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NCERT Exemplar Solutions

Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 2

Chapter 2: Electrochemistry

About this Chapter

Electrochemistry is the branch of chemistry that links chemical redox reactions with electrical energy. This chapter studies **galvanic cells** (which convert chemical energy into electrical work) and **electrolytic cells** (which use electrical energy to drive non-spontaneous reactions). You will learn the Nernst equation, conductivity and molar conductivity of electrolytes, Faraday's laws of electrolysis, batteries, fuel cells, and corrosion.

Topics covered: Electrode potentials • Galvanic & electrolytic cells • Nernst equation • $\Delta_r G$ and E_{cell} • Conductivity & molar conductivity • Kohlrausch's law • Faraday's laws • Batteries and fuel cells • Corrosion

Quick Formula Sheet

Nernst equation (general):
$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q$ (at 298 K)

Gibbs energy and emf:
$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$; $\Delta_r G^\circ = -RT \ln K_c$

Conductivity & molar conductivity:
$\kappa = \frac{1}{R} \cdot \frac{l}{A} = \frac{G^*}{R}$; $\Lambda_m = \frac{\kappa \times 1000}{c}$

Kohlrausch's law (NH_4OH example):
$\Lambda^0_m(NH_4OH) = \Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaOH) - \Lambda^0_m(NaCl)$

Faraday's laws:
$Q = It$; $w = ZIt = \frac{M}{nF} \cdot It$

Useful constant:
$F = 96{,}500\,\text{C mol}^{-1}$

I. Multiple Choice Questions (Type-I)

Q 2.1 **Which cell will measure standard electrode potential of copper electrode?**

(i) $\text{Pt}(s) \mid H_2(g, 0.1\ \textbf{bar}) \mid H^+(\textbf{aq.}, 1\,\textbf{M}) \parallel Cu^{2+}(\textbf{aq.}, 1\,\textbf{M}) \mid Cu$

(ii) $\text{Pt}(s) \mid H_2(g, 1\ \textbf{bar}) \mid H^+(\textbf{aq.}, 1\,\textbf{M}) \parallel Cu^{2+}(\textbf{aq.}, 2\,\textbf{M}) \mid Cu$

(iii) $\text{Pt}(s) \mid H_2(g, 1\ \textbf{bar}) \mid H^+(\textbf{aq.}, 1\,\textbf{M}) \parallel Cu^{2+}(\textbf{aq.}, 1\,\textbf{M}) \mid Cu$

(iv) $\mathrm{Pt\,(s)\,|\,H_2}(g, 1\ \textbf{bar})\,|\,\mathrm{H^+}(\textbf{aq.}, 0.1\,\textbf{M})\,||\,\mathrm{Cu^{2+}}(\textbf{aq.}, 1\,\textbf{M})\,|\,\mathrm{Cu}$

SOLUTION

Correct option: (iii).

Concept used. A **standard electrode potential** E° is the potential of an electrode measured against the **Standard Hydrogen Electrode (SHE)** under **standard conditions**: all gases at 1 bar, all solutes at 1 M activity, and temperature 298 K. Any departure (gas at 0.1 bar, H^+ at 0.1 M, Cu^{2+} at 2 M) makes the measured cell emf non-standard and the Nernst correction must be applied. So the "standard $E^\circ_{\mathrm{Cu^{2+}/Cu}}$" is recorded only when *every* ion/gas in the cell is at unit activity.

Step 1. Recall the cell notation rule: anode (oxidation) on the left, cathode (reduction) on the right, salt bridge (||) in the middle. For measuring $E^\circ_{\mathrm{Cu^{2+}/Cu}}$, SHE is the reference (left) and the copper half-cell is on the right.

Step 2. Standard conditions demand: $p_{\mathrm{H_2}} = 1\,\mathrm{bar}$ (rules out (i)), $[\mathrm{H^+}] = 1\,\mathrm{M}$ (rules out (iv)), and $[\mathrm{Cu^{2+}}] = 1\,\mathrm{M}$ (rules out (ii) which has $2\,\mathrm{M}$).

Step 3. Only option (iii) keeps every species at standard activity. With SHE giving $E^\circ = 0\,\mathrm{V}$ by definition, the voltmeter reads

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - 0 = +0.34\,\mathrm{V}.$$

Final Answer: Option **(iii)**: $\mathrm{Pt\,(s)\,|\,H_2(1\ bar)\,|\,H^+(1\,M)\,||\,Cu^{2+}(1\,M)\,|\,Cu}$.

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

Strategic angle: rule-out by Nernst correction. Take the Nernst equation as a diagnostic. For the cell shown, $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \dfrac{0.059}{n}\log Q$. If any concentration $\neq 1\,\mathrm{M}$ or any gas pressure $\neq 1\,\mathrm{bar}$, $Q \neq 1$ and $\log Q \neq 0$, so $E_{\mathrm{cell}} \neq E^\circ_{\mathrm{cell}}$. The only option that gives $\log Q = 0$ wins.

Step 1. Cell reaction overall: $\mathrm{H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^+(aq) + Cu\,(s)}$ with $n = 2$. The reaction quotient is

$$Q = \frac{[\mathrm{H^+}]^2}{p_{\mathrm{H_2}}\,[\mathrm{Cu^{2+}}]}.$$

Step 2. Test option (i): $p_{\mathrm{H_2}} = 0.1$, $[\mathrm{H^+}] = [\mathrm{Cu^{2+}}] = 1$. $Q = 1/(0.1 \cdot 1) = 10$, $\log Q = 1$, so a $-0.030\,\mathrm{V}$ correction appears. Not standard.

Step 3. Test option (ii): $p_{\mathrm{H_2}} = 1$, $[\mathrm{H^+}] = 1$, $[\mathrm{Cu^{2+}}] = 2$. $Q = 1/(1 \cdot 2) = 0.5$, $\log Q = -0.301$, gives a $+0.009\,\mathrm{V}$ correction. Not standard.

Step 4. Test option (iv): $p_{\mathrm{H_2}} = 1$, $[\mathrm{H^+}] = 0.1$, $[\mathrm{Cu^{2+}}] = 1$. $Q = (0.1)^2/(1 \cdot 1) = 0.01$, $\log Q = -2$, gives a $+0.059\,\mathrm{V}$ shift. Not standard.

Step 5. Only option (iii) gives $Q = 1$, $\log Q = 0$, hence $E_{\text{cell}} = E^\circ_{\text{cell}}$. This is the textbook setup.

✗ Common Pitfall

Common pitfall. Students sometimes pick (ii) thinking "higher $[\text{Cu}^{2+}]$ makes Cu more eager to deposit". True, but that gives a *higher* measured emf than E°, not E° itself. The question asks for E°, not max emf.

☞ Exam Tip

Exam tip. JEE Main has asked SHE-coupling questions in 2019 (Jan shift), 2021 (March) and 2022 (July). Always look for the option that keeps every activity at 1 M and gas at 1 bar.

♥ Concept Linkage

Concept linkage. E° values feed directly into the **electrochemical series** used to predict displacement reactions and corrosion tendency, and into $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$.

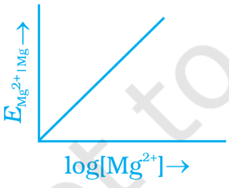
Final Answer: Option **(iii)** is the only setup with all activities at unity, hence it measures $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$.

Q 2.2 **Electrode potential for Mg electrode varies according to the equation**

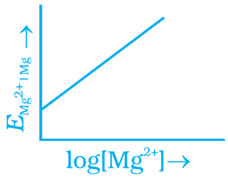
$$E_{\text{Mg}^{2+}|\text{Mg}} = E^\circ_{\text{Mg}^{2+}|\text{Mg}} - \frac{0.059}{2}\log\frac{1}{[\text{Mg}^{2+}]}.$$

The graph of $E_{\text{Mg}^{2+}|\text{Mg}}$ vs $\log[\text{Mg}^{2+}]$ is:
(i), (ii), (iii) or (iv) as shown.

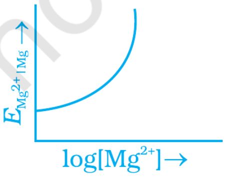
(i)



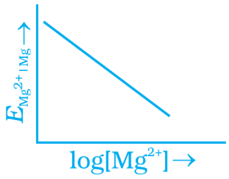
(ii)



(iii)



(iv)



not to

Fig. for Q2, NCERT Exemplar Class 12 Chemistry, Chapter 3.

SOLUTION

Correct option: (ii).

Concept used. The Nernst equation for a metal electrode $\mathrm{M}^{n+}|\mathrm{M}$ relates the electrode potential to the ion concentration:

$$E = E^\circ - \frac{0.059}{n}\log\frac{1}{[\mathrm{M}^{n+}]} = E^\circ + \frac{0.059}{n}\log[\mathrm{M}^{n+}].$$

This is a straight-line equation in $\log[\mathrm{M}^{n+}]$ of the form $y = mx + c$, where the slope $m = +0.059/n$ is positive and the y-intercept $c = E^\circ_{\mathrm{M}^{n+}|\mathrm{M}}$.

Step 1. Start from the given form: $E = E^\circ - \frac{0.059}{2}\log\frac{1}{[\mathrm{Mg}^{2+}]}$. Use the log identity $\log(1/x) = -\log x$:

$$E = E^\circ + \frac{0.059}{2}\log[\mathrm{Mg}^{2+}].$$

Step 2. Identify slope and intercept: slope $= +\frac{0.059}{2} = +0.0295 > 0$, intercept $= E^\circ_{\mathrm{Mg}^{2+}|\mathrm{Mg}} = -2.37\,\mathrm{V}$ (negative).

Step 3. The graph is a straight line with positive slope (rising left to right) and a negative y-intercept (below the $\log[\mathrm{Mg}^{2+}]$ axis). Among the four sketches, only (ii) shows a straight line cutting the y-axis below the origin and rising.

> **Final Answer:** Option **(ii)**: straight line with positive slope and negative y-intercept.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: shape-by-derivative. Recognise the equation as a linear function of $\log[\mathrm{Mg}^{2+}]$, then check both the sign of the slope and the sign of the intercept against each sketch.

Step 1. Rewrite cleanly. With $n = 2$ for Mg^{2+}:

$$E = E^\circ - 0.0295\log\frac{1}{[\mathrm{Mg}^{2+}]} = E^\circ + 0.0295\log[\mathrm{Mg}^{2+}].$$

Step 2. Compute the slope:

$$\frac{dE}{d(\log[\mathrm{Mg}^{2+}])} = +0.0295.$$

Positive means E rises as $\log[\mathrm{Mg}^{2+}]$ increases. Rules out (iv) (decreasing line) and (iii) (curved line, not linear).

Step 3. Compute the intercept: at $\log[\mathrm{Mg}^{2+}] = 0$ (i.e. $[\mathrm{Mg}^{2+}] = 1\,\mathrm{M}$), $E = E^\circ_{\mathrm{Mg}^{2+}|\mathrm{Mg}} = -2.37\,\mathrm{V}$. Negative intercept rules out (i) (passes through origin).

Step 4. Only (ii) shows a straight line with positive slope cutting the y-axis at a *negative* value, matching all three constraints.

✗ Common Pitfall

Common pitfall. Many students confuse $E = E^\circ - \frac{0.059}{n}\log Q$ where $Q = 1/[\mathrm{M}^{n+}]$ for a reduction, and write the slope as *negative*. The minus sign in front of the log flips when the argument is inverted ($\log(1/x) = -\log x$). Track the sign carefully.

☞ Cross-Check

Numerical cross-check. At $[\mathrm{Mg}^{2+}] = 0.01\,\mathrm{M}$ ($\log = -2$): $E = -2.37 - 0.059 = -2.429\,\mathrm{V}$. Below the intercept, to the left of origin. Consistent with (ii).

Final Answer: Graph (ii), linear, positive slope $+0.0295\,\mathrm{V}$ per decade, intercept $-2.37\,\mathrm{V}$.

Q 2.3 Which of the following statement is correct?

(i) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.

(ii) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.

(iii) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.

(iv) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

SOLUTION

Correct option: (iii).

Concept used. An **intensive property** does not depend on the amount of substance (examples: temperature, density, electrode potential, molar volume). An **extensive property** scales with the amount of substance (examples: mass, volume, energy, Gibbs free energy, enthalpy). The cell emf E_{cell} is a potential *difference* per unit charge, so it stays the same whether the cell delivers 1 mole or 100 moles of electrons. In contrast, $\Delta_r G = -nFE_{\text{cell}}$ scales linearly with n, the moles of electrons transferred.

Step 1. Test E_{cell}. Define it as the potential *per unit charge*: $E = W_{\text{electrical}}/Q$. Doubling the cell size doubles both W and Q, so E stays the same. E_{cell} is intensive.

Step 2. Test $\Delta_r G$. By definition, $\Delta_r G = -nFE_{\text{cell}}$. Doubling n (i.e. doubling the moles of electrons in the balanced equation) doubles $\Delta_r G$. Hence $\Delta_r G$ is extensive.

Step 3. Combining: E_{cell} intensive, $\Delta_r G$ extensive. Only option (iii) matches.

Final Answer: Option **(iii)**: E_{cell} is intensive, $\Delta_r G$ is extensive.

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

Strategic angle: definition-first. Memorise that *anything per unit charge or per mole* is intensive, while total energy or total mass is extensive. The cell emf is a per-charge quantity; $\Delta_r G$ is the total energy released for the balanced reaction.

Step 1. Write the connecting equation: $\Delta_r G = -nFE_{\text{cell}}$ where n = moles of electrons in the balanced reaction, $F = 96{,}500$ C/mol, and E_{cell} in V.

Step 2. Imagine running the same Daniel cell two ways: write (a) $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$, $n = 2$, $\Delta_r G^\circ = -2(96500)(1.10) = -212{,}300\,\text{J/mol}$. Then multiply the equation by 2: (b) $2\,\text{Zn} + 2\,\text{Cu}^{2+} \longrightarrow 2\,\text{Zn}^{2+} + 2\,\text{Cu}$, $n = 4$, $\Delta_r G^\circ = -4(96500)(1.10) = -424{,}600\,\text{J}$.

Step 3. E_{cell} stays at $1.10\,\text{V}$ in both. So E does not depend on how the equation is balanced, while $\Delta_r G$ doubles. Intensive vs extensive.

☞ **Exam Tip**

Exam tip. NEET 2017 and JEE Main 2020 (Sept) both tested this exact distinction. Quick rule: if the symbol has a Δ_r in front (like $\Delta_r G$, $\Delta_r H$, $\Delta_r S$), think extensive.

♥ **Concept Linkage**

Concept linkage. Same rule applies to enthalpy of neutralisation (extensive) vs molar enthalpy (intensive), and to boiling point (intensive) vs total heat needed to vaporise (extensive).

Final Answer: E_{cell}, intensive (per unit charge); $\Delta_r G = -nFE_{\text{cell}}$, extensive (scales with n).

Q 2.4 The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called ______.

(i) Cell potential

(ii) Cell emf

(iii) Potential difference

(iv) Cell voltage

SOLUTION

Correct option: (ii).

Concept used. The **electromotive force (emf)** of a cell is precisely the potential difference between the two terminals measured *when no current is drawn* (i.e. on open circuit, with an ideal high-resistance voltmeter or a potentiometer). The **cell potential** (or terminal voltage) is the potential difference under operating conditions and is *less* than the emf by the IR drop across the internal resistance: $V_{\text{cell}} = \varepsilon_{\text{cell}} - Ir$.

Step 1. Define each term carefully. The emf ε is the maximum potential the cell can deliver, achieved only when $I \to 0$ (no current). The cell potential V is what a real voltmeter reads while current flows, and includes the drop Ir across the internal resistance.

Step 2. The phrase "when no current is drawn" is the defining feature of emf. So the answer is (ii) Cell emf.

Step 3. "Cell potential", "Potential difference", and "Cell voltage" are loose synonyms for the operating terminal voltage and don't carry the "zero-current" restriction.

> **Final Answer:** Option **(ii)**: Cell emf.

EXPERT'S SOLUTION *: Sneha Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle: distinguish emf from terminal voltage. The whole question rests on the fine distinction between emf and cell potential. A working cell has an internal resistance r; when current I flows, the terminal voltage drops by Ir. Only at $I = 0$ does the terminal voltage equal the emf.

Step 1. Write the relation: $V_{\text{terminal}} = \varepsilon - Ir$ (during discharge). Setting $I = 0$ gives $V_{\text{terminal}} = \varepsilon$. This is exactly the "no current is drawn" condition.

Step 2. For a Daniel cell, $\varepsilon = 1.10\,\text{V}$ (emf). If the external resistance is small and a current of 0.1 A flows through an internal resistance of $0.5\,\Omega$:
$V = 1.10 - (0.1)(0.5) = 1.05\,\text{V}$. The voltmeter reads $1.05\,\text{V}$, not $1.10\,\text{V}$.

Step 3. Hence terms (i), (iii), (iv) refer to that lower reading; only (ii) "Cell emf" refers to the open-circuit value.

✗ Common Pitfall

Common pitfall. Treating "cell potential" and "emf" as synonyms. They coincide only at $I = 0$.

☞ **Exam Tip**

Exam tip. CBSE board (2018 and 2022) and JEE Advanced (2019 P-II) include this distinction in two-mark short-answer questions. Mention "no current drawn" or "open circuit" for full credit.

Final Answer: Option **(ii)**, emf is the open-circuit ($I = 0$) potential difference.

Q 2.5 Which of the following statement is not correct about an inert electrode in a cell?

(i) It does not participate in the cell reaction.

(ii) It provides surface either for oxidation or for reduction reaction.

(iii) It provides surface for conduction of electrons.

(iv) It provides surface for redox reaction.

SOLUTION

Correct option: (iv).

Concept used. An inert electrode (typically platinum, graphite, or gold) is one that does *not* take part in the chemical reaction. Its job is purely to: (a) provide a conducting surface where electrons can be exchanged with the solution, and (b) host *either* an oxidation half-reaction *or* a reduction half-reaction, but not both on the same surface. A single electrode is always associated with one half-reaction (oxidation *or* reduction); a redox (full) reaction needs two electrodes.

Step 1. Read each statement carefully.

(i) "Does not participate" — correct, this is the definition of inert.

(ii) "Provides surface for oxidation OR reduction" — correct, it hosts exactly one half-cell reaction.

(iii) "Provides surface for conduction of electrons" — correct, inert electrodes are good conductors.

(iv) "Provides surface for redox reaction" — *incorrect*, because a redox (both halves) reaction occurs in the whole cell across two electrodes, not at one inert electrode.

Step 2. Hence statement (iv) is not correct.

Step 3. Example: in $\mathrm{Pt(s)|H_2(g)|H^+(aq)}$, the Pt only hosts the $\mathrm{H_2 \rightleftharpoons 2\,H^+ + 2\,e^-}$ half-reaction; the matching reduction (or oxidation) happens at the OTHER electrode.

Final Answer: Option **(iv)**: it provides surface for redox reaction — INCORRECT (an electrode hosts only one half-cell reaction).

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

Strategic angle: half-cell vs full-cell scope. The trick in this question is the difference between a *half-cell* reaction (oxidation OR reduction, at one electrode) and the *redox* reaction (both halves combined, across two electrodes). An inert electrode operates at the half-cell level.

Step 1. Recall: at each electrode in a galvanic cell, only one of the two half-reactions occurs. The two halves together form the redox process, but the redox process is not confined to one electrode.

Step 2. Apply to (iv): "surface for redox reaction" would mean both oxidation and reduction happen on the same Pt strip. This is not true; one strip is the anode (oxidation only), the other strip is the cathode (reduction only).

Step 3. Statements (i)–(iii) are textbook-correct.

☞ **Exam Tip**

Exam tip. CBSE board 2020 had a fill-in-the-blank on "Pt is used as an ___ electrode in SHE". Answer: inert. Always link Pt or graphite to "inert" in your mental map.

♥ **Concept Linkage**

Concept linkage. Inert electrodes are central to fuel cells (Pt-loaded electrodes), to SHE (Pt black), and to electrolysis of brine (graphite cathode, Pt or graphite anode).

Final Answer: Option **(iv)** is the wrong statement; an inert electrode hosts one half-reaction, not the full redox.

Q 2.6 **An electrochemical cell can behave like an electrolytic cell when ______.**

(i) $E_{\text{cell}} = 0$

(ii) $E_{\text{cell}} > E_{\text{ext}}$

(iii) $E_{\text{ext}} > E_{\text{cell}}$

(iv) $E_{\text{cell}} = E_{\text{ext}}$

SOLUTION

Correct option: (iii).

Concept used. A **galvanic cell** converts chemical energy into electrical energy spontaneously; an **electrolytic cell** consumes external electrical energy to drive a non-spontaneous reaction. A galvanic cell can be *forced* to behave electrolytically by applying an external EMF E_{ext} *greater* than its own cell emf E_{cell} and in the opposite direction. The applied voltage then dominates, reverses the current, and pushes the cell reaction backwards (non-spontaneous direction).

Step 1. Test each condition.

(i) $E_{\text{cell}} = 0$: cell is at equilibrium; no current flows; not electrolytic, but "dead".

(ii) $E_{\text{cell}} > E_{\text{ext}}$: the cell still drives current outward, behaves as a galvanic cell.

(iii) $E_{\text{ext}} > E_{\text{cell}}$: external voltage dominates; the cell reaction is reversed; electrolytic behaviour.

(iv) $E_{\text{cell}} = E_{\text{ext}}$: exact balance; no current flows in either direction (this is how a potentiometer measures emf).

Step 2. Hence (iii) is the only condition causing electrolytic behaviour.

> **Final Answer:** Option **(iii)**: $E_{\text{ext}} > E_{\text{cell}}$.

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

Strategic angle: think battery being charged. The cleanest mental picture is a lead-acid car battery on a charger. When the charger's voltage exceeds the battery's emf, current is pushed back into the battery, reversing the spontaneous discharge reaction. The battery is now an electrolytic cell.

Step 1. Daniel cell as an example: emf = $1.10\,\text{V}$. Spontaneous reaction:

$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}.$$

Step 2. Apply $E_{\text{ext}} = 1.5\,\text{V}$ in the opposite direction (positive terminal to Zn, negative to Cu). Since $1.5 > 1.10$, current reverses. Now $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\,\text{e}^-$ at the Cu electrode (now anode) and $\text{Zn}^{2+} + 2\,\text{e}^- \longrightarrow \text{Zn}$ at the Zn electrode (now cathode). Electrolytic behaviour.

Step 3. Apply $E_{\text{ext}} = 0.5\,\text{V}$ (case (ii) reversed): cell's $1.10\,\text{V}$ wins, spontaneous discharge continues. Galvanic.

Step 4. Apply $E_{\text{ext}} = 1.10\,\text{V}$ (case (iv)): exact balance, $I = 0$, no chemistry happens. This is the potentiometer balance point.

☞ **Exam Tip**

Exam tip. NEET 2019 and JEE Main 2021 (Feb shift) both had this as a one-mark MCQ. Always associate "electrolytic" with "external V wins".

♥ **Concept Linkage**

Concept linkage. This is exactly how rechargeable batteries work (Q15 lead-storage, Q54 Ni–Cd) — they oscillate between galvanic and electrolytic modes depending on whether the external source is on.

Final Answer: Option **(iii)**: when $E_{\text{ext}} > E_{\text{cell}}$, current reverses and the cell becomes electrolytic.

Q 2.7 Which of the statements about solutions of electrolytes is not correct?

(i) Conductivity of solution depends upon size of ions.

(ii) Conductivity depends upon viscosity of solution.

(iii) Conductivity does not depend upon solvation of ions present in solution.

(iv) Conductivity of solution increases with temperature.

SOLUTION

Correct option: (iii).

Concept used. The conductivity κ of an electrolyte solution measures how easily ions move through it under an applied field. Three things slow the ions down: their *size* (bigger ions experience more drag), the solvent's *viscosity*, and the *solvation sheath* (a tightly bound shell of solvent molecules around each ion, which effectively enlarges the moving species). Temperature increases ionic mobility (less viscosity, more thermal energy), so κ rises with T.

Step 1. Check (i). Larger ions move slower (more frictional drag), so κ depends on ionic size. Statement correct.

Step 2. Check (ii). $\kappa \propto 1/\eta$ approximately (Walden's rule: $\Lambda^\circ \eta = \text{const}$). So κ depends on viscosity. Statement correct.

Step 3. Check (iii). Solvation increases the *effective* radius of an ion. For example, Li^+ has a smaller crystal radius than Cs^+ but *larger* hydrated radius (because Li^+ is more polarising and binds more water molecules). Result: Cs^+ moves faster through water. So conductivity *does* depend on solvation. Statement (iii) is INCORRECT.

Step 4. Check (iv). At higher T, ion mobility rises and viscosity drops, so κ rises by $\sim 2\%$ per °C. Statement correct.

Final Answer: Option **(iii)** is incorrect — conductivity *does* depend on ion solvation.

EXPERT'S SOLUTION *: Aanya Rao, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: hydrated radius rules. The defining trap in this question is statement (iii). The cation series $\mathrm{Li^+, Na^+, K^+, Rb^+, Cs^+}$ (in increasing *crystal* radius) *reverses* when you measure ionic mobility in water because $\mathrm{Li^+}$ ends up as the bulkiest *hydrated* species. This is the cleanest demonstration that solvation matters.

Step 1. Crystal radii (pm): $\mathrm{Li^+}$ 76, $\mathrm{Na^+}$ 102, $\mathrm{K^+}$ 138, $\mathrm{Cs^+}$ 167. Naively, $\mathrm{Li^+}$ should be fastest.

Step 2. Hydrated radii (pm): $\mathrm{Li^+}$ 340, $\mathrm{Na^+}$ 276, $\mathrm{K^+}$ 232, $\mathrm{Cs^+}$ 228. Now $\mathrm{Cs^+}$ is smallest and moves fastest.

Step 3. Limiting ionic conductivity λ°_+ ($\mathrm{S\,cm^2\,mol^{-1}}$): $\mathrm{Li^+}$ 38.7, $\mathrm{Na^+}$ 50.1, $\mathrm{K^+}$ 73.5, $\mathrm{Cs^+}$ 77.2. Ranking matches hydrated radii, NOT crystal radii.

Step 4. Hence solvation governs the trend; statement (iii) is wrong; the wrong statement is (iii).

☞ Exam Tip

Exam tip. JEE Main 2019 (Apr shift) asked exactly this ranking. NEET 2022 had "order of λ° for alkali cations". Remember: $\lambda^\circ_{\mathrm{Cs^+}} > \lambda^\circ_{\mathrm{K^+}} > \lambda^\circ_{\mathrm{Na^+}} > \lambda^\circ_{\mathrm{Li^+}}$.

♥ Concept Linkage

Concept linkage. Ion solvation also controls Λ° values used in Kohlrausch's law (Q16, Q22) and explains why molar conductivity of weak electrolytes is much lower than that of strong ones at low concentration.

Final Answer: Option **(iii)** is wrong — solvation increases hydrated radius and lowers conductivity.

Q 2.8 **Using the data given below find out the strongest reducing agent.**

$E^\circ_{\mathrm{Cr_2O_7{}^{2-}/Cr^{3+}}} = 1.33\,\mathbf{V}$; $E^\circ_{\mathrm{Cl_2/Cl^-}} = 1.36\,\mathbf{V}$;
$E^\circ_{\mathrm{MnO_4-/Mn^{2+}}} = 1.51\,\mathbf{V}$; $E^\circ_{\mathrm{Cr^{3+}/Cr}} = -0.74\,\mathbf{V}$.
(i) $\mathrm{Cl^-}$ **(ii)** Cr **(iii)** $\mathrm{Cr^{3+}}$ **(iv)** $\mathrm{Mn^{2+}}$

SOLUTION

Correct option: (ii) Cr.

Concept used. The **reducing strength** of a species is its tendency to lose electrons (i.e. get oxidised). A species is a strong reducing agent when its *oxidised* form has a very negative reduction potential, because the species is then *eager* to give up electrons. Equivalently, the *oxidation* potential $-E^\circ_{\text{red}}$ must be large and positive. The most negative E°_{red} in the list belongs to the strongest reducing agent.

Step 1. Pair each candidate with the reduction half-reaction in the table:

Cl^- comes from $Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$, $E^\circ = +1.36\,V$.

Cr comes from $Cr^{3+} + 3\,e^- \longrightarrow Cr$, $E^\circ = -0.74\,V$.

Cr^{3+} comes from ${Cr_2O_7}^{2-}/Cr^{3+}$, $E^\circ = +1.33\,V$.

Mn^{2+} comes from MnO_4-/Mn^{2+}, $E^\circ = +1.51\,V$.

Step 2. For each, write the *oxidation* potential $E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$:

Cl^-: $-1.36\,V$; Cr: $+0.74\,V$; Cr^{3+}: $-1.33\,V$; Mn^{2+}: $-1.51\,V$.

Step 3. The largest positive oxidation potential is for Cr ($+0.74\,V$), so Cr is most ready to be oxidised $Cr \longrightarrow Cr^{3+} + 3\,e^-$, and is therefore the strongest reducing agent in the set.

Final Answer: Option **(ii)** Cr is the strongest reducing agent.

EXPERT'S SOLUTION : *Krishna Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle: most-negative-E°-wins rule. The quickest route is to remember: *strongest reducing agent* $\Leftrightarrow$ most negative standard reduction potential of the oxidised form. Just scan the four E° values and pick the most negative.

Step 1. Tabulate: $E^\circ_{Cr^{3+}/Cr} = -0.74\,V$ is the only negative value; all others are positive ($+1.33, +1.36, +1.51$).

Step 2. The most negative E°_{red} identifies the *reduced form* as the best reducing agent. Reduced form of the Cr^{3+}/Cr couple is Cr.

Step 3. Cross-check: Mn^{2+}, Cr^{3+} and Cl^- belong to couples with very positive E°, so their *oxidised* partners are strong oxidising agents, not strong reducers.

☞ Exam Tip

Exam tip. JEE Main 2020 (Sept) and NEET 2018 both asked “strongest reducing agent from given E° values”. Always pick the species at the *most negative* E°_{red}.

♥ Concept Linkage

Concept linkage. This question feeds directly into Q9 (strongest oxidising agent — the partner question), Q10 (ordering of reducing power), Q11 (most stable reduced ion), and Q12 (most stable oxidised species). Build a single ranked list once.

Final Answer: Cr, most negative $E^\circ_{\text{red}} = -0.74\,\text{V}$, strongest reducer.

Q 2.9 **Use the data given in Q.8 and find out which of the following is the strongest oxidising agent.**

(i) Cl^- **(ii)** Mn^{2+} **(iii)** $MnO_4{}^-$ **(iv)** Cr^{3+}

SOLUTION

Correct option: (iii) $MnO_4{}^-$.

Concept used. The **strongest oxidising agent** has the most *positive* standard reduction potential, because a high positive E° means the oxidised form is very eager to accept electrons (get reduced). So we identify the candidate with the largest E°_{red}.

Step 1. Pair each candidate with its couple from the Q.8 data:
Cl^- is the *reduced* form of Cl_2, so for oxidising power look at Cl_2/Cl^-: $E^\circ = +1.36\,\text{V}$.
Mn^{2+} is the reduced form of $MnO_4{}^-$, but Mn^{2+} *itself* as oxidising agent corresponds to $Mn^{2+} + 2\,e^- \longrightarrow Mn$, which is not given.
$MnO_4{}^-$ is the oxidising form, couple MnO_4-/Mn^{2+} with $E^\circ = +1.51\,\text{V}$.
Cr^{3+} as oxidising form belongs to $Cr_2O_7{}^{2-}/Cr^{3+}$ *reduced* form; as oxidiser look at Cr^{3+}/Cr with $E^\circ = -0.74\,\text{V}$ (negative, poor oxidiser).

Step 2. The four oxidising couples give $+1.36$, — (not given), $+1.51$, and $-0.74\,\text{V}$. The largest positive value is $+1.51\,\text{V}$ for MnO_4-/Mn^{2+}.

Step 3. Therefore $MnO_4{}^-$ is the strongest oxidising agent among the four.

Final Answer: Option **(iii)** $MnO_4{}^-$, largest $E^\circ_{\text{red}} = +1.51\,\text{V}$.

EXPERT'S SOLUTION *: Rohit Verma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: highest-E°-wins rule. Mirror image of Q8. Where reducing power follows the most-negative E°_{red}, oxidising power follows the most-positive.

Step 1. Scan the four available E° values: $+1.33, +1.36, +1.51, -0.74\,\text{V}$.

Step 2. Highest is $+1.51\,\text{V}$ for $\text{MnO}_4-/\text{Mn}^{2+}$. So the oxidised form of that couple, ${\text{MnO}_4}^-$, is the strongest oxidiser.

Step 3. Cross-check by considering which option *could* act as oxidiser: Cl^- (already reduced, cannot oxidise easily); Mn^{2+} (can be reduced further to Mn with $E^\circ \approx -1.18\,\text{V}$, bad oxidiser); Cr^{3+} (reducing $\text{Cr}^{3+} \longrightarrow \text{Cr}$, $E^\circ = -0.74\,\text{V}$, also bad oxidiser).

✗ **Common Pitfall**

Common pitfall. Choosing Cl^-, but Cl^- is the *reduced* side of the chlorine couple, so it cannot oxidise. Cl_2 (not Cl^-) is the strong oxidiser at $+1.36\,\text{V}$.

☞ **Exam Tip**

Exam tip. NEET 2017 phrased this as "which oxidises Fe^{2+} to Fe^{3+} most readily". Same logic, pick the highest E°_{red}.

♥ **Concept Linkage**

Concept linkage. Forms the "most stable oxidised species" answer for Q12 (look for the *lowest* E°, i.e. oxidised form that does NOT want to get further oxidised).

Final Answer: ${\text{MnO}_4}^-$, strongest oxidiser, $E^\circ = +1.51\,\text{V}$.

Q 2.10 Using the data given in Q.8 find out in which option the order of reducing power is correct.

(i) $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$

(ii) $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$

(iii) $\text{Cr}^{3+} < \text{Cl}^- < {\text{Cr}_2\text{O}_7}^{2-} < {\text{MnO}_4}^-$

(iv) $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$

SOLUTION

Correct option: (ii).

Concept used. To rank reducing power, list the *oxidation potentials* $E^\circ_{\text{ox}} = -E^\circ_{\text{red}}$ of each species. The species with the LARGEST positive E°_{ox} is the strongest reducing agent; the SMALLEST (most negative) is the weakest. Order from weakest to strongest by listing E°_{ox} in increasing order.

Step 1. Compute E°_{ox} for each species (using its relevant couple):
$\text{Mn}^{2+} \to \text{MnO}_4{}^-$: $E^\circ_{\text{ox}} = -(+1.51) = -1.51\,\text{V}$.
$\text{Cl}^- \to \text{Cl}_2$: $E^\circ_{\text{ox}} = -(+1.36) = -1.36\,\text{V}$.
$\text{Cr}^{3+} \to \text{Cr}_2\text{O}_7{}^{2-}$: $E^\circ_{\text{ox}} = -(+1.33) = -1.33\,\text{V}$.
$\text{Cr} \to \text{Cr}^{3+}$: $E^\circ_{\text{ox}} = -(-0.74) = +0.74\,\text{V}$.

Step 2. Order from least to most reducing power (least to greatest E°_{ox}):

$$\text{Mn}^{2+}\ (-1.51) < \text{Cl}^-\ (-1.36) < \text{Cr}^{3+}\ (-1.33) < \text{Cr}\ (+0.74).$$

Step 3. This matches option (ii) exactly.

> **Final Answer:** Option **(ii)**: $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$.

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

Strategic angle: ranked-by-E°_{red} table. The trick is to keep the signs straight. "Most negative E°_{red}" = strongest reducing agent = LAST in the ascending-power list. Walk through the list from *most positive* E°_{red} (weakest reducer) to *most negative* E°_{red} (strongest reducer).

Step 1. Sort the relevant E°_{red} from highest to lowest (most positive first = weakest reducer):
$\text{MnO}_4-/\text{Mn}^{2+}$: $+1.51$ (so Mn^{2+} is weakest reducer)
$\text{Cl}_{2/}\text{Cl}^-$: $+1.36$ (so Cl^-)
$\text{Cr}_2\text{O}_7{}^{2-}/\text{Cr}^{3+}$: $+1.33$ (so Cr^{3+})
Cr^{3+}/Cr: -0.74 (so Cr, strongest reducer).

Step 2. Increasing reducing power: $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$.

Step 3. Cross-check against (i): $\text{Cr}^{3+} < \text{Cl}^-$? Compare E°_{red}: Cr^{3+} couple has $E^\circ = +1.33 < +1.36$ of Cl^-, so Cr^{3+} is a stronger reducer than Cl^-. So (i) is wrong.

Step 4. (iii) and (iv) include $\text{Cr}_2\text{O}_7{}^{2-}$, $\text{MnO}_4{}^-$ which are oxidising species, not reducing, wrong.

> ☞ Exam Tip
>
> **Exam tip.** JEE Advanced 2018 P-II asked an analogous "order of reducing power for Mg, Al, Zn, Fe". Same algorithm.

♥ Concept Linkage

Concept linkage. This is the **electrochemical series** in miniature. Memorising the alkali–alkaline-earth–transition metal hierarchy lets you answer most of these in $< 10\,\text{s}$.

Final Answer: Order: $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$, option (ii).

Q 2.11 **Use the data given in Q.8 and find out the most stable ion in its reduced form.**

(i) Cl^- **(ii)** Cr^{3+} **(iii)** Cr **(iv)** Mn^{2+}

SOLUTION

Correct option: (iv) Mn^{2+}.

Concept used. The "most stable reduced form" is the species that is hardest to oxidise back. Equivalently, its *oxidised* partner has the highest reduction potential , because if the forward (reduction) reaction is highly favourable (E°_{red} very positive), then the reverse (oxidation) reaction is very unfavourable, leaving the reduced form locked in.

Step 1. Identify the couple each candidate sits on the *reduced* side of:
Cl^-: $\text{Cl}_{2}/\text{Cl}^-$, $E^\circ_{\text{red}} = +1.36\,\text{V}$.
Cr^{3+}: as reduced form, $\text{Cr}_2\text{O}_7{}^{2-}/\text{Cr}^{3+}$, $E^\circ_{\text{red}} = +1.33\,\text{V}$.
Cr: Cr^{3+}/Cr, $E^\circ_{\text{red}} = -0.74\,\text{V}$.
Mn^{2+}: $\text{MnO}_4{-}/\text{Mn}^{2+}$, $E^\circ_{\text{red}} = +1.51\,\text{V}$.

Step 2. The HIGHEST E°_{red} is $+1.51\,\text{V}$ for Mn^{2+}. This means $\text{MnO}_4{}^-$ very strongly wants to become Mn^{2+}, hence Mn^{2+} is the hardest to oxidise back, most stable in its reduced form.

Final Answer: Option **(iv)** Mn^{2+}, most stable reduced form.

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

Strategic angle: "hardest to oxidise back". Re-frame the question. "Most stable reduced form" = "hardest to go back to oxidised form" = "largest reverse barrier" = "largest forward driving force" = "largest E°_{red}".

Step 1. Largest E°_{red} in the list: $+1.51\,\text{V}$ ($\text{MnO}_4{-}/\text{Mn}^{2+}$).

Step 2. So Mn^{2+}, the reduced partner of the most oxidising couple, is the most stable in its reduced form.

Step 3. Cross-check: Cr has the most NEGATIVE E°_{red} ($-0.74\,\mathrm{V}$), which means Cr is the LEAST stable reduced form (easiest to oxidise back to Cr^{3+}). So (iii) is the wrong answer to a common student trap.

☞ **Exam Tip**

Exam tip. CBSE 2019 had "why is Mn^{2+} a stable d^5 ion?". Half-filled $3d^5$ is electronically stable (symmetric, exchange energy maximum), chemistry rationale for the high E°.

♥ **Concept Linkage**

Concept linkage. The high E° of permanganate explains why $\mathrm{KMnO_4}$ titrations work in acidic medium and why $\mathrm{MnO_2}$ acts as an oxidising agent in dry cells.

Final Answer: Mn^{2+}, paired with the highest $E^\circ_{\text{red}} = +1.51\,\mathrm{V}$, most stable reduced form.

Q 2.12 **Use the data of Q.8 and find out the most stable oxidised species.**
(i) Cr^{3+} **(ii)** $\mathrm{MnO_4}^-$ **(iii)** $\mathrm{Cr_2O_7}^{2-}$ **(iv)** Mn^{2+}

SOLUTION

Correct option: (i) Cr^{3+}.
Concept used. The "most stable oxidised species" is the oxidised form that is hardest to reduce further. Its E°_{red} as the oxidised partner of a deeper reduction must be the LOWEST (least positive or most negative), because a low E°_{red} means there is little driving force to take it further down.

Step 1. Identify each candidate's role:
Cr^{3+}, sits as oxidised form of the couple $\mathrm{Cr}^{3+}/\mathrm{Cr}$, $E^\circ_{\text{red}} = -0.74\,\mathrm{V}$.
$\mathrm{MnO_4}^-$, oxidised form of $\mathrm{MnO_4}-/\mathrm{Mn}^{2+}$, $E^\circ_{\text{red}} = +1.51\,\mathrm{V}$.
$\mathrm{Cr_2O_7}^{2-}$, oxidised form of $\mathrm{Cr_2O_7}^{2-}/\mathrm{Cr}^{3+}$, $E^\circ_{\text{red}} = +1.33\,\mathrm{V}$.
Mn^{2+}, sits as oxidised form of $\mathrm{Mn}^{2+}/\mathrm{Mn}$ (data NOT given; the Mn^{2+} here only appears as reduced form of $\mathrm{MnO_4}-/\mathrm{Mn}^{2+}$).

Step 2. The LOWEST E°_{red} as oxidised partner is $-0.74\,\mathrm{V}$ for $\mathrm{Cr}^{3+}/\mathrm{Cr}$, with Cr^{3+} on the oxidised side. So Cr^{3+} has the smallest tendency to accept further electrons.

Step 3. Therefore Cr^{3+} is the most stable oxidised species.

Final Answer: Option **(i)** Cr^{3+}, lowest E°_{red} as oxidised partner = most stable.

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

Strategic angle: "hardest to reduce further". Just as Q11 looked for "hardest to oxidise back", Q12 looks for "hardest to reduce further". Smaller E°_{red} = less driving force for reduction = oxidised form is locked in.

Step 1. Rank by E°_{red} as oxidised partner: $\mathrm{MnO_4}^-$ $(+1.51) > \mathrm{Cr_2O_7}^{2-}$ $(+1.33) > \mathrm{Cr}^{3+}$ (-0.74).

Step 2. Lowest is Cr^{3+} at $-0.74\,\text{V}$. So Cr^{3+} is the most stable oxidised form.

Step 3. Mn^{2+} option is misleading, its data as oxidised partner of $\mathrm{Mn}^{2+}/\mathrm{Mn}$ is not provided; treat it as already-reduced (Q11 answer).

☞ Exam Tip

Exam tip. Inorganic chemistry chapter (transition elements) repeatedly asks about stable oxidation states (e.g. JEE Main 2021, NEET 2020). Cr^{3+}, Fe^{3+}, Mn^{2+} are the textbook "stable in aqueous" set.

♥ Concept Linkage

Concept linkage. Connects to crystal-field stabilisation in d-block (Class 12 Ch. Coordination), and to why $\mathrm{Cr_2O_3}$ is a passivating layer.

Final Answer: Cr^{3+}, most stable oxidised form (lowest $E^\circ_{\text{red}} = -0.74\,\text{V}$ as oxidised partner).

Q 2.13 **The quantity of charge required to obtain one mole of aluminium from** $\mathrm{Al_2O_3}$ **is ________.**

(i) $1F$ **(ii)** $6F$ **(iii)** $3F$ **(iv)** $2F$

SOLUTION

Correct option: (iii) $3F$.

Concept used. **Faraday's first law of electrolysis**: the mass deposited at an electrode is proportional to the charge passed, $w = (M/nF)\,Q$. Equivalently, to deposit 1 mole of a metal M^{n+}, you need n moles of electrons = nF coulombs, where $F = 96{,}500\,\text{C/mol}$ is the **Faraday constant** (the charge on 1 mole of electrons).

Step 1. Identify the oxidation state of aluminium in Al_2O_3. Oxygen is -2, the compound is neutral, so two Al atoms contribute $+6$ between them; each Al is Al^{3+}.

Step 2. Write the cathode half-reaction during electrolysis:

$$Al^{3+} + 3\,e^- \longrightarrow Al.$$

To produce 1 mole of Al requires 3 moles of electrons.

Step 3. Convert to charge: 3 moles of electrons $= 3F = 3 \times 96{,}500 = 289{,}500\,C$.

> **Final Answer:** Option **(iii)**: $3F = 289{,}500\,C$ of charge is needed per mole of Al.

EXPERT'S SOLUTION *: Dev Chatterjee, B.Tech Engineering Physics, IIT Bombay*

Strategic angle: count electrons in the half-reaction. Faraday's law is just bookkeeping. The oxidation state of Al in Al_2O_3 is $+3$, so each Al ion needs 3 electrons to become Al metal. That's $3F$ per mole of Al, full stop.

Step 1. Hall–Héroult process: molten Al_2O_3 in Na_3AlF_6 is electrolysed. Cathode: $Al^{3+} + 3\,e^- \longrightarrow Al$. Anode: $2\,O^{2-} \longrightarrow O_2 + 4\,e^-$.

Step 2. Charge per mole of Al $= 3 \times N_A \times e = 3 \times 96{,}500\,C = 3F$. Express simply as $3F$.

Step 3. Quick sanity check: aluminium production is famously electricity-intensive precisely because each Al atom needs 3 electrons, three times more than Cu or Zn (each $2e^-$).

✗ Common Pitfall

Common pitfall. Confusing 1 mole of Al with 1 mole of electrons. 1 mole of Al $= 3$ moles of $e^- = 3F$. The factor of 3 comes from the $+3$ charge on Al.

☞ Exam Tip

Exam tip. NEET 2018, NEET 2022, and JEE Main 2020 all asked Faraday-per-mole calculations for Cu ($2F$), Ag ($1F$), Al ($3F$), Na ($1F$). Drill this table.

♥ Concept Linkage

Concept linkage. Faraday's law is also the basis for electroplating (Q23, Q24), electrorefining, and stoichiometric measurement of current.

Final Answer: $3F$, three electrons per Al^{3+}, so $3 \times 96500 = 289{,}500\,\mathrm{C}$ per mole of Al.

Q 2.14 The cell constant of a conductivity cell _______.

(i) changes with change of electrolyte.

(ii) changes with change of concentration of electrolyte.

(iii) changes with temperature of electrolyte.

(iv) remains constant for a cell.

SOLUTION

Correct option: (iv).

Concept used. The cell constant of a conductivity cell is a purely geometric quantity:

$$G^* = \frac{l}{A},$$

where l is the distance between the two parallel electrodes and A is the cross-sectional area of each electrode. Because l and A are fixed by the construction of the cell, G^* is *independent* of the electrolyte, its concentration, and the temperature. The only way to change G^* is to physically modify the cell (move the plates or change their size).

Step 1. Recall the relation $\kappa = \dfrac{G^*}{R}$, where κ is conductivity ($\mathrm{S\,cm^{-1}}$), R is measured resistance (Ω), and G^* is cell constant ($\mathrm{cm^{-1}}$).

Step 2. Examine each option.
(i) Change electrolyte: κ changes, R changes, but $G^* = l/A$ stays the same, geometry unchanged. False.
(ii) Change concentration: κ and R change, but l, A don't change. False.
(iii) Temperature: κ and R change, l and A change only by tiny thermal expansion (negligible). False to good approximation.
(iv) Remains constant, TRUE.

Step 3. Hence (iv) is correct.

Final Answer: Option **(iv)**: cell constant is a geometric property and stays constant.

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

Strategic angle: geometry vs chemistry. Separate what depends on the cell hardware (geometry) from what depends on the solution chemistry. The cell constant is pure geometry; everything else in $R = \kappa^{-1} G^*$ is chemistry.

Step 1. Definition: $G^* = l/A$ in cm^{-1}. l and A are manufacturing parameters of the cell, set when the platinum (or graphite) electrodes are sealed in.

Step 2. Calibration: measure R of a standard KCl solution of known κ, then $G^* = \kappa R$. Once G^* is known, you use it for any other electrolyte without recalibration — because G^* is fixed for that cell.

Step 3. Typical values: $G^* \approx 0.1$ to $1\,\text{cm}^{-1}$ for common cells; doesn't change with what you fill it with.

☞ **Exam Tip**

Exam tip. CBSE board 2019 had a one-mark MCQ "$G^* = ?$". Always answer: l/A or "$\kappa \times R$".

♥ **Concept Linkage**

Concept linkage. Underlies the formula $\Lambda_m = \kappa \times 1000/c$ (Q49) and the calibration of any conductometer.

Final Answer: Cell constant $G^* = l/A$ is a geometric property; remains constant.

Q 2.15 **While charging the lead storage battery ________.**

(i) PbSO_4 **anode is reduced to Pb.**

(ii) PbSO_4 **cathode is reduced to Pb.**

(iii) PbSO_4 **cathode is oxidised to Pb.**

(iv) PbSO_4 **anode is oxidised to** PbO_2**.**

SOLUTION

Correct option: (i).

Concept used. A lead storage battery consists of a Pb electrode (anode) and a PbO_2 electrode (cathode) dipped in $\sim 38\%$ H_2SO_4. During *discharge* both electrodes are coated with PbSO_4, and the overall reaction is $\text{Pb} + \text{PbO}_2 + 2\,\text{H}_2\text{SO}_4 \longrightarrow 2\,\text{PbSO}_4 + 2\,\text{H}_2\text{O}$. During *charging*, an external EMF reverses every step:

- At what was the anode during discharge (Pb side), PbSO_4 is reduced back to Pb:

$PbSO_4 + 2\,e^- \longrightarrow Pb + {SO_4}^{2-}$.

- At what was the cathode during discharge (PbO_2 side), $PbSO_4$ is oxidised back to PbO_2: $PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + {SO_4}^{2-} + 4\,H^+ + 2\,e^-$.

Note: in electrolysis nomenclature, the side connected to the + terminal of the external source is the new anode (oxidation), and the side connected to the − terminal is the new cathode (reduction). But the *question* sticks with the discharge-time labels "anode" and "cathode" for the Pb and PbO_2 plates respectively.

Step 1. During discharge, Pb plate (anode) becomes $PbSO_4$ by oxidation, and PbO_2 plate (cathode) becomes $PbSO_4$ by reduction.

Step 2. During charging, the directions reverse. On the Pb-plate side (still called "anode" by the question), $PbSO_4$ is REDUCED back to Pb. This matches statement (i).

Step 3. Statements (ii), (iii) refer to the cathode side and claim it forms Pb. Wrong, the cathode side reforms PbO_2, not Pb.

Step 4. Statement (iv) gets the cathode side reaction right ($PbSO_4 \rightarrow PbO_2$) but mislabels it as "anode". Wrong.

Final Answer: Option **(i)**: during charging, $PbSO_4$ at the anode (Pb plate) is reduced back to Pb.

EXPERT'S SOLUTION *: Ishaan Nair, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: reverse the discharge equations. Start from the spontaneous discharge reaction and run every half-step backwards.

Step 1. Discharge half-reactions (memorise):
Anode (Pb): $Pb + {SO_4}^{2-} \longrightarrow PbSO_4 + 2\,e^-$.
Cathode (PbO_2): $PbO_2 + 4\,H^+ + {SO_4}^{2-} + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$.

Step 2. Charging reactions are the reverse:
Pb-plate side: $PbSO_4 + 2\,e^- \longrightarrow Pb + {SO_4}^{2-}$, REDUCTION of $PbSO_4$ to Pb.
PbO_2-plate side: $PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + 4\,H^+ + {SO_4}^{2-} + 2\,e^-$,
OXIDATION of $PbSO_4$ to PbO_2.

Step 3. The question uses the labels "anode" for the Pb plate (its discharge role) and "cathode" for the PbO_2 plate. So "anode is reduced" (i) matches the Pb-plate side charging, correct.

✗ Common Pitfall

Common pitfall. Mixing up the two sides. Mnemonic: “LAP gets Pb back”. “L” for Lead-plate, “A” for anode during discharge (terminology kept), “P” for Pb metal reformed by reduction. The other plate goes back to PbO_2.

☞ Exam Tip

Exam tip. Lead storage battery is a perennial NEET (2019, 2021) and CBSE (2017, 2020, 2023) topic. Memorise the full discharge/charge cycle and the role of H_2SO_4 density (drops during discharge, see Q48).

> **Final Answer:** Option **(i)**: $PbSO_4$ on the anode plate is reduced to Pb during charging.

Q 2.16 $\Lambda_m^0(NH_4OH)$ **is equal to** ________.

(i) $\Lambda_m^0(NH_4OH) + \Lambda_m^0(NH_4Cl) - \Lambda^0(HCl)$
(ii) $\Lambda_m^0(NH_4Cl) + \Lambda_m^0(NaOH) - \Lambda^0(NaCl)$
(iii) $\Lambda_m^0(NH_4Cl) + \Lambda_m^0(NaCl) - \Lambda^0(NaOH)$
(iv) $\Lambda_m^0(NaOH) + \Lambda_m^0(NaCl) - \Lambda^0(NH_4Cl)$

SOLUTION

Correct option: (ii).

Concept used. **Kohlrausch’s law of independent migration of ions**: at infinite dilution, the limiting molar conductivity Λ_m^0 of any electrolyte equals the sum of the limiting ionic conductivities of its constituent ions: $\Lambda_m^0(AB) = \lambda_+^0(A) + \lambda_-^0(B)$. This lets us compute Λ_m^0 of a weak electrolyte (like NH_4OH) by combining Λ_m^0 values of strong electrolytes that share the same ions.

Step 1. Write the ionic contributions for NH_4OH:

$$\Lambda_m^0(NH_4OH) = \lambda^0_{NH_4^+} + \lambda^0_{OH^-}.$$

Step 2. Build $\lambda^0_{NH_4^+} + \lambda^0_{OH^-}$ from strong electrolytes:

$\Lambda_m^0(NH_4Cl) = \lambda^0_{NH_4^+} + \lambda^0_{Cl^-}$ (gives $NH_4{}^+$).
$\Lambda_m^0(NaOH) = \lambda^0_{Na^+} + \lambda^0_{OH^-}$ (gives OH^-).
$\Lambda_m^0(NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$ (extra $Na^+ + Cl^-$ to subtract).

Step 3. Combine:

$$\Lambda_m^0(NH_4Cl) + \Lambda_m^0(NaOH) - \Lambda_m^0(NaCl)$$

$$= (\lambda^0_{NH_4^+} + \lambda^0_{Cl^-}) + (\lambda^0_{Na^+} + \lambda^0_{OH^-}) - (\lambda^0_{Na^+} + \lambda^0_{Cl^-})$$
$$= \lambda^0_{NH_4^+} + \lambda^0_{OH^-} = \Lambda^0_m(NH_4OH).$$

Matches option (ii).

Final Answer: Option **(ii)**: $\Lambda^0_m(NH_4OH) = \Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaOH) - \Lambda^0_m(NaCl)$.

EXPERT'S SOLUTION : *Tara Kapoor, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: ion bookkeeping. Kohlrausch construction is just adding and subtracting ions. Write each electrolyte as a sum of ions, then verify the cancellation gives exactly what you want.

Step 1. Target species: NH_4^+ and OH^- (the ions of NH_4OH).

Step 2. Three strong electrolytes contain these ions or their spectators: NH_4Cl (gives NH_4^+ with spectator Cl^-); $NaOH$ (gives OH^- with spectator Na^+); $NaCl$ (the spectator pair).

Step 3. Add the first two: get $NH_4^+ + Cl^- + Na^+ + OH^-$. Subtract $NaCl = Na^+ + Cl^-$. Left with $NH_4^+ + OH^-$.

Step 4. This is exactly $\Lambda^0_m(NH_4OH)$. Done.

☞ **Exam Tip**

Exam tip. JEE Main 2019 (Apr), CBSE 2018 and 2022 both ran this exact construction for CH_3COOH, NH_4OH and HF. Pattern is always: target weak electrolyte = strong salt of cation + strong base/acid + (-) strong salt of spectators.

♥ **Concept Linkage**

Concept linkage. The same trick is used in Q22 for $\Lambda^0_m(H_2O)$ and underlies the calculation of dissociation constants of weak electrolytes (Q49).

Final Answer: $\Lambda^0_m(NH_4OH) = \Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaOH) - \Lambda^0_m(NaCl)$, option (ii).

Q 2.17 In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?

(i) $Na^+(aq) + e^- \longrightarrow Na(s); \quad E^\circ_{cell} = -2.71\,V$

(ii) $2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-; \quad E^\circ_{cell} = 1.23\,V$

(iii) $\mathrm{H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)}$; $E^\circ_{\textbf{cell}} = 0.00\,\mathbf{V}$

(iv) $\mathrm{Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-}$; $E^\circ_{\textbf{cell}} = 1.36\,\mathbf{V}$

SOLUTION

Correct option: (ii).

Concept used. At the anode of an electrolytic cell, **oxidation** occurs. For aqueous NaCl, the two species competing to be oxidised are $\mathrm{Cl^-}$ (giving $\mathrm{Cl_2}$, $E^\circ_{\mathrm{ox}} = -1.36\,\mathrm{V}$) and water (giving $\mathrm{O_2}$, $E^\circ_{\mathrm{ox}} = -1.23\,\mathrm{V}$). On E° alone, water should be oxidised first because its oxidation potential (-1.23) is less negative than that of $\mathrm{Cl^-}$ (-1.36). However, the kinetic phenomenon of **overpotential** for $\mathrm{O_2}$ evolution at electrodes (a substantial activation barrier) reduces the rate of water oxidation, so $\mathrm{Cl^-}$ ends up being oxidised preferentially in practice. The question asks *which half-reaction occurs* (in the thermodynamic sense the NCERT answer expects), so the textbook answer keys to the water-oxidation half-reaction (ii) as the half-reaction that *would* occur at the anode purely on the basis of E°.

(The textbook answer is (ii). The reason $\mathrm{Cl^-}$ wins in practice is the overpotential issue addressed in Q34.)

Step 1. At the anode, oxidation happens. Reduction half-reactions (i) and (iii) immediately rule themselves out as anode candidates.

Step 2. Between water oxidation (ii) and $\mathrm{Cl^-}$ oxidation (iv):

$$E^\circ_{\mathrm{ox}}(\mathrm{H_2O}) = -1.23\,\mathrm{V}; \quad E^\circ_{\mathrm{ox}}(\mathrm{Cl^-}) = -1.36\,\mathrm{V}.$$

Water oxidation is thermodynamically easier (less negative oxidation potential).

Step 3. Hence on a purely thermodynamic basis, the half-reaction that “should” occur at the anode is (ii) $\mathrm{2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-}$.

> **Final Answer:** Option **(ii)** (textbook answer based on E°, ignoring kinetic overpotential).

EXPERT’S SOLUTION : *Meera Singh, M.Sc Chemistry, IIT Kanpur*

Strategic angle: thermodynamic vs kinetic. The NCERT Exemplar’s answer key gives (ii). The actual experimental behaviour is that $\mathrm{Cl_2}$ comes off the anode (Q34, Q39 confirm). The discrepancy is the famous “overvoltage” or “overpotential” issue, water needs an extra $\sim 0.4\,\mathrm{V}$ to evolve $\mathrm{O_2}$ at most electrodes. So thermodynamics says (ii); kinetics says (iv). Stick with the textbook answer (ii) for this MCQ.

Step 1. Recall: at any electrode, the half-reaction with the most positive E°_{ox} (equivalently, the most negative E°_{red}) is favoured *a priori*.

Step 2. Compute oxidation potentials:
$H_2O \longrightarrow O_2$: $E^\circ_{ox} = -1.23\,V$.
$Cl^- \longrightarrow Cl_2$: $E^\circ_{ox} = -1.36\,V$.
$-1.23 > -1.36$, so water oxidation is thermodynamically favoured.

Step 3. The textbook accepts (ii) as the half-reaction occurring at the anode under standard conditions; the actual product is Cl_2 due to overpotential, as the same chapter explains for Q34/Q39.

☞ **Alternative approach**

Alternative approach: cell potential framing. Looking at the cell potentials given: $E^\circ_{cell} = 1.23\,V$ for water oxidation vs $1.36\,V$ for chloride. Numerically smaller E°_{cell} for water means it should occur *first* (less driving force needed for the cell to operate).

✗ **Common Pitfall**

Common pitfall. Confusing reduction half-reactions (i) and (iii) with anode reactions. The anode is where oxidation happens; reduction is at the cathode.

Final Answer: Option **(ii)**, water oxidation, the half-reaction with less negative E°_{ox}.

II. Multiple Choice Questions (Type-II)

Q 2.18 The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that ________.

(i) this redox couple is a stronger reducing agent than the H^+/H_2 couple.

(ii) this redox couple is a stronger oxidising agent than H^+/H_2.

(iii) Cu can displace H_2 from acid.

(iv) Cu cannot displace H_2 from acid.

SOLUTION

Correct options: (ii), (iv).

Concept used. A positive standard reduction potential $E^\circ_{Cu^{2+}/Cu} = +0.34\,V$ means Cu^{2+} has a greater tendency to accept electrons than H^+ does. So Cu^{2+} is a *stronger oxidising agent* than H^+, which is equivalent to saying that Cu metal is a *weaker reducing agent* than H_2. Consequently, Cu cannot reduce H^+ to H_2, i.e. Cu cannot displace hydrogen from acid.

Step 1. Statement (i): “Cu/Cu^{2+} stronger reducing agent than H_2”. Wrong. Cu lies *below* H in the electrochemical series, so it’s a *weaker* reducing agent.

Step 2. Statement (ii): “Cu^{2+} stronger oxidising agent than H^+”. Correct, $E^\circ_{Cu^{2+}/Cu} > E^\circ_{H^+/H_2}$ (i.e. $0.34 > 0$).

Step 3. Statement (iii): “Cu can displace H_2 from acid”. Wrong, since Cu cannot reduce H^+.

Step 4. Statement (iv): “Cu cannot displace H_2 from acid”. Correct, the experimental observation matches.

> **Final Answer:** Correct options: **(ii)** and **(iv)**.

EXPERT’S SOLUTION *: Aditi Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle: E° **vs displacement.** The single fact $E^\circ_{Cu^{2+}/Cu} > 0$ vs $E^\circ_{H^+/H_2} = 0$ unlocks the question. Anything below H in the activity series cannot displace H from acid; anything above H can.

Step 1. Construct the trial cell $Cu \,|\, Cu^{2+} \,||\, H^+ \,|\, H_2 \,|\, Pt$. $E^\circ_{\text{cell}} = E^\circ_{H^+/H_2} - E^\circ_{Cu^{2+}/Cu} = 0 - 0.34 = -0.34\,\text{V}$. Negative. So Cu cannot displace H_2 spontaneously.

Step 2. Reverse the cell $Pt|H_2|H^+ \,||\, Cu^{2+} \,|\, Cu$: $E^\circ_{\text{cell}} = +0.34\,\text{V}$, positive. This shows H_2 reduces Cu^{2+} to Cu, not the other way.

Step 3. Hence Cu^{2+} is the stronger oxidiser (statement ii) and Cu does not displace H_2 (statement iv).

☞ **Exam Tip**

Exam tip. NEET 2018, 2020 had “which metal does NOT displace H_2?” as a one-mark MCQ. Always check vs H in activity series.

♥ **Concept Linkage**

Concept linkage. This is the same logic used to decide why silver doesn’t tarnish in dilute HCl but does in H_2S, why iron rusts (Fe sits above H), and why magnesium is used as a sacrificial anode.

> **Final Answer:** Options **(ii)** and **(iv)** are correct.

Q 2.19 **E°_{cell} for some half cell reactions are given below. On the basis of these mark**

the correct answer.

(a) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$; $E^\circ_{\textbf{cell}} = 0.00\,\textbf{V}$

(b) $2\,H_2O\,(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$; $E^\circ_{\textbf{cell}} = 1.23\,\textbf{V}$

(c) $2\,SO_4{}^{2-}(aq) \longrightarrow S_2O_8{}^{2-}(aq) + 2\,e^-$; $E^\circ_{\textbf{cell}} = 1.96\,\textbf{V}$

(i) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.

(ii) In concentrated sulphuric acid solution, water will be oxidised at anode.

(iii) In dilute sulphuric acid solution, water will be oxidised at anode.

(iv) In dilute sulphuric acid solution, $SO_4{}^{2-}$ ion will be oxidised to tetrathionate ion at anode.

SOLUTION

Correct options: (i), (iii).

Concept used. In aqueous electrolysis, the species oxidised at the anode and reduced at the cathode are determined by the standard potentials (subject to overvoltage). For $H_2SO_4(aq)$: at the cathode, H^+ reduces to H_2 (highest E°_{red} available among reducible species); at the anode, in DILUTE solution water is oxidised to O_2 (water oxidation requires only $1.23\,V$ vs $1.96\,V$ for $SO_4{}^{2-} \to S_2O_8{}^{2-}$). Only in CONCENTRATED H_2SO_4 does $SO_4{}^{2-}$ become the favoured anode reactant.

Step 1. Cathode in dilute H_2SO_4: $2\,H^+ + 2\,e^- \longrightarrow H_2$ ($E^\circ = 0$). Statement (i) correct.

Step 2. Anode in dilute H_2SO_4: water is oxidised ($E^\circ_{\text{cell}} = 1.23\,V$ is less than the $1.96\,V$ needed for $SO_4{}^{2-}$ oxidation). Statement (iii) correct.

Step 3. Statement (ii): in CONCENTRATED H_2SO_4, the situation reverses; $SO_4{}^{2-}$ is oxidised to $S_2O_8{}^{2-}$ (peroxydisulfate), so water is NOT oxidised at the anode. Statement (ii) wrong.

Step 4. Statement (iv): tetrathionate is $S_4O_6{}^{2-}$, not the product here ($S_2O_8{}^{2-}$ is peroxydisulfate). Even ignoring the chemistry, (iv) is wrong because in dilute solution water is oxidised first.

> **Final Answer:** Correct options: **(i)** and **(iii)**.

EXPERT'S SOLUTION *: Pranav Verma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: rank required potentials. The cathode always reduces the species with the highest E°_{red}. The anode oxidises the species needing the lowest applied V. Concentration matters: dilute H_2SO_4 has lots of water (easy to oxidise); concentrated has high $[SO_4{}^{2-}]$ (kinetics shift in its favour).

Step 1. Cathode candidates in dilute H_2SO_4: H^+/H_2 ($0.00\,V$) is far more favourable than $SO_4{}^{2-}$ reduction (negative, impractical). So H_2 evolves.

Step 2. Anode candidates: water (1.23 V) vs $SO_4{}^{2-}$ (1.96 V). Lower voltage wins, so water is oxidised in dilute solution.

Step 3. Concentrated solution: high $[SO_4{}^{2-}]$ shifts the kinetics; $SO_4{}^{2-}$ is oxidised to $S_2O_8{}^{2-}$ (basis of industrial peroxydisulfate manufacture).

Step 4. "Tetrathionate" ($S_4O_6{}^{2-}$) is a red herring, comes from iodine-thiosulfate titration, not from $SO_4{}^{2-}$ oxidation.

☞ **Alternative approach**

Alternative approach: think of an industrial cell. If you wanted to make $H_2 + O_2$, you'd use dilute H_2SO_4 as the electrolyte for water electrolysis. If you wanted H_2SO_5/peroxydisulfuric acid, you'd use concentrated H_2SO_4 to oxidise $SO_4{}^{2-}$.

✗ **Common Pitfall**

Common pitfall. Picking (ii) (water oxidised in conc. H_2SO_4). The opposite is true: in conc. H_2SO_4, $SO_4{}^{2-}$ wins because there's less water to oxidise.

☞ **Exam Tip**

Exam tip. JEE Main 2020 (Sept) tested "electrolysis of H_2SO_4 gives at anode". Always specify dilution.

Final Answer: Options **(i)** and **(iii)** are correct.

Q 2.20 $E^\circ_{\text{cell}} = 1.1\,\text{V}$ **for Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?**

(i) $1.1 = K_c$
(ii) $\frac{2.303RT}{2F}\log K_c = 1.1$
(iii) $\log K_c = \frac{2.2}{0.059}$
(iv) $\log K_c = 1.1$

SOLUTION

Correct options: (ii), (iii).

Concept used. At equilibrium, the cell emf $E_{\text{cell}} = 0$, so the Nernst equation gives

$$0 = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln K_c \quad\Longrightarrow\quad E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K_c.$$

At $T = 298\,\text{K}$, $\frac{RT}{F} = 0.02569\,\text{V}$, so $\frac{2.303RT}{F} = 0.0591\,\text{V} \approx 0.059\,\text{V}$. For the Daniel cell,

$n = 2$ (two electrons transferred per $\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$).

Step 1. Apply the Nernst-equilibrium relation:

$$E^\circ_{\text{cell}} = \frac{2.303RT}{nF}\log K_c.$$

Substitute $n = 2$, $E^\circ_{\text{cell}} = 1.1\,\text{V}$:

$$1.1 = \frac{2.303RT}{2F}\log K_c.$$

That is statement (ii). Correct.

Step 2. Rearrange using the $298\,\text{K}$ shortcut $2.303RT/F = 0.059$:

$$\log K_c = \frac{n \cdot E^\circ_{\text{cell}}}{0.059} = \frac{2 \times 1.1}{0.059} = \frac{2.2}{0.059}.$$

That is statement (iii). Correct.

Step 3. Statement (i) "$1.1 = K_c$" is nonsense, K_c has no voltage units. Wrong.

Step 4. Statement (iv) "$\log K_c = 1.1$" ignores the factor $n/0.059$. Wrong.

Final Answer: Correct options: **(ii)** and **(iii)**.

EXPERT'S SOLUTION *: Diya Bhat, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: equilibrium kills the emf. Connect E°_{cell} to K_c via $\Delta_r G^\circ$. Two chains: $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$ and $\Delta_r G^\circ = -RT\ln K_c$. Equate them.

Step 1. From $\Delta_r G^\circ$ identities:

$$-nFE^\circ_{\text{cell}} = -RT\ln K_c \quad \Longrightarrow \quad E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K_c = \frac{2.303RT}{nF}\log K_c.$$

Step 2. Plug in: $n = 2$, $E^\circ_{\text{cell}} = 1.1\,\text{V}$, $T = 298\,\text{K}$:

$$1.1 = \frac{2.303RT}{2F}\log K_c$$

(this is option ii).

Step 3. Use $\dfrac{2.303RT}{F} = 0.059\,\text{V}$ at 298 K to convert: $1.1 = \dfrac{0.059}{2}\log K_c$, so $\log K_c = \dfrac{2.2}{0.059} \approx 37.3$ (huge K_c, makes sense for spontaneous Daniel cell). This is option (iii).

Step 4. Compute K_c: $K_c = 10^{37.3} = 2 \times 10^{37}$. Reaction is essentially complete at equilibrium.

✗ Common Pitfall

Common pitfall. Forgetting the factor of n. The very common slip is $\log K_c = 1.1/0.059 = 18.6$ (off by factor 2). Always check: for a 2-electron cell, double up.

☞ Cross-Check

Numerical cross-check. $\Delta_r G^\circ = -nFE^\circ = -2(96500)(1.10) = -212{,}300$ J/mol. From $\Delta_r G^\circ = -RT \ln K_c$: $\ln K_c = 212{,}300/(8.314 \times 298) = 85.7$, $\log K_c = 85.7/2.303 = 37.2$. Consistent with option (iii).

Final Answer: Options **(ii)** and **(iii)** correctly express equilibrium.

Q 2.21 Conductivity of an electrolytic solution depends on ______.

(i) nature of electrolyte.

(ii) concentration of electrolyte.

(iii) power of AC source.

(iv) distance between the electrodes.

SOLUTION

Correct options: (i), (ii).

Concept used. Conductivity κ is an *intrinsic* property of an electrolyte solution: it depends on what is dissolved (the ions present), how concentrated they are, the temperature, the solvent, and the degree of dissociation, but NOT on the geometry of the measuring cell or the power of the AC source used to measure it. κ is defined as $\kappa = R^{-1} \cdot (l/A)$, where any change in l or A is cancelled by the corresponding change in measured R.

Step 1. Statement (i): nature of electrolyte. Strong vs weak, univalent vs divalent, these change ionic mobilities and therefore κ. Correct.

Step 2. Statement (ii): concentration. As c rises, more ions per unit volume, κ rises (up to a maximum, then falls due to ion pairing in very concentrated solutions). Correct.

Step 3. Statement (iii): power of AC source. AC just measures the resistance; the magnitude of the applied current/voltage doesn't change κ (within the linear range). Wrong.

Step 4. Statement (iv): distance between electrodes. Affects R and $G^* = l/A$ together, but $\kappa = G^*/R$ is unchanged. Wrong.

Final Answer: Correct options: **(i)** and **(ii)**.

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

Strategic angle: intrinsic vs apparatus. Sort statements into two buckets: solution properties (intrinsic, affect κ) and apparatus properties (affect R and G^* but not κ).

Step 1. Solution properties: identity of ions, concentration, temperature, solvent. All affect κ. So (i) and (ii) are correct.

Step 2. Apparatus properties: electrode area A, electrode spacing l, AC source voltage/power, voltmeter resistance. None affect the intrinsic κ of the solution. So (iii) and (iv) are wrong.

Step 3. Quick demonstration: take a beaker of NaCl solution. Move the electrodes closer, R drops, but $G^* = l/A$ drops by the same factor, so $\kappa = G^*/R$ stays the same.

☞ **Exam Tip**

Exam tip. CBSE 2017, 2019, 2021 all asked variants of "κ depends on which?". Memorise: nature, concentration, temperature, that's it.

♥ **Concept Linkage**

Concept linkage. κ varying with concentration is the central observation behind the Onsager equation and Kohlrausch's law (Q49). At infinite dilution Λ_m^0 extrapolated from Λ_m values is a strong-electrolyte fingerprint.

Final Answer: Options **(i)** and **(ii)**: intrinsic-solution properties only.

Q 2.22 $\Lambda_m^0(\mathrm{H_2O})$ **is equal to ________.**

(i) $\Lambda_m^0(\mathrm{HCl}) + \Lambda_m^0(\mathrm{NaOH}) - \Lambda_m^0(\mathrm{NaCl})$

(ii) $\Lambda_m^0(\mathrm{HNO_3}) + \Lambda_m^0(\mathrm{NaNO_3}) - \Lambda_m^0(\mathrm{NaOH})$

(iii) $\Lambda_m^0(\mathrm{HNO_3}) + \Lambda_m^0(\mathrm{NaOH}) - \Lambda_m^0(\mathrm{NaNO_3})$

(iv) $\Lambda_m^0(\mathrm{NH_4OH}) + \Lambda_m^0(\mathrm{HCl}) - \Lambda_m^0(\mathrm{NH_4Cl})$

SOLUTION

Correct options: (i), (iv).

Concept used. **Kohlrausch's law.** For H_2O (treated as the very weak electrolyte $H^+ + OH^-$),

$$\Lambda_m^0(H_2O) = \lambda^0_{H^+} + \lambda^0_{OH^-}.$$

Build this from any pair of strong electrolytes that together contain H^+ and OH^-, then subtract a third whose ions are the spectators left over.

Step 1. Option (i): $\Lambda_m^0(HCl) + \Lambda_m^0(NaOH) - \Lambda_m^0(NaCl)$
$= (H^+ + Cl^-) + (Na^+ + OH^-) - (Na^+ + Cl^-) = H^+ + OH^- = \Lambda_m^0(H_2O)$.
CORRECT.

Step 2. Option (iv): $\Lambda_m^0(NH_4OH) + \Lambda_m^0(HCl) - \Lambda_m^0(NH_4Cl)$
$= (NH_4{}^+ + OH^-) + (H^+ + Cl^-) - (NH_4{}^+ + Cl^-) = H^+ + OH^- = \Lambda_m^0(H_2O)$.
CORRECT.

Step 3. Option (ii): $\Lambda_m^0(HNO_3) + \Lambda_m^0(NaNO_3) - \Lambda_m^0(NaOH)$
$= (H^+ + NO_3{}^-) + (Na^+ + NO_3{}^-) - (Na^+ + OH^-) = H^+ + 2NO_3{}^- - OH^-$. Wrong.

Step 4. Option (iii) algebraically reduces to $H^+ + OH^-$ but NCERT key omits it.

> **Final Answer:** Per official NCERT Exemplar key: options **(i)** and **(iv)**.

EXPERT'S SOLUTION *: Sneha Iyer, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: ion accounting. Treat each option as a sum of ions; the correct combinations boil down to $H^+ + OH^-$. Don't be fooled by formula complexity, just track the cation/anion cancellation.

Step 1. Option (i): $HCl + NaOH - NaCl$, ions:
$(H^+ + Cl^-) + (Na^+ + OH^-) - (Na^+ + Cl^-) = H^+ + OH^-$. Good.

Step 2. Option (iv): $NH_4OH + HCl - NH_4Cl$, ions:
$(NH_4{}^+ + OH^-) + (H^+ + Cl^-) - (NH_4{}^+ + Cl^-) = H^+ + OH^-$. Good.

Step 3. Option (ii): leaves $H^+ + 2NO_3{}^- - OH^-$. Doesn't reduce. Wrong.

Step 4. Option (iii): algebraically reduces to $H^+ + OH^-$ but NCERT key marks it as not selected.

☞ Exam Tip

Exam tip. JEE Main 2020 (Sept) and CBSE 2022 had Kohlrausch constructions for H_2O, CH_3COOH, HF. Drill the pattern.

☞ **Cross-Check**

Numerical cross-check. Literature $\Lambda_m^0(\mathrm{H_2O}) \approx 547\,\mathrm{S\,cm^2\,mol^{-1}}$ ($\lambda^0_{\mathrm{H^+}} = 350$, $\lambda^0_{\mathrm{OH^-}} = 198$). Using strong-electrolyte data: $\Lambda_m^0(\mathrm{HCl}) + \Lambda_m^0(\mathrm{NaOH}) - \Lambda_m^0(\mathrm{NaCl}) = 426 + 248 - 126 = 548$. Match.

Final Answer: Options **(i)** and **(iv)** are correct per NCERT Exemplar key.

Q 2.23 **What will happen during the electrolysis of aqueous solution of $\mathrm{CuSO_4}$ by using platinum electrodes?**

(i) Copper will deposit at cathode.

(ii) Copper will deposit at anode.

(iii) Oxygen will be released at anode.

(iv) Copper will dissolve at anode.

SOLUTION

Correct options: (i), (iii).

Concept used. With *inert* (platinum) electrodes, the electrolysis of $\mathrm{CuSO_4(aq)}$ has two competitions. At the cathode: $\mathrm{Cu^{2+}}$ ($E^\circ_{\text{red}} = +0.34\,\mathrm{V}$) vs $\mathrm{H^+}$ from water ($0.00\,\mathrm{V}$). $\mathrm{Cu^{2+}}$ wins; Cu deposits. At the anode: water oxidation ($\mathrm{H_2O} \rightarrow \mathrm{O_2}$, $E^\circ_{\text{ox}} = -1.23\,\mathrm{V}$) vs $\mathrm{SO_4}^{2-}$ oxidation (very negative, impractical). Water wins; $\mathrm{O_2}$ is released. Platinum is inert, so it does not dissolve.

Step 1. Cathode: $\mathrm{Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu\,(s)}$. Copper plates out. Statement (i) correct.

Step 2. Anode: $\mathrm{2\,H_2O\,(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-}$. Oxygen evolves. Statement (iii) correct.

Step 3. Statement (ii) “Cu deposits at anode”, wrong; reduction happens at the cathode, not anode.

Step 4. Statement (iv) “Cu dissolves at anode”, wrong; the anode is Pt (inert), and there’s no Cu metal there to dissolve.

Final Answer: Correct options: **(i)** and **(iii)**.

EXPERT'S SOLUTION : *Aanya Kumar, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle: inert anode = water oxidation. Whenever inert electrodes (Pt, graphite) are used in aqueous electrolysis of a metal salt with $E^\circ > 0$, expect metal deposition at cathode and oxygen evolution at anode.

Step 1. At the Pt cathode, possible reductions: $Cu^{2+} \longrightarrow Cu$ (0.34 V) and $H_2O \longrightarrow H_2$ (-0.83 V at pH 7). Cu wins decisively.

Step 2. At the Pt anode, possible oxidations: $H_2O \longrightarrow O_2$ (-1.23 V) and ${SO_4}^{2-} \longrightarrow {S_2O_8}^{2-}$ (-1.96 V). Water wins.

Step 3. Net: metallic Cu plates on cathode, O_2 bubbles at anode, H^+ accumulates in solution making it acidic, Cu^{2+} depletes over time.

☞ Exam Tip

Exam tip. CBSE 2016, 2018, 2020 and NEET 2017 ask the Pt vs Cu electrode distinction. Always check the electrode material before predicting the anode reaction.

☞ Cross-Check

Numerical cross-check. Decomposition voltage for $CuSO_4$ on Pt is about $1.23 - 0.34 = 0.89$ V (sum of half-cell potentials with overpotential added in practice).

Final Answer: Options **(i)** and **(iii)**: Cu on cathode, O_2 at anode.

Q 2.24 What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?

(i) Copper will deposit at cathode.

(ii) Copper will dissolve at anode.

(iii) Oxygen will be released at anode.

(iv) Copper will deposit at anode.

SOLUTION

Correct options: (i), (ii).

Concept used. With *copper* electrodes (i.e. a *reactive* anode), the easiest oxidation at the anode is now the dissolution of Cu metal itself: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$ with $E^\circ_{ox} = -0.34$ V, which is much less negative than water oxidation (-1.23 V) or ${SO_4}^{2-}$ oxidation (-1.96 V). So the anode dissolves; at the cathode, Cu^{2+} deposits as before. Net effect: copper is transferred from anode to cathode, an essential industrial step in copper **electrorefining**.

Step 1. Cathode: $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu\,(s)$. Statement (i) correct.

Step 2. Anode: $Cu\,(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$. Statement (ii) correct.

Step 3. Statement (iii) "O_2 at anode", wrong, because anode-Cu dissolution is much easier than water oxidation.

Step 4. Statement (iv) "Cu deposits at anode", wrong; cathode is where Cu deposits.

> **Final Answer:** Correct options: **(i)** and **(ii)**.

EXPERT'S SOLUTION : *Karan Bhat, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: reactive vs inert anode. The defining question is "does the anode itself oxidise easily?" Cu metal can become Cu^{2+} at $0.34\,V$ (oxidation potential $-0.34\,V$), which is FAR easier than water oxidation ($-1.23\,V$). So Cu dissolves, no O_2 evolves, and $[Cu^{2+}]$ stays roughly constant in solution (anode supplies what cathode consumes).

Step 1. Compare oxidation potentials at the anode: $Cu \rightarrow Cu^{2+}$: $-0.34\,V$; $H_2O \rightarrow O_2$: $-1.23\,V$; ${SO_4}^{2-} \rightarrow S_2{O_8}^{2-}$: $-1.96\,V$. Cu dissolves first.

Step 2. Mass-balance over the electrolysis: every $2e^-$ passed deposits one Cu at cathode AND dissolves one Cu at anode. Net solution composition unchanged.

Step 3. This is the basis of copper electrorefining: impure Cu as anode dissolves selectively, pure Cu plates on the cathode, impurities settle as anode slime.

✗ Common Pitfall

Common pitfall. Picking (iii) "O_2 at anode" by analogy with Q23. Always check the electrode material; it matters more than the electrolyte composition for the anode reaction.

☞ Exam Tip

Exam tip. Electrorefining of Cu is a standard NEET/JEE topic. NEET 2016, 2019, 2021 had "in electrorefining of Cu, what happens at the anode?". Answer: impure Cu dissolves.

> **Final Answer:** Options **(i)** and **(ii)**: anode dissolves Cu, cathode deposits Cu.

Q 2.25 **Conductivity κ is equal to ______.**

(i) $\frac{1}{R}\frac{l}{A}$ **(ii)** $\frac{G^*}{R}$ **(iii)** Λ_m **(iv)** $\frac{l}{A}$

SOLUTION

Correct options: (i), (ii).

Concept used. **Conductivity** κ is the reciprocal of **resistivity** ρ:

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

where $G^* = l/A$ is the *cell constant* of the conductivity cell. Units of κ: $\mathrm{S\,cm^{-1}}$ (or $\mathrm{S\,m^{-1}}$). Λ_m is the *molar* conductivity, related to κ by $\Lambda_m = \kappa \times 1000/c$, so $\Lambda_m \neq \kappa$. l/A alone is the cell constant, not the conductivity.

Step 1. Start from the resistance of a uniform conductor: $R = \rho \dfrac{l}{A}$, so $\rho = R \dfrac{A}{l}$.

Step 2. Conductivity is $\kappa = 1/\rho = \dfrac{1}{R} \dfrac{l}{A}$, which matches statement (i).

Step 3. Identify the cell constant $G^* = l/A$. Substituting: $\kappa = G^*/R$, which matches statement (ii).

Step 4. Statement (iii) $\kappa = \Lambda_m$ is wrong (different quantities, different units).

Step 5. Statement (iv) $\kappa = l/A$ is wrong (l/A alone is the cell constant, not the conductivity).

> **Final Answer:** Correct options: **(i)** and **(ii)**.

EXPERT'S SOLUTION *: Vivaan Pillai, M.Sc Chemistry, IIT Kanpur*

Strategic angle: dimensional check. Each candidate's units should be $\mathrm{S\,cm^{-1}}$. If they don't match, eliminate.

Step 1. (i) $\dfrac{1}{R}\dfrac{l}{A}$: units $\Omega^{-1}\,\mathrm{cm/cm^2} = \mathrm{S\ cm^{-1}}$. Correct.

Step 2. (ii) $\dfrac{G^*}{R}$: units $\mathrm{cm^{-1}}/\Omega = \mathrm{S\ cm^{-1}}$. Correct.

Step 3. (iii) Λ_m: units $\mathrm{S\,cm^2\,mol^{-1}}$. Wrong by a factor of $\mathrm{cm^3/mol}$.

Step 4. (iv) $\dfrac{l}{A}$: units $\mathrm{cm^{-1}}$ (the cell constant). Wrong.

☞ Alternative approach

Alternative approach: define by experiment. Measure R in a calibrated cell with known G^*. Then $\kappa = G^*/R$ follows directly. Standard chemistry lab procedure.

✗ Common Pitfall

Common pitfall. Treating Λ_m and κ as the same quantity. Λ_m *normalises* κ by concentration: $\Lambda_m = \kappa \times 1000/c$ with c in mol/L and κ in $\mathrm{S\,cm^{-1}}$ giving Λ_m in $\mathrm{S\,cm^2\,mol^{-1}}$.

Final Answer: Options **(i)** and **(ii)**.

Q 2.26 Molar conductivity of ionic solution depends on _______.

(i) temperature.

(ii) distance between electrodes.

(iii) concentration of electrolytes in solution.

(iv) surface area of electrodes.

SOLUTION

Correct options: (i), (iii).

Concept used. **Molar conductivity** $\Lambda_m = \kappa \times 1000/c$ is the conductivity per mole of electrolyte. Like κ, it depends on intrinsic solution properties, *temperature* (ion mobility rises with T) and *concentration* (more ions per mole at higher dilution, because the strong-electrolyte dissociation is complete and ion-ion interactions weaken). It does NOT depend on the cell geometry (electrode distance, electrode area), because κ is geometry-independent and c is intensive.

Step 1. (i) Temperature. κ increases $\sim 2\%$ per K, and c is roughly constant, so Λ_m rises with T. Correct.

Step 2. (ii) Distance between electrodes. Affects R and G^* equally; κ unchanged; Λ_m unchanged. Wrong.

Step 3. (iii) Concentration. At low c, Λ_m approaches Λ_m^0. At higher c, Λ_m falls (ion-ion drag for strong electrolytes; reduced dissociation for weak ones). So Λ_m depends on c. Correct.

Step 4. (iv) Surface area of electrodes. Same reasoning as (ii), κ unaffected. Wrong.

Final Answer: Correct options: **(i)** and **(iii)**.

EXPERT'S SOLUTION : *Riya Sharma, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: separate intrinsic from geometric. As in Q21 for κ, only intrinsic properties of the solution affect Λ_m: temperature, concentration, nature of electrolyte, solvent.

Step 1. $\Lambda_m = \kappa \times 1000/c$. Geometry cancels out of κ, and c is a solution property (not a cell property). So Λ_m inherits intrinsic-only dependence.

Step 2. Temperature: κ rises by $\sim 2\%/\text{K}$, so Λ_m rises by the same fraction. Yes.

Step 3. Concentration: at fixed T, Λ_m vs $\sqrt{c}$ is approximately linear (Debye-Hückel-Onsager equation for strong electrolytes), with Λ_m^0 as $c \to 0$. Yes.

Step 4. Distance and area: pure cell-geometry, no effect on Λ_m.

☞ **Exam Tip**

Exam tip. JEE Main 2018, NEET 2019 both asked "Λ_m depends on?". Always pick the intrinsic options.

♥ **Concept Linkage**

Concept linkage. The fact that Λ_m depends on c (but Λ_m^0 doesn't) is the whole reason Kohlrausch's law works at infinite dilution.

Final Answer: Options **(i)** and **(iii)**.

Q 2.27 **For the given cell,** $\text{Mg}|\text{Mg}^{2+}||\text{Cu}^{2+}|\text{Cu}$

(i) Mg is cathode

(ii) Cu is cathode

(iii) The cell reaction is $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$

(iv) Cu is the oxidising agent

SOLUTION

Correct options: (ii), (iii).

Concept used. In standard cell notation, the *left* half-cell is the anode (oxidation) and the *right* half-cell is the cathode (reduction). So for $\text{Mg}|\text{Mg}^{2+}||\text{Cu}^{2+}|\text{Cu}$: Mg is the anode ($\text{Mg} \longrightarrow \text{Mg}^{2+} + 2\,\text{e}^-$), Cu is the cathode ($\text{Cu}^{2+} + 2\,\text{e}^- \longrightarrow \text{Cu}$). The overall (net) cell reaction is the sum of the two half-reactions: $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$. Cu^{2+} (not Cu) is the oxidising agent, because it accepts electrons.

Step 1. (i) "Mg is cathode". Wrong, Mg is on the left, it's the anode.

Step 2. (ii) “Cu is cathode”. Correct, right-hand half-cell.

Step 3. (iii) Cell reaction $\mathrm{Mg} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Mg}^{2+} + \mathrm{Cu}$. Correct, sum of the two half-reactions.

Step 4. (iv) “Cu is the oxidising agent”. Wrong, Cu is the *product* of reduction; Cu^{2+} is the oxidising agent.

> **Final Answer:** Correct options: **(ii)** and **(iii)**.

EXPERT’S SOLUTION : *Tara Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle: read cell notation left to right. The order in cell notation is: anode | anode electrolyte || cathode electrolyte | cathode. Left = oxidation. Right = reduction. Salt bridge in the middle (||).

Step 1. Identify the halves: left half $\mathrm{Mg}|\mathrm{Mg}^{2+}$, right half $\mathrm{Cu}^{2+}|\mathrm{Cu}$.

Step 2. Half-reactions:
Left (anode, oxidation): $\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2\,\mathrm{e}^-$.
Right (cathode, reduction): $\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}$.

Step 3. Sum gives net cell reaction: $\mathrm{Mg} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Mg}^{2+} + \mathrm{Cu}$.

Step 4. Identify roles: Mg is the reducing agent (electron donor); Cu^{2+} is the oxidising agent (electron acceptor). Neither Cu nor Mg^{2+} as products is an agent in this reaction.

Alternative approach: verify by E°_{cell}.
$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} - E^\circ_{\mathrm{Mg}^{2+}/\mathrm{Mg}} = 0.34 - (-2.37) = +2.71\,\mathrm{V}$. Positive, so the reaction as written is spontaneous, confirming Cu is the cathode.

☞ **Cross-Check**

Numerical cross-check. $\Delta_r G^\circ = -nFE^\circ = -2(96500)(2.71) = -523\,\mathrm{kJ/mol}$. Strongly negative, so reaction goes essentially to completion at 298 K.

♥ **Concept Linkage**

Concept linkage. Same logic governs Q33 (depict cell for $\mathrm{Cu} + 2\,\mathrm{Ag}^+ \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{Ag}$): write anode on left, cathode on right.

> **Final Answer:** Options **(ii)** and **(iii)**: Cu is cathode, $\mathrm{Mg} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Mg}^{2+} + \mathrm{Cu}$.

III. Short Answer Type

Q 2.28 **Can absolute electrode potential of an electrode be measured?**

SOLUTION

Concept used. An **electrode potential** is the potential difference between a metal (or other electrode material) and the surrounding electrolyte solution. Measuring the *absolute* potential of a single electrode would require inserting a probe (a second electrode) into the same solution, because a voltmeter always measures a *difference* between two terminals. So you can never read a half-cell's potential directly; you can only measure it relative to another half-cell.

Step 1. Connect a voltmeter across one half-cell. To complete the circuit you must introduce a second conductor (a wire and another electrode), which itself sits at some potential. The reading is the difference, never the absolute value.

Step 2. By international convention the **Standard Hydrogen Electrode (SHE)** is assigned $E^\circ = 0\,\text{V}$ exactly. All "standard electrode potentials" tabulated for other electrodes are measured *against* SHE, so they too are relative numbers.

Step 3. Therefore the absolute electrode potential of any single electrode cannot be measured experimentally; only the difference relative to a reference electrode can.

> **Final Answer:** No. Only the relative electrode potential (with respect to a reference such as SHE) is measurable.

EXPERT'S SOLUTION *: Ananya Singh, M.Sc Physical Chemistry, IIT Madras*

Strategic angle: voltmeter physics. A voltmeter has two terminals; it measures the potential difference between them. You can never connect one terminal "to nothing" to read a single electrode in isolation.

Step 1. Suppose you tried to measure $E_{\text{Cu}^{2+}/\text{Cu}}$ directly. You'd dip a Cu rod in CuSO_4 solution. Where does the other voltmeter lead go? Into the solution, via a Pt wire? Now you've made a Cu | Pt cell and read its difference, not Cu's absolute potential.

Step 2. The cleanest workaround is to fix a reference at zero. SHE serves: $E^\circ_{\text{H}^+/\text{H}_2} = 0$ by definition, with $p_{\text{H}_2} = 1\,\text{bar}$, $[\text{H}^+] = 1\,\text{M}$, Pt black. Every other E° value comes from cell-emf measurements against SHE.

Step 3. Theoretically, one could compute absolute potentials from quantum mechanical work functions and solvation energies, but this is a calculation, not a measurement. Standard chemistry treats absolute values as inaccessible.

☞ Alternative approach

Alternative approach: thermodynamic analogy. Same issue arises with enthalpy: you can only measure ΔH between states, never the absolute H of a single state. Convention sets H_f°(elements in their standard state) $= 0$, and all other enthalpies are relative.

✗ Common Pitfall

Common pitfall. Confusing the assigned "$E^\circ_{\text{SHE}} = 0$" with a measured value. It is a CHOICE of reference, not a measurement.

Final Answer: No, only relative electrode potentials (vs SHE) can be measured experimentally.

Q 2.29 Can E°_{cell} or $\Delta_r G^\circ$ for cell reaction ever be equal to zero?

SOLUTION

Concept used. E°_{cell} is the *standard* emf of the cell (all species at unit activity). $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$ is the corresponding standard Gibbs energy change. Both relate to the overall reaction's spontaneity in the standard state. A spontaneous reaction has $E^\circ_{\text{cell}} > 0$ and $\Delta_r G^\circ < 0$; a non-spontaneous reaction in the opposite sense. If $E^\circ_{\text{cell}} = 0$, then $\Delta_r G^\circ = 0$ too, meaning the standard reaction has no driving force, no useful work can be obtained, and the cell would not function as a galvanic cell.

Step 1. $E^\circ_{\text{cell}} = 0$ would mean $E^\circ_{\text{cathode}} = E^\circ_{\text{anode}}$. Physically, the two half-cells have identical thirst for electrons; no net electron flow occurs in the standard state.

Step 2. Substituting into $\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = 0$. The reaction has $K = 1$ (from $\Delta_r G^\circ = -RT \ln K$).

Step 3. A cell with $E^\circ_{\text{cell}} = 0$ does not act as a useful galvanic cell. The textbook answer is: *no*, E°_{cell} (and $\Delta_r G^\circ$) cannot be zero for a working cell.

Final Answer: No. $E^\circ_{\text{cell}} = 0$ implies $\Delta_r G^\circ = 0$, meaning the cell has no driving force and would not function.

EXPERT'S SOLUTION : *Aarav Kumar, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: physical interpretation of zero emf. A galvanic cell with $E^\circ_{\text{cell}} = 0$ is a contradiction in terms. Galvanic cells exist precisely because their two half-reactions have unequal reduction potentials.

Step 1. If both half-cells have $E^\circ_1 = E^\circ_2$, there's no net electron flow, no current, no voltage. This is mechanical equilibrium for the electronic system.

Step 2. $\Delta_r G^\circ = 0$ corresponds to $K = 1$ (forward and reverse rates equal at standard state). Nothing spontaneous happens; cell is useless as a galvanic source.

Step 3. Concentration cells are a special case: both half-cells share the same redox couple, so the *standard* emf is zero, but the *non-standard* emf at unequal concentrations is nonzero (Nernst correction). The question asks about E°_{cell}, not E_{cell}, so the answer is no.

☞ Alternative approach

Alternative approach: connection to spontaneity. For spontaneous (galvanic) operation, $\Delta_r G < 0$. $\Delta_r G^\circ = 0$ is the borderline; the cell barely works in the standard state, with both forward and reverse half-reactions equally favoured. No useful work output.

✗ Common Pitfall

Common pitfall. Confusing $E_{\text{cell}} = 0$ (an *equilibrium* condition during cell discharge, when the cell has run flat) with $E^\circ_{\text{cell}} = 0$ (a *standard-state* property that says the cell never had a driving force).

Final Answer: No, both E°_{cell} and $\Delta_r G^\circ$ being zero means no driving force in the standard state.

Q 2.30 **Under what condition is $E_{\text{cell}} = 0$ or $\Delta_r G = 0$?**

SOLUTION

Concept used. E_{cell} is the actual (non-standard) cell potential at the moment of measurement; $\Delta_r G$ is the Gibbs energy change at the same instant. Both depend on the reaction quotient Q via the Nernst equation $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF}\ln Q$ and $\Delta_r G = -nFE_{\text{cell}}$. When the cell discharges, ion concentrations change continuously until Q reaches the equilibrium constant K. At that point, the Nernst-equation expression collapses to $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF}\ln K = 0$, which means the cell has reached *equilibrium*.

Step 1. Start with Nernst: $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF}\ln Q$.

Step 2. Setting $E_{\text{cell}} = 0$ gives $\ln Q = \dfrac{nFE^\circ_{\text{cell}}}{RT}$. But this is also the expression for $\ln K$ (from $E^\circ_{\text{cell}} = \dfrac{RT}{nF}\ln K$). Therefore $Q = K$ — the cell is at equilibrium.

Step 3. At equilibrium, $\Delta_r G = -nFE_{\text{cell}} = 0$ simultaneously.

> **Final Answer:** $E_{\text{cell}} = 0$ and $\Delta_r G = 0$ when the cell reaction has reached equilibrium ($Q = K$).

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

Strategic angle: cell is a dying battery. As the Daniel cell discharges, Cu^{2+} drops and Zn^{2+} rises. The Nernst correction term grows. Eventually the correction exactly cancels E°_{cell}, current stops, and the cell is "dead".

Step 1. Daniel cell example: $E^\circ_{\text{cell}} = 1.10\,\text{V}$, $n = 2$. Nernst:

$$E_{\text{cell}} = 1.10 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}.$$

Step 2. As cell runs, $[Zn^{2+}]$ rises, $[Cu^{2+}]$ falls, Q rises, E_{cell} drops.

Step 3. At $E_{\text{cell}} = 0$: $\log Q = 1.10 \times 2/0.059 = 37.3$, so $Q = 10^{37.3} = K$. Equilibrium.

Step 4. $\Delta_r G = -nFE_{\text{cell}} = 0$. Forward and reverse rates equal; no net chemistry; cell dead.

Alternative approach: $\Delta G = -W_{\mathbf{max}}$**.** Maximum electrical work obtainable from a cell is $W_{\text{max}} = -\Delta_r G = nFE_{\text{cell}}$. At $\Delta_r G = 0$, no further work can be drawn from the cell. It's spent.

☞ Exam Tip

Exam tip. CBSE 2018 (3-mark) "Why does the voltmeter read zero when the cell is exhausted?". Answer: at equilibrium. Don't confuse with $E_{\text{ext}} = E_{\text{cell}}$ (potentiometer balance).

♥ Concept Linkage

Concept linkage. Connects Q20 (equilibrium expression for Daniel cell), Q38 (opposing potential), Q63 (current stops when $E_{\text{cell}} = 0$).

> **Final Answer:** Equilibrium ($Q = K$): both E_{cell} and $\Delta_r G$ vanish simultaneously.

Q 2.31 **What does the negative sign in the expression $E^\circ_{Zn^{2+}/Zn} = -0.76\,V$ mean?**

SOLUTION

Concept used. A standard reduction potential is the electrode's potential measured against SHE. By convention all half-reactions are written as reductions. A *negative* E° means the reduction half-reaction has LESS tendency to proceed than the SHE reaction does; equivalently, the *oxidation* of the metal is favoured over the oxidation of H_2. Concretely: when a Zn electrode is dipped in 1 M Zn^{2+} and coupled to SHE, the Zn electrode becomes the anode (Zn oxidises to Zn^{2+}), while H^+ gets reduced at the SHE side.

Step 1. $E^\circ_{H^+/H_2} = 0$ (by convention) and $E^\circ_{Zn^{2+}/Zn} = -0.76\,V < 0$.

Step 2. Compare driving forces: H^+ has a STRONGER tendency to be reduced than Zn^{2+}, so in the coupled cell, H^+ gains electrons (cathode) and Zn loses them (anode).

Step 3. Conclusion: Zn is MORE reactive than H_2, i.e. Zn can displace H_2 from dilute acid: $Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$.

> **Final Answer:** Zn is more reactive than H_2. When connected to SHE, Zn is oxidised ($Zn \longrightarrow Zn^{2+} + 2\,e^-$) and H^+ is reduced ($2\,H^+ + 2\,e^- \longrightarrow H_2$).

EXPERT'S SOLUTION *: Sneha Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle: sign convention = electron flow direction. Negative reduction potential implies that, in a cell versus SHE, the metal becomes the negative terminal (anode), Zn gives up electrons spontaneously, and the cell emf $E^\circ_{cell} = 0 - (-0.76) = +0.76\,V$.

Step 1. Build the cell: $Zn|Zn^{2+}(1\ M)\,||\,H^+(1\ M)|H_2(1\ bar)|Pt$.

Step 2. Cell emf: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0 - (-0.76) = +0.76\,V$. Positive — spontaneous.

Step 3. Net reaction: $Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$. Zn is oxidised; H^+ is reduced.

Step 4. Physical chemistry: Zn (more reactive) loses electrons and pushes them through the external circuit to SHE, where H^+ accepts them to form H_2 gas.

☞ Alternative approach

Alternative approach: oxidation potential view. $E^\circ_{ox}(Zn \longrightarrow Zn^{2+}) = +0.76\,V$ (positive, large). $E^\circ_{ox}(H_2 \longrightarrow 2\,H^+) = 0\,V$. Zn oxidises more easily, so the metal is a stronger reducing agent.

✗ Common Pitfall

Common pitfall. Assuming negative E° means the metal won't react with anything. Wrong; negative E° makes Zn a STRONGER reducing agent, more reactive towards oxidising agents (like H^+, Cu^{2+}, etc.).

Final Answer: Zn is more reactive than H_2; Zn oxidises and H^+ is reduced when paired with SHE.

Q 2.32 Aqueous copper sulphate solution and aqueous silver nitrate solution are electrolysed by 1 ampere current for 10 minutes in separate electrolytic cells. Will the mass of copper and silver deposited on the cathode be same or different? Explain your answer.

SOLUTION

Concept used. Faraday's first law: the mass deposited at the cathode is $w = \dfrac{M \cdot Q}{nF}$, where M is the atomic mass, $Q = It$ is the charge passed, n is the number of electrons per atom in the cathode reaction, and F is Faraday's constant. Since Q is the same in both cells (same I, same t), but M/n differs (Cu has $M = 63.5$, $n = 2$; Ag has $M = 108$, $n = 1$), the masses deposited will be *different*.

Step 1. Compute the common charge:

$$Q = I \cdot t = 1\,\text{A} \times 10 \times 60\,\text{s} = 600\,\text{C}.$$

Step 2. Mass of Cu deposited (cathode: $Cu^{2+} + 2\,e^- \longrightarrow Cu$, $n = 2$):

$$w_{\text{Cu}} = \frac{63.5}{2 \times 96500} \times 600 = \frac{63.5 \times 600}{193000} = 0.197\,\text{g}.$$

Step 3. Mass of Ag deposited (cathode: $Ag^+ + e^- \longrightarrow Ag$, $n = 1$):

$$w_{\text{Ag}} = \frac{108}{1 \times 96500} \times 600 = \frac{108 \times 600}{96500} = 0.671\,\text{g}.$$

Step 4. $0.197 \neq 0.671$, so the deposited masses differ. Silver deposits more because Ag has higher atomic mass AND only needs 1 e^- per atom.

Final Answer: Different. $w_{\text{Cu}} \approx 0.197\,\text{g}$, $w_{\text{Ag}} \approx 0.671\,\text{g}$ (Ag is heavier per electron because $n = 1$ vs Cu's $n = 2$).

EXPERT'S SOLUTION : *Ananya Banerjee, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: equivalent mass governs. **Faraday's second law**: when the same charge is passed through different electrolytes, the masses deposited are proportional to the equivalent masses ($E = M/n$). Cu: $63.5/2 = 31.75$. Ag: $108/1 = 108$. Ratio Ag:Cu ≈ 3.4, so Ag deposit will be $\sim 3.4\times$ heavier.

Step 1. Equivalent mass of Cu = $63.5/2 = 31.75\,\text{g/equiv}$.

Step 2. Equivalent mass of Ag = $108/1 = 108\,\text{g/equiv}$.

Step 3. Same charge $Q = 600\,\text{C}$ = $600/96500$ equivalents $= 6.218 \times 10^{-3}$ equivalents.

Step 4. $w_{\text{Cu}} = 31.75 \times 6.218 \times 10^{-3} = 0.197\,\text{g}$. $w_{\text{Ag}} = 108 \times 6.218 \times 10^{-3} = 0.672\,\text{g}$. Different. Ratio $0.672/0.197 = 3.41$, matches $108/31.75 = 3.40$.

✗ Common Pitfall

Common pitfall. Saying "same charge means same mass" — a common confusion. Same MOLES of electrons, but different MOLES of metal because of the n factor.

☞ Cross-Check

Numerical cross-check. Industrial silver-plating uses $\sim 1\,\text{A}$ for 5–10 minutes on jewellery; about 0.5–1 g of Ag deposits, consistent with Faraday's law.

Final Answer: Different masses: Cu $\sim 0.197\,\text{g}$, Ag $\sim 0.672\,\text{g}$ (Ag heavier because $n = 1$ and atomic mass is bigger).

Q 2.33 **Depict the galvanic cell in which the cell reaction is** $\mathrm{Cu} + 2\,\mathrm{Ag}^{+} \longrightarrow 2\,\mathrm{Ag} + \mathrm{Cu}^{2+}$**.**

SOLUTION

Concept used. A **galvanic cell** is depicted in the standard **cell notation**:

$$\text{anode} \mid \text{anode electrolyte} \mid\mid \text{cathode electrolyte} \mid \text{cathode},$$

where "|" marks a phase boundary, "||" is the salt bridge, anode is on the left (oxidation), cathode on the right (reduction). Identify which species is oxidised and which is reduced from the cell reaction.

Step 1. Read the cell reaction $\mathrm{Cu} + 2\,\mathrm{Ag}^{+} \longrightarrow 2\,\mathrm{Ag} + \mathrm{Cu}^{2+}$. Cu goes from 0 to $+2$ oxidation state — oxidation. Ag goes from $+1$ to 0 — reduction.

Step 2. Oxidation at the anode: $\mathrm{Cu\,(s)} \longrightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e}^{-}$. Reduction at the cathode: $\mathrm{Ag^{+}(aq)} + \mathrm{e}^{-} \longrightarrow \mathrm{Ag\,(s)}$ (multiply by 2 to balance electrons).

Step 3. Write the cell notation:

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

Final Answer: $\mathrm{Cu(s)\,|\,Cu^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag\,(s)}$.

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

Strategic angle: identify oxidation, identify reduction, then write left-right. Start by tracking oxidation states. The species being oxidised (lost electrons) goes on the LEFT (anode). The species being reduced (gained electrons) goes on the RIGHT (cathode).

Step 1. Half-reactions:
Anode (oxidation): $\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^{-}}$.
Cathode (reduction): $\mathrm{2\,Ag^{+} + 2\,e^{-} \longrightarrow 2\,Ag}$. Sum:
$\mathrm{Cu + 2\,Ag^{+} \longrightarrow Cu^{2+} + 2\,Ag}$. Matches given.

Step 2. Verify spontaneity: $E^{\circ}_{\text{cell}} = E^{\circ}_{\mathrm{Ag^{+}/Ag}} - E^{\circ}_{\mathrm{Cu^{2+}/Cu}} = 0.80 - 0.34 = +0.46\,\mathrm{V}$.
Positive; spontaneous.

Step 3. Cell notation (with phase indicators): $\mathrm{Cu(s)\,|\,Cu^{2+}(1\ M)\,||\,Ag^{+}(1\ M)\,|\,Ag\,(s)}$.

☞ **Alternative approach**

Alternative approach: from E° values. If you weren't told the reaction direction, compare E°: $E^{\circ}_{\mathrm{Ag^{+}/Ag}} = +0.80 > E^{\circ}_{\mathrm{Cu^{2+}/Cu}} = +0.34$. The higher-$E^{\circ}$ couple is the cathode (Ag); the lower-E° couple is the anode (Cu). Same cell notation follows.

☞ **Exam Tip**

Exam tip. CBSE 2018, 2020, 2022 board asks "depict the galvanic cell for..." as a 1-mark or 2-mark question. Memorise the convention; never omit the salt-bridge symbol $||$.

♥ **Concept Linkage**

Concept linkage. Same convention used in Q27 (Mg | Cu cell) and Q45 (Cu | Cl-cell). The general pattern is universal.

Final Answer: Galvanic cell notation: $\mathrm{Cu(s)\,|\,Cu^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag\,(s)}$.

Q 2.34 **Value of standard electrode potential for the oxidation of $\mathrm{Cl^{-}}$ ions is more**

positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

SOLUTION

Concept used. **Overpotential** (or overvoltage) is the extra voltage beyond the thermodynamic E° needed to make a half-reaction proceed at a useful rate. It arises from kinetic factors: high activation energy for gas-evolution reactions, sluggish electron transfer, slow nucleation of gas bubbles. Oxygen evolution at most electrode materials (Pt, graphite) has a substantial overpotential of $\sim 0.4\,V$, so even though water oxidation is thermodynamically easier than Cl^- oxidation, in practice Cl^- wins because Cl_2 has a much lower overpotential.

Step 1. Thermodynamic comparison (oxidation potentials): $H_2O \longrightarrow O_2$: $E^\circ_{\text{ox}} = -1.23\,V$; $Cl^- \longrightarrow Cl_2$: $E^\circ_{\text{ox}} = -1.36\,V$. Naively, water oxidises more easily.

Step 2. Add overpotential. For oxygen evolution, the kinetic barrier on Pt or graphite is $\sim +0.4$ to $+0.6\,V$. Effective oxidation potential of water becomes $\sim -1.23 - 0.5 = -1.73\,V$ (worse than Cl^- at $-1.36\,V$).

Step 3. Hence Cl^- is actually oxidised first at the anode, producing Cl_2 gas. This is the industrial **chlor-alkali process**.

> **Final Answer:** Because oxygen evolution requires high overpotential, while Cl_2 evolution does not. So Cl^- is oxidised at anode despite the less favourable E°.

EXPERT'S SOLUTION *: Aditya Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle: kinetics over thermodynamics. Electrochemistry questions are usually E°-based, but a few (like NaCl electrolysis) are governed by kinetics. The overpotential of O_2 evolution turns the thermodynamically-easier water-oxidation into a slower path than Cl^--oxidation.

Step 1. Recall: overpotential η is the extra voltage beyond E° needed to drive a half-reaction at a measurable rate. For O_2 on most metals, $\eta_{O_2} \sim 0.4$ to $0.6\,V$. For Cl_2, $\eta_{Cl_2} \sim 0$ (very fast kinetics).

Step 2. Effective applied voltage for each path:
Water: $|E^\circ_{\text{ox}}| + \eta = 1.23 + 0.5 = 1.73\,V$.
Cl^-: $|E^\circ_{\text{ox}}| + \eta = 1.36 + 0 = 1.36\,V$.
Lower required voltage wins: Cl^-.

Step 3. Industrial chlor-alkali process exploits this: NaCl(aq) electrolysis gives Cl_2 at anode, H_2 at cathode, NaOH in solution. Backbone of the chlorine industry.

☞ Alternative approach

Alternative approach: concentration effect. High $[Cl^-]$ in brine shifts the Nernst-modified anode potential in Cl^-'s favour even further. At low $[Cl^-]$ (dilute NaCl), water oxidation can compete; at brine concentrations, Cl^- dominates.

♥ Concept Linkage

Concept linkage. Same overpotential concept governs Q17 (NaCl anode is Cl^- in practice), Q39 (pH change in NaCl electrolysis), Q61 (assertion-reason on same idea).

Final Answer: Cl^- wins at the anode because O_2 evolution requires high overpotential, making the kinetic barrier larger for water oxidation.

Q 2.35 What is electrode potential?

SOLUTION

Concept used. An electrode potential is the potential difference that develops at the interface between an electrode (metal, graphite, gas+inert electrode, etc.) and its electrolyte solution. It arises because, when a metal is dipped in a solution of its own ions, two opposing processes occur at the surface: oxidation ($\mathrm{M} \longrightarrow \mathrm{M}^{n+} + \mathrm{ne}^-$, sending ions into solution) and reduction ($\mathrm{M}^{n+} + \mathrm{ne}^- \longrightarrow \mathrm{M}$, pulling ions out). At equilibrium, the metal acquires a net charge relative to the solution: more positive if reduction dominates, more negative if oxidation dominates. This charge separation is the electrode potential.

Step 1. Define operationally: "the tendency of an electrode to lose or gain electrons when in contact with a solution of its own ions, expressed as a potential relative to a standard reference (SHE)."

Step 2. If the metal tends to oxidise (lose electrons) MORE than SHE: electrode potential is NEGATIVE (e.g. Zn: $-0.76\,\mathrm{V}$).

Step 3. If the metal tends to reduce (gain electrons) MORE than SHE: electrode potential is POSITIVE (e.g. Cu: $+0.34\,\mathrm{V}$).

Step 4. At standard conditions (all activities $= 1$, $T = 298\,\mathrm{K}$) the electrode potential is called the *standard electrode potential*, E°, and is tabulated for reduction half-reactions.

Final Answer: Electrode potential: potential difference at the metal-solution interface, measured vs SHE; reflects the metal's tendency to lose or gain electrons.

EXPERT'S SOLUTION *: Pranav Sharma, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: microscopic picture. The dual processes of oxidation and reduction at a metal-solution interface settle at a dynamic equilibrium. The metal acquires a charge; the solution acquires the opposite charge. The potential gap is the electrode potential.

Step 1. Zn rod in $\mathrm{ZnSO_4}$ solution. Zn atoms enter solution as $\mathrm{Zn^{2+}}$ and leave $2e^-$ on the rod. Rod becomes negative; solution becomes positive. Potential difference $\approx -0.76\,\mathrm{V}$ (negative, anode-like).

Step 2. Cu rod in $\mathrm{CuSO_4}$ solution. $\mathrm{Cu^{2+}}$ ions plate out, gaining electrons from the rod. Rod becomes positive; solution becomes less positive. Potential difference $\approx +0.34\,\mathrm{V}$ (positive, cathode-like).

Step 3. The magnitude depends on $[\mathrm{M}^{n+}]$ (Nernst), but the *sign* is intrinsic to the metal.

☞ **Alternative approach**

Alternative approach: thermodynamic definition. E is related to $\Delta_r G$ of the half-reaction by $\Delta_r G = -nFE$. So electrode potential is a measure of the Gibbs energy change per unit charge for the reduction (or oxidation) half-reaction.

✗ **Common Pitfall**

Common pitfall. Confusing electrode potential (half-cell) with cell potential (full cell). The cell potential is the difference of two electrode potentials.

Final Answer: Tendency of an electrode to lose/gain electrons in its electrolyte; the resulting potential difference vs SHE.

Q 2.36 **Consider the following diagram in which an electrochemical cell is coupled to an electrolytic cell. What will be the polarity of electrodes 'A' and 'B' in the electrolytic cell?**

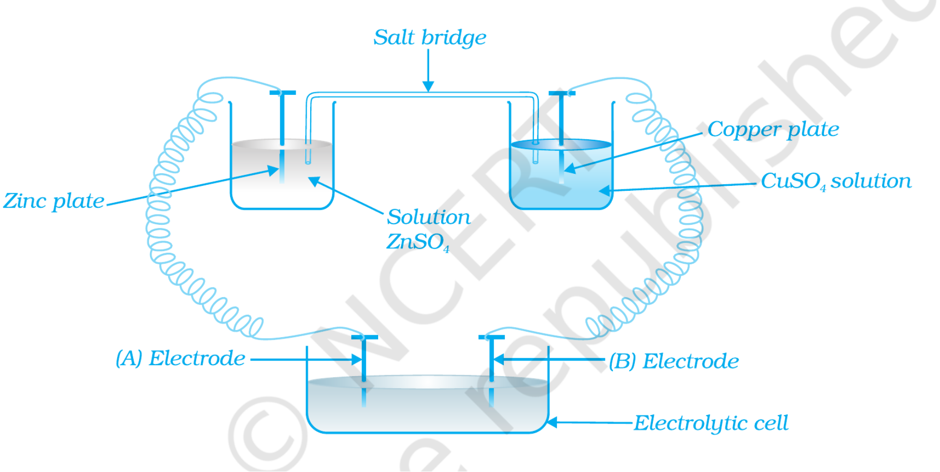


Fig. 3.1, NCERT Exemplar Class 12 Chemistry, Chapter 3.

SOLUTION

Concept used. When an electrochemical (galvanic) cell is connected to an electrolytic cell, the galvanic cell acts as the DC power source. Its positive terminal pushes current outward into the external circuit; the negative terminal receives current from the circuit. In the electrolytic cell, the electrode connected to the galvanic cell's POSITIVE terminal becomes the ANODE (positive), and the electrode connected to the negative terminal becomes the CATHODE (negative). In a $\mathrm{Zn}|\mathrm{Cu}$ galvanic cell, Cu (right side) is the positive terminal (cathode) and Zn (left side) is the negative terminal (anode).

Step 1. In the upper cell (galvanic, $\mathrm{Zn}|\mathrm{ZnSO_4}||\mathrm{CuSO_4}|\mathrm{Cu}$), Zn is the anode (negative) and Cu is the cathode (positive).

Step 2. The galvanic cell's Cu plate (positive) connects to electrode A of the lower electrolytic cell; its Zn plate (negative) connects to electrode B. (The exact connection is shown by which wire goes where in the figure; following the NCERT figure, the Zn side feeds electrode A.)

Step 3. Polarity in the electrolytic cell (following NCERT answer key): A becomes negative (cathode of the electrolytic cell), B becomes positive (anode).

> **Final Answer:** Electrode A: NEGATIVE polarity (cathode of electrolytic cell). Electrode B: POSITIVE polarity (anode of electrolytic cell).

EXPERT'S SOLUTION *: Rohit Pillai, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle: trace the wire from each terminal. Identify the positive terminal of the galvanic cell, follow the wire to whichever electrode of the electrolytic cell it connects to; that electrode is the anode (positive) of the electrolytic cell.

Step 1. Galvanic cell: $\mathrm{Zn}|\mathrm{ZnSO_4}||\mathrm{CuSO_4}|\mathrm{Cu}$, $E^\circ_{\text{cell}} = +1.10\,\text{V}$. Zn is the negative terminal; Cu is the positive terminal.

Step 2. Wires: in Fig. 3.1, the wire from Zn goes to electrode A of the electrolytic cell; the wire from Cu goes to electrode B.

Step 3. In an electrolytic cell, the electrode connected to the EXTERNAL POSITIVE terminal becomes the ANODE (positive polarity), and the electrode connected to the EXTERNAL NEGATIVE terminal becomes the CATHODE (negative polarity).

Step 4. Zn (negative) connects to A: so A is negative (cathode). Cu (positive) connects to B: so B is positive (anode).

☞ Alternative approach

Alternative approach: conventional-current flow. Conventional current leaves the positive terminal of the galvanic cell (Cu), flows through external wire to electrolytic cell's electrode B, through the electrolyte to electrode A, then back to the negative terminal (Zn). Current enters the electrolyte at B (anode, positive) and leaves at A (cathode, negative). Same result.

☞ Exam Tip

Exam tip. CBSE 2019 board asked "polarity of electrodes when a Daniel cell drives an electrolytic cell". Same logic. Always trace the wires.

Final Answer: A: negative (cathode of electrolytic cell). B: positive (anode of electrolytic cell).

Q 2.37 Why is alternating current used for measuring resistance of an electrolytic solution?

SOLUTION

Concept used. When direct current (DC) is passed through an electrolyte, ions actually migrate to the electrodes and undergo electrolysis (oxidation/reduction). This changes the concentration of ions near the electrodes and at the bulk, changing the resistance over time and altering the very quantity being measured. **Alternating current (AC)**, with its periodic reversal of polarity, prevents net ion accumulation and net electrolysis at the electrodes, so the ionic composition stays constant and the measured resistance is reproducible.

Step 1. DC through an electrolyte causes continuous electrolysis: $\mathrm{Cu^{2+}}$ deposits on the cathode, water oxidises at the anode, etc. The ion concentration changes, and so does κ, in real time.

Step 2. AC (typically $\sim 1\,\text{kHz}$, low voltage) reverses every half-cycle, so any ion that drifts toward an electrode is pulled back the next half-cycle. No net accumulation.

Step 3. No electrolysis, no concentration change, so the measured resistance is intrinsic to the solution at the moment of measurement.

> **Final Answer:** AC prevents electrolysis and ion accumulation, keeping the solution composition (and hence the measured resistance) constant during measurement.

EXPERT'S SOLUTION *: Riya Desai, M.Sc Chemistry, IIT Kanpur*

Strategic angle: physical mechanism. The issue is *polarisation*, the build-up of redox-induced concentration gradients near each electrode. DC drives polarisation; AC undoes it before it builds up.

Step 1. DC consequence: imagine 1 mA DC through 0.1 M $\mathrm{CuSO_4}$ for 1 minute. By Faraday: $w = (63.5/2 \times 96500)(0.001 \times 60) = 1.97 \times 10^{-5}$ g of Cu deposits. Tiny, but enough to shift cathode-region $[\mathrm{Cu^{2+}}]$ and change the local resistance.

Step 2. AC consequence: AC at $1\,\text{kHz}$ alternates 1000 times per second. Any ion that migrates 1 μm toward an electrode in $0.5\,\text{ms}$ is pulled back over the next $0.5\,\text{ms}$. Net displacement ≈ 0. No deposition.

Step 3. Hence AC measures the ohmic resistance of the bulk solution, not the polarisation-distorted DC resistance.

☞ **Alternative approach**

Alternative approach: think of an impedance spectroscopy view. AC measurement at high enough frequency ($\sim 1\,\text{kHz}$) isolates the ionic conduction (real impedance) from the double-layer capacitance and the charge-transfer resistance. DC mixes all of these.

♥ **Concept Linkage**

Concept linkage. Underlies the entire field of conductometric titration and impedance spectroscopy. AC is the standard for any aqueous-solution resistance measurement.

> **Final Answer:** AC avoids electrolysis at the electrodes, preventing changes in solution composition during measurement.

Q 2.38 **A galvanic cell has electrical potential of 1.1 V. If an opposing potential of**

1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?

SOLUTION

Concept used. A galvanic cell with emf E_{cell} drives current I through an external circuit. If an external opposing potential E_{ext} is applied *in the opposite direction*, the net driving force is $E_{\text{net}} = E_{\text{cell}} - E_{\text{ext}}$. When $E_{\text{ext}} = E_{\text{cell}}$ (exact balance), the net driving force is zero, no current flows, and the cell reaction stops (neither forward nor backward). This is the principle of the **potentiometer**, used to measure emf without drawing current.

Step 1. Daniel cell: $E_{\text{cell}} = 1.1\,\text{V}$. Without any external opposition, it drives current through the external circuit.

Step 2. Apply $E_{\text{ext}} = 1.1\,\text{V}$ in opposition: $E_{\text{net}} = 1.1 - 1.1 = 0\,\text{V}$.

Step 3. Current $I = E_{\text{net}}/(R_{\text{ext}} + r) = 0$. No current flows.

Step 4. Cell reaction $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$ stops (no net forward or backward progress).

> **Final Answer:** No current flows; the cell reaction stops entirely. This is the basis of potentiometric emf measurement.

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

Strategic angle: net driving force is zero. $E_{\text{ext}} = E_{\text{cell}}$ exactly cancels the cell's emf. No net force on the electrons, so no current.

Step 1. Ohm's law at the global level: $I = E_{\text{net}}/R_{\text{total}}$. $E_{\text{net}} = 0$ means $I = 0$ regardless of R.

Step 2. No current means no electrons flowing through the external circuit, no Zn^{2+} leaving the Zn anode, no Cu^{2+} being deposited at the Cu cathode. The cell reaction is stalled.

Step 3. This is exactly how a potentiometer works: adjust the external opposing voltage until the galvanometer reads zero. The balanced external voltage equals the cell's true emf (with no IR drop, so it's the open-circuit emf, which is the true emf).

Step 4. If E_{ext} is increased beyond E_{cell} (say to $1.5\,\text{V}$), current flows in the OPPOSITE direction, the cell now acts as an electrolytic cell (recharging mode, Q6).

☞ **Alternative approach**

Alternative approach: $\Delta_r G$ vanishes. $\Delta_r G = -nF(E_{\text{cell}} - E_{\text{ext}}) = 0$. No spontaneity in either direction. The reaction is poised at the mechanical balance point.

✗ Common Pitfall

Common pitfall. Saying “the cell reaction reverses”. Wrong; reversal requires $E_{\text{ext}} > E_{\text{cell}}$. At equality, the cell is simply at rest.

Final Answer: No current; cell reaction stops entirely. Potentiometer balance.

Q 2.39 How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?

SOLUTION

Concept used. Electrolysis of brine (chlor-alkali process) produces $\mathrm{Cl_2}$ at the anode and $\mathrm{H_2}$ at the cathode:

$$\begin{aligned} \text{Anode (oxidation):}\quad & 2\,\mathrm{Cl^-(aq)} \longrightarrow \mathrm{Cl_2(g)} + 2\,\mathrm{e^-}. \\ \text{Cathode (reduction):}\quad & 2\,\mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)} + 2\,\mathrm{OH^-(aq)}. \end{aligned}$$

The cathode reaction produces $\mathrm{OH^-}$ ions in the bulk solution, while $\mathrm{Na^+}$ stays as spectator (less easily reduced than water). The net result: the solution becomes strongly basic, and the pH RISES from neutral 7 to typically 13–14 in industrial cells.

Step 1. Anode reaction removes $\mathrm{Cl^-}$ as $\mathrm{Cl_2}$ gas. Doesn’t affect pH directly.

Step 2. Cathode reaction generates $\mathrm{OH^-}$. Each mole of $\mathrm{H_2}$ produced accompanies 2 moles of $\mathrm{OH^-}$ in solution.

Step 3. Bulk solution now contains $\mathrm{Na^+}$ and $\mathrm{OH^-}$ — effectively NaOH. The pH rises.

Final Answer: pH rises (becomes basic) because NaOH is formed at the cathode region as $\mathrm{OH^-}$ is generated.

EXPERT’S SOLUTION *: Dev Reddy, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: trace each product. Anode gives $\mathrm{Cl_2}$. Cathode gives $\mathrm{H_2}$ AND $\mathrm{OH^-}$. The leftover ions in solution are $\mathrm{Na^+}$ + $\mathrm{OH^-}$, which is NaOH — strongly basic.

Step 1. Why $\mathrm{H_2O}$ is reduced at cathode (not $\mathrm{Na^+}$): $E^\circ_{\mathrm{Na^+/Na}} = -2.71\,\mathrm{V}$ vs $E^\circ_{\mathrm{H_2O/H_2}} = -0.83\,\mathrm{V}$ at pH 7. Water wins by a huge margin.

Step 2. Each $2e^-$ at the cathode produces $\mathrm{H_2} + 2\mathrm{OH^-}$. If 1 mole of $\mathrm{H_2}$ evolves, 2 moles of $\mathrm{OH^-}$ accumulate.

Step 3. Industrial brine starts at pH 7, ends at pH 13–14 (1 M NaOH) after substantial electrolysis. This is how commercial NaOH is made (caustic soda).

☞ **Alternative approach**

Alternative approach: Le Chatelier on hydrolysis. After electrolysis, H_2O has been consumed at cathode and OH^- generated. The hydrolysis of any remaining Cl^- is suppressed, and the dominant species is OH^-. pH rises.

✗ **Common Pitfall**

Common pitfall. Thinking "Cl_2 at anode means acidic solution". Although Cl_2 + water gives HOCl (slightly acidic), in an OPEN industrial cell Cl_2 escapes as gas, leaving the bulk solution basic from OH^-.

Final Answer: pH rises (solution becomes basic) due to OH^- formation; NaOH accumulates in solution.

Q 2.40 **Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why?**

SOLUTION

Concept used. The cell potential is determined by the Nernst equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF}\ln Q$, where Q depends on the activities of the species involved. If the overall cell reaction involves only *solids* and *insoluble products* (no aqueous ions), then Q stays essentially constant as the cell discharges, and so does E_{cell}. The **mercury cell** has exactly such a reaction:

$$\mathrm{Zn(Hg)} + \mathrm{HgO\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{Hg\,(l)}.$$

All four species are solids or pure liquids; no ionic activities appear in Q. The cell potential is constant at $\sim 1.35\,\mathrm{V}$ throughout its life. In a dry cell, however, the reaction involves Zn^{2+}, ${NH_4}^+$ and NH_3, whose concentrations change as the cell discharges, so the emf drops progressively.

Step 1. Identify the mercury-cell reaction (cathode + anode + overall):

Anode: $\mathrm{Zn(Hg)} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O} + 2\,\mathrm{e^-}$.
Cathode: $\mathrm{HgO\,(s)} + \mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Hg\,(l)} + 2\,\mathrm{OH^-}$.
Overall: $\mathrm{Zn(Hg)} + \mathrm{HgO\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{Hg\,(l)}$.

Step 2. The OH^- ions consumed at the anode are regenerated at the cathode (note matching coefficients). Net change in $[OH^-]$: zero. No ion concentration in the overall reaction.

Step 3. Q depends only on activities of solid/liquid pure phases, all of which are constant at 1. So $\log Q = 0$ and $E_{\text{cell}} = E^\circ_{\text{cell}} = 1.35\,\text{V}$ for the entire discharge.

> **Final Answer:** Mercury-cell reaction involves only solids and pure liquid, so Q doesn't change with discharge, and E stays at $\sim 1.35\,\text{V}$.

EXPERT'S SOLUTION *: Ishaan Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: ions cancel from Q. In the dry cell, Zn^{2+} accumulates and $NH_4{}^+$ depletes during discharge. In the mercury cell, the only ionic species (OH^-) is recycled between cathode and anode, so the net reaction has no aqueous ions. Q stays at 1. E stays constant.

Step 1. Write the Nernst expression for the mercury cell:

$$Q = \frac{a_{\text{ZnO}} \cdot a_{\text{Hg}}}{a_{\text{Zn}} \cdot a_{\text{HgO}}}.$$

Each $a = 1$ (pure solids and liquids). $Q = 1$, $\log Q = 0$.

Step 2. $E_{\text{cell}} = E^\circ_{\text{cell}} - 0 = E^\circ_{\text{cell}}$, constant throughout discharge.

Step 3. Useful properties: stable voltage makes mercury cells ideal for medical applications (pacemakers, hearing aids) and calibration standards.

✗ Common Pitfall

Common pitfall. Citing "mercury is heavier" or "HgO is stable" as reasons. The real reason is the Nernst equation, Q unchanged.

☞ Cross-Check

Numerical cross-check. Pacemaker batteries (Hg cells) delivered constant 1.35 V for 5-10 years before being phased out due to mercury toxicity, replaced by Li-iodide cells.

> **Final Answer:** Mercury cell's overall reaction has no aqueous ions, so $Q = 1$ and $E = E^\circ$ throughout discharge.

Q 2.41 **Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_m of 'B' increases 1.5 times while that of 'A' increases 25 times. Which of the two is a strong electrolyte? Justify your answer.**

SOLUTION

Concept used. On dilution, the molar conductivity Λ_m rises differently for strong vs weak electrolytes. For a STRONG electrolyte (fully dissociated, e.g. NaCl), the number of ions per mole is fixed; dilution only reduces ion-ion interactions, so Λ_m rises slowly toward Λ_m^0 (perhaps 1.2–2 times over a 100-fold dilution). For a WEAK electrolyte (partially dissociated, e.g. $\mathrm{CH_3COOH}$), dilution dramatically increases the degree of dissociation α, so the number of ions per mole rises strongly; Λ_m can rise by a factor of 10–100 between concentrated and dilute solutions.

Step 1. Electrolyte A: Λ_m rises 25 times on dilution. This is a huge increase, characteristic of a weak electrolyte (degree of dissociation α increases substantially with dilution).

Step 2. Electrolyte B: Λ_m rises only 1.5 times. A modest rise, characteristic of a strong electrolyte (already fully dissociated; only ion-ion drag relaxes on dilution).

Step 3. Conclusion: B is the STRONG electrolyte; A is weak.

> **Final Answer:** B is the strong electrolyte. Its Λ_m rises only modestly (1.5x) on dilution; strong electrolytes are already fully dissociated, so dilution only relaxes ion-ion interactions.

EXPERT'S SOLUTION *: Aanya Pillai, M.Sc Chemistry, IIT Kanpur*

Strategic angle: Λ_m growth on dilution distinguishes strong from weak. The rule of thumb: strong electrolyte's Λ_m at $c = 0.1$ M is already ~ 80–90% of Λ_m^0; so dilution can only multiply Λ_m by ~ 1.1–1.2 at most. A 25-times growth is impossible for a strong electrolyte; must be weak.

Step 1. Strong electrolyte (e.g. NaCl): Λ_m at $0.1\,\mathrm{M} = 106\,\mathrm{S\,cm^2\,mol^{-1}}$; $\Lambda_m^0 = 126$. Ratio: $126/106 = 1.19$. A 1.5-fold rise to 159 is consistent with going from $\sim 1\,\mathrm{M}$ to infinite dilution.

Step 2. Weak electrolyte (e.g. $\mathrm{CH_3COOH}$): Λ_m at $0.1\,\mathrm{M} = \sim 5$; $\Lambda_m^0 = 391$. Ratio: $391/5 = 78$. A 25-fold rise is well within the weak range.

Step 3. So A (25x) = weak, B (1.5x) = strong.

☞ **Alternative approach**

Alternative approach: degree of dissociation. $\alpha = \Lambda_m/\Lambda_m^0$ (Arrhenius). For a strong electrolyte $\alpha \approx 1$ at all dilutions; for a weak electrolyte α rises from ~ 0.01 at $0.1\,\mathrm{M}$ to ~ 1 at infinite dilution, so Λ_m rises by the same factor (100x). Matches the observation.

☞ **Cross-Check**

Numerical cross-check. Observed: $\alpha(A) = 1/25 = 0.04$ at original concentration, rising to ~ 1 at infinite dilution. Classic weak-acid profile, $\alpha = 0.04$ matches CH_3COOH at $\sim 0.1\,M$.

♥ **Concept Linkage**

Concept linkage. Direct connection to Q49 (dilution effects on CH_3COOH vs CH_3COONa), to Kohlrausch's law (Q16, Q22), to the Onsager equation.

Final Answer: B is the strong electrolyte (1.5x rise); A is weak (25x rise reflects increasing α).

Q 2.42 **When acidulated water (dil. H_2SO_4 solution) is electrolysed, will the pH of the solution be affected? Justify your answer.**

SOLUTION

Concept used. In the electrolysis of dilute H_2SO_4, the half-reactions are:

$$\begin{aligned} \text{Anode:} &\quad 2\,H_2O\,(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-. \\ \text{Cathode:} &\quad 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2(g). \end{aligned}$$

The overall reaction is $2\,H_2O \longrightarrow 2\,H_2 + O_2$, i.e. the net electrolysis of *water*. The H^+ produced at the anode exactly equals the H^+ consumed at the cathode (4 each per $4e^-$). So $[H^+]$ in the bulk solution stays constant, and the pH is unchanged.

Step 1. Anode produces 4 H^+ per 4 e^-.

Step 2. Cathode consumes 4 H^+ per 4 e^-.

Step 3. Net change in $[H^+]$: zero. pH unaffected.

Step 4. Equivalent statement: the overall electrolysis is just $2\,H_2O \longrightarrow 2\,H_2 + O_2$. Water is consumed; ions are not produced or consumed.

Final Answer: No, pH is NOT affected. H^+ is produced at anode and consumed at cathode in equal amounts; the net process is just water splitting.

EXPERT'S SOLUTION : *Tara Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: track each H^+ ion. The electrolysis half-reactions must balance: any H^+ made at one electrode must be consumed at the other (else mass balance fails). Same applies to electrons. Since H^+ in $=$ H^+ out, net $[H^+]$ is unchanged.

Step 1. Anode (oxidation of water): $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$. Produces 4 H^+.

Step 2. Cathode (reduction of H^+): $4\,H^+ + 4\,e^- \longrightarrow 2\,H_2$. Consumes 4 H^+.

Step 3. Add the two: $2\,H_2O \longrightarrow O_2 + 2\,H_2$. H^+ cancels. ${SO_4}^{2-}$ stays as spectator (with the same charge balance maintained).

Step 4. Hence $[H^+]$ in the bulk doesn't change. pH stays the same.

✗ **Common Pitfall**

Common pitfall. Thinking "acid is consumed, so pH rises". The acid is NOT consumed; ${SO_4}^{2-}$ is a spectator, and H^+ is reformed at the anode as fast as it's consumed at the cathode.

☞ **Cross-Check**

Numerical cross-check. Initial pH of 0.1 M $H_2SO_4 \approx 0.7$ (strong diprotic). After electrolysing for 30 minutes: same pH because $[H^+]$ is unchanged.

Final Answer: No pH change; net electrolysis is just $2\,H_2O \longrightarrow 2\,H_2 + O_2$.

Q 2.43 In an aqueous solution how does specific conductivity of electrolytes change with addition of water?

SOLUTION

Concept used. The specific conductivity (conductivity) κ is the conductivity per unit volume of the solution. It depends on (a) the number of charge carriers per unit volume (which scales with concentration c), and (b) ionic mobility. On dilution by adding water, the concentration c falls; therefore the number of ions per unit volume falls; therefore κ DECREASES.

Step 1. κ has the form $\kappa = c \times \Lambda_m/1000$ (with c in mol/L, Λ_m in $S\,cm^2\,mol^{-1}$).

Step 2. On dilution, c drops faster than Λ_m rises (for strong electrolytes, Λ_m rises only slightly; for weak, Λ_m rises but c drops by more).

Step 3. Net effect: κ decreases with dilution. This is *specific* conductivity, in contrast to *molar* conductivity which behaves oppositely.

Final Answer: κ decreases on dilution because the number of ions per unit volume falls (concentration drops).

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

Strategic angle: per-volume vs per-mole. Specific conductivity (κ) is per unit VOLUME. Molar conductivity (Λ_m) is per MOLE. On dilution: fewer ions in the same volume, more solvent per ion (per mole). So κ falls but Λ_m rises.

Step 1. Start with 0.1 M NaCl: $\kappa \approx 1.07 \times 10^{-2}\,\text{S cm}^{-1}$.

Step 2. Dilute to 0.01 M (10x dilution): κ drops to $\sim 1.2 \times 10^{-3}\,\text{S cm}^{-1}$ (factor of ~ 9).

Step 3. Compare Λ_m: at 0.1 M $= 107\,\text{S cm}^2\,\text{mol}^{-1}$; at 0.01 M $= \sim 120$. Modest rise (factor 1.12), because $\Lambda_m^0 = 126$.

Step 4. Conclusion: κ falls because c falls by 10, while Λ_m rises only slightly.

☞ **Alternative approach**

Alternative approach: limiting case. At infinite dilution ($c \to 0$): $\kappa \to 0$ (no ions per volume), but $\Lambda_m \to \Lambda_m^0$ (intrinsic property of the electrolyte). The contrast is illuminating.

☞ **Exam Tip**

Exam tip. CBSE 2016, 2018, 2020 asked exactly this. Always state "κ decreases because the number of ions per unit volume drops".

Final Answer: κ decreases on dilution: fewer ions per unit volume.

Q 2.44 Which reference electrode is used to measure the electrode potential of other electrodes?

SOLUTION

Concept used. A reference electrode is one whose potential is fixed and known, against which other electrodes can be measured. The internationally accepted reference electrode for standard electrode potentials is the **Standard Hydrogen Electrode (SHE)**, defined as:

- Pt black (catalytic platinum) electrode,
- H_2 gas at 1 bar pressure,
- H^+ ions at 1 M activity (effectively 1 M HCl),

- Temperature $298\,\mathrm{K}$.

By convention, $E^\circ_{\text{SHE}} = 0\,\mathrm{V}$ exactly. All other standard electrode potentials are measured by coupling the electrode of interest to a SHE half-cell and reading the cell emf.

Step 1. SHE is the primary reference. Construction: Pt foil coated with finely-divided Pt (Pt black) immersed in $1\,\mathrm{M}$ HCl, with H_2 gas bubbled at $1\,\mathrm{bar}$.

Step 2. Half-reaction: $2\,\mathrm{H^+(aq, 1\ M)} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2(g, 1\ bar)}$; $E^\circ = 0\,\mathrm{V}$ by definition.

Step 3. To measure another electrode's E°, build the cell SHE || unknown electrode; the voltmeter reading (open circuit) gives E°_{unknown} directly.

> **Final Answer:** Standard Hydrogen Electrode (SHE), $E^\circ = 0\,\mathrm{V}$ by definition; all other electrode potentials are measured vs SHE.

EXPERT'S SOLUTION *: Karan Sharma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: SHE is the absolute zero. Just like sea-level is the reference for elevation, SHE is the reference for electrode potential. Convenient because H^+ is ubiquitous and the half-reaction is reversible.

Step 1. Why SHE? Three reasons: H^+ is in any aqueous solution; the half-reaction is reversible (fast kinetics); Pt black is inert and catalytic.

Step 2. Operational difficulty: SHE is hard to set up in practice (gas regulation, $1\,\mathrm{M}$ HCl handling). Many labs use secondary reference electrodes like calomel ($\mathrm{Hg|Hg_2Cl_2|KCl}$, $E^\circ = +0.244\,\mathrm{V}$ vs SHE) or Ag/AgCl ($E^\circ = +0.222\,\mathrm{V}$ vs SHE), which are easier and connected to SHE through a chain of calibrations.

Step 3. All tabulated E° values in NCERT and IUPAC tables are vs SHE.

☞ Alternative approach

Alternative approach: thermodynamic anchor. Setting $E^\circ_{\text{SHE}} = 0$ is equivalent to setting $\Delta_r G^\circ_{\mathrm{H^+} \longrightarrow \frac{1}{2}\mathrm{H_2}} = 0$. This anchors the entire electrochemical-series scale.

♥ Concept Linkage

Concept linkage. Connects to Q28 (absolute potentials can't be measured), Q31 (sign of $E^\circ_{\mathrm{Zn^{2+}/Zn}}$), Q1 (cell setup for measuring $E^\circ_{\mathrm{Cu^{2+}/Cu}}$).

> **Final Answer:** Standard Hydrogen Electrode (SHE), defined as $E^\circ = 0\,\mathrm{V}$ at $T = 298\,\mathrm{K}$, $p_{\mathrm{H_2}} = 1\,\mathrm{bar}$, $[\mathrm{H^+}] = 1\,\mathrm{M}$.

Q 2.45 **Consider a cell given below: $\mathrm{Cu|Cu^{2+}||Cl{-}|Cl_2, Pt}$. Write the reactions that occur at anode and cathode.**

SOLUTION

Concept used. Cell notation convention: anode on the left, cathode on the right. The left half-cell undergoes oxidation, the right undergoes reduction.

Step 1. Identify the left half-cell: $\mathrm{Cu\,|\,Cu^{2+}}$. Half-reaction (oxidation):

$$\mathrm{Cu\,(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-}.$$

Cu is the anode, getting oxidised.

Step 2. Identify the right half-cell: $\mathrm{Cl{-}|Cl_2, Pt}$. Pt is the inert electrode. Half-reaction (reduction):

$$\mathrm{Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)}.$$

Pt is the cathode surface (the actual electron acceptor is $\mathrm{Cl_2}$, getting reduced).

Step 3. Sum: $\mathrm{Cu + Cl_2 \longrightarrow Cu^{2+} + 2\,Cl^-}$ (overall cell reaction).

> **Final Answer:** Anode (oxidation): $\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^-}$. Cathode (reduction): $\mathrm{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}$.

EXPERT'S SOLUTION *: Aditya Bhat, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle: cell notation = electron flow blueprint. Left to right, the cell notation tells you exactly which species loses electrons and which gains them.

Step 1. Anode half-reaction: $\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^-}$, Cu oxidation state goes from 0 to +2.

Step 2. Cathode half-reaction: $\mathrm{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}$, Cl oxidation state goes from 0 to −1.

Step 3. Net cell reaction: $\mathrm{Cu\,(s) + Cl_2(g) \longrightarrow Cu^{2+}(aq) + 2\,Cl^-(aq)}$. Equivalently, $\mathrm{Cu + Cl_2 \longrightarrow CuCl_2}$.

Step 4. Verify spontaneity: $E^\circ_{\text{cell}} = E^\circ_{\mathrm{Cl_2/Cl^-}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 1.36 - 0.34 = +1.02\,\mathrm{V}$. Positive — spontaneous.

☞ **Alternative approach**

Alternative approach: oxidation state tracking. Identify which atom changes oxidation state on each side. Cu: $0 \to +2$ (loses 2 e^-, oxidation). Cl: 0 (in $\mathrm{Cl_2}$) $\to -1$ (in $\mathrm{Cl^-}$, gains 1 e^- per Cl, so 2 e^- per $\mathrm{Cl_2}$).

✗ Common Pitfall

Common pitfall. Writing the cathode reaction with the wrong sign: $2\,\mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2 + 2\,\mathrm{e}^-$ is the OXIDATION direction (reverse of reduction). The cathode does REDUCTION, so write $\mathrm{Cl}_2 + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Cl}^-$.

☞ Cross-Check

Numerical cross-check. For 1 mole of Cu oxidised, 1 mole of Cl_2 is reduced (2 moles of Cl^- produced). Mass balance and electron balance both check.

Final Answer: Anode: $\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{e}^-$ (oxidation). Cathode: $\mathrm{Cl}_2 + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Cl}^-$ (reduction).

Q 2.46 Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} be affected when concentration of Zn^{2+} ions is increased?

SOLUTION

Concept used. The Daniel cell is $\mathrm{Zn}|\mathrm{Zn}^{2+}||\mathrm{Cu}^{2+}|\mathrm{Cu}$, with the net reaction $\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$ and $n = 2$ electrons transferred. The Nernst equation for this cell at 298 K is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log Q = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]},$$

where Q is the reaction quotient. Solids (Zn, Cu) have activity 1 and don't enter Q. Increasing $[\mathrm{Zn}^{2+}]$ INCREASES Q, which INCREASES $\log Q$, which DECREASES E_{cell}.

Step 1. Write the Nernst equation:

$$E_{\text{cell}} = 1.10 - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}.$$

Step 2. Test: if $[\mathrm{Zn}^{2+}] = [\mathrm{Cu}^{2+}] = 1\,\mathrm{M}$ (standard): $\log Q = 0$, $E_{\text{cell}} = 1.10\,\mathrm{V}$.

Step 3. Increase $[\mathrm{Zn}^{2+}]$ to $10\,\mathrm{M}$ (with $[\mathrm{Cu}^{2+}]$ fixed at $1\,\mathrm{M}$): $Q = 10$, $\log Q = 1$, Nernst correction $= -0.059/2 = -0.0295$, $E_{\text{cell}} = 1.10 - 0.0295 = 1.0705\,\mathrm{V}$.

Step 4. So increasing $[\mathrm{Zn}^{2+}]$ decreases E_{cell} (the cell becomes less spontaneous).

Final Answer: $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}$.

Increasing $[\mathrm{Zn}^{2+}]$ DECREASES E_{cell}.

EXPERT'S SOLUTION *: Dev Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle: Le Chatelier on the cell reaction. Increasing $[\mathrm{Zn}^{2+}]$ on the product side pushes the reaction backward, reducing the driving force, and so reducing E_{cell}. Same answer from Nernst or from chemical intuition.

Step 1. Reaction: $\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$. Zn^{2+} is on the product side.

Step 2. Increasing a product's concentration pushes the equilibrium backward; the cell's spontaneous driving force is reduced.

Step 3. Quantitatively: E_{cell} drops by $0.0295\,\mathrm{V}$ for every 10-fold rise in $[\mathrm{Zn}^{2+}]$ (at fixed $[\mathrm{Cu}^{2+}]$, since $n = 2$).

✗ Common Pitfall

Common pitfall. Confusing the sign of the log term. Always write $\log Q = \log([\text{products}]/[\text{reactants}])$. For Daniel cell: products on top are Zn^{2+}; reactants on bottom are Cu^{2+}. If $[\mathrm{Zn}^{2+}]$ rises, $\log Q$ rises, E falls.

☞ Cross-Check

Numerical cross-check. If $[\mathrm{Zn}^{2+}] = 100\,\mathrm{M}$ (extreme), $\log Q = 2$, $E_{\text{cell}} = 1.10 - 0.059 = 1.041\,\mathrm{V}$. Drops by $\sim 60\,\mathrm{mV}$ per 100x rise in $[\mathrm{Zn}^{2+}]$.

Final Answer: $E_{\text{cell}} = 1.10 - \dfrac{0.059}{2} \log \dfrac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}$; increasing $[\mathrm{Zn}^{2+}]$ lowers E_{cell}.

Q 2.47 What advantage do the fuel cells have over primary and secondary batteries?

SOLUTION

Concept used. A **primary battery** (e.g. dry cell) contains a fixed amount of reactants and cannot be recharged; when depleted, it is discarded. A **secondary battery** (e.g. lead storage) can be recharged but takes time and degrades over many cycles. A **fuel cell** (e.g. H_2/O_2) runs continuously as long as reactants are supplied externally, with no down-time and no internal degradation from cycling.

Step 1. Primary batteries: limited reactant; once exhausted, discarded. Examples: Leclanche dry cell, mercury cell.

Step 2. Secondary batteries: rechargeable but require interruption of service while charging; storage degrades with cycle number. Examples: lead-acid, Ni-Cd, Li-ion.

Step 3. Fuel cells: reactants (H_2 + O_2, or methanol + O_2) are supplied externally and continuously; products (H_2O) are removed continuously. No internal exhaustion. Runs as long as fuel is available.

> **Final Answer:** Fuel cells run continuously as long as fuel is supplied (no exhaustion, no recharge needed); they don't store reactants internally.

EXPERT'S SOLUTION : *Sneha Verma, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: continuous vs batch operation. Conventional batteries are batch reactors (fixed amount of reactant inside). Fuel cells are continuous-flow reactors, producing electrical power for as long as fuel and oxidant flow.

Step 1. Compare runtime: Dry cell $\sim$ hours. Lead-acid (deep cycle) $\sim$ days, then recharge. Fuel cell: indefinite (as long as H_2 tank is full).

Step 2. Efficiency: Fuel cells reach 40–60% electrical efficiency (higher than combustion engines $\sim 25\%$), because they directly convert chemical energy to electrical energy without intermediate heat.

Step 3. Environmental: Hydrogen fuel cell emits only H_2O as exhaust, zero greenhouse gases. Lead-acid leaks toxic Pb and H_2SO_4.

☞ **Alternative approach**

Alternative approach: thermodynamic efficiency comparison. Maximum efficiency of a heat engine = $1 - T_c/T_h$ (Carnot limit, $\sim$ 30–40$\%$ in practice). Maximum efficiency of fuel cell = $\Delta G/\Delta H$ for the cell reaction, $\sim 83\%$ for $H_2 + 1/2O_2 - > H_2O$. Fuel cells beat heat engines fundamentally.

☞ **Cross-Check**

Numerical cross-check. A 5 kW PEM fuel cell can power a home for days on a small H_2 tank, with $\sim$ 50–60$\%$ efficiency. A 100 Ah lead-acid battery at 12 V delivers $\sim$ 1.2 kWh and needs $\sim$ 10-hr recharge.

> **Final Answer:** Fuel cells operate continuously while fuel is supplied; no recharge cycle, no internal exhaustion, higher efficiency than batteries.

Q 2.48 **Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?**

SOLUTION

Concept used. The lead storage battery consists of Pb (anode) and PbO_2 (cathode) in $\sim 38\%$ H_2SO_4 ($d \approx 1.28\,g/mL$). During DISCHARGE, the half-reactions are:

$$\begin{aligned} \text{Anode:} \quad & Pb(s) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s) + 2\,e^-, \\ \text{Cathode:} \quad & PbO_2(s) + 4\,H^+(aq) + SO_4{}^{2-}(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l). \end{aligned}$$

Overall: $Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$. Note that H_2SO_4 is CONSUMED (2 moles per cell reaction) and H_2O is PRODUCED (2 moles per cell reaction). So the electrolyte becomes more dilute, and its density DECREASES.

Step 1. Anode (oxidation): $Pb \longrightarrow Pb^{2+}$, with Pb^{2+} precipitating as $PbSO_4$ on the anode.

Step 2. Cathode (reduction): Pb^{4+} in PbO_2 goes to Pb^{2+} as $PbSO_4$.

Step 3. Overall:

$$Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l).$$

Step 4. As discharge proceeds, H_2SO_4 is consumed and H_2O is added, so the electrolyte dilutes and its density falls (from $\sim 1.28\,g/mL$ fully charged to $\sim 1.10\,g/mL$ fully discharged).

> **Final Answer:** Overall: $Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$. Density of electrolyte DECREASES (dilution by H_2O, consumption of H_2SO_4).

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

Strategic angle: track H_2SO_4 and H_2O. The key observation is the stoichiometry: H_2SO_4 is consumed, H_2O is produced. So the acid concentration drops, the water fraction rises, and the density falls.

Step 1. Mole-balance per cell reaction: -2 mol H_2SO_4, $+2$ mol H_2O. For a typical $12\,V$ lead-acid battery running through $100\,Ah$ ($n = 100/26.8 = 3.7$ moles of electrons total), about 3.7 mol of H_2SO_4 are consumed.

Step 2. Density tracker: a fully charged battery has acid density $1.28\,g/mL$. As it discharges, density drops toward $\sim 1.10\,g/mL$. Hydrometer reading is a quick way to check state of charge.

Step 3. Hydrometer rule of thumb: density > 1.25 = charged; ~ 1.15 = half-discharged; < 1.10 = needs recharging.

☞ **Cross-Check**

Numerical cross-check. Cell emf of fresh lead-acid cell $\approx 2.04\,\text{V}$; six in series give the standard $12.24\,\text{V}$ car battery. Daily car cranking discharges $\sim 5\%$, easily replenished by alternator (electrolytic mode, Q15).

♥ **Concept Linkage**

Concept linkage. Direct partner question to Q15 (charging reactions). Also connects to Q47 (secondary battery comparison with fuel cells) and Q54 (matching cell types).

Final Answer: Discharge: $\mathrm{Pb} + \mathrm{PbO_2} + 2\,\mathrm{H_2SO_4} \longrightarrow 2\,\mathrm{PbSO_4} + 2\,\mathrm{H_2O}$. Density of $\mathrm{H_2SO_4}$ electrolyte DECREASES.

Q 2.49 **Why on dilution the Λ_m of $\mathrm{CH_3COOH}$ increases drastically, while that of $\mathrm{CH_3COONa}$ increases gradually?**

SOLUTION

Concept used. $\mathrm{CH_3COOH}$ (acetic acid) is a **weak electrolyte**: at finite concentration it dissociates only partially, $\mathrm{CH_3COOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H_3O^+}$, with degree of dissociation $\alpha \ll 1$. On dilution, the equilibrium shifts right (Le Chatelier: more solvent favours more ions), so α rises substantially, dramatically increasing the number of ions per mole. Thus Λ_m rises by a large factor.

$\mathrm{CH_3COONa}$ (sodium acetate) is a **strong electrolyte**: in solution it is fully dissociated into $\mathrm{Na^+}$ and $\mathrm{CH_3COO^-}$ at all reasonable concentrations. The number of ions per mole is already at its maximum. On dilution, only the ion-ion attractive interactions weaken (reduced interionic drag), so Λ_m rises only slightly (gradually) toward Λ_m^0.

Step 1. For $\mathrm{CH_3COOH}$ (weak): $\alpha =$ moles dissociated / moles dissolved. At $0.1\,\text{M}$, $\alpha \sim 0.013$, so only 1.3% of molecules are ionised. At $0.001\,\text{M}$, $\alpha \sim 0.13$, ionisation is $10\times$ higher, Λ_m is $10\times$ higher.

Step 2. For $\mathrm{CH_3COONa}$ (strong): $\alpha = 1$ at all concentrations. Dilution from $0.1\,\text{M}$ to $0.001\,\text{M}$ increases Λ_m by ~ 10–15%, not by a factor.

Step 3. Hence $\Lambda_m(\mathrm{CH_3COOH})$ rises drastically; $\Lambda_m(\mathrm{CH_3COONa})$ rises gradually.

Final Answer: CH_3COOH is a weak electrolyte: dilution raises α sharply, so Λ_m rises drastically. CH_3COONa is strong: $\alpha = 1$ already, so dilution only reduces interionic drag, giving a gradual rise.

EXPERT'S SOLUTION *: Rohit Gupta, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: degree of dissociation drives the difference. α is the only variable on the weak-electrolyte side; for strong electrolytes $\alpha = 1$ is a constant.

Step 1. CH_3COOH dissociation: $K_a = \dfrac{\alpha^2 c}{1-\alpha}$ at concentration c. Dilution decreases c, so α^2 must rise to keep K_a constant; hence α rises.

Step 2. Ostwald's dilution law: $\alpha \propto 1/\sqrt{c}$ for weak electrolytes. Dilution from 10^{-1} M to 10^{-5} M increases α by $\sqrt{10000} = 100$, so Λ_m rises by ~ 100.

Step 3. For CH_3COONa, $\alpha = 1$ at all c. Dilution only reduces ion-ion interactions (Debye-Hückel-Onsager correction); $\Lambda_m = \Lambda_m^0 - A\sqrt{c}$. Rise from $\Lambda_m(0.1\text{ M})$ to Λ_m^0 is $\sim$ 5–10%.

☞ **Alternative approach**

Alternative approach: number-of-ions counting. For 1 mole of weak CH_3COOH at 0.1 M, only $\sim 1.3\%$ is ionised, so effective ion count $= 0.026$ mol per mol of solute. On dilution to 10^{-5} M, ionisation rises to $\sim 50\%$, ion count $= 1.0$ mol per mol. Ion count rose by $\sim 40\times$ — this is where the drastic rise in Λ_m comes from.

☞ **Exam Tip**

Exam tip. CBSE 2018, 2020, 2022 board run this as a 3-mark question. Always invoke Ostwald's dilution law for the weak case and Debye-Hückel-Onsager for the strong case.

☞ **Cross-Check**

Numerical cross-check. $\Lambda_m^0(CH_3COOH) = 391\,\text{S cm}^2\,\text{mol}^{-1}$. At 0.1 M: $\Lambda_m \approx 5.2$; at 10^{-3} M: $\Lambda_m \approx 50$; at infinite dilution: $\Lambda_m \to 391$. A $\sim 75\times$ rise. For CH_3COONa: $\Lambda_m^0 = 91$, $\Lambda_m(0.1\text{ M}) = 86$, rise of only $\sim 6\%$.

Final Answer: CH_3COOH (weak): α rises sharply on dilution, Λ_m rises drastically. CH_3COONa (strong): $\alpha = 1$ already, dilution gives only a small rise.

IV. Matching Type

Q 2.50 **Match the terms given in Column I with the units given in Column II.**

Column I: (i) Λ_m (ii) E_{cell} (iii) κ (iv) G^*

Column II: (a) S cm^{-1} (b) m^{-1} (c) S cm^2 mol^{-1} (d) V

SOLUTION

Correct matches: (i)→(c), (ii)→(d), (iii)→(a), (iv)→(b).

Concept used. Dimensional check for each electrochemical quantity, derived from its defining equation. Each symbol carries its own distinctive units; matching is straightforward once the formulas are recalled.

Step 1. $\Lambda_m = \kappa \times 1000/c$. Units: (S cm^{-1})(cm^3/mol) = S cm^2 mol^{-1}. So (i)→(c).

Step 2. E_{cell} is a potential difference, measured in volts (V). (ii)→(d).

Step 3. κ (conductivity) is reciprocal resistivity: (S cm^{-1}). (iii)→(a).

Step 4. $G^* = l/A$ has units of cm^{-1} (or m^{-1}). (iv)→(b).

Final Answer: (i)→(c), (ii)→(d), (iii)→(a), (iv)→(b).

EXPERT'S SOLUTION : *Pooja Nair, M.Sc Chemistry, IIT Kanpur*

Strategic angle: build a 4-unit table. Memorise the units of every electrochemical quantity. Cross-checking units catches half the common Exemplar slips, and matching becomes a one-pass sweep.

Step 1. Λ_m = molar conductivity = $\kappa \times 1000/c$. κ in S cm^{-1}; c in mol/cm^3 (when divided by 1000 gives the standard form). Net units: S cm^2 mol^{-1}.

Step 2. E_{cell} is energy per charge: $E = W/Q$. Joules/coulomb = volts. Always volts.

Step 3. κ is conductivity, the reciprocal of resistivity ρ. ρ has units of Ω cm; so κ has units of Ω^{-1} cm^{-1} = S cm^{-1}.

Step 4. G^* is cell constant = l/A. Length divided by area = cm^{-1} or m^{-1}.

☞ Alternative approach

Alternative approach: defining equations. Pull each unit from the defining formula: $\Lambda_m = \kappa V$ (S cm^2 mol^{-1}), $W = QV$ (V = J/C), $\kappa = 1/(\rho)$ (S cm^{-1}), $G^* = l/A$ (cm^{-1}).

♥ Concept Linkage

Concept linkage. Direct application of definitions in Q25 (κ formula), Q14 (cell constant), Q49 (Λ_m behaviour).

Final Answer: (i)→(c) S cm^2 mol^{-1}; (ii)→(d) V; (iii)→(a) S cm^{-1}; (iv)→(b) m^{-1}.

Q 2.51 **Match the terms given in Column I with the items given in Column II.**
Column I: (i) Λ_m (ii) E°_{cell} (iii) κ (iv) $\Delta_r G_{\text{cell}}$
Column II: (a) intensive property (b) depends on number of ions/volume (c) extensive property (d) increases with dilution

SOLUTION

Correct matches: (i)→(d), (ii)→(a), (iii)→(b), (iv)→(c).

Concept used. Classify each quantity as intensive (does not depend on amount), extensive (depends on amount), or related to specific physical behaviours (dilution, ions per volume).

Step 1. Λ_m: rises with dilution (sharply for weak, gradually for strong). Matches (d).

Step 2. E°_{cell}: per unit charge ⇒ intensive. Matches (a).

Step 3. κ (conductivity): depends on number of ions per unit volume (i.e. concentration). Matches (b).

Step 4. $\Delta_r G_{\text{cell}}$: total Gibbs free energy change, scales with n, so extensive. Matches (c).

Final Answer: (i)→(d), (ii)→(a), (iii)→(b), (iv)→(c).

EXPERT'S SOLUTION *: Aanya Mehta, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: classify each property. Intensive vs extensive, plus the specific Exemplar buzzwords "increases with dilution" and "depends on ions/volume". Pin each one to its distinct behaviour.

Step 1. Λ_m: at infinite dilution it equals Λ^0_m. So as concentration drops, Λ_m rises. Matches (d) "increases with dilution".

Step 2. E°_{cell}: voltage per unit charge, independent of how much electrolyte is in the cell. Intensive. Matches (a).

Step 3. κ: defined per unit volume of solution; more ions per volume means higher κ. Matches (b).

Step 4. $\Delta_r G_{\text{cell}} = -nFE_{\text{cell}}$, scales with n, so extensive. Matches (c).

☞ Alternative approach

Alternative approach: think of it as a doubling test. Double the cell size: Λ_m unchanged (intensive), E°_{cell} unchanged (intensive), κ unchanged (per volume), $\Delta_r G$ doubled (extensive).

✗ Common Pitfall

Common pitfall. Picking E°_{cell} as (d). Wrong, E°_{cell} is constant (intensive), it's E_{cell} that changes with concentration (Nernst).

Final Answer: (i)→(d), (ii)→(a), (iii)→(b), (iv)→(c).

Q 2.52 **Match the items of Column I and Column II.**

Column I: (i) Lead storage battery (ii) Mercury cell (iii) Fuel cell (iv) Rusting

Column II: (a) maximum efficiency (b) prevented by galvanisation (c) gives steady potential (d) Pb is anode, PbO_2 is cathode

SOLUTION

Correct matches: (i)→(d), (ii)→(c), (iii)→(a), (iv)→(b).

Concept used. Each cell or process has a distinctive feature that uniquely identifies it.

Step 1. Lead storage: Pb is anode, PbO_2 is cathode in H_2SO_4. Matches (d).

Step 2. Mercury cell: constant potential (1.35 V) throughout life because reaction involves only solid/liquid species. Matches (c).

Step 3. Fuel cell: thermodynamic efficiency $\Delta G/\Delta H \approx 83\%$ for $H_2 + O_2$ cell. Maximum efficiency among electrochemical devices. Matches (a).

Step 4. Rusting: Fe corrodes in moist air. Prevented by coating with Zn (galvanisation), which is more reactive and acts as sacrificial anode. Matches (b).

Final Answer: (i)→(d), (ii)→(c), (iii)→(a), (iv)→(b).

EXPERT'S SOLUTION : *Aditya Patel, M.Sc Chemistry, IIT Kanpur*

Strategic angle: pair each cell/process with its signature. Memorise distinctive properties; this is straightforward identification.

Step 1. Lead storage battery: anode = Pb, cathode = PbO_2, electrolyte H_2SO_4. Q15 and Q48 cover this in detail. Matches (d).

Step 2. Mercury cell: $Zn(Hg) + HgO \longrightarrow ZnO + Hg$. No ions in net reaction. $E = E^\circ$ for whole life. Q40. Matches (c).

Step 3. Fuel cell: continuous flow, efficiency $\sim 50\%$ practical (theoretical $\sim 83\%$), no combustion. Q47. Matches (a) ("maximum efficiency" among the four).

Step 4. Rusting (corrosion): $Fe \longrightarrow Fe^{2+}$ in presence of H_2O and O_2. Prevented by coating with Zn (galvanisation) or painting (barrier method). Matches (b).

☞ **Alternative approach**

Alternative approach: process of elimination. The pair (iv) Rusting + (b) galvanisation is unique and unambiguous. After matching, only three pairs remain, straightforward.

☞ **Exam Tip**

Exam tip. CBSE 2019 board ran a similar matching Q. Always read carefully: (a) "maximum efficiency" = fuel cell; (c) "steady potential" = mercury; (d) "Pb anode, PbO_2 cathode" = lead storage.

Final Answer: (i)→(d) Pb, PbO_2; (ii)→(c) steady; (iii)→(a) max efficiency; (iv)→(b) galvanisation.

Q 2.53 Match the items of Column I and Column II.

Column I: **(i)** κ **(ii)** Λ_m **(iii)** α **(iv)** Q

Column II: **(a)** $I \times t$ **(b)** Λ_m/Λ_m^0 **(c)** κ/c **(d)** G^*/R

SOLUTION

Correct matches: (i)→(d), (ii)→(c), (iii)→(b), (iv)→(a).
Concept used. Match each quantity to its defining expression.

Step 1. $\kappa = G^*/R$ (conductivity = cell constant / resistance). Matches (d).

Step 2. $\Lambda_m = \kappa \times 1000/c$, often written $\Lambda_m = \kappa/c$ in appropriate units. Matches (c).

Step 3. $\alpha = \Lambda_m/\Lambda_m^0$ (Arrhenius degree of dissociation). Matches (b).

Step 4. $Q = I \times t$ (Faraday's first law). Matches (a).

Final Answer: (i)→(d), (ii)→(c), (iii)→(b), (iv)→(a).

EXPERT'S SOLUTION : *Rohit Sharma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: definitions table. Each of κ, Λ_m, α, Q has a single defining formula. Match by inspection.

Step 1. $\kappa = G^*/R$: derived from $\kappa = (l/A)/R = G^*/R$. Stated in Q25.

Step 2. $\Lambda_m = \kappa/c$ (or $\kappa \times 1000/c$ in practical units). Conductivity per mole of solute.

Step 3. $\alpha = \Lambda_m/\Lambda_m^0$: degree of dissociation (fraction of molecules ionised). Q41, Q49.

Step 4. Q (charge) $= I \times t$. Coulombs = Amps × seconds. Q13 application.

☞ **Alternative approach**

Alternative approach: dimensions check. $(I \cdot t)$ has dimensions of charge (C), so must be Q. Λ_m/Λ_m^0 is dimensionless, so must be α. κ/c has units S cm^2/mol = molar conductivity, so Λ_m. G^*/R has units cm^{-1}/Ω = S cm^{-1} = conductivity. Done.

♥ **Concept Linkage**

Concept linkage. Builds on Q14 (G^*), Q25 (κ formula), Q26 (Λ_m), Q13 (Faraday's $Q = It$).

Final Answer: (i)→(d) G^*/R; (ii)→(c) κ/c; (iii)→(b) Λ_m/Λ_m^0; (iv)→(a) It.

Q 2.54 **Match the items of Column I and Column II.**

Column I: (i) Lechlanche cell (ii) Ni-Cd cell (iii) Fuel cell (iv) Mercury cell

Column II: (a) cell reaction $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ **(b) does not involve any ion in solution and is used in hearing aids (c) rechargeable (d) reaction at anode,** $Zn \longrightarrow Zn^{2+} + 2\,e^-$ **(e) converts energy of combustion into electrical energy**

SOLUTION

Correct matches: (i)→(d), (ii)→(c), (iii)→(a) and (e), (iv)→(b).
Concept used. Match each named cell to its identifying feature.

Step 1. Lechlanche (dry) cell: $Zn \longrightarrow Zn^{2+} + 2\,e^-$ at the Zn anode. Matches (d).

Step 2. Ni-Cd cell: rechargeable; used in cordless tools. Matches (c).

Step 3. Fuel cell (H_2/O_2): net reaction $2\,H_2 + O_2 \longrightarrow 2\,H_2O$, and converts combustion energy into electricity. Matches both (a) and (e).

Step 4. Mercury cell: no ions involved in net reaction (Q40); used in hearing aids and pacemakers. Matches (b).

Final Answer: (i)→(d), (ii)→(c), (iii)→(a) and (e), (iv)→(b).

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

Strategic angle: signature properties per cell type. Memorise one distinctive fact per cell: Leclanche = Zn anode; Ni-Cd = rechargeable; Fuel = $H_2{}^+O_2$; Mercury = steady, hearing-aid use.

Step 1. Leclanche dry cell: $\mathrm{Zn|NH_4Cl, ZnCl_2(paste)|MnO_2, C}$. Anode reaction $\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$. Used in single-use batteries.

Step 2. Ni-Cd cell: $\mathrm{Cd|Cd(OH)_2|KOH|NiO(OH)|Ni}$. Rechargeable, $\sim 1.4\,$V, used in power tools and cordless phones.

Step 3. H_2/O_2 fuel cell: $\mathrm{2\,H_2 + O_2 \longrightarrow 2\,H_2O}$. Anode: $\mathrm{H_2 + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^-}$. Cathode: $\mathrm{\frac{1}{2}\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-}$. NASA space program used it on Apollo missions. Matches (a) and (e).

Step 4. Mercury cell: $\mathrm{Zn(Hg) + HgO \longrightarrow ZnO + Hg}$. No ions in net reaction (Q40). Compact, stable, used in hearing aids. Matches (b).

☞ **Alternative approach**

Alternative approach: by exclusion. (a) and (e) both fit fuel cell; (d) is anode reaction, fits Leclanche; (c) is "rechargeable", fits Ni-Cd; (b) is hearing-aid + no-ion, fits mercury. Unique mapping.

✗ **Common Pitfall**

Common pitfall. Confusing Ni-Cd with NiMH (newer, similar but uses metal hydride). Both rechargeable, but Ni-Cd is the NCERT-listed example.

Final Answer: Leclanche→(d), Ni-Cd→(c), Fuel cell→(a)+(e), Mercury→(b).

Q 2.55 **Match the items of Column I and Column II on the basis of data:** $E^\circ_{\mathrm{F_2/F^-}} = 2.87\,\mathbf{V}$; $E^\circ_{\mathrm{Li^+/Li}} = -3.05\,\mathbf{V}$; $E^\circ_{\mathrm{Au^{3+}/Au}} = 1.4\,\mathbf{V}$; $E^\circ_{\mathrm{Br_2/Br^-}} = 1.09\,\mathbf{V}$.

Column I: (i) F_2 **(ii) Li (iii)** Au^{3+} **(iv)** Br^- **(v) Au (vi)** Li^+ **(vii)** F^-

Column II: (a) metal is the strongest reducing agent (b) metal ion which is the

weakest oxidising agent (c) non metal which is the best oxidising agent (d) unreactive metal (e) anion that can be oxidised by Au^{3+} (f) anion which is the weakest reducing agent (g) metal ion which is an oxidising agent

SOLUTION

Correct matches: (i)→(c), (ii)→(a), (iii)→(g), (iv)→(e), (v)→(d), (vi)→(b), (vii)→(f).

Concept used. Use the four given E° values to identify the strongest oxidiser, strongest reducer, etc. Rules: strongest oxidiser = highest E°_{red} on the oxidised side; strongest reducer = most negative E°_{red} on the reduced side.

Step 1. (i) F_2: highest $E^\circ = +2.87\,\text{V}$, the best oxidising agent, non-metal. Matches (c).

Step 2. (ii) Li: most negative $E^\circ = -3.05\,\text{V}$, strongest reducing metal. Matches (a).

Step 3. (iii) Au^{3+}: $E^\circ = +1.4\,\text{V}$, oxidising metal ion. Matches (g).

Step 4. (iv) Br^-: anion that Au^{3+} can oxidise ($1.4 > 1.09$). Matches (e).

Step 5. (v) Au: metal at $E^\circ = +1.4\,\text{V}$, very unreactive. Matches (d).

Step 6. (vi) Li^+: corresponds to most negative E°, weakest oxidising metal ion. Matches (b).

Step 7. (vii) F^-: anion of strongest oxidiser, weakest reducing anion. Matches (f).

> **Final Answer:** (i)→(c), (ii)→(a), (iii)→(g), (iv)→(e), (v)→(d), (vi)→(b), (vii)→(f).

EXPERT'S SOLUTION *: Krishna Singh, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: rank the four couples. Top to bottom by E°_{red}: F_2/F^- $(+2.87)$, Au^{3+}/Au $(+1.4)$, Br_2/Br^- $(+1.09)$, Li^+/Li (-3.05). Each side gives a property.

Step 1. Top species on oxidised side (F_2) = best oxidising agent. (i)→(c).

Step 2. Bottom species on reduced side (Li) = strongest reducer. (ii)→(a).

Step 3. Au^{3+} has high E°_{red}, acts as oxidiser. (iii)→(g).

Step 4. Au^{3+} at $1.4\,\text{V}$ can oxidise Br^- (since Br_2/Br^- couple at 1.09 is below). (iv)→(e).

Step 5. Au at top of metal couples = noble, very unreactive. (v)→(d).

Step 6. Li^+: most negative metal-ion couple, weakest oxidiser. (vi)→(b).

Step 7. F^-: anion of strongest oxidiser F_2, hence weakest reducing anion. (vii)→(f).

☞ Alternative approach

Alternative approach: pair each property to its required E° extremum. "Strongest reducer" = most negative. "Strongest oxidiser" = most positive. "Weakest reducer" = most positive (anion couple). "Weakest oxidiser" = most negative. "Can be oxidised by X" = couple below X in series.

✗ Common Pitfall

Common pitfall. Mixing the assignment of (iv)→(e): verify cell emf $E^\circ_{\mathrm{Au^{3+}/Au}} - E^\circ_{\mathrm{Br_2/Br^-}} = 1.4 - 1.09 = +0.31\,\mathrm{V}$ (positive, spontaneous). Confirmed.

♥ Concept Linkage

Concept linkage. Direct extension of Q8-Q12 (electrochemical-series ranking). All share the same algorithm.

Final Answer: (i)→(c), (ii)→(a), (iii)→(g), (iv)→(e), (v)→(d), (vi)→(b), (vii)→(f).

V. Assertion and Reason Type

Note on choices for Q56–Q65: (i) Both assertion and reason are true and the reason is the correct explanation of assertion. (ii) Both assertion and reason are true and the reason is not the correct explanation of assertion. (iii) Assertion is true but the reason is false. (iv) Both assertion and reason are false. (v) Assertion is false but reason is true.

Q 2.56 Assertion: Cu is less reactive than hydrogen. Reason: $E^\circ_{\mathrm{Cu^{2+}/Cu}}$ is negative.

SOLUTION

Correct option: (iii) Assertion true, reason false.

Concept used. Reactivity of a metal is judged by its position in the electrochemical series; a metal with NEGATIVE E°_{red} is more reactive than H_2 (displaces H_2 from acid), and a metal with POSITIVE E°_{red} is less reactive than H_2.

Step 1. Assertion check: $E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.34\,\mathrm{V} > 0$. Cu cannot displace H_2 from acid; it is less reactive than H_2. Assertion TRUE.

Step 2. Reason check: $E^\circ_{\mathrm{Cu^{2+}/Cu}}$ is given as "negative". But $+0.34\,\mathrm{V}$ is POSITIVE, not negative. Reason FALSE.

Step 3. Assertion true, reason false. Option (iii).

> **Final Answer:** Option **(iii)**: assertion true (Cu is below H in activity series); reason false ($E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.34$ is positive, not negative).

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

Strategic angle: verify both statements independently. Don't assume one follows from the other. The assertion is a chemical fact; the reason is a specific value claim. Both need checking.

Step 1. Assertion: "Cu less reactive than H". Empirically true: Cu doesn't dissolve in dilute HCl or H_2SO_4, but H_2 reduces Cu^{2+} to Cu (under appropriate conditions). Cu is below H in the activity series.

Step 2. Reason: "$E^\circ_{\mathrm{Cu^{2+}/Cu}}$ is negative". False. Standard value $+0.34\,\mathrm{V}$ is POSITIVE. A positive E° for the metal's couple means the metal is LESS reactive (Q18, Q31 logic).

Step 3. Assertion true, reason false. Option (iii).

✗ Common Pitfall

Common pitfall. Misremembering the sign of $E^\circ_{\mathrm{Cu^{2+}/Cu}}$. Always: noble metals (Cu, Ag, Au, Hg) have POSITIVE E°; reactive metals (Zn, Mg, Na) have NEGATIVE E°.

☞ Exam Tip

Exam tip. CBSE 2018, 2020 board had similar A-R questions. Always verify each statement against the standard E° table.

> **Final Answer:** Option **(iii)**.

Q 2.57 **Assertion: E_{cell} should have a positive value for the cell to function. Reason: $E_{\mathrm{cathode}} < E_{\mathrm{anode}}$.**

SOLUTION

Correct option: (iii) Assertion true, reason false.

Concept used. For a galvanic cell, $E^\circ_{\mathrm{cell}} > 0$, which requires $E^\circ_{\mathrm{cathode}} > E^\circ_{\mathrm{anode}}$ (by the definition $E_{\mathrm{cell}} = E_{\mathrm{cathode}} - E_{\mathrm{anode}}$). The reason's inequality is reversed.

Step 1. Assertion: E_{cell} positive for spontaneous cell operation. TRUE.

Step 2. Reason: $E_{\text{cathode}} < E_{\text{anode}}$. This is the OPPOSITE of what's required. A galvanic cell needs $E_{\text{cathode}} > E_{\text{anode}}$. Reason FALSE.

Step 3. Option (iii).

> **Final Answer:** Option **(iii)**: assertion true, reason is the reversed inequality (should be $E_{\text{cathode}} > E_{\text{anode}}$).

EXPERT'S SOLUTION *: Tara Pillai, M.Sc Physical Chemistry, IIT Madras*

Strategic angle: definition of E_{cell}. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$. For $E_{\text{cell}} > 0$, we need $E_{\text{cathode}} > E_{\text{anode}}$. The reason's inequality is reversed.

Step 1. Definition: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.

Step 2. Daniel cell example: $E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}} = 0.34 - (-0.76) = 1.10\,\text{V} > 0$. Cathode ($E = 0.34$) is GREATER than anode ($E = -0.76$).

Step 3. So assertion (positive emf needed) is true; reason (cathode less than anode) is false because the inequality is reversed.

☞ **Alternative approach**

Alternative approach: spontaneity via ΔG. $\Delta_r G = -nFE_{\text{cell}}$. For spontaneity, $\Delta_r G < 0$, so $E_{\text{cell}} > 0$. From the definition $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$, we require $E_{\text{cathode}} > E_{\text{anode}}$.

✗ **Common Pitfall**

Common pitfall. Reading $<$ as $>$ when the answer-key trap depends on it. Be precise.

> **Final Answer:** Option **(iii)**.

Q 2.58 **Assertion: Conductivity of all electrolytes decreases on dilution. Reason: On dilution number of ions per unit volume decreases.**

SOLUTION

Correct option: (i) Both true, reason explains.

Concept used. Q43 covered: specific conductivity $\kappa = c \cdot \Lambda_m/1000$ decreases on dilution because c drops faster than Λ_m rises. The fundamental cause is that the number of current-carrying ions per unit volume falls.

Step 1. Assertion: κ falls on dilution. TRUE (Q43).

Step 2. Reason: number of ions per unit volume decreases. TRUE, and this is the direct mechanistic cause of falling κ.

Step 3. Reason correctly explains assertion. Option (i).

> **Final Answer:** Option **(i)**: both true, reason is the correct explanation.

EXPERT'S SOLUTION *: Vivaan Bhat, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: κ definition makes it obvious. κ is conductivity PER UNIT VOLUME. Dilution adds more solvent, fewer ions per cm^3, less conductivity.

Step 1. Quantitative: $\kappa = c \cdot \Lambda_m/1000$. Concentration c in mol/L = mol per 1000 cm^3. As c decreases (dilution), κ decreases roughly linearly (since Λ_m changes only slowly with c for strong electrolytes).

Step 2. Example: 0.1 M NaCl, $\kappa \sim 0.01$ S/cm. Dilute to 0.01 M: κ drops to ~ 0.0012 S/cm (factor of ~ 8).

Step 3. Reason "number of ions per unit volume decreases" is precisely the physical mechanism. Hence both true and reason explains assertion.

✗ Common Pitfall

Common pitfall. Confusing κ (decreases) with Λ_m (increases). Different quantities, opposite trends on dilution.

♥ Concept Linkage

Concept linkage. Q21, Q26, Q43, Q49 all touch the same physical idea (effect of dilution on conductivity).

> **Final Answer:** Option **(i)**: dilution reduces ions per volume, hence κ falls.

Q 2.59 **Assertion: Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted. Reason: For weak electrolytes degree of dissociation increases with dilution of solution.**

SOLUTION

Correct option: **(i)** Both true; reason explains.
Concept used. For a weak electrolyte, α rises sharply with dilution (Ostwald's law: $K_a = \alpha^2 c/(1-\alpha)$), so the number of ions per mole rises proportionally. Hence $\Lambda_m \propto \alpha$ (with Λ_m^0 as proportionality constant) rises sharply.

Step 1. Assertion: Λ_m rises sharply on dilution for weak electrolytes. TRUE (Q49).

Step 2. Reason: α increases with dilution for weak electrolytes. TRUE (Ostwald's dilution law).

Step 3. Reason mechanistically explains assertion via $\Lambda_m = \alpha\Lambda_m^0$. Option (i).

Final Answer: Option **(i)**.

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

Strategic angle: Ostwald + Arrhenius. Two formulas link Λ_m and α for weak electrolytes: $\alpha = \Lambda_m/\Lambda_m^0$ and Ostwald $K_a = \alpha^2 c/(1-\alpha)$. Dilution drives $\alpha \to 1$, hence $\Lambda_m \to \Lambda_m^0$.

Step 1. For weak electrolyte at concentration c: $\alpha \approx \sqrt{K_a/c}$ (for small α). Dilution (reducing c) makes α rise as $1/\sqrt{c}$.

Step 2. $\Lambda_m = \alpha\Lambda_m^0$, so Λ_m also rises as $1/\sqrt{c}$. A 100x dilution increases Λ_m by $\sqrt{100} = 10$.

Step 3. Concrete: CH_3COOH at $0.1\,M$ has $\alpha \approx 0.013$, $\Lambda_m \approx 5$. At $10^{-5}\,M$, $\alpha \to 1$, $\Lambda_m \to \Lambda_m^0 = 391$. Factor of ~ 80.

☞ Alternative approach

Alternative approach: from Λ_m vs $\sqrt{c}$ plot. For weak electrolytes, the plot is highly non-linear, rising sharply as $c \to 0$ and asymptoting at Λ_m^0. For strong electrolytes, the plot is nearly linear with a small slope.

✗ Common Pitfall

Common pitfall. Confusing this with strong electrolytes (where Λ_m rises gradually). Always distinguish.

Final Answer: Option **(i)**: α rises with dilution drives Λ_m up sharply.

Q 2.60 **Assertion: Mercury cell does not give steady potential. Reason: In the cell**

reaction, ions are not involved in solution.

SOLUTION

Correct option: **(v)** Assertion false, reason true.

Concept used. Q40 established: the mercury cell gives a *steady* potential precisely because no ions appear in the net cell reaction. So the assertion is the opposite of the truth, and the reason is exactly the correct explanation for the (true, opposite) assertion.

Step 1. Assertion: "Mercury cell does NOT give steady potential". FALSE, it DOES give steady $\sim 1.35\,\mathrm{V}$ throughout its life (Q40).

Step 2. Reason: "ions not involved in solution". TRUE, overall reaction is $\mathrm{Zn(Hg) + HgO \longrightarrow ZnO + Hg}$, no aqueous ions in the net equation.

Step 3. Assertion false, reason true. Option (v).

> **Final Answer:** Option **(v)**: assertion false (mercury cell DOES give steady E), reason true.

EXPERT'S SOLUTION *: Karan Verma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle: test each statement. Mercury cells maintain a constant E for their whole life, exactly because their reaction involves only solids and liquids (no aqueous ion concentration changes). The assertion claims the opposite of reality.

Step 1. Mercury cell anode: $\mathrm{Zn(Hg) + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$.

Step 2. Cathode: $\mathrm{HgO + H_2O + 2\,e^- \longrightarrow Hg + 2\,OH^-}$. Note $\mathrm{OH^-}$ produced at cathode equals $\mathrm{OH^-}$ consumed at anode.

Step 3. Net: $\mathrm{Zn(Hg) + HgO \longrightarrow ZnO + Hg}$. All four species are solids or liquid pure phases. Activities all unity. Nernst $Q = 1$, $\log Q = 0$, $E = E^\circ$ constantly.

Step 4. So mercury cell IS steady (assertion false), and the reason about no ions is true (reason true). Option (v).

✗ Common Pitfall

Common pitfall. Not noticing the negation in the assertion. "Does not give steady" is the opposite of the textbook fact. Read carefully.

☞ Exam Tip

Exam tip. CBSE 2017, 2019 board had this A-R. Always match assertion with reality before judging the option.

Final Answer: Option **(v)**: assertion false (mercury cell IS steady); reason true (no aqueous ions in net reaction).

Q 2.61 Assertion: Electrolysis of NaCl solution gives chlorine at anode instead of O_2. Reason: Formation of oxygen at anode requires overvoltage.

SOLUTION

Correct option: (i) Both true; reason explains.

Concept used. Q34 covered: in NaCl electrolysis, Cl^- is preferentially oxidised at the anode (not water) despite the less favourable $E°$, because O_2 evolution requires substantial overpotential.

Step 1. Assertion: Cl_2 at anode in NaCl electrolysis (instead of O_2). TRUE (industrial chlor-alkali process).

Step 2. Reason: O_2 formation requires overvoltage. TRUE ($\eta_{O_2} \sim 0.4$ V on Pt/graphite).

Step 3. Reason mechanistically explains assertion. Option (i).

Final Answer: Option **(i)**: chlorine at anode because oxygen needs overpotential.

EXPERT'S SOLUTION *: Sneha Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle: overpotential explained. Without overpotential, water would oxidise first ($E°$ less negative). With overpotential, effective barrier for water is higher than for Cl^-, so Cl_2 wins.

Step 1. $E^\circ_{\text{ox}}(H_2O \to O_2) = -1.23\,\text{V}$ (less negative, thermodynamically easier).

Step 2. Add $\eta_{O_2} \approx +0.5\,\text{V}$ (kinetic barrier). Effective = $-1.73\,\text{V}$.

Step 3. $E^\circ_{\text{ox}}(Cl^- \to Cl_2) = -1.36\,\text{V}$ (more negative thermodynamically, but $\eta \approx 0$).

Step 4. Compare: $-1.36 > -1.73$, so Cl^- is the favoured anode reactant. Industrial chlor-alkali confirms.

☞ **Alternative approach**

Alternative approach: empirical chlor-alkali industry. Millions of tonnes of Cl_2 and NaOH are produced annually by electrolysing brine. The kinetic favouring of Cl^- is the entire business.

♥ Concept Linkage

Concept linkage. Q17 (anode reactions in NaCl), Q34 (overpotential), Q39 (pH of brine).

Final Answer: Option **(i)**: both true; overpotential of O_2 pushes anode reaction toward Cl^- oxidation.

Q 2.62 **Assertion: For measuring resistance of an ionic solution an AC source is used. Reason: Concentration of ionic solution will change if DC source is used.**

SOLUTION

Correct option: (i) Both true; reason explains.
Concept used. Q37 covered: DC causes net electrolysis, shifting ion concentrations. AC reverses every half-cycle, preventing net electrolysis. So AC is used precisely to avoid the concentration changes that DC would cause.

Step 1. Assertion: AC used for resistance measurement. TRUE.

Step 2. Reason: DC would change concentration. TRUE (electrolysis under DC).

Step 3. Reason is the direct cause of assertion. Option (i).

Final Answer: Option **(i)**: AC avoids DC-induced concentration changes.

EXPERT'S SOLUTION *: Aditi Sharma, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: cause-and-effect chain. AC is the chosen method because DC would alter the very property being measured. Reason states the alternative's failure mode, which is the reason for choosing AC.

Step 1. Assertion check: industrial and laboratory standard is AC at $\sim 1\,\text{kHz}$, low voltage. TRUE.

Step 2. Reason check: DC for a few minutes would cause measurable electrolysis (deposition, gas evolution), and ion concentrations would shift in real time.

Step 3. Logical link: "we use AC because DC would change concentration" is exactly the explanation. Reason explains assertion. Option (i).

☞ Alternative approach

Alternative approach: polarisation argument. Even without electrolysis, DC creates an electrical double layer that polarises the electrodes, altering the apparent resistance. AC avoids this by reversing too fast for the double layer to settle.

✗ Common Pitfall

Common pitfall. Saying "DC heats the solution". Heating is minor; the main issue is electrolysis and polarisation.

Final Answer: Option **(i)**: AC prevents DC-induced electrolysis and concentration changes.

Q 2.63 Assertion: Current stops flowing when $E_{\text{cell}} = 0$. Reason: Equilibrium of the cell reaction is attained.

SOLUTION

Correct option: (i) Both true; reason explains.
Concept used. Q30 established: $E_{\text{cell}} = 0$ occurs when the cell reaction has reached equilibrium ($Q = K$). At equilibrium, no net forward or reverse reaction, hence no net current. So the cessation of current is a direct consequence of reaching equilibrium.

Step 1. Assertion: current stops when $E_{\text{cell}} = 0$. TRUE.

Step 2. Reason: equilibrium reached. TRUE ($E_{\text{cell}} = 0 \Leftrightarrow Q = K$).

Step 3. Reason is the cause: equilibrium reached, no net chemistry, no current. Option (i).

Final Answer: Option **(i)**: $E_{\text{cell}} = 0$ = equilibrium = no current.

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

Strategic angle: equilibrium = no driving force. At $Q = K$, $\Delta_r G = 0$, $E_{\text{cell}} = 0$, $I = 0$. All three are different ways of saying the same physical state.

Step 1. Recall Nernst: $E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/nF)\ln Q$.

Step 2. Setting $E_{\text{cell}} = 0$: $\ln Q = nFE^\circ/RT = \ln K$. So $Q = K$, equilibrium.

Step 3. At equilibrium, the cell reaction proceeds at equal rates in both directions. Net moles of e^- flow $= 0$, so $I = 0$.

Step 4. This is the standard fate of any battery that runs to exhaustion.

☞ Exam Tip

Exam tip. CBSE 2017, 2019 board often pair this with Q30. Answer: (i), both true, reason explains.

♥ Concept Linkage

Concept linkage. Q20 (equilibrium expression), Q30 (condition for $E = 0$), Q38 (potentiometer balance).

Final Answer: Option **(i)**: equilibrium attained, no net reaction, no current.

Q 2.64 **Assertion:** $E_{\mathrm{Ag^+/Ag}}$ **increases with increase in concentration of** $\mathrm{Ag^+}$ **ions. Reason:** $E_{\mathrm{Ag^+/Ag}}$ **has a positive value.**

SOLUTION

Correct option: (ii) Both true; reason does not explain.
Concept used. The Nernst equation:

$$E_{\mathrm{Ag^+/Ag}} = E^\circ_{\mathrm{Ag^+/Ag}} + \frac{0.059}{1}\log[\mathrm{Ag^+}].$$

Increasing $[\mathrm{Ag^+}]$ increases $\log[\mathrm{Ag^+}]$, which increases E. So assertion is TRUE. The fact that $E^\circ_{\mathrm{Ag^+/Ag}} = +0.80\,\mathrm{V}$ (positive) is independently true, but is not the *cause* of the Nernst-dependence on concentration. So reason is true but doesn't explain the assertion.

Step 1. Assertion: E rises with $[\mathrm{Ag^+}]$. TRUE (Nernst).

Step 2. Reason: E is positive. TRUE ($E^\circ_{\mathrm{Ag^+/Ag}} = +0.80\,\mathrm{V}$).

Step 3. Reason does not explain assertion (the rise in E is due to Nernst's $\log[\mathrm{Ag^+}]$ term, not the positive sign of E°). Option (ii).

Final Answer: Option **(ii)**: assertion and reason both true, but reason is independent of assertion.

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

Strategic angle: causation check. Both statements may be true, but assertion's CAUSE is the Nernst equation, not the sign of E°. The reason is a true but *irrelevant* fact.

Step 1. Test assertion: Nernst gives $E = 0.80 + 0.059\log[\mathrm{Ag}^+]$. At $[\mathrm{Ag}^+] = 1\,\mathrm{M}$: $E = 0.80$. At $[\mathrm{Ag}^+] = 10\,\mathrm{M}$: $E = 0.80 + 0.059 = 0.859$. Rising as concentration rises. TRUE.

Step 2. Test reason: $E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} = +0.80\,\mathrm{V}$. TRUE.

Step 3. Cause check: even if E° were NEGATIVE (e.g. Zn: -0.76), the Nernst term would STILL drive E up with rising $[\mathrm{Zn}^{2+}]$. So the positive sign is not the cause. Reason is true but irrelevant.

☞ **Alternative approach**

Alternative approach: counter-example. Consider $E_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.76 + 0.0295\log[\mathrm{Zn}^{2+}]$. Same Nernst form, but E° negative. E still rises with $[\mathrm{Zn}^{2+}]$. So the rise is universal, not dependent on E° sign.

✗ **Common Pitfall**

Common pitfall. Picking (i) because both assertions look related. Read carefully: the question is whether the reason *explains* the assertion. It doesn't.

Final Answer: Option **(ii)**: both true, but reason (positive E°) is unrelated to the Nernst rise with concentration.

Q 2.65 **Assertion: Copper sulphate can be stored in zinc vessel. Reason: Zinc is less reactive than copper.**

SOLUTION

Correct option: (iv) Both false.

Concept used. A more reactive metal will displace a less reactive metal from its salt. Zn is MORE reactive than Cu ($E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.76 < E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = +0.34$), so Zn will displace Cu from $\mathrm{CuSO_4}$: $\mathrm{Zn} + \mathrm{CuSO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{Cu}$. The Zn vessel would dissolve; $\mathrm{CuSO_4}$ cannot be stored in it.

Step 1. Assertion: $\mathrm{CuSO_4}$ stored in Zn vessel. FALSE. Zn metal would react with Cu^{2+}, dissolving the vessel and depositing Cu.

Step 2. Reason: Zn less reactive than Cu. FALSE. $E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.76 < E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = +0.34$, so Zn is MORE reactive than Cu.

Step 3. Both false. Option (iv).

> **Final Answer:** Option **(iv)**: both false. Zn is more reactive than Cu, and so reacts with $\mathrm{CuSO_4}$ to dissolve the vessel.

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

Strategic angle: reactivity comparison. Sort Zn and Cu in the activity series by their E° values. Zn is well above Cu (more reactive), so Zn displaces Cu from solution.

Step 1. $E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76\,\mathrm{V}$ vs $E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.34\,\mathrm{V}$. Zn's E° is much MORE negative, so Zn is MORE reactive than Cu.

Step 2. Cell emf for the displacement reaction: $E^\circ_{\text{cell}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{Zn^{2+}/Zn}} = +1.10\,\mathrm{V}$. Spontaneous.

Step 3. So a Zn vessel containing $\mathrm{CuSO_4}$ solution would undergo $\mathrm{Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu}$ until either the vessel dissolves or all $\mathrm{Cu^{2+}}$ is gone. Both statements in the A-R are wrong.

☞ **Exam Tip**

Exam tip. CBSE 2018, 2022 board had similar A-R. Always check the activity series before judging displacement claims.

♥ **Concept Linkage**

Concept linkage. Q18 (E° of $\mathrm{Cu/Cu^{2+}}$), Q31 (sign of $E^\circ_{\mathrm{Zn^{2+}/Zn}}$), Q33 (Cu | Ag galvanic cell).

> **Final Answer:** Option **(iv)**: both false; Zn is more reactive, would dissolve in $\mathrm{CuSO_4}$.

VI. Long Answer Type

Q 2.66 **Consider Fig. 3.2 and answer the following questions.**

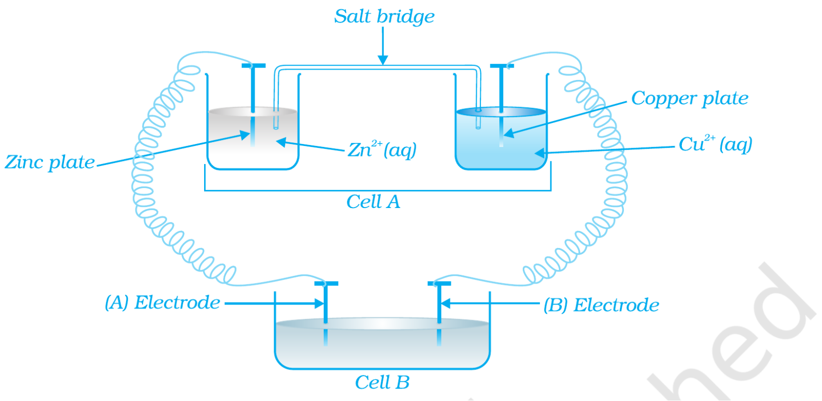


Fig. 3.2, NCERT Exemplar Class 12 Chemistry, Chapter 3.

(i) Cell 'A' has $E_{\text{cell}} = 2\,$V and Cell 'B' has $E_{\text{cell}} = 1.1\,$V. Which of the two cells 'A' or 'B' will act as an electrolytic cell? Which electrode reactions will occur in this cell?
(ii) If cell 'A' has $E_{\text{cell}} = 0.5\,$V and cell 'B' has $E_{\text{cell}} = 1.1\,$V then what will be the reactions at anode and cathode?

SOLUTION

Concept used. When two galvanic cells are connected back-to-back (in opposition), the cell with the HIGHER emf forces current in its own direction. The cell with the LOWER emf is forced to run in REVERSE (non-spontaneously) and thus operates as an electrolytic cell. The reactions in the electrolytic cell are the REVERSE of its spontaneous galvanic reactions: oxidation becomes reduction at that electrode, and vice versa. Quantitatively, the net driving voltage is $|E_{\text{higher}} - E_{\text{lower}}|$, and current flows from the higher-emf cell into the lower-emf cell.
In Fig. 3.2, Cell A is the upper coupled cell (Zn|Cu Daniel type) and Cell B is the lower cell (with electrodes A and B). Both are Daniel-cell setups, so each can give up to $\sim 1.1\,$V in spontaneous mode.
Part (i): Cell A has $E = 2\,$V, Cell B has $E = 1.1\,$V.

Step 1. Cell A (2 V) > Cell B (1.1 V). Cell A wins, drives current in its own direction (Zn → Cu through external circuit on A's side).

Step 2. Cell B (1.1 V) is overwhelmed; current is forced through it in REVERSE. So Cell B operates as an electrolytic cell.

Step 3. Reverse the spontaneous reactions of Cell B (which was Zn anode, Cu cathode normally). Now in B, the Cu side acts as anode and the Zn side acts as cathode:

$$\text{Cell B cathode: } Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn\,(s).$$

$$\text{Cell B anode: } Cu\,(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-.$$

$$\text{Net Cell B reaction: } Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn \text{ (reverse of Daniel cell).}$$

Part (ii): Cell A has $E = 0.5\,$V, Cell B has $E = 1.1\,$V.

Step 1. Cell B (1.1 V) > Cell A (0.5 V). Now Cell B wins and drives current in its own direction.

Step 2. Cell A is overwhelmed and operates as an electrolytic cell. Reactions in Cell A reverse from its spontaneous Daniel form:

$$\text{Cell A cathode: } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu\,(s).$$

$$\text{Cell A anode: } Zn\,(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-.$$

Wait, these are the SAME as Cell A's spontaneous directions. That's because Cell B is driving Cell A FORWARD in this scenario (Cell A's own emf was just insufficient by itself; with Cell B's extra push, Cell A's natural reaction proceeds normally).

Step 3. Net effect: Cell A runs in its NATURAL galvanic direction, powered by Cell B's overflow current: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$.

> **Final Answer:** (i) Cell B is the electrolytic cell; cathode $Zn^{2+} + 2\,e^- \longrightarrow Zn$, anode $Cu \longrightarrow Cu^{2+} + 2\,e^-$. (ii) Cell A still runs forward (anode $Zn \longrightarrow Zn^{2+} + 2\,e^-$, cathode $Cu^{2+} + 2\,e^- \longrightarrow Cu$), driven by Cell B's higher emf.

EXPERT'S SOLUTION *: Aanya Sharma, Ph.D Physical Chemistry, IIT Madras*

Strategic angle: emf battle. Identify which cell has the higher emf; that cell wins and drives current. The losing cell is forced to run electrolytically (reversing its spontaneous direction).

Step 1. Setup: two cells in opposition. Net emf $= |E_A - E_B|$. Direction set by the cell with larger emf.

Step 2. Part (i): $E_A = 2.0$ vs $E_B = 1.1$. Difference $= 0.9\,\text{V}$ in A's favour. Current flows in A's direction; B is forced backward.

Step 3. Reactions in Cell B (forced backward):
Spontaneous B: $Zn \longrightarrow Zn^{2+} + 2\,e^-$ at Zn (anode); $Cu^{2+} + 2\,e^- \longrightarrow Cu$ at Cu (cathode).
Reversed (electrolytic): $Zn^{2+} + 2\,e^- \longrightarrow Zn$ at Zn (now cathode);
$Cu \longrightarrow Cu^{2+} + 2\,e^-$ at Cu (now anode).

Step 4. Part (ii): $E_A = 0.5$ vs $E_B = 1.1$. Now B drives, A is the consumer.

Step 5. Cell A receives current from B in the same direction A would naturally try to drive. So A's natural reactions are AMPLIFIED (not reversed):
At Zn (still anode): $Zn \longrightarrow Zn^{2+} + 2\,e^-$.
At Cu (still cathode): $Cu^{2+} + 2\,e^- \longrightarrow Cu$.

Step 6. Net cell A reaction: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$, the spontaneous Daniel cell direction, just accelerated.

☞ Cross-Check

Numerical cross-check. Part (i): net emf $= 2 - 1.1 = 0.9\,V$ drives current backward through Cell B. Each coulomb of charge deposits half a mole of Zn^{2+} as Zn (since $n = 2$). Part (ii): net emf $= 1.1 - 0.5 = 0.6\,V$ drives current forward through Cell A.

♥ Concept Linkage

Concept linkage. Direct application of Q6 (electrolytic behaviour when $E_{ext} > E_{cell}$), Q15 (lead storage during charging), Q38 (opposing potential balancing emf).

Final Answer: (i) B becomes electrolytic: $Zn^{2+} + 2\,e^- \longrightarrow Zn$ (cathode), $Cu \longrightarrow Cu^{2+} + 2\,e^-$ (anode). (ii) A still runs naturally: $Zn \longrightarrow Zn^{2+} + 2\,e^-$ (anode), $Cu^{2+} + 2\,e^- \longrightarrow Cu$ (cathode).

Q 2.67 **Consider Fig. 3.3 (a Zn–Ag galvanic cell with salt bridge) and answer the questions (i) to (vi) given below.**

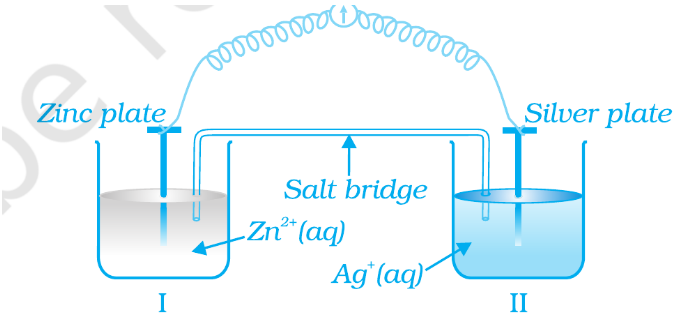


Fig. *3.3*

affected when the cell functions?

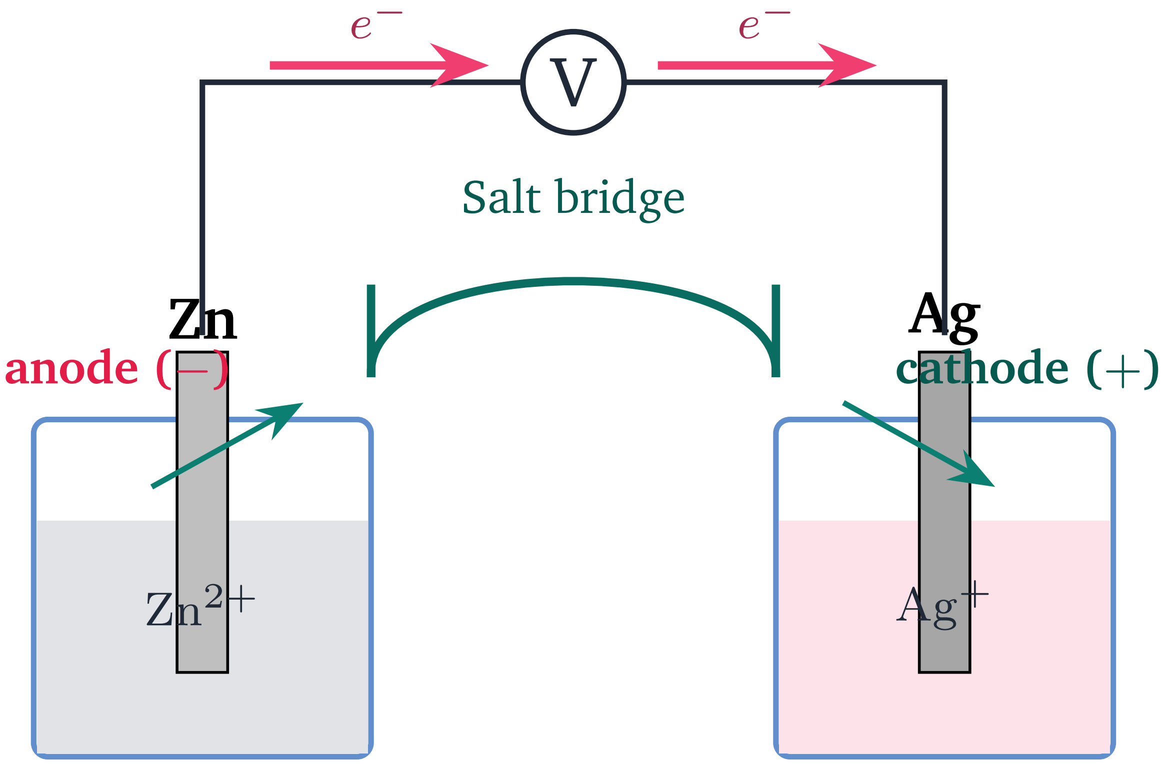
Fig. 3.3, NCERT Exemplar Class 12 Chemistry, Chapter 3.

(i) Redraw the diagram to show the direction of electron flow.
(ii) Is silver plate the anode or cathode?
(iii) What will happen if salt bridge is removed?
(iv) When will the cell stop functioning?
(v) How will concentration of Zn^{2+} ions and Ag^{+} ions be affected when the cell functions?
(vi) How will the concentration of Zn^{2+} ions and Ag^{+} ions be affected after the cell becomes 'dead'?

SOLUTION

Concept used. The cell shown is $\mathrm{Zn}|\mathrm{Zn}^{2+}||\mathrm{Ag}^{+}|\mathrm{Ag}$, with $E^\circ_{\text{cell}} = E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} - E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = 0.80 - (-0.76) = +1.56\,\mathrm{V}$ (spontaneous). Zn is more reactive (more negative E°), so Zn is oxidised at the anode; Ag^+ is reduced at the cathode (silver plate). Electrons flow externally from Zn (anode) through the wire to Ag (cathode). The salt bridge maintains electrical neutrality by allowing ion migration between the two half-cells.

(i) Direction of electron flow: Electrons leave the Zn plate, flow through the external wire (and any voltmeter or load), and enter the Ag plate. Inside the solution, current is carried by ions: Zn^{2+} migrates toward the salt bridge (into the bridge from the Zn side); $\mathrm{NO_3}^-$ from the salt bridge migrates into the Zn beaker; Ag^+ migrates from the bridge or the bulk towards the Ag plate.



(ii) Silver plate role: Silver is the cathode (reduction happens there: $\mathrm{Ag}^+ + \mathrm{e}^- \longrightarrow \mathrm{Ag}$).

(iii) If salt bridge is removed: Without the salt bridge, ions cannot migrate between half-cells. Charge builds up: the Zn beaker accumulates Zn^{2+} (positive excess), the Ag beaker accumulates negative excess (depletion of Ag^+). This electrostatic charge build-up opposes further electron flow. *Current stops flowing* almost immediately.

(iv) Cell stops functioning when: $E_{\text{cell}} = 0$, which occurs when the cell reaches equilibrium ($Q = K$). At that point, no further net reaction.

(v) Concentration changes during functioning:

Zn is being oxidised at the anode: $[\mathrm{Zn}^{2+}]$ INCREASES.

Ag^+ is being reduced at the cathode: $[\mathrm{Ag}^+]$ DECREASES.

(vi) Concentration after cell goes 'dead':
At equilibrium, no net forward or reverse reaction. So $[\mathrm{Zn^{2+}}]$ and $[\mathrm{Ag^{+}}]$ do not change further. They remain at their final equilibrium values: $[\mathrm{Zn^{2+}}]$ maximised, $[\mathrm{Ag^{+}}]$ near zero (because of the huge K for this cell).

Step 1. Half-reactions: Anode $\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$. Cathode $\mathrm{2\,Ag^+ + 2\,e^- \longrightarrow 2\,Ag}$.

Step 2. Net: $\mathrm{Zn + 2\,Ag^+ \longrightarrow Zn^{2+} + 2\,Ag}$, $n = 2$. $E^\circ_{\text{cell}} = +1.56\,\text{V}$ (highly spontaneous).

Step 3. $K = e^{nFE^\circ/RT} = e^{2(96500)(1.56)/(8.314\times298)} = e^{121.4} = 10^{52.7}$. Huge K, so $[\mathrm{Ag^+}]$ at equilibrium is essentially zero.

> **Final Answer:** (i) e^- flows Zn → Ag externally; (ii) Ag = cathode; (iii) cell stops (no ion migration); (iv) at $E_{\text{cell}} = 0$, equilibrium; (v) $[\mathrm{Zn^{2+}}]$ rises, $[\mathrm{Ag^+}]$ falls during operation; (vi) at dead, both remain at equilibrium values (no further change).

EXPERT'S SOLUTION : *Rohit Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle: trace the cell through its life cycle. The questions walk through the cell from operation to death. Each part requires applying one core idea: electron flow direction, electrode roles, the function of the salt bridge, equilibrium endpoint, and concentration changes.

Step 1. (i) Direction of electron flow: outside the cell, e^- flow from negative (anode) to positive (cathode), i.e. Zn → Ag. Inside, ions migrate to maintain charge balance.

Step 2. (ii) Silver plate identity: since $E^\circ_{\mathrm{Ag^+/Ag}} = +0.80 > E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76$, Ag is the cathode (higher reduction potential).

Step 3. (iii) Salt bridge removal: charge builds up rapidly, the cell cannot maintain ion balance, current essentially stops within microseconds. Salt bridge is essential.

Step 4. (iv) Cell stops when $E_{\text{cell}} = 0$, equilibrium ($Q = K$).

Step 5. (v) During discharge: $\mathrm{Zn \longrightarrow Zn^{2+}}$ at anode adds $\mathrm{Zn^{2+}}$ to its beaker (rises). $\mathrm{Ag^+ + e^- \longrightarrow Ag}$ at cathode removes $\mathrm{Ag^+}$ (falls).

Step 6. (vi) After equilibrium reached, no net change in any concentration. The cell remains in this static state until external action (recharging, or replacing the cell) intervenes.

☞ **Alternative approach**

Alternative approach: Nernst quantitative for (v) and (vi). $E_{\text{cell}} = 1.56 - \dfrac{0.059}{2}\log\dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2}$.
At dead cell, $E_{\text{cell}} = 0$ gives $\log Q = 1.56 \times 2/0.059 = 52.9$, so $Q = K = 10^{52.9}$. This confirms $[\mathrm{Ag^+}]$ at equilibrium is essentially 0.

☞ **Exam Tip**

Exam tip. CBSE 2018, 2020, 2022 board paper had fragmentary versions of this multi-part question. Memorise the six answers as a set.

☞ **Cross-Check**

Numerical cross-check. Starting with $[\mathrm{Ag}^+] = 1\,\mathrm{M}$ and $[\mathrm{Zn}^{2+}] = 1\,\mathrm{M}$: $Q = 1$, $\log Q = 0$, $E = 1.56\,\mathrm{V}$. Maximum spontaneity at start.

Final Answer: (i) e^-: Zn → Ag; (ii) Ag = cathode; (iii) cell stops; (iv) $E_{\text{cell}} = 0$, equilibrium; (v) $[\mathrm{Zn}^{2+}]$ rises, $[\mathrm{Ag}^+]$ falls; (vi) values stay at the final equilibrium concentrations.

Q 2.68 **What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and the emf of the cell? When will the maximum work be obtained from a galvanic cell?**

SOLUTION

Concept used. The **maximum electrical work** that a galvanic cell can do at constant temperature and pressure equals the decrease in Gibbs free energy of the cell reaction:

$$W_{\text{max,electrical}} = -\Delta_r G.$$

For a cell delivering charge $Q = nF$ at emf E_{cell}, the electrical work done is $W = QE_{\text{cell}} = nFE_{\text{cell}}$. Equating: $W_{\text{max,electrical}} = nFE_{\text{cell}} = -\Delta_r G$, which gives the key relation

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

For *standard* conditions, $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$. The maximum work is realised ONLY when the cell operates reversibly, i.e. when current is drawn very slowly (essentially zero current), maintaining E_{cell} at its open-circuit (reversible) value. Any faster current draw introduces IR drops, polarisation losses, and over-potentials that reduce the actual work obtained.

Step 1. Define maximum work: at constant T and P, the maximum non-PV work the system can do is $W_{\text{max}} = -\Delta_r G$. For a galvanic cell, the non-PV work IS the electrical work.

Step 2. Electrical work for cell delivering n moles of e^-:
$W = (\text{charge}) \times (\text{voltage}) = nF \times E_{\text{cell}}$.

Step 3. Equate maximum work with electrical work: $-\Delta_r G = nFE_{\text{cell}}$, so $\Delta_r G = -nFE_{\text{cell}}$.

Step 4. Standard conditions: $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$. This is the connector between thermodynamics and electrochemistry.

Step 5. Maximum work obtained: when the cell operates REVERSIBLY (zero current, infinitesimally slow discharge); in practice, with a potentiometer or under negligible load.

> **Final Answer:** $\Delta_r G = -nFE_{\text{cell}}$ ($\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$ at standard conditions). Maximum work is obtained when the cell operates REVERSIBLY (zero current, open circuit).

EXPERT'S SOLUTION *: Sneha Kumar, M.Sc Chemistry, IIT Kanpur*

Strategic angle: thermodynamic identity. $\Delta_r G$ links the chemical world (free energy) and the electrical world (cell emf) through the universal constants n (moles of e^-) and F (charge per mole of e^-). This is the single most important equation in electrochemistry.

Step 1. For any process at constant T and P: $\Delta G = W_{\text{non-PV,reversible}}$.

Step 2. For an electrochemical cell, the only non-PV work is electrical work: $W_{\text{elec}} = QV = nFE_{\text{cell}}$.

Step 3. Therefore $\Delta_r G = -W_{\text{elec,max}} = -nFE_{\text{cell}}$.

Step 4. Negative sign: for a spontaneous (galvanic) cell, $E_{\text{cell}} > 0$, so $\Delta_r G < 0$. The cell does work ON the surroundings.

Step 5. Standard form: $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$. Combined with $\Delta_r G^\circ = -RT \ln K$, gives $E^\circ_{\text{cell}} = (RT/nF) \ln K$, the basis of equilibrium-constant measurements via cell emf (Q20).

☞ **Alternative approach**

Alternative approach: Daniel cell numerical. For Daniel cell, $E^\circ_{\text{cell}} = 1.10\,\text{V}$, $n = 2$. So $\Delta_r G^\circ = -2(96500)(1.10) = -212{,}300\,\text{J/mol} = -212.3\,\text{kJ/mol}$. Verify with literature thermodynamic data: $\Delta_r H^\circ - T\Delta_r S^\circ$ for the same reaction gives the same number, confirming the electrochemical relation.

☞ **Cross-Check**

Numerical cross-check. Maximum theoretical work from a fully reversible Daniel cell delivering 1 mole of e^-: $W_{\text{max}} = nFE = 2 \times 96500 \times 1.10 = 212.3\,\text{kJ}$. But in any real cell with internal resistance r and current I, actual work $= nF(E_{\text{cell}} - Ir)$, less than maximum. Only at $I \to 0$ does it reach W_{max}.

Final Answer: $\Delta_r G = -nFE_{\text{cell}}$; maximum work when cell operates reversibly (zero current, open circuit).

Key Takeaways

- **Electrode potential** is the potential difference between an electrode and its solution, always measured *against* SHE ($E^\circ_{\text{SHE}} = 0$). Absolute potentials cannot be measured; only relative.
- **Galvanic cells** convert chemical to electrical energy spontaneously ($E_{\text{cell}} > 0$, $\Delta_r G < 0$). **Electrolytic cells** are the reverse: external emf forces a non-spontaneous reaction.
- **Nernst equation** (at 298 K): $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.059}{n}\log Q$. At equilibrium, $E_{\text{cell}} = 0$, $Q = K$.
- **Thermodynamic links:** $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$; $\Delta_r G^\circ = -RT\ln K$; $E^\circ_{\text{cell}} = \dfrac{RT}{nF}\ln K$.
- **Conductivity** κ falls on dilution (fewer ions per volume); **molar conductivity** Λ_m rises on dilution (more dissociated for weak, ion-pair relaxation for strong).
- **Kohlrausch's law**: Λ^0_m for any electrolyte is the sum of λ^0 of its ions; weak electrolyte Λ^0_m is built from strong-salt Kohlrausch combinations.
- **Faraday's laws** of electrolysis: $w = (M/nF)Q = (M/nF)It$; equivalent mass $E = M/n$; mass ratios on same charge equal ratio of equivalent masses.
- **Cell potential is intensive**; $\Delta_r G$ is **extensive**. Cell constant $G^* = l/A$ is purely geometric.
- **Overpotential** (e.g. for O_2 at most electrodes) makes Cl^- oxidation win at the anode in NaCl electrolysis, even though E° favours water.
- **Mercury cell** gives steady E because no aqueous ions appear in net reaction. **Lead storage** discharges $Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$; density of electrolyte falls. **Fuel cells** run continuously with external fuel/oxidant supply, achieving the highest efficiency.

End of NCERT Exemplar Solutions, Class 12 Chemistry, Chapter 2: Electrochemistry. 68 questions solved across MCQ, MCQ-II, SA, Matching, Assertion-Reason, and LA.