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PHYSICAL

CH 03

Electrochemistry — Cells, Nernst Equation & Conductance

03

Cells and electrode potentials, the Nernst equation, the E°–ΔG°–K triangle, conductance and Kohlrausch's law, electrolysis and Faraday's laws — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Write cell notation, pick the anode and cathode, and calculate E°cell from the series
- Use the Nernst equation for any concentration, including concentration cells and pH
- Move between E°, ΔG° and K, and explain why E° values can't simply be added
- Calculate κ, Λm, α and Ka from conductivity data using Kohlrausch's law
- Predict electrolysis products and solve every type of Faraday's-law numerical

INSIDE

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C Electrode potentials
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E The E°–ΔG°–K triangle
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H Batteries and corrosion
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HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Two kinds of cell, one redox reaction. Everything else in the chapter is bookkeeping for the electrons.

IN ONE LINE

A spontaneous redox reaction pushes electrons through a wire (galvanic cell); a battery can push them the other way (electrolysis). E°, ΔG° and K are three views of the same driving force.

THINK OF IT LIKE THIS

A galvanic cell is a waterfall: electrons fall downhill from the metal that gives them up easily (zinc) to the ion that grabs them (Cu^{2+}), and you put a turbine in the wire. Electrolysis is a pump: you spend energy to push them uphill.

	Galvanic (voltaic) cell	Electrolytic cell
Energy change	Chemical → electrical	Electrical → chemical
Reaction	Spontaneous, $\Delta G < 0$	Non-spontaneous, driven by an external source
Anode (oxidation)	Negative	Positive
Cathode (reduction)	Positive	Negative
Examples	Daniell cell, dry cell, fuel cell	Electroplating, extraction of Na and Al, refining Cu

KEY IDEA

In both cells, oxidation is at the anode and reduction at the cathode. Only the signs change. Remember "**An Ox, Red Cat**".

SECTION B

Cells and cell notation

B

How to write a cell, and what the salt bridge is really doing.

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

Anode on the left, cathode on the right. | = phase boundary, ‖ = salt bridge

- **Anode reaction:** $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
- **Cathode reaction:** $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)
- **Cell reaction:** $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
- **Salt bridge** (KCl or KNO_3 in agar): completes the circuit and keeps both solutions electrically neutral. Without it, the zinc side builds up positive charge and the current stops within seconds.

> **EXAM TRAP**
> Students write the salt bridge as a source of electrons. It carries **ions**, not electrons. Electrons travel only through the external wire.

SECTION C

C

Electrode potentials and the series

One number per half-cell tells you who gives electrons to whom.

The **standard hydrogen electrode (SHE)** is the zero of the scale: $2H^+(aq, 1\ M) + 2e^- \rightarrow H_2(g, 1\ bar)$, $E° = 0.00$ V at 298 K. Every other standard reduction potential is measured against it.

Half-reaction (reduction)	E° (V)	What it tells you
$F_2 + 2e^- \rightarrow 2F^-$	+2.87	Strongest oxidising agent
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23	
$Ag^+ + e^- \rightarrow Ag$	+0.80	Silver is a poor reducing agent
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	Cu does not displace H_2 from acids
$2H^+ + 2e^- \rightarrow H_2$	0.00	Reference
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44	Fe displaces H_2 from dilute acids
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76	
$Na^+ + e^- \rightarrow Na$	−2.71	
$Li^+ + e^- \rightarrow Li$	−3.05	Strongest reducing agent

$$E°_{cell} = E°_{(cathode)} - E°_{(anode)}$$

Use reduction potentials for both. Positive $E°_{cell}$ → spontaneous as written.

Four things the series predicts

1. **Which electrode is the anode:** the one with the lower (more negative) E°.

2. **Displacement:** a metal displaces another from solution if it is lower in the series. Zn displaces Cu from $CuSO_4$; Cu does not displace Zn.
3. **Reaction with acids:** metals with E° < 0 release H_2 from dilute acids (Zn, Fe); metals with E° > 0 don't (Cu, Ag).
4. **Storage:** $CuSO_4$ solution can't be kept in a zinc pot (zinc would dissolve), but can be kept in a silver one.

SOLVED EXAMPLE 01 — CHOOSING THE ANODE

A cell is made from Ag^+/Ag (E° = +0.80 V) and Cu^{2+}/Cu (E° = +0.34 V). Identify the anode and find E°cell.

SOLUTION

1. Lower E° → oxidised → anode: Cu.
2. Cathode: $Ag^+ + e^- \rightarrow Ag$.
3. E°cell = 0.80 − 0.34 = 0.46 V.

ANSWER Cu is the anode; E°cell = 0.46 V; cell reaction $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$.

CHECK YOURSELF

C1 Can you store $AgNO_3$ solution in a copper vessel?

C2 Which is the stronger reducing agent: Zn or Fe?

C3 Will dilute HCl react with silver?

Answers at the end of the chapter.

SECTION D

The Nernst equation

D

E° is for 1 M solutions. Real cells aren't standard; the Nernst equation corrects for that.

$$E = E^\circ - (0.059 / n) \log Q \text{ (at 298 K)}$$

n = electrons in the balanced cell reaction. Pure solids and liquids are left out of Q.

For the Daniell cell, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, so $Q = [Zn^{2+}] / [Cu^{2+}]$.

KEY IDEA

Read the equation as a see-saw: **more reactant ions (smaller Q) → higher E; more product ions (larger Q) → lower E.** At equilibrium the cell is flat: E = 0.

Three special cases examiners love

- **Concentration cell:** the same electrode in two concentrations, so E° = 0 and E = (0.059/n) log(c(cathode)/c(anode)). The more concentrated side is the cathode.

- **Hydrogen electrode at other pH:** E = −0.059 × pH (with H_2 at 1 bar). At pH 10, E = −0.59 V.
- **Metal ion electrode:** $E(M^{2+}/M) = E^\circ - (0.059/2)\log(1/[M^{2+}])$. Diluting the ions makes the potential more negative.

SOLVED EXAMPLE 02 — NERNST WITH REAL CONCENTRATIONS

Find E for Mg | Mg^{2+}(0.001 M) ‖ Cu^{2+}(0.0001 M) | Cu. E°_{cell} = 2.71 V.

SOLUTION

1. Mg + Cu^{2+} → Mg^{2+} + Cu, n = 2.
2. Q = $[Mg^{2+}]/[Cu^{2+}]$ = 0.001/0.0001 = 10.
3. E = 2.71 − (0.059/2) × log 10 = 2.71 − 0.0295.

ANSWER E ≈ 2.68 V.

SOLVED EXAMPLE 03 — A CONCENTRATION CELL

Find E for Cu | Cu^{2+}(0.01 M) ‖ Cu^{2+}(0.1 M) | Cu.

SOLUTION

1. E° = 0 (same electrode both sides), n = 2.
2. E = (0.059/2) log(0.1/0.01) = 0.0295 × 1.

ANSWER E = 0.0295 V; the 0.1 M side is the cathode.

CHECK YOURSELF

C4 What happens to E of a Daniell cell if $[Zn^{2+}]$ is increased?

C5 A hydrogen electrode dips into a solution of pH 3. What is its potential?

Answers at the end of the chapter.

SECTION E

The E°–ΔG°–K triangle

E

Three quantities, one driving force. Know any one and you have the other two.

$$\Delta G^\circ = -nFE^\circ$$

$$E^\circ_{cell} = (0.059 / n) \log K \text{ (at 298 K)}$$

$$\Delta G^\circ = -2.303\ RT \log K$$

F = 96,487 C mol^{-1} (≈ 96,500)

E°_{cell}	ΔG°	K	Meaning
Positive	Negative	> 1	Products favoured; spontaneous

E°cell	ΔG°	K	Meaning
Zero	Zero	1	At equilibrium
Negative	Positive	< 1	Reactants favoured

EXAM TRAP

E° is intensive; ΔG° is extensive. Doubling a half-reaction doubles ΔG° but leaves E° unchanged. So you can add ΔG° values, but never add E° values of half-reactions directly.

SOLVED EXAMPLE 04 — K FROM E°

For the Daniell cell, E° = 1.10 V. Find K and ΔG°.

SOLUTION

1. log K = nE°/0.059 = 2 × 1.10/0.059 = 37.29.
2. K = antilog(37.29) ≈ 1.9×10^{37}.
3. ΔG° = −2 × 96,487 × 1.10 = −212,271 J mol^{-1}.

ANSWER K ≈ 1.9×10^{37}; ΔG° ≈ −212.3 kJ mol^{-1}. The reaction goes essentially to completion.

SECTION F

Conductance

F

How well a solution carries current, and how to use that to measure dissociation.

Quantity	Symbol and unit	What it means
Resistance	R (Ω)	Opposition to current
Conductance	G = 1/R (S)	Ease of current flow
Cell constant	G* = l/A (cm^{-1})	Geometry of the conductivity cell
Conductivity	κ = G* / R (S cm^{-1})	Conductance of a 1 cm cube of solution
Molar conductivity	Λm = κ × 1000 / M (S cm^2 mol^{-1})	Conductance of 1 mol of electrolyte

What happens on dilution

- **κ decreases:** fewer ions per cm^3.
- **Λm increases:** ions move more freely, and weak electrolytes dissociate more.
- **Strong electrolyte:** Λm = Λ°m − A√c. A plot of Λm against √c is a straight line; extrapolate to c = 0 to get Λ°m.
- **Weak electrolyte:** Λm rises steeply near zero concentration, so it can't be extrapolated. Use Kohlrausch's law.

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

Kohlrausch: at infinite dilution, each ion contributes independently

Ion	λ° (S cm² mol⁻¹)
H^+	349.6
OH^-	199.1
Na^+	50.1
Cl^-	76.3
CH_3COO^-	40.9

Why are H^+ and OH^- so fast? They don't travel themselves; protons hop from one water molecule to the next along hydrogen bonds (the Grotthuss mechanism).

Uses of Kohlrausch's law

1. Λ°_m of a weak electrolyte: $\Lambda^\circ(CH_3COOH) = \Lambda^\circ(HCl) + \Lambda^\circ(CH_3COONa) - \Lambda^\circ(NaCl)$.
2. Degree of dissociation: $\alpha = \Lambda_m / \Lambda^\circ_m$.
3. Dissociation constant: $K_a = c\alpha^2 / (1 - \alpha)$.

SOLVED EXAMPLE 05 — CELL CONSTANT AND ΛM

A cell filled with 0.1 M KCl (κ = 0.0129 S cm⁻¹) has R = 100 Ω. Filled with 0.02 M of another electrolyte, R = 520 Ω. Find Λ_m of the second solution.

SOLUTION

1. $G^* = \kappa R = 0.0129 \times 100 = 1.29$ cm⁻¹.
2. $\kappa(\text{new}) = G^*/R = 1.29/520 = 2.48 \times 10^{-3}$ S cm⁻¹.
3. $\Lambda_m = \kappa \times 1000/M = 2.48 \times 10^{-3} \times 1000/0.02$.

ANSWER $\Lambda_m \approx 124$ S cm² mol⁻¹.

SOLVED EXAMPLE 06 — α AND K_A OF ACETIC ACID

0.001028 M acetic acid has $\kappa = 4.95 \times 10^{-5}$ S cm⁻¹. $\Lambda^\circ_m(CH_3COOH) = 390.5$ S cm² mol⁻¹.

SOLUTION

1. $\Lambda_m = 4.95 \times 10^{-5} \times 1000/0.001028 = 48.15$ S cm² mol⁻¹.
2. $\alpha = 48.15/390.5 = 0.1233$.
3. $K_a = c\alpha^2/(1 - \alpha) = 0.001028 \times 0.1233^2/0.8767$.

ANSWER $\alpha \approx 0.123$; $K_a \approx 1.78 \times 10^{-5}$.

CHECK YOURSELF

C6 Why does κ fall but Λm rise on dilution?

C7 Find Λ°m of CH_3COOH from the ion table above.

Answers at the end of the chapter.

SECTION G

Electrolysis and Faraday's laws

G

Pushing electrons uphill, and counting exactly how much you get for your charge.

$$m = (M / nF) \times I \times t$$

First law: mass ∝ charge. Second law: for the same charge, masses ∝ M/n.

1 F = 96,487 C ≈ 96,500 C = the charge on 1 mol of electrons. Charge Q = I × t (amperes × seconds).

Predicting the products

Electrolyte	Cathode	Anode	Why
Molten NaCl	Na	Cl_2	Only Na^+ and Cl^- present
Aqueous NaCl (concentrated)	H_2	Cl_2	Water (−0.83 V) is far easier to reduce than Na^+ (−2.71 V); O_2 has a high overpotential, so Cl_2 forms
Dilute H_2SO_4	H_2	O_2	Water is oxidised; SO_4^{2-} is very hard to oxidise
Concentrated H_2SO_4	H_2	$S_2O_8^{2-}$	At high concentration, HSO_4^- is oxidised to peroxodisulphate
Aqueous $CuSO_4$, Pt electrodes	Cu	O_2	Cu^{2+} is easier to reduce than water
Aqueous $CuSO_4$, Cu electrodes	Cu deposits	Cu dissolves	Basis of copper refining and electroplating

KEY IDEA

At the cathode, the species with the **highest reduction potential** is reduced. At the anode, the species **easiest to oxidise** is oxidised, unless overpotential intervenes (O_2 from water usually needs extra voltage).

SOLVED EXAMPLE 07 — MASS DEPOSITED

2.0 A flows through $CuSO_4$ solution for 965 s. Find the mass of copper deposited (Cu = 63.5).

SOLUTION

1. Q = 2.0 × 965 = 1930 C = 1930/96,500 = 0.020 mol e^-.
2. $Cu^{2+} + 2e^- \rightarrow Cu$, so mol Cu = 0.010.
3. Mass = 0.010 × 63.5.

ANSWER 0.635 g of copper.

SOLVED EXAMPLE 08 — TIME REQUIRED

How long does a 2.0 A current take to deposit 1.27 g of copper?

SOLUTION

1. mol Cu = 1.27/63.5 = 0.020; mol e^- = 0.040.
2. Q = 0.040 × 96,500 = 3860 C.
3. t = Q/I = 3860/2.0 = 1930 s.

ANSWER 1930 s ≈ 32.2 min.

SOLVED EXAMPLE 09 — VOLUME OF GAS AND THE SECOND LAW

965 C is passed through dilute H_2SO_4. What volume of O_2 (at STP) forms at the anode? If the same charge passes through $AgNO_3$, what mass of Ag deposits?

SOLUTION

1. 965 C = 0.010 mol e^-.
2. $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$: mol O_2 = 0.010/4 = 0.0025 → 0.0025 × 22,400 mL.
3. $Ag^+ + e^- \rightarrow Ag$: mol Ag = 0.010 → 0.010 × 108 g.

ANSWER 56 mL of O_2; 1.08 g of Ag.

SECTION H

Batteries, fuel cells and corrosion

H

The same chemistry in your torch, your car and on a rusting gate.

Device	Anode	Cathode	Notes
Dry (Leclanché) cell	$Zn \rightarrow Zn^{2+} + 2e^-$	$MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$	About 1.5 V; not rechargeable
Mercury cell	Zn(Hg)	$HgO \rightarrow Hg$	Steady 1.35 V; hearing aids, watches

Device	Anode	Cathode	Notes
Lead storage battery	Pb	PbO_2	Discharge: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$; rechargeable
H_2–O_2 fuel cell	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Product is water; used in spacecraft; about 70% efficient

Corrosion (rusting) is a tiny galvanic cell on the iron surface. At one spot (the anode) $Fe \rightarrow Fe^{2+} + 2e^-$; at another (the cathode) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. Fe^{2+} is later oxidised to rust, $Fe_2O_3 \cdot xH_2O$. Salt water speeds it up by carrying ions.

- **Barrier protection:** paint, oil, plastic coating.
- **Sacrificial protection:** galvanising with zinc, or attaching Mg blocks to ships and pipelines. The more reactive metal is oxidised instead of iron, even if the coating is scratched.

SECTION I

Exam trap gallery

I

The mistakes that cost the most marks in this chapter, side by side with the fix.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Doubling a half-reaction doubles its E°.	E° stays the same; only ΔG° doubles.
WHY E° is intensive (per electron); ΔG° is extensive.	

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$E°(Fe^{3+}/Fe) = E°(Fe^{3+}/Fe^{2+}) + E°(Fe^{2+}/Fe) = 0.77 + (-0.44) = 0.33$ V.	Add ΔG°, then divide: $E° = (1 \times 0.77 + 2 \times (-0.44))/3 = -0.037$ V.
WHY E° values of half-reactions can't be added; their ΔG° values can.	

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In a galvanic cell, the anode is positive.	In a galvanic cell the anode is **negative**; in an electrolytic cell it is positive.
WHY Oxidation is always at the anode; only the sign changes.	

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$E°_{cell} = E°(anode) - E°(cathode)$.	$E°_{cell} = E°(cathode) - E°(anode)$, both as reduction potentials.
WHY Positive $E°_{cell}$ must mean spontaneous.	

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
On dilution, both κ and Λm increase.	κ decreases; Λm increases.

WHY Fewer ions per cm^3, but each mole of electrolyte conducts better.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aqueous NaCl gives Na at the cathode.	It gives H_2; only molten NaCl gives Na.

WHY Water is reduced far more easily than Na^+.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$\Lambda_m = \kappa/M$.	$\Lambda_m = \kappa \times 1000/M$ when κ is in S cm^{-1} and M in mol L^{-1}.

WHY The 1000 converts litres to cm^3.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
The salt bridge supplies electrons to the cathode.	The salt bridge carries ions to keep each half-cell neutral.

WHY Electrons flow only through the external wire.

MEMORY HOOK

"**An Ox, Red Cat**" — Anode Oxidation, Reduction Cathode.

"**LEO says GER**" — Lose Electrons Oxidation, Gain Electrons Reduction.

"**E° stays, ΔG° pays**" — only ΔG° scales with the equation.

"**κ falls, Λ climbs**" — what dilution does.

SECTION J

Practice MCQs

Levels: Easy checks recall, Moderate needs one reasoning step, Tough combines two ideas. Full explanations follow.

Q01 In a galvanic cell, electrons flow: [EASY]

(a) from cathode to anode through the salt bridge

(b) from anode to cathode through the external wire

(c) from cathode to anode through the external wire

(d) in both directions

Q02 The function of a salt bridge is to: [EASY]

(a) supply electrons
(b) maintain electrical neutrality in each half-cell
(c) increase the cell voltage
(d) act as a catalyst

Q03 Which metal can displace copper from $CuSO_4$ solution? [EASY]

(a) Ag
(b) Au
(c) Zn
(d) Pt

Q04 E° for Cu^{2+}/Cu is +0.34 V and for Ag^{+}/Ag is +0.80 V. E°cell for the cell made from them is: [EASY]

(a) 1.14 V
(b) 0.46 V
(c) -0.46 V
(d) 0.23 V

Q05 The unit of molar conductivity is: [EASY]

(a) S cm^{-1}
(b) S cm^2 mol^{-1}
(c) S mol cm^{-2}
(d) Ω cm

Q06 On dilution of an aqueous KCl solution: [MODERATE]

(a) κ and Λm both increase
(b) κ increases, Λm decreases
(c) κ decreases, Λm increases
(d) both decrease

Q07 The potential of a hydrogen electrode (H_2 at 1 bar) in a solution of pH 4 at 298 K is: [MODERATE]

(a) +0.236 V
(b) -0.236 V
(c) -0.059 V
(d) 0.00 V

Q08 For Zn | Zn^{2+}(0.1 M) ‖ Ag^{+}(0.01 M) | Ag, E°cell = 1.56 V. Ecell at 298 K is about: [MODERATE]

(a) 1.56 V
(b) 1.62 V
(c) 1.47 V
(d) 1.50 V

Q09 Electrolysis of aqueous NaCl gives at the cathode: [MODERATE]

(a) Na
(b) Cl_2
(c) H_2
(d) O_2

Q10 The charge needed to deposit 1 mol of Al from Al^{3+} is: [MODERATE]

(a) 1 F
(b) 2 F
(c) 3 F
(d) 6 F

Q11 When a lead storage battery discharges: [MODERATE]

(a) $PbSO_4$ is formed at both electrodes
(b) H_2SO_4 concentration increases
(c) PbO_2 is formed
(d) Pb is deposited

Q12 Which protects iron even when the coating is scratched? [MODERATE]

(a) Tin plating (b) Painting
(c) Zinc coating (d) Oiling

Q13 $E°(Fe^{3+}/Fe^{2+})$ = +0.77 V and $E°(Fe^{2+}/Fe)$ = −0.44 V. $E°(Fe^{3+}/Fe)$ is: [TOUGH]

(a) +0.33 V (b) −0.037 V
(c) +1.21 V (d) −0.11 V

Q14 For the cell reaction $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$, $E° = 0.46$ V. log K at 298 K is about: [TOUGH]

(a) 7.8 (b) 15.6
(c) 31.2 (d) 3.9

Q15 A current is passed through $AgNO_3$ and $CuSO_4$ solutions in series. 1.08 g Ag is deposited. The mass of Cu deposited is: [TOUGH]

(a) 0.635 g (b) 0.3175 g
(c) 1.27 g (d) 0.108 g

Answer key with explanations

Q01 **(b) from anode to cathode through the external wire** — Electrons leave the anode (oxidation) and travel through the wire to the cathode.

Q02 **(b) maintain electrical neutrality in each half-cell** — It carries ions, not electrons.

Q03 **(c) Zn** — Zn ($E° = -0.76$ V) is lower in the series than Cu.

Q04 **(b) 0.46 V** — 0.80 − 0.34 = 0.46 V; Cu is the anode.

Q05 **(b) S cm² mol⁻¹** — $\Lambda m = \kappa \times 1000/M$ gives S cm² mol⁻¹.

Q06 **(c) κ decreases, Λm increases** — Fewer ions per cm³, but each mole conducts better.

Q07 **(b) −0.236 V** — $E = -0.059 \times pH = -0.236$ V.

Q08 **(c) 1.47 V** — $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$, n = 2, $Q = 0.1/(0.01)^2 = 1000$; $E = 1.56 - 0.0295 \times 3 = 1.47$ V.

Q09 **(c) H_2** — Water is reduced far more easily than Na^+.

Q10 **(c) 3 F** — $Al^{3+} + 3e^- \rightarrow Al$.

Q11 **(a) $PbSO_4$ is formed at both electrodes** — $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$; the acid is used up.

Q12 **(c) Zinc coating** — Zinc is more reactive and is oxidised first (sacrificial). A scratched tin coating speeds rusting.

Q13 **(b) −0.037 V** — Add $\Delta G°$: $-3FE = -F(0.77) - 2F(-0.44) \rightarrow E = -0.037$ V.

Q14 **(b) 15.6** — $\log K = nE°/0.059 = 2 \times 0.46/0.059 = 15.6$.

Q15 **(b) 0.3175 g** — Same charge: 0.010 mol e^- → 0.005 mol Cu = 0.3175 g.

SECTION K

Advanced problems

TGT/PGT and JEE level: each combines two ideas from this chapter.

SOLVED EXAMPLE 10 — NON-ADDITIVE E°

Given $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V and $E°(Fe^{2+}/Fe) = -0.44$ V, find $E°(Fe^{3+}/Fe)$.

SOLUTION

1. Write $\Delta G°$ for each: $Fe^{3+} + e^- \rightarrow Fe^{2+}$, $\Delta G°_1 = -1 \times F \times 0.77$.
2. $Fe^{2+} + 2e^- \rightarrow Fe$, $\Delta G°_2 = -2 \times F \times (-0.44) = +0.88F$.
3. $Fe^{3+} + 3e^- \rightarrow Fe$: $\Delta G°_3 = \Delta G°_1 + \Delta G°_2 = -0.77F + 0.88F = +0.11F$.
4. $E°_3 = -\Delta G°_3/3F = -0.11/3$.

ANSWER $E°(Fe^{3+}/Fe) \approx -0.037$ V.

SOLVED EXAMPLE 11 — NERNST WITH UNEQUAL COEFFICIENTS

Find Ecell for $Zn \mid Zn^{2+}(0.1\ M) \parallel Ag^+(0.01\ M) \mid Ag$. $E°(Ag^+/Ag) = +0.80$ V, $E°(Zn^{2+}/Zn) = -0.76$ V.

SOLUTION

1. $E°cell = 0.80 - (-0.76) = 1.56$ V.
2. $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$, so n = 2 and $Q = [Zn^{2+}]/[Ag^+]^2 = 0.1/(0.01)^2 = 1000$.
3. $E = 1.56 - (0.059/2) \times \log 1000 = 1.56 - 0.0885$.

ANSWER Ecell ≈ 1.47 V. (The trap: forgetting to square $[Ag^+]$.)

Check-yourself answers

C1 No. Cu ($E° = +0.34$ V) is lower than Ag (+0.80 V), so copper would reduce Ag^+ and dissolve.

C2 Zn ($E° = -0.76$ V vs −0.44 V for Fe).

C3 No. Silver has $E° > 0$, so it can't reduce H^+.

C4 E decreases ($Q = [Zn^{2+}]/[Cu^{2+}]$ gets larger).

C5 $E = -0.059 \times 3 = -0.177$ V.

C6 κ counts ions per cm^3 (fewer on dilution); Λm is per mole, and each mole conducts better when ions are far apart.

C7 $\Lambda° = 349.6 + 40.9 = 390.5\ S\ cm^2\ mol^{-1}$.

QUICK REVISION

One-page revision

Read this page the night before the exam. Every line points back to a section in these notes.

Cells

- Galvanic: chemical → electrical, $\Delta G < 0$, anode −
- Electrolytic: electrical → chemical, anode +
- Oxidation always at the anode (An Ox, Red Cat)
- Salt bridge carries ions, not electrons

Potentials

- $E°_{cell} = E°_{(cathode)} - E°_{(anode)}$
- Lower $E°$ = anode = better reducing agent
- $E < 0$ metals release H_2 from dilute acid
- $E°$ intensive; add $\Delta G°$, never $E°$

Nernst and the triangle

- $E = E° - (0.059/n) \log Q$
- Concentration cell: $E = (0.059/n) \log(c_2/c_1)$
- H_2 electrode: $E = -0.059\ pH$
- $\Delta G° = -nFE°$; $\log K = nE°/0.059$

Conductance

- $\kappa = G^*/R$; $\Lambda_m = \kappa \times 1000/M$
- Dilution: κ falls, Λ_m rises
- Strong: $\Lambda_m = \Lambda°_m - A\sqrt{c}$
- $\alpha = \Lambda_m/\Lambda°_m$; $K_a = c\alpha^2/(1 - \alpha)$

Electrolysis

- $m = (M/nF) \times I \times t$; 1 F = 96,500 C
- Aq. NaCl → $H_2 + Cl_2$; molten NaCl → $Na + Cl_2$
- Dilute H_2SO_4 → $H_2 + O_2$
- Same charge: masses ∝ M/n

Devices and corrosion

- Dry cell 1.5 V; mercury cell 1.35 V steady
- Lead battery: $PbSO_4$ on both plates when discharged
- Fuel cell product: water
- Zinc protects iron sacrificially

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