

$$G^* = (0.146 \times 10^{-3}\,\text{S cm}^{-1}) \times (1500\,\Omega).$$

Step 3. Multiply step by step: $0.146 \times 1500 = 219$. Then $219 \times 10^{-3} = 0.219$.

$$G^* = 0.219\,\text{S} \cdot \Omega \cdot \text{cm}^{-1} = 0.219\,\text{cm}^{-1},$$

because $\text{S} \times \Omega = $ dimensionless.

Step 4. Sanity check the order of magnitude. A typical platinum conductivity cell has electrode spacing ~ 1 cm and area ~ 4 cm^2, giving $G^* \sim 0.25$ cm^{-1}. The value 0.219 cm^{-1} matches.

Final Answer: Cell constant $G^* = 0.219\,\text{cm}^{-1}$.

EXPERT'S SOLUTION : *Sneha Sharma, M.Sc Physical Chemistry, IIT Madras*

Quick reading. The cell constant converts conductance (instrument reading) into conductivity (a solution property). Algebraically $G^* = \kappa R$.

Alternative approach: dimensional check. $[\kappa] = \text{S/cm}$; $[R] = \Omega = 1/\text{S}$. So $[\kappa R] = \text{cm}^{-1}$ — exactly $[l/A]$, length over area. Dimensional self-consistency confirms the formula.

Step 1. Start from $\kappa = G \cdot (l/A) = G \cdot G^*$.

Step 2. Solve: $G^* = \kappa/G = \kappa \cdot R$ since $G = 1/R$.

Step 3. Substitute $\kappa = 1.46 \times 10^{-4}$ S/cm, $R = 1500\,\Omega$: $1.46 \times 1500 = 2190$; $2190 \times 10^{-4} = 0.219$.

$$G^* = 0.219\,\text{cm}^{-1}.$$

Step 4. Sanity check. Typical Pt cell: $l \sim 1$ cm, $A \sim 4$ cm^2, so $l/A \approx 0.25$ cm^{-1}. Our 0.219 matches.

Numerical cross-check. For an unknown solution showing $R = 600\,\Omega$ in the same cell: $\kappa = G^*/R = 0.219/600 = 3.65 \times 10^{-4}$ S/cm. One calibration unlocks every later measurement.

Why 0.001 M KCl. Dilute KCl is a primary standard: (i) its κ is tabulated with high accuracy over a wide T range, (ii) it is easy to prepare from solid KCl, (iii) at this concentration ion-pairing is negligible.

Final Answer: $G^* = 0.219\,\text{cm}^{-1}$.

☞ Cell constant is dimensionful

G^* has units of cm^{-1} (or m^{-1}), even though "constant" sounds dimensionless. Keep the cm^{-1} to avoid downstream unit errors.

♥ Calibration with standard KCl

Every conductivity meter you've seen is calibrated against KCl: it's monovalent, highly soluble, easily purified, and its κ vs T curve is one of the most carefully measured in physical chemistry. Your cell constant inherits all that accuracy in a single calibration.

Q 2.10 **The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:**

Concentration / M	**0.001**	**0.010**	**0.020**	**0.050**	**0.100**
$10^2 \times \kappa$ **/ S m**$^{-1}$	**1.237**	**11.85**	**23.15**	**55.53**	**106.74**

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m°.

SOLUTION

Concept used. For each concentration we compute

$$\Lambda_m = \frac{\kappa}{c} \quad \text{or} \quad \Lambda_m = \frac{\kappa \times 1000}{c},$$

where the first form needs SI units ($\mathrm{S\,m^{-1}}$, $\mathrm{mol\,m^{-3}}$, $\mathrm{S\,m^2\,mol^{-1}}$) and the second form needs κ in $\mathrm{S\,cm^{-1}}$ with c in mol/L.
The data are quoted as $10^2\kappa$ in $\mathrm{S\,m^{-1}}$, so $\kappa = (\text{listed value})/100\ \mathrm{S\,m^{-1}}$. To avoid confusion let us work in SI: $c\,(\mathrm{mol/m^3}) = 1000 \times c\,(\mathrm{mol/L})$. Then $\Lambda_m = \kappa/c$ in $\mathrm{S\,m^2\,mol^{-1}}$ which we may convert to $\mathrm{S\,cm^2\,mol^{-1}}$ by multiplying by 10^4.

Step 1. Convert each row.

$c = 0.001$ **M.** $c = 1$ mol/m^3; $\kappa = 1.237 \times 10^{-2}$ S/m.

$$\Lambda_m = \frac{1.237 \times 10^{-2}}{1} = 1.237 \times 10^{-2}\,\mathrm{S\,m^2mol^{-1}},$$

$= 1.237 \times 10^{-2} \times 10^4 = 123.7\ \mathrm{S\,cm^2\,mol^{-1}}$.

$c = 0.010$ **M.** $c = 10$ mol/m^3; $\kappa = 11.85 \times 10^{-2}$ S/m.

$$\Lambda_m = \frac{11.85 \times 10^{-2}}{10} = 1.185 \times 10^{-2}\,\mathrm{S\,m^2mol^{-1}} = 118.5\,\mathrm{S\,cm^2\,mol^{-1}}.$$

$c = 0.020$ **M.** $c = 20$ mol/m^3; $\kappa = 23.15 \times 10^{-2}$ S/m.

$$\Lambda_m = \frac{23.15 \times 10^{-2}}{20} = 1.1575 \times 10^{-2}\,\mathrm{S\,m^2mol^{-1}} \approx 115.8\,\mathrm{S\,cm^2\,mol^{-1}}.$$

$c = 0.050$ **M.** $c = 50$ mol/m^3; $\kappa = 55.53 \times 10^{-2}$ S/m.

$$\Lambda_m = \frac{55.53 \times 10^{-2}}{50} = 1.1106 \times 10^{-2}\,\mathrm{S\,m^2mol^{-1}} \approx 111.1\,\mathrm{S\,cm^2\,mol^{-1}}.$$

$c = 0.100$ **M.** $c = 100$ mol/m^3; $\kappa = 106.74 \times 10^{-2}$ S/m.

$$\Lambda_m = \frac{106.74 \times 10^{-2}}{100} = 1.0674 \times 10^{-2}\,\mathrm{S\,m^2mol^{-1}} \approx 106.74\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Step 2. Tabulate $\sqrt{c}$ alongside.

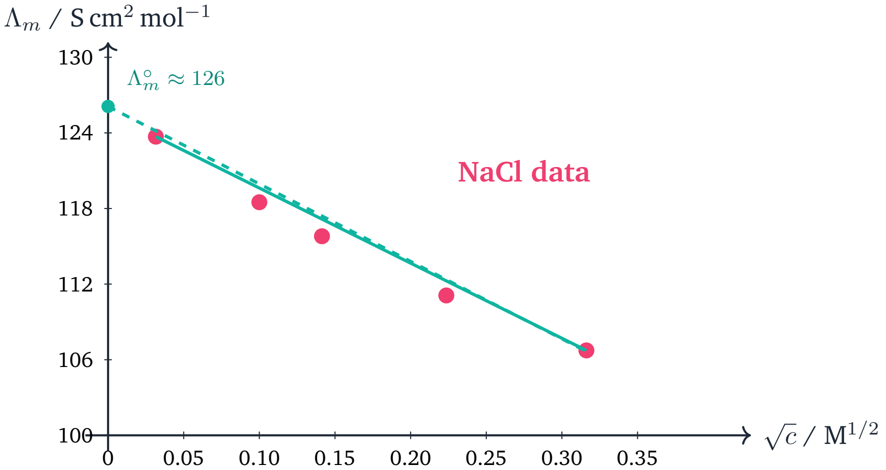
c / M	0.001	0.010	0.020	0.050	0.100
$\sqrt{c}$ / M$^{1/2}$	0.0316	0.1000	0.1414	0.2236	0.3162
Λ_m / $\mathrm{S\,cm^2\,mol^{-1}}$	123.7	118.5	115.8	111.1	106.74

Step 3. Plot Λ_m vs $\sqrt{c}$. NaCl is a strong electrolyte; the plot is essentially a straight line.

Step 4. Extrapolate to $\sqrt{c} = 0$. From the first two points: slope $\approx (123.7 - 118.5)/(0.0316 - 0.1000) = 5.2/(-0.0684) = -76$ (units: $\mathrm{S\,cm^2\,mol^{-1}}$ per $\mathrm{M^{1/2}}$). Using $\Lambda_m = 123.7$ at $\sqrt{c} = 0.0316$,

$$\Lambda_m^\circ = 123.7 - (-76) \times 0.0316 = 123.7 + 2.4 = 126.1.$$

So $\Lambda_m^\circ(\mathrm{NaCl}) \approx 126\,\mathrm{S\,cm^2\,mol^{-1}}$.



Linear plot; dashed segment is the extrapolation to $\sqrt{c} = 0$.

Final Answer: $\Lambda_m = 123.7,\ 118.5,\ 115.8,\ 111.1,\ 106.74\,\mathrm{S\,cm^2\,mol^{-1}}$; $\Lambda_m^\circ(\mathrm{NaCl}) \approx 126\,\mathrm{S\,cm^2\,mol^{-1}}$.

EXPERT'S SOLUTION : *Pranav Banerjee, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Convert every conductivity, divide by the matching molar concentration, plot Λ_m vs $\sqrt{c}$, and extrapolate to $\sqrt{c} = 0$. Working in SI keeps the arithmetic clean; convert at the end. NaCl is a strong electrolyte, so the plot is essentially a straight line and a two-point extrapolation gives a good Λ_m°.

Alternative approach: cm-based per-row. Multiply listed $10^2\kappa$ by 10^{-2} to get S/m, again by 10^{-2} to get S/cm, then $\Lambda_m = \kappa \cdot 1000/c$.

Step 1. SI conversion. Listed $10^2\kappa$ in S/m $\Rightarrow \kappa = \text{value}/100$ in S/m. Molarity $\times 1000$ gives mol/m^3. Divide for Λ_m in $\mathrm{S\,m^2/mol}$, then $\times 10^4$ for $\mathrm{S\,cm^2/mol}$.

Step 2. Row-by-row. $\Lambda_m(0.001) = 1.237 \times 10^{-2}/1 = 1.237 \times 10^{-2}\,\mathrm{S\,m^2/mol} = 123.7\,\mathrm{S\,cm^2/mol}$. Similarly $\Lambda_m(0.010) = 118.5$; $\Lambda_m(0.020) = 115.8$; $\Lambda_m(0.050) = 111.1$; $\Lambda_m(0.100) = 106.74$.

Step 3. Tabulate $\sqrt{c}$.

c / M	0.001	0.010	0.020	0.050	0.100
$\sqrt{c}$	0.0316	0.1000	0.1414	0.2236	0.3162
Λ_m	123.7	118.5	115.8	111.1	106.74

Step 4. **Extrapolate.** First and last points: slope $= (123.7 - 106.74)/(0.0316 - 0.3162) = 16.96/(-0.2846) = -59.6\ \mathrm{S\,cm^2\,mol^{-1}\,M^{-1/2}}$. Intercept (using first point): $\Lambda_m^\circ = 123.7 - (-59.6) \times 0.0316 = 123.7 + 1.88 = 125.6 \approx 126\ \mathrm{S\,cm^2/mol}$.

Step 5. **Linearity check.** Predicted vs actual at middle points: $\sqrt{c} = 0.1$ predicts $125.6 - 5.96 = 119.6$ (actual 118.5, -1%); $\sqrt{c} = 0.1414$ predicts 117.2 (actual 115.8, -1%). Excellent fit — strong-electrolyte signature.

Comparison with literature. $\Lambda_m^\circ(\mathrm{NaCl}) = 126.45\ \mathrm{S\,cm^2/mol}$ at 298 K (NCERT Table 2.4). Our extrapolation ≈ 126 matches within 0.5%.

Cross-check via Kohlrausch. $\Lambda^\circ(\mathrm{Na^+}) = 50.1$ and $\Lambda^\circ(\mathrm{Cl^-}) = 76.3$ at 298 K; sum $= 126.4\ \mathrm{S\,cm^2/mol}$ — excellent agreement. The per-ion view rebuilds the salt's limiting conductivity.

Concept linkage. The DHO slope $|A| = 59.6$ matches the universal value ≈ 60 for 1:1 strong electrolytes in water at 298 K. The slope is theory-determined by long-range ion-ion interaction, so its closeness to the textbook value validates the data.

JEE/NEET relevance. "Plot, then extrapolate" is a stock NEET diagram task. Never try to extrapolate a weak-electrolyte curve linearly — the curvature near $\sqrt{c} = 0$ gives garbage; use Kohlrausch's law instead.

> **Final Answer:** Λ_m values: $123.7, 118.5, 115.8, 111.1, 106.74\ \mathrm{S\,cm^2/mol}$; $\Lambda_m^\circ \approx 126\ \mathrm{S\,cm^2/mol}$.

☞ Choice of extrapolation points

Best-fit through all five points gives $\Lambda_m^\circ \approx 125$, close to the two-endpoint value. In an exam, use the first *and* last data points: the longest lever arm minimises slope sensitivity to measurement errors.

☞ Convert κ data cleanly

"$10^2\kappa$ in $\mathrm{S\,m^{-1}}$" means actual $\kappa =$ listed $/100$. Forgetting the $/100$ inflates every Λ_m by $100\times$ — a classic data-parsing mistake.

Q 2.11 **Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$. Calculate its molar conductivity. If Λ_m° for acetic acid is $390.5\ \mathrm{S\,cm^2\,mol^{-1}}$, what is its dissociation constant?**

SOLUTION

Concept used. For a weak electrolyte at concentration c, the **degree of dissociation** α is the fraction of the electrolyte that has split into ions. It is given by the ratio of the molar conductivity at that concentration to the molar conductivity at infinite dilution:

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

For $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, the dissociation constant is

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}.$$

When $\alpha \ll 1$, this simplifies to $K_a \approx c\alpha^2$.

Step 1. Molar conductivity.

$$\Lambda_m = \frac{\kappa \times 1000}{c}.$$

Substitute $\kappa = 7.896 \times 10^{-5}$ S/cm, $c = 0.00241$ mol/L:

$$\Lambda_m = \frac{7.896 \times 10^{-5} \times 1000}{0.00241} = \frac{0.07896}{0.00241}.$$

Long division: $0.07896/0.00241 = 7896/241 = 32.76$.

$$\Lambda_m = 32.76\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Step 2. Degree of dissociation:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{32.76}{390.5}.$$

$390.5 \times 0.08 = 31.24$; $390.5 \times 0.084 = 32.80$ (close to numerator). So $\alpha \approx 0.0839 \approx 0.084$.

$$\alpha = 0.0839.$$

Step 3. Apply $K_a = c\alpha^2/(1-\alpha)$. $\alpha^2 = 0.0839^2 = 0.00704$. Numerator: $c\alpha^2 = 0.00241 \times 0.00704 = 1.697 \times 10^{-5}$. $1 - \alpha = 1 - 0.0839 = 0.9161$.

$$K_a = \frac{1.697 \times 10^{-5}}{0.9161} = 1.853 \times 10^{-5} \approx 1.85 \times 10^{-5}.$$

Step 4. Compare with the literature: $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ at 298 K. Excellent agreement.

Final Answer: $\Lambda_m = 32.76\,\mathrm{S\,cm^2\,mol^{-1}}$; $\alpha \approx 0.084$; $K_a \approx 1.85 \times 10^{-5}$.

EXPERT'S SOLUTION : *Karan Gupta, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. A single chain: $\kappa \to \Lambda_m \to \alpha \to K_a$. Each arrow uses one definition; keep significant figures through the chain so K_a does not lose precision.

Alternative approach: small-α shortcut. Since $\alpha \approx 0.08 \ll 1$, $K_a \approx c\alpha^2 = 1.70 \times 10^{-5}$, within 8% of the exact value. Useful when $\alpha < 0.05$.

Step 1. Λ_m. $\Lambda_m = \kappa \cdot 1000/c = 7.896 \times 10^{-5} \times 1000/(2.41 \times 10^{-3}) = 0.07896/0.00241 = 32.76\ \mathrm{S\,cm^2/mol}$.

Step 2. α. $\alpha = \Lambda_m/\Lambda_m^\circ = 32.76/390.5 = 0.0839$. Only $\sim 8.4\%$ is dissociated.

Step 3. K_a. $K_a = c\alpha^2/(1-\alpha)$. $(0.0839)^2 = 0.007039$.
$c\alpha^2 = 2.41 \times 10^{-3} \times 0.007039 = 1.697 \times 10^{-5}$. Divide by 0.9161:
$K_a = 1.853 \times 10^{-5} \approx 1.85 \times 10^{-5}$.

Cross-check via pH. $[\mathrm{H^+}] = c\alpha = 2.02 \times 10^{-4}$; $\mathrm{pH} = 3.69$. Substitute into $K_a = [\mathrm{H^+}]^2/([\mathrm{HA}] - [\mathrm{H^+}])$: $(2.02 \times 10^{-4})^2/(2.21 \times 10^{-3}) = 1.85 \times 10^{-5}$. Match.
Reading the result. $K_a \approx 1.8 \times 10^{-5}$ corresponds to $pK_a \approx 4.74$, the textbook value. $\Lambda_m^\circ = 390.5$ is built from ionic conductivities $\lambda^\circ(\mathrm{H^+}) = 349.6$ and $\lambda^\circ(\mathrm{CH_3COO^-}) = 40.9$; almost 90% of Λ_m° comes from $\mathrm{H^+}$ hopping via the Grotthuss mechanism.
JEE/NEET relevance. Computing K_a from Λ_m is JEE Mains classic. Often only κ and c are given — remember to fetch Λ_m° from the data table or compute it via Kohlrausch.

Final Answer: $\Lambda_m = 32.76\ \mathrm{S\,cm^2/mol}$; $\alpha \approx 0.084$; $K_a \approx 1.85 \times 10^{-5}$.

☞ Weak electrolyte recipe

$$\Lambda_m = \frac{\kappa \cdot 1000}{c}; \quad \alpha = \frac{\Lambda_m}{\Lambda_m^\circ}; \quad K_a = \frac{c\alpha^2}{1-\alpha}\ \text{(exact)} \approx c\alpha^2 \text{ if } \alpha \ll 1.$$

☞ Hold 4 significant figures

Rounding α to 0.08 instead of 0.0839 makes $\alpha^2 = 0.0064$ not 0.00704, an 11% error in K_a. Round only at the final answer.

Q 2.12 **How much charge is required for the following reductions:**
(i) 1 **mol of Al^{3+} to Al?**
(ii) 1 **mol of Cu^{2+} to Cu?**
(iii) 1 **mol of MnO_4^- to Mn^{2+}?**

SOLUTION

Concept used. The total charge needed to reduce one mole of ions is given by Faraday's law:

$$Q = nF,$$

where n is the number of electrons required *per ion* (read off the half-reaction) and $F = 96\,500\,\mathrm{C/mol}$ is the charge on one mole of electrons.

Step 1. Identify n for each half-reaction.

$$\begin{aligned} &(i) && \mathrm{Al^{3+}} + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al} && \Rightarrow && n = 3 \\ &(ii) && \mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu} && \Rightarrow && n = 2 \\ &(iii) && \mathrm{MnO_4{}^-} + 8\,\mathrm{H^+} + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O} && \Rightarrow && n = 5 \end{aligned}$$

For (iii) the manganese centre goes from $+7$ in MnO_4^- to $+2$ in Mn^{2+}, a five-electron reduction.

Step 2. Compute $Q = nF$ for each:

$$\begin{aligned} (i) \quad & Q = 3 \times 96500 = 2.895 \times 10^5\,\mathrm{C} \\ (ii) \quad & Q = 2 \times 96500 = 1.93 \times 10^5\,\mathrm{C} \\ (iii) \quad & Q = 5 \times 96500 = 4.825 \times 10^5\,\mathrm{C} \end{aligned}$$

Step 3. Cross-check by computing the number of moles of electrons needed: 3 for (i), 2 for (ii), 5 for (iii). Each mole of electrons carries 96500 C.

> **Final Answer:** (i) 2.895×10^5 C; (ii) 1.93×10^5 C; (iii) 4.825×10^5 C.

EXPERT'S SOLUTION : *Ishita Desai, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. For each reduction, read the electron count from the balanced half-reaction and multiply by Faraday's constant. The whole problem reduces to "what is n?".

Alternative approach: oxidation-state arithmetic. (i) Al: $+3 \to 0$, drop 3, $n = 3$. (ii) Cu: $+2 \to 0$, drop 2, $n = 2$. (iii) Mn in MnO_4^-: $+7 \to +2$, drop 5, $n = 5$.

Step 1. **(i) Al.** $\mathrm{Al^{3+}} + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}$: $Q = 3 \times 96500 = 2.895 \times 10^5$ C.

Step 2. **(ii) Cu.** $\mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}$: $Q = 2 \times 96500 = 1.93 \times 10^5$ C.

Step 3. **(iii) Permanganate.** $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$: $n = 5$ (Mn: $+7 \to +2$). $Q = 5 \times 96500 = 4.825 \times 10^5$ C.

Reading the numbers. Each electron costs $\sim 9.65 \times 10^4$ C per mole. The result scales linearly with n: Al needs 50% more charge than Cu for the same mole count; permanganate needs $2.5\times$ as much as Cu.

Cross-check (iii). 4.825×10^5 C $= 134$ Ah. A 1 A current must run for 134 hours to reduce one mole (~ 100 g) of MnO_4^- — a real industrial number.

JEE/NEET relevance. "Charge to deposit x moles of M" is a classroom staple. The trap: mis-counting electrons for couples like $Cr_2O_7^{2-}/Cr^{3+}$ (6, not 3 or 7).

Final Answer: (i) 2.895×10^5 C; (ii) 1.93×10^5 C; (iii) 4.825×10^5 C.

✗ Wrong n for MnO_4^-

Some students count $n = 7$ (oxidation state of Mn in the reactant) or $n = 2$ (in the product). Both wrong. n = *change* $= 7 - 2 = 5$.

☞ Faraday's first law

$Q = nF = z \cdot n_{\text{ion}} \cdot F$, z = electrons per ion, $F = 96{,}500$ C/mol. For 1 mol of M^{+z}, $Q = zF$ exactly.

Q 2.13 How much electricity in terms of Faraday is required to produce

(i) $20.0\,\text{g}$ **of Ca from molten $CaCl_2$?**

(ii) $40.0\,\text{g}$ **of Al from molten Al_2O_3?**

SOLUTION

Concept used. The relation between mass deposited at a cathode and charge passed is

$$n_{\text{electrons}} = z \times \text{moles of product},$$

where z is the number of electrons per ion in the reduction half-reaction. The number of Faradays equals the number of moles of electrons:

$$\text{Faradays} = z \times \text{moles of product}.$$

Atomic masses needed: $M(\text{Ca}) = 40$ g/mol; $M(\text{Al}) = 27$ g/mol.

Part (i): $20.0\,\text{g}$ **of Ca.**

Step 1. Half-reaction: $Ca^{2+} + 2\,e^- \longrightarrow Ca$. So $z = 2$.

Step 2. Moles of Ca:

$$n_{\text{Ca}} = \frac{m}{M} = \frac{20.0\,\text{g}}{40\,\text{g/mol}} = 0.5\,\text{mol}.$$

Step 3. Faradays required:

$$\mathrm{F} = z \times n_{\mathrm{Ca}} = 2 \times 0.5 = 1.0\,\mathrm{F}.$$

Step 4. Optionally in coulombs: $Q = 1.0 \times 96500 = 96500$ C.

> **Final Answer:** (i) 1.0 Faraday $= 96500$ C.

Part (ii): $40.0\,\mathrm{g}$ **of Al.**

Step 1. Half-reaction: $\mathrm{Al^{3+}} + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}$. So $z = 3$.

Step 2. Moles of Al:

$$n_{\mathrm{Al}} = \frac{40.0\,\mathrm{g}}{27\,\mathrm{g/mol}} = 1.481\,\mathrm{mol}.$$

Step 3. Faradays required:

$$\mathrm{F} = z \times n_{\mathrm{Al}} = 3 \times 1.481 = 4.444\,\mathrm{F}.$$

Step 4. In coulombs: $Q = 4.444 \times 96500 = 428886$ C $\approx 4.29 \times 10^5$ C.

> **Final Answer:** (ii) 4.44 Faradays $\approx 4.29 \times 10^5$ C.

EXPERT'S SOLUTION *: Yash Rao, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Moles of product → moles of electrons. Convert at the end if coulombs are needed. "1 Faraday" = 1 mole of electrons $= 96{,}500$ C.
Alternative approach: equivalents. Mass per Faraday $= M_w/z$. For Ca: $40/2 = 20$ g/F; Al: $27/3 = 9$ g/F. So 20 g Ca → 1 F; 40 g Al → $40/9 = 4.44$ F. The equivalent route is the fastest mental computation.

Step 1. **(i) Ca.** $\mathrm{Ca^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ca}$, $z = 2$. Moles of Ca $= 20/40 = 0.5$. Moles of $e^- = 1$. $\Rightarrow$ **1 Faraday**.

Step 2. **(ii) Al.** $\mathrm{Al^{3+}} + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}$, $z = 3$. Moles of Al $= 40/27 = 1.481$. Moles of $e^- = 4.444$. $\Rightarrow$ **4.44 Faradays**.

Step 3. **Sanity check (i).** One Faraday gives half a mole of any divalent metal; half a mole of Ca $= 20$ g.

Step 4. **Sanity check (ii).** One Faraday gives one-third mole of any trivalent metal; $4.44/3 = 1.48$ mol Al $= 40$ g.

Numerical cross-check (industrial). 1 tonne of Al (3.70×10^4 mol) needs $3 \times 3.70 \times 10^4 = 1.11 \times 10^5$ F $\approx 1.07 \times 10^{10}$ C. At 4.5 V cell voltage, energy = 4.83×10^{10} J $= 13.4$ MWh per tonne. This matches the "$\sim 15{,}000$ kWh/tonne" industrial figure. The 3-electron reduction is exactly why aluminium is so energy-intensive vs sodium ($z = 1$) or magnesium ($z = 2$).

Final Answer: (i) 1.0 Faraday $= 96{,}500$ C; (ii) 4.44 Faradays $\approx 4.29 \times 10^5$ C.

♥ Why aluminium is so expensive

World Al production is $\sim$ 70 million tonnes/year. Multiplied by $13{,}400$ kWh/tonne $= 940$ TWh/year, about 3% of global electricity. The 3-electron reduction sets the thermodynamic floor. Recycling Al re-melts the metal and saves $\sim 95\%$ of the energy — which is why aluminium recycling is universally profitable.

☞ "Faraday" is electrons, not coulombs

"How many Faradays" = moles of electrons. Convert to coulombs only if the question explicitly asks. Don't lose a mark writing $96{,}500$ C when the question wanted "1".

Q 2.14 **How much electricity is required in coulomb for the oxidation of**
(i) 1 mol of H_2O to O_2?
(ii) 1 mol of FeO to Fe_2O_3?

SOLUTION

Concept used. For an oxidation, balance the half-reaction to count the electrons *released* per mole of substance. The charge that must be removed equals nF, where n is the electron count and $F = 96500$ C/mol.

Part (i): $\mathrm{H_2O \to O_2}$.

Step 1. Balance the half-reaction. Oxygen goes from -2 in H_2O to 0 in O_2: a loss of 2 electrons per O atom. The balanced anodic half-reaction (acidic medium) is

$$2\,\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-}.$$

Step 2. Per mole of O_2, 4 mol of electrons are released; per *mole of H_2O*, that is 2 mol of electrons.

$$n = 2 \quad \text{per mole of H}_2\text{O}.$$

Step 3. Charge required:

$$Q = nF = 2 \times 96500 = 1.93 \times 10^5\,\text{C}.$$

Final Answer: (i) $Q = 1.93 \times 10^5$ C per mole of H_2O.

Part (ii): $\mathrm{FeO \to Fe_2O_3}$.

Step 1. Identify the oxidation-state change of Fe. In FeO, Fe is $+2$; in Fe_2O_3, Fe is $+3$. Per mole of FeO, one Fe atom is oxidised by 1 electron:

$$\mathrm{FeO} \longrightarrow \frac{1}{2}\,\mathrm{Fe_2O_3} + \mathrm{e^-} \quad \text{(schematic)}.$$

Step 2. Per mole of FeO, $n = 1$. Charge required:

$$Q = 1 \times 96500 = 96500\,\mathrm{C} = 9.65 \times 10^4\,\mathrm{C}.$$

Final Answer: (ii) $Q = 9.65 \times 10^4$ C per mole of FeO.

EXPERT'S SOLUTION *: Riya Kapoor, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Balance the half-reaction, count electrons *per mole of starting material*, multiply by F. The trap is the basis: the question says "per mole of H_2O", not "per mole of O_2".

Alternative approach: oxidation-state arithmetic. (i) O: $-2 \to 0$ per atom, 2 per H_2O; $n = 2$. (ii) Fe: $+2 \to +3$, $n = 1$ per FeO.

Step 1. **(i) Water oxidation.** $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$: 4 electrons for 2 mol H_2O, i.e. 2 per mole of H_2O. $Q = 2 \times 96500 = 1.93 \times 10^5$ C.

Step 2. **(ii) FeO to Fe_2O_3.** Fe goes $+2 \to +3$: 1 e^- per Fe, 1 per mole of FeO. $Q = 1 \times 96500 = 9.65 \times 10^4$ C.

Connection to corrosion. Both reactions appear together in rusting: Fe/FeO is oxidised by atmospheric O_2 in moist air. Each turnover transfers exactly the electrons we counted — 4 from the O_2-reduction cathode (matching 4 Fe^{2+}-to-Fe^{3+} oxidations).

Numerical cross-check. Industrial water electrolysis at ~ 2.0 V producing 1 mol/s of H_2 draws $4 \times 96500/(2) = 193{,}000$ A per cell (using $n = 4$ per net reaction $2\,H_2O \longrightarrow 2\,H_2 + O_2$). The factor-of-2 between H_2O and O_2 specifications is exactly why "per mole of" phrasing matters.

JEE/NEET relevance. "Per mole of O_2" would give $Q = 4 \times 96500 = 3.86 \times 10^5$ C, exactly double. A 1-mark difference between right and wrong.

Final Answer: (i) 1.93×10^5 C per mole of H_2O; (ii) 9.65×10^4 C per mole of FeO.

✗ "per mole H_2O" vs "per mole O_2"

$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$ gives 4 electrons *per 2 mol H_2O* = 2 per mole of H_2O. Per mole of O_2 it's 4. The question fixed the basis as H_2O, so $n = 2$.

☞ **Oxidation-state shortcut**

n per formula unit $= |\Sigma|$ oxidation-number changes of all redox-active atoms in that formula unit. Faster than full half-equation balancing for single-atom couples.

Q 2.15 **A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?**

SOLUTION

Concept used. Faraday's first law of electrolysis states that the mass w of a substance deposited at an electrode is proportional to the charge passed:

$$w = Z \cdot I \cdot t, \quad \text{where} \quad Z = \frac{M_w}{nF}$$

is the electrochemical equivalent. Equivalently,

$$w = \frac{M_w \cdot I \cdot t}{nF}.$$

For Ni^{2+} the cathode reaction is $Ni^{2+} + 2\,e^- \longrightarrow Ni$, so $n = 2$; $M(\mathrm{Ni}) = 58.7$ g/mol.

Step 1. Convert time to seconds:

$$t = 20\,\text{min} \times 60\,\text{s/min} = 1200\,\text{s}.$$

Step 2. Total charge passed:

$$Q = I \cdot t = 5\,\text{A} \times 1200\,\text{s} = 6000\,\text{C}.$$

Step 3. Moles of electrons:

$$n_e = \frac{Q}{F} = \frac{6000}{96500} = 0.06218\,\text{mol}.$$

Step 4. Moles of Ni deposited (each Ni needs 2 electrons):

$$n_{\text{Ni}} = \frac{n_e}{2} = \frac{0.06218}{2} = 0.03109\,\text{mol}.$$

Step 5. Mass of Ni:

$$w = n_{\text{Ni}} \times M(\text{Ni}) = 0.03109 \times 58.7 = 1.825\,\text{g} \approx 1.83\,\text{g}.$$

Step 6. Cross-check with the single-step formula:

$$w = \frac{M_w It}{nF} = \frac{58.7 \times 5 \times 1200}{2 \times 96500}.$$

Numerator: $58.7 \times 5 = 293.5$; $293.5 \times 1200 = 352200$. Denominator: $2 \times 96500 = 193000$.

$$w = \frac{352200}{193000} = 1.825\,\text{g}.$$

Final Answer: Mass of Ni deposited ≈ 1.83 g.

EXPERT'S SOLUTION : *Diya Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Charge → moles of electrons → moles of metal → mass. Each arrow is one division. The composite formula $w = M_w It/(nF)$ collapses the chain, but knowing the chain helps debug arithmetic errors.

Alternative approach: equivalent weight. Ni's chemical equivalent: $58.7/2 = 29.35$ g/F. Coulombs $= 5 \times 1200 = 6000$; Faradays $= 6000/96500 = 0.0622$. Mass $= 0.0622 \times 29.35 = 1.83$ g. Fastest mental computation.

Step 1. **Charge passed.** $t = 20$ min $\times\ 60 = 1200$ s. $Q = It = 5 \times 1200 = 6000$ C.

Step 2. **Moles of e^-.** $n_e = Q/F = 6000/96500 = 0.0622$ mol.

Step 3. **Moles of Ni.** $\mathrm{Ni}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Ni}$, so $n_{\mathrm{Ni}} = 0.0622/2 = 0.0311$ mol.

Step 4. **Mass.** $w = 0.0311 \times 58.7 = 1.83$ g.

Cross-check via master formula.
$w = M_w It/(nF) = (58.7 \times 5 \times 1200)/(2 \times 96500) = 352{,}200/193{,}000 = 1.825$ g; three sig. fig. $= 1.83$ g.

Reading the result. 5 A for 20 min deposits under 2 g of Ni. For a watch-case coat of ~ 5 g, you'd need either 25 min at 10 A or 50 min at 5 A. Industry uses the linear scaling to size plants.

Concept linkage — inert electrodes. The Pt electrodes are *inert*; they pass current without dissolving. If the anode were Ni metal instead, the anode reaction $\mathrm{Ni} \longrightarrow \mathrm{Ni}^{2+} + 2\,\mathrm{e}^-$ would replenish bulk Ni^{2+}, an electrorefining cell.

JEE/NEET relevance. End-to-end Faraday-first-law problems appear in nearly every JEE Mains paper. The most common trap: not converting minutes to seconds. $Q = It$ needs t in seconds.

Final Answer: Mass of Ni deposited ≈ 1.83 g.

✗ Forgetting min → s

"5 amp for 20 minutes" becomes $Q = 5 \times 20 = 100$ C without the $\times 60$ factor — off by a factor of 60. Always: $t(\mathrm{s}) = t(\mathrm{min}) \times 60$.

☞ Single-formula vs four-step chain

$w = M_w It/(nF)$ is faster than the chain, but only if you've drilled it. Use the chain when debugging — each line gives a checkable intermediate.

Q 2.16 **Three electrolytic cells *A*, *B*, *C* containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively, are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell *B*. How long**

did the current flow? What mass of copper and zinc were deposited?

SOLUTION

Concept used. In cells connected in series the *same current* flows for the *same time*, so each cell passes the same charge $Q = It$. Faraday's law then gives the mass of each metal:

$$w = \frac{M_w \cdot Q}{nF},$$

with n depending on the ionic charge: Ag^+: $n = 1$; Cu^{2+}: $n = 2$; Zn^{2+}: $n = 2$. Atomic masses: $M(\text{Ag}) = 108$ g/mol; $M(\text{Cu}) = 63.5$ g/mol; $M(\text{Zn}) = 65.4$ g/mol.

Step 1. Find total charge Q from the silver deposition (cell B). $Ag^+ + e^- \longrightarrow Ag$, so $n = 1$. From $w = M_w Q/(nF)$:

$$Q = \frac{w \cdot nF}{M_w} = \frac{1.45 \times 1 \times 96500}{108}.$$

Numerator: 1.45×96500. $1 \times 96500 = 96500$; $0.45 \times 96500 = 43425$; sum $= 139925$.

$$Q = \frac{139925}{108} = 1295.6\,\text{C}.$$

Step 2. Find time t:

$$t = \frac{Q}{I} = \frac{1295.6}{1.5} = 863.7\,\text{s}.$$

Convert to minutes: $863.7/60 = 14.4$ min, or 14 min 24 s.

Step 3. Mass of Cu deposited (cell C). $n = 2$:

$$w_{\text{Cu}} = \frac{M(\text{Cu}) \cdot Q}{2F} = \frac{63.5 \times 1295.6}{2 \times 96500}.$$

Numerator: $63.5 \times 1295.6 = 82270.6$. Denominator: 193000.

$$w_{\text{Cu}} = \frac{82270.6}{193000} = 0.4263\,\text{g} \approx 0.426\,\text{g}.$$

Step 4. Mass of Zn deposited (cell A). $n = 2$:

$$w_{\text{Zn}} = \frac{M(\text{Zn}) \cdot Q}{2F} = \frac{65.4 \times 1295.6}{193000}.$$

Numerator: $65.4 \times 1295.6 = 84732.2$.

$$w_{\text{Zn}} = \frac{84732.2}{193000} = 0.439\,\text{g}.$$

Step 5. Quick equivalent-mass check. Equivalents of each metal deposited are the same (same Q): eq. $= Q/F = 1295.6/96500 = 0.01343$ eq.
$w(\text{Ag}) = 0.01343 \times 108 = 1.450$ g (matches); $w(\text{Cu}) = 0.01343 \times 31.75 = 0.426$ g (matches); $w(\text{Zn}) = 0.01343 \times 32.7 = 0.439$ g (matches).

Final Answer: Time $t \approx 863.7$ s (≈ 14.4 min); $w(\text{Cu}) \approx 0.426$ g; $w(\text{Zn}) \approx 0.439$ g.

EXPERT'S SOLUTION : *Rahul Chatterjee, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Three cells in *series* receive the *same charge* in the same time. Compute charge from one cell (here cell B, silver), then use it to find masses in the other two.

Alternative approach: equivalents. eq deposited $= Q/F$, same for all three cells. eq $= 1.45/108 = 0.01343$. $w(\text{Cu}) = 0.01343 \times 31.75 = 0.426$ g. $w(\text{Zn}) = 0.01343 \times 32.7 = 0.439$ g. Faraday's second law in three lines.

Step 1. **Charge from Ag.** Moles Ag $= 1.45/108 = 0.01343$; moles $e^- = 0.01343$ (since $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$); $Q = 0.01343 \times 96500 = 1295.6$ C.

Step 2. **Time.** $t = Q/I = 1295.6/1.5 = 863.7$ s $= 14$ min 24 s.

Step 3. **Mass of Cu.** 2 e^- per Cu, so moles Cu $= 0.01343/2 = 0.006716$.
$w(\text{Cu}) = 0.006716 \times 63.5 = 0.426$ g.

Step 4. **Mass of Zn.** 2 e^- per Zn, so moles Zn $= 0.006716$.
$w(\text{Zn}) = 0.006716 \times 65.4 = 0.439$ g.

Cross-check. Sum of moles of electrons across the three cells must equal $Q/F = 0.01343$. Independent calculation: Ag $0.01343 \times 1 = 0.01343$; Cu $0.006716 \times 2 = 0.01343$; Zn $0.006716 \times 2 = 0.01343$. All identical, as required by series connection.

Generalisation. The series circuit is the classic demonstration of **Faraday's second law**: same charge through different electrolytes deposits masses in the ratio of *chemical equivalents* M_w/z. Zn is heavier than Cu, but only slightly more Zn is deposited because M_w/z values (32.7 vs 31.75) are close.

JEE/NEET relevance. Series-cell problems are favourite multi-part JEE Mains questions: they bundle time, charge, mass, and the second law. A common variant: given two deposit masses, find the ratio of atomic weights or charges.

Final Answer: $t \approx 864$ s (≈ 14 min 24 s); $w(\text{Cu}) \approx 0.426$ g; $w(\text{Zn}) \approx 0.439$ g.

☞ Series vs parallel

Series: same current, same time ⇒ same charge in every cell. Use Faraday's *second* law.

Parallel: same voltage; current splits between cells. Charges and masses are no longer equal across cells.

♥ Electrolytic refining at scale

Copper refining stacks many series cells with impure-Cu anodes and pure-Cu cathodes sharing one current. Ag, Au, Pt impurities settle as "anode mud" — often worth more than the labour of running the cells. This is why electrorefined copper is the standard for electrical wiring.

Q 2.17 Using the standard electrode potentials given in NCERT Table 2.1, predict if the reaction between the following is feasible:

(i) Fe^{3+}(aq) and I^-(aq)

(ii) Ag^+(aq) and Cu(s)

(iii) Fe^{3+}(aq) and Br^-(aq)

(iv) Ag(s) and Fe^{3+}(aq)

(v) Br_2(aq) and Fe^{2+}(aq).

SOLUTION

Concept used. For any postulated reaction, write the oxidation half (anode) and the reduction half (cathode) using the standard reduction potentials. Compute

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}.$$

If $E^\circ_{\text{cell}} > 0$ the reaction is feasible (spontaneous in the standard state), since $\Delta_r G^\circ = -nFE^\circ$ would then be negative. If $E^\circ_{\text{cell}} < 0$, the reaction is not feasible.
Required potentials (NCERT Table 2.1): $E^\circ(\mathrm{Fe^{3+}/Fe^{2+}}) = +0.77$ V; $E^\circ(\mathrm{I_2/I^-}) = +0.54$ V; $E^\circ(\mathrm{Ag^+/Ag}) = +0.80$ V; $E^\circ(\mathrm{Cu^{2+}/Cu}) = +0.34$ V; $E^\circ(\mathrm{Br_2/Br^-}) = +1.08$ V.

Part (i): Fe^{3+} + I^-. Postulate Fe^{3+} oxidises I^- to I_2; itself reduced to Fe^{2+}.

Step 1. Cathode (reduction): $\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$, $E^\circ = +0.77$ V.

Step 2. Anode (oxidation): $\mathrm{2\,I^- \longrightarrow I_2 + 2\,e^-}$. Use the reduction potential $E^\circ(\mathrm{I_2/I^-}) = +0.54$ V.

Step 3. $E^\circ_{\text{cell}} = 0.77 - 0.54 = +0.23\text{ V} > 0$. **Feasible.**

Part (ii): Ag^+ + Cu. Postulate Ag^+ oxidises Cu to Cu^{2+}; itself reduced to Ag.

Step 1. Cathode: $\mathrm{Ag^+ + e^- \longrightarrow Ag}$, $E^\circ = +0.80$ V.

Step 2. Anode: $\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^-}$; $E^\circ(\mathrm{Cu^{2+}/Cu}) = +0.34$ V.

Step 3. $E^\circ_{\text{cell}} = 0.80 - 0.34 = +0.46\text{ V} > 0$. **Feasible.**

Part (iii): Fe^{3+} + Br^-. Postulate Fe^{3+} oxidises Br^- to Br_2.

Step 1. Cathode: $\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$, $E^\circ = +0.77$ V.

Step 2. Anode: $\mathrm{2\,Br^- \longrightarrow Br_2 + 2\,e^-}$; $E^\circ(\mathrm{Br_2/Br^-}) = +1.08$ V.

Step 3. $E^\circ_{\text{cell}} = 0.77 - 1.08 = -0.31\text{ V} < 0$. **Not feasible.**

Part (iv): Ag + Fe^{3+}. Postulate Fe^{3+} oxidises Ag to Ag^+.

Step 1. Cathode: $\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$, $E^\circ = +0.77$ V.

Step 2. Anode: $\mathrm{Ag \longrightarrow Ag^+ + e^-}$; $E^\circ(\mathrm{Ag^+/Ag}) = +0.80$ V.

Step 3. $E^\circ_{\text{cell}} = 0.77 - 0.80 = -0.03\text{ V} < 0$. **Not feasible** (barely).

Part (v): Br_2 + Fe^{2+}. Postulate Br_2 oxidises Fe^{2+} to Fe^{3+}.

Step 1. Cathode: $\mathrm{Br_2 + 2\,e^- \longrightarrow 2\,Br^-}$, $E^\circ = +1.08$ V.

Step 2. Anode: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$; $E^\circ(Fe^{3+}/Fe^{2+}) = +0.77$ V.

Step 3. $E^\circ_{\text{cell}} = 1.08 - 0.77 = +0.31\text{ V} > 0$. **Feasible.**

> **Final Answer:** (i) feasible (+0.23 V); (ii) feasible (+0.46 V); (iii) not feasible (-0.31 V); (iv) not feasible (-0.03 V); (v) feasible (+0.31 V).

EXPERT'S SOLUTION *: Sanya Iyer, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The species written first in the question is the oxidising agent (cathode side); the second is the reducing agent (anode side). Compute E°_{cell}; positive means feasible:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} > 0 \Leftrightarrow \Delta_r G^\circ < 0 \Leftrightarrow \text{spontaneous}.$$

Alternative approach: "higher reduces lower". The couple with the higher E°_{red} will oxidise the couple with the lower one. Use this to predict the spontaneous direction first, then check if the postulated reaction matches.

Step 1. **(i)** Fe^{3+} (0.77) vs I_2/I^- (0.54): higher is Fe^{3+}. $E^\circ_{\text{cell}} = 0.77 - 0.54 = +0.23$ V. **Feasible.**

Step 2. **(ii)** Ag^+ (0.80) vs Cu^{2+}/Cu (0.34): higher is Ag^+. $E^\circ_{\text{cell}} = 0.80 - 0.34 = +0.46$ V. **Feasible.**

Step 3. **(iii)** Fe^{3+} (0.77) vs Br_2/Br^- (1.08): higher is Br_2, so Br_2 would oxidise Fe^{2+}, but the question asks the reverse. $E^\circ_{\text{cell}} = 0.77 - 1.08 = -0.31$ V. **Not feasible.**

Step 4. **(iv)** Fe^{3+} (0.77) vs Ag^+/Ag (0.80): higher is Ag^+ (just barely). $E^\circ_{\text{cell}} = 0.77 - 0.80 = -0.03$ V. **Not feasible** (barely).

Step 5. **(v)** Br_2 (1.08) vs Fe^{3+}/Fe^{2+} (0.77): higher is Br_2, so Br_2 oxidises Fe^{2+}. $E^\circ_{\text{cell}} = 1.08 - 0.77 = +0.31$ V. **Feasible.**

Numerical sanity (iv). $E^\circ_{\text{cell}} = -0.03$ V gives $\Delta_r G^\circ = -F \times (-0.03) = +2.9$ kJ/mol. With $RT = 2.5$ kJ/mol at 298 K, $K = e^{-2.9/2.5} = 0.31$ — only $\sim 31\%$ of equilibrium completion in the forward direction. Not feasible in the standard state, but at non-standard concentrations (high Fe^{3+}, very low Ag^+) the Nernst equation could flip the sign.

Concept linkage — the ladder. On the standard reduction- potential ladder:

$$Br_2/Br^- > Ag^+/Ag > Fe^{3+}/Fe^{2+} > I_2/I^- > Cu^{2+}/Cu.$$

Higher couples oxidise lower; the converse is non-spontaneous.

JEE/NEET relevance. "Predict feasibility from E°" is a 1-mark MCQ workhorse. The trick: identify which species is being oxidised in the postulated reaction — it is the reducing agent, not the oxidising one.

Final Answer: Feasible: (i), (ii), (v). Not feasible: (iii), (iv).

✗ Mixing reduction and oxidation signs

A student writes $E^\circ_{\text{ox}}(\text{I}^-) = -0.54$ V and $E^\circ_{\text{red}}(\text{Fe}^{3+}) = +0.77$ V, then *adds*: $0.77 + (-0.54) = 0.23$ V. Coincidentally right, conceptually wrong. The correct rule: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode,red}} - E^\circ_{\text{anode,red}}$, *both as reductions.*

☞ Feasibility shortcut

$E^\circ_{\text{cell}} > 0 \Leftrightarrow \Delta_r G^\circ < 0 \Leftrightarrow K > 1 \Leftrightarrow$ feasible in standard state. Higher-E° couple is the oxidising agent.

Q 2.18 **Predict the products of electrolysis in each of the following:**
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of H_2SO_4 with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

SOLUTION

Concept used. The products of aqueous electrolysis depend on which species can be oxidised most easily at the anode and which species can be reduced most easily at the cathode. Two factors decide the outcome.

- **Standard electrode potentials.** At each electrode the species with the highest reduction potential is preferred for reduction; the species with the lowest reduction potential (most readily oxidised) is preferred for oxidation.
- **Overpotential.** For gas-producing reactions (especially O_2, H_2, Cl_2), the practical voltage needed is higher than the thermodynamic prediction. Oxygen has a particularly high overpotential at platinum.

The electrodes themselves matter: *inert* electrodes (Pt) simply pass current; *reactive* electrodes (Ag, Cu) can be oxidised in preference to water.

Part (i): aqueous $AgNO_3$ with Ag electrodes.

Step 1. At the cathode, possible reductions are $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$ $(+0.80\text{ V})$ and $2\,\text{H}_2\text{O} + 2\,\text{e}^- \longrightarrow \text{H}_2 + 2\,\text{OH}^-$ $(-0.83\text{ V}$ at pH 7$)$. The higher-E° option wins: Ag^+ is reduced to Ag.

Step 2. At the anode, possible oxidations are oxidation of the silver electrode itself $(\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-$, $E^\circ_{\text{ox}} = -0.80\text{ V})$ or water $(2\,\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\,\text{H}^+ + 4\,\text{e}^-$, $E^\circ_{\text{ox}} = -1.23\text{ V})$ or $\text{NO}_3{}^-$ (very stable, requires high potential). The least negative oxidation potential wins (lowest cost): oxidation of *silver metal*.

Step 3. Products: **cathode: Ag metal** deposited; **anode: Ag metal** dissolves as Ag^+. The cell effectively transfers silver from the anode to the cathode; the concentration of $AgNO_3$ stays constant. This is the principle of **electrorefining** and **silver plating**.

Part (ii): aqueous $AgNO_3$ with Pt electrodes.

Step 1. Cathode: same as (i). Ag^+ is reduced to Ag, which deposits on the Pt cathode.

Step 2. Anode: the Pt is inert, so the choices are oxidation of H_2O (-1.23 V) or ${NO_3}^-$ (very negative). Water wins: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$.

Step 3. Products: **cathode: Ag**; **anode: O_2**. The solution becomes acidic as H^+ accumulates around the anode and silver is depleted from the bulk.

Part (iii): dilute H_2SO_4 with Pt electrodes.

Step 1. Cathode: only H^+ (from H_2SO_4) and H_2O are available for reduction. H^+ has the higher reduction potential, so $2\,H^+ + 2\,e^- \longrightarrow H_2$.

Step 2. Anode: choices are ${SO_4}^{2-}$ (very stable; oxidation to peroxodisulphate ${S_2O_8}^{2-}$ needs $E^\circ_{ox} = -2.05$ V) or H_2O ($2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$, $E^\circ_{ox} = -1.23$ V). Water wins: O_2 is released.

Step 3. Products: **cathode: H_2**; **anode: O_2**. Net reaction: $2\,H_2O \longrightarrow 2\,H_2 + O_2$ (electrolysis of water; H_2SO_4 only carries the current).

Part (iv): aqueous $CuCl_2$ with Pt electrodes.

Step 1. Cathode: choices are $Cu^{2+} + 2\,e^- \longrightarrow Cu$ ($+0.34$ V) and $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$ (-0.83 V at pH 7). Cu^{2+} wins (higher E°). Copper is deposited.

Step 2. Anode: choices are $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$ ($E^\circ(Cl_2/Cl^-) = +1.36$ V, so $E^\circ_{ox} = -1.36$ V) or $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$ (-1.23 V). Thermodynamically, water would be the easier oxidation. In practice the **overpotential** for O_2 at Pt is large (~ 0.5 V), so the practical anode product is Cl_2.

Step 3. Products: **cathode: Cu**; **anode: Cl_2** (in concentrated Cl^-; if very dilute, some O_2 also forms).

(i) $AgNO_3$ / Ag

Cathode: Ag deposit
Anode: Ag dissolves

(ii) $AgNO_3$ / Pt

Cathode: Ag deposit
Anode: O_2 gas

(iii) H_2SO_4 / Pt

Cathode: H_2 gas
Anode: O_2 gas

(iv) $CuCl_2$ / Pt

Cathode: Cu deposit
Anode: Cl_2 gas

Final Answer: (i) Cathode: Ag; Anode: Ag dissolves. (ii) Cathode: Ag; Anode: O_2. (iii) Cathode: H_2; Anode: O_2. (iv) Cathode: Cu; Anode: Cl_2.

EXPERT'S SOLUTION *: Meera Pillai, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. For aqueous electrolysis, list every species that could be oxidised (or reduced) at each electrode and pick by the rule: *highest reduction potential wins at the cathode; lowest reduction potential wins at the anode*, with **overpotential** as a real-world tiebreaker. Reactive electrodes (Ag, Cu) can also dissolve in preference to water.

Alternative approach. For each cell, list (a) cathode candidates as reductions and (b) anode candidates as oxidations, each with its E°_{red}. Cathode picks the highest E°_{red}; anode picks the lowest (equivalently, highest E°_{ox}). Overpotential reorders winners when two candidates are within ~ 0.5 V.

Step 1. **(i) $AgNO_3$ / Ag electrodes.** *Cathode:* Ag^+ $(+0.80)$ vs H_2O $(-0.83$ at pH $7)$. Ag^+ wins. *Anode:* dissolution of Ag electrode ($E^\circ_{\text{ox}} = -0.80$) vs H_2O (-1.23) vs ${NO_3}^-$ (very inert). Ag dissolves (least-negative oxidation potential). **Effect:** Ag moves from anode to cathode; bulk $AgNO_3$ concentration unchanged. This is the basis of **silver electroplating** and electrorefining.

Step 2. **(ii) $AgNO_3$ / Pt electrodes.** Cathode: same as (i); Ag deposits on Pt. Anode: Pt is inert; H_2O oxidation wins over inert ${NO_3}^-$: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. **Products: Ag at cathode, O_2 at anode.** Solution slowly becomes acidic and depleted in silver.

Step 3. **(iii) Dilute H_2SO_4 / Pt.** Cathode: only H^+ and H_2O compete; H^+ wins. $2\,H^+ + 2\,e^- \longrightarrow H_2$. Anode: ${SO_4}^{2-}$ oxidation to peroxodisulphate needs $E^\circ_{\text{red}} = +2.05$ V (very hard); H_2O wins: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. **Products: H_2/O_2.** Net: $2\,H_2O \longrightarrow 2\,H_2 + O_2$. H_2SO_4 merely carries current — **electrolysis of water**.

Step 4. **(iv) Aqueous $CuCl_2$ / Pt.** Cathode: Cu^{2+} $(+0.34)$ vs H_2O (-0.83); Cu^{2+} wins. Copper deposits. Anode: thermodynamic comparison gives $2\,Cl^- \longrightarrow Cl_2$

($E^\circ_{\text{ox}} = -1.36$) vs H_2O (-1.23). H_2O would win on thermodynamics — but the **overpotential** for O_2 at Pt is large (~ 0.5 V), so practical anode product is Cl_2. **Products: Cu / Cl_2.**

Numerical anchor for overpotential. O_2 evolution at Pt needs $E_{\text{anode}} \geq 1.23 + \eta(O_2) \approx 1.73$ V. Cl_2 evolution needs $\geq 1.36 + \eta(Cl_2) \approx 1.41$ V — lower. Cl_2 wins on kinetics. This is exactly why the chlor-alkali industry electrolyses brine for chlorine.

Reading the four cases together. Cases (i) and (ii) differ only at the anode: the choice of electrode material flips whether the salt is consumed (Pt) or merely shuttled (Ag). Cases (iii) and (iv) emphasise that the dissolved anion matters: stable ${SO_4}^{2-}$ forces H_2O oxidation; kinetically active Cl^- wins over H_2O thanks to overpotential, even though thermodynamics favours H_2O.

Concept linkage. The same overpotential effect explains why brine (not pure water) is electrolysed for chlorine, why Hg-cathode chlor-alkali cells produce NaOH without Na escape, and why electrolytic vs catalytic synthesis depends on the electrode metal.

JEE/NEET relevance. “Predict products of electrolysis” appears every year and rewards systematic candidate listing. Two classic surprises tested: (a) reactive metal electrodes (Ag, Cu) dissolving instead of water oxidising, and (b) Cl_2 winning over O_2 at Pt anodes due to overpotential.

Final Answer: (i) Ag/Ag (plating); (ii) Ag/O_2; (iii) H_2/O_2 (water electrolysis); (iv) Cu/Cl_2 (overpotential).

♥ Electrolysis in industry

Case (i): **electroplating** — thin silver on cheap metals using a bath of $AgNO_3$ and a sacrificial Ag anode. Case (iii): **water electrolysis** for hydrogen production — a growing market for green-hydrogen fuel. Case (iv): why the chlor-alkali industry chooses Cl^- solutions over neutral H_2O for chlorine production — Cl_2 kinetics beat O_2 thermodynamics at Pt.

☞ Two-rule recipe for electrolysis

Cathode: pick the species with the *highest* E°_{red}.

Anode: pick the species with the *lowest* E°_{red} (highest E°_{ox}), *unless* overpotential at the electrode material reorders the winners (Cl_2 vs O_2 at Pt).

☞ Reactive vs inert electrodes

Inert (Pt, graphite): pass current only; chemistry on dissolved species.

Reactive (Ag, Cu, Ni): the electrode can be oxidised in preference to water/anion — basis of electrorefining and plating.

Key Takeaways

- **Galvanic cells.** A galvanic cell converts a spontaneous redox reaction into electricity. The anode (where oxidation occurs) is the negative terminal; the cathode (reduction) is positive. Cell notation: anode | anode-solution || cathode-solution | cathode.
- **Standard cell potential.** $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, with all potentials measured as *reductions* against the standard hydrogen electrode (SHE, $E^\circ = 0$ V at $a_{\text{H}^+} = 1$, $p_{\text{H}_2} = 1$ bar).
- **Gibbs energy and K.** $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$; $\log K = nE^\circ_{\text{cell}}/0.0591$ at 298 K. Positive E° $\Leftrightarrow$ negative $\Delta_r G^\circ \Leftrightarrow K > 1 \Leftrightarrow$ spontaneous.
- **Nernst equation.** $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$ at 298 K. Use to correct for non-standard concentrations and to predict EMF in concentration cells.
- **Conductivity.** $\kappa = G \cdot l/A$, units S/cm. Decreases on dilution (fewer ions per cm^3).
- **Molar conductivity.** $\Lambda_m = \kappa \times 1000/c$, units $\text{S cm}^2\,\text{mol}^{-1}$. Increases on dilution. For strong electrolytes, Λ_m vs $\sqrt{c}$ is linear and extrapolates to Λ°_m (Debye-Huckel-Onsager). For weak electrolytes, use Kohlrausch's law, $\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$.
- **Weak electrolytes.** $\alpha = \Lambda_m/\Lambda^\circ_m$; $K_a = c\alpha^2/(1-\alpha)$ (Ostwald's dilution law).
- **Faraday's first law.** $w = M_w It/(nF)$. To deposit one mole of M^{n+} requires n Faradays of charge.
- **Faraday's second law.** For cells in series, the masses of substances deposited are in the ratio of their chemical equivalents (M_w/n).
- **Products of electrolysis.** At the cathode, the species with the highest reduction potential wins. At the anode, the species with the lowest reduction potential (or with low overpotential) wins. Reactive electrodes (Ag, Cu) compete with water/aqueous species at the anode and can dissolve in preference.

End of Chapter 2 Exercises