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Introduction

Overview

- Electrochemistry studies electricity production from spontaneous chemical reactions.
- It also covers using electrical energy to drive non-spontaneous chemical changes.

Solved Examples

- Ex 1: Identify the type of reaction in a battery producing electricity spontaneously.
 - Answer: Spontaneous redox reaction producing electrical energy.

Practice Set

- Q1: Electrochemistry primarily deals with:
 - A. Heat energy from reactions
 - B. Electrical energy from chemical reactions
 - C. Light energy from reactions
 - D. Sound energy from reactions
- Q2: Which process is studied in electrochemistry?
 - A. Combustion
 - B. Photosynthesis
 - C. Electrolysis and galvanic reactions
 - D. Nuclear fission
- Q3: Electrochemistry involves the study of:
 - A. Spontaneous and non-spontaneous redox reactions
 - B. Only spontaneous reactions
 - C. Only non-spontaneous reactions
 - D. Acid-base reactions

Answer Key

- Q1: B - Electrochemistry focuses on electrical energy from chemical reactions.
- Q2: C - It studies electrolysis (non-spontaneous) and galvanic (spontaneous) reactions.

- Q3: A - Both spontaneous and non-spontaneous redox reactions are studied.

Memory Aids

- Electrochemistry = Electricity + Chemistry (study of electrical energy and chemical reactions)
- Remember: Spontaneous → galvanic cell; Non-spontaneous → electrolytic cell

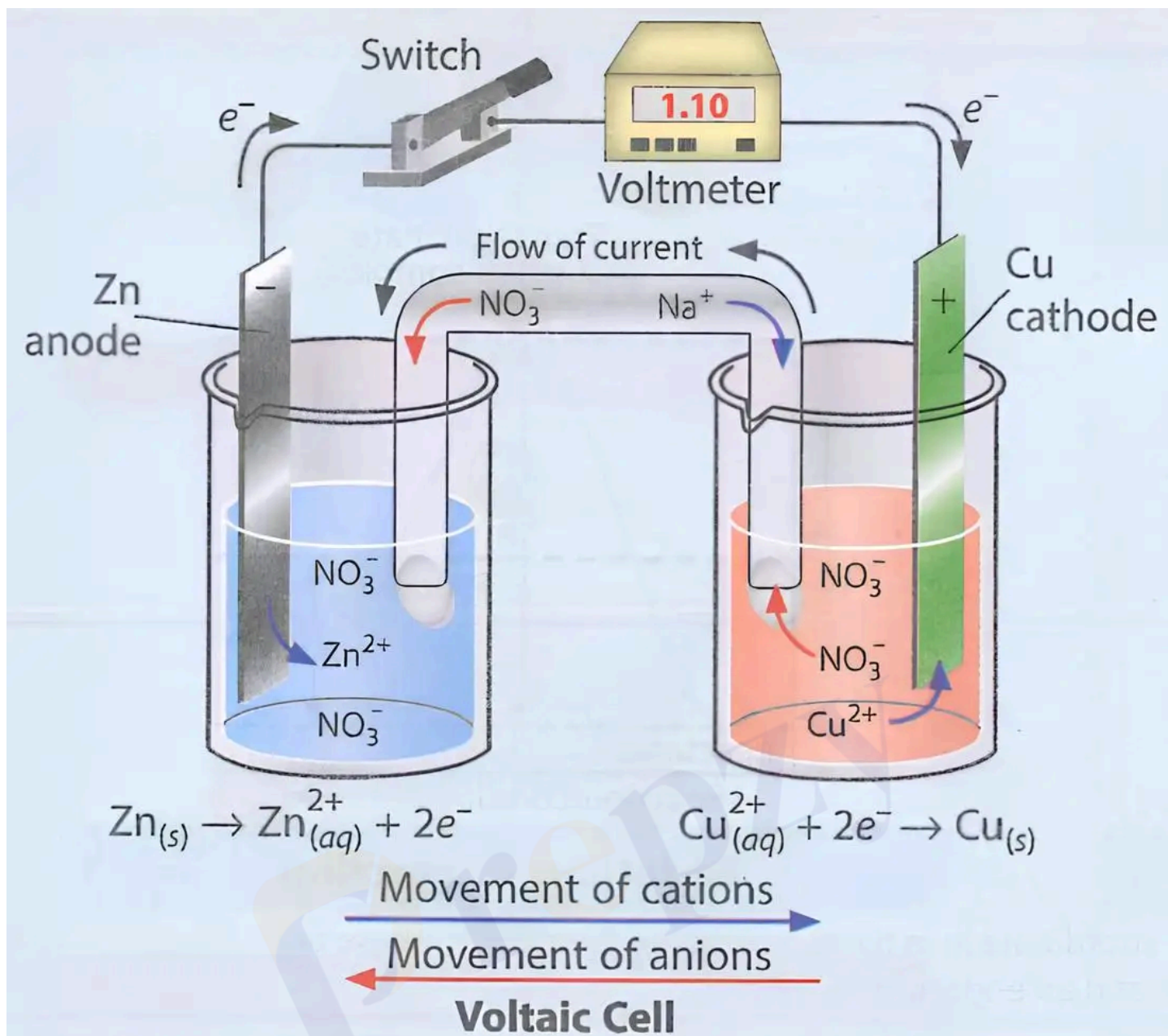
Electrochemical Cells

Definition and Types

- Electrochemical cell converts chemical energy from redox reactions into electrical energy.
- Also called galvanic or voltaic cells (e.g., Daniell cell).
- Daniell cell reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
- Standard potential of Daniell cell = 1.1 V (1 M ion concentration).

Working of Daniell Cell

- Anode (Zn): $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (oxidation)
- Cathode (Cu): $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (reduction)
- Electrons flow from Zn to Cu through external circuit.
- Salt bridge maintains charge balance by ion flow (NO_3^- , Na^+).
- Electric current is produced and measured by voltmeter.



Solved Examples

- Ex 1: Write the half reactions in Daniell cell.
 - Anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$
 - Cathode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

Practice Set

- Q1: In Daniell cell, the anode is:
 - A. Copper electrode
 - B. Zinc electrode

- C. Salt bridge
- D. Voltmeter
- Q2: The overall reaction in Daniell cell is:
 - A. $\text{Zn}^{2+} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{2+}$
 - B. $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
 - C. $\text{Zn} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}$
 - D. $\text{Zn}^{2+} + \text{Cu}^{2+} \rightarrow \text{Zn} + \text{Cu}$
- Q3: The salt bridge in Daniell cell:
 - A. Prevents electron flow
 - B. Maintains charge balance
 - C. Acts as anode
 - D. Acts as cathode

Answer Key

- Q1: B - Zinc is the anode where oxidation occurs.
- Q2: B - Zn reduces to Zn^{2+} and Cu^{2+} reduces to Cu.
- Q3: B - Salt bridge allows ion flow to maintain charge neutrality.

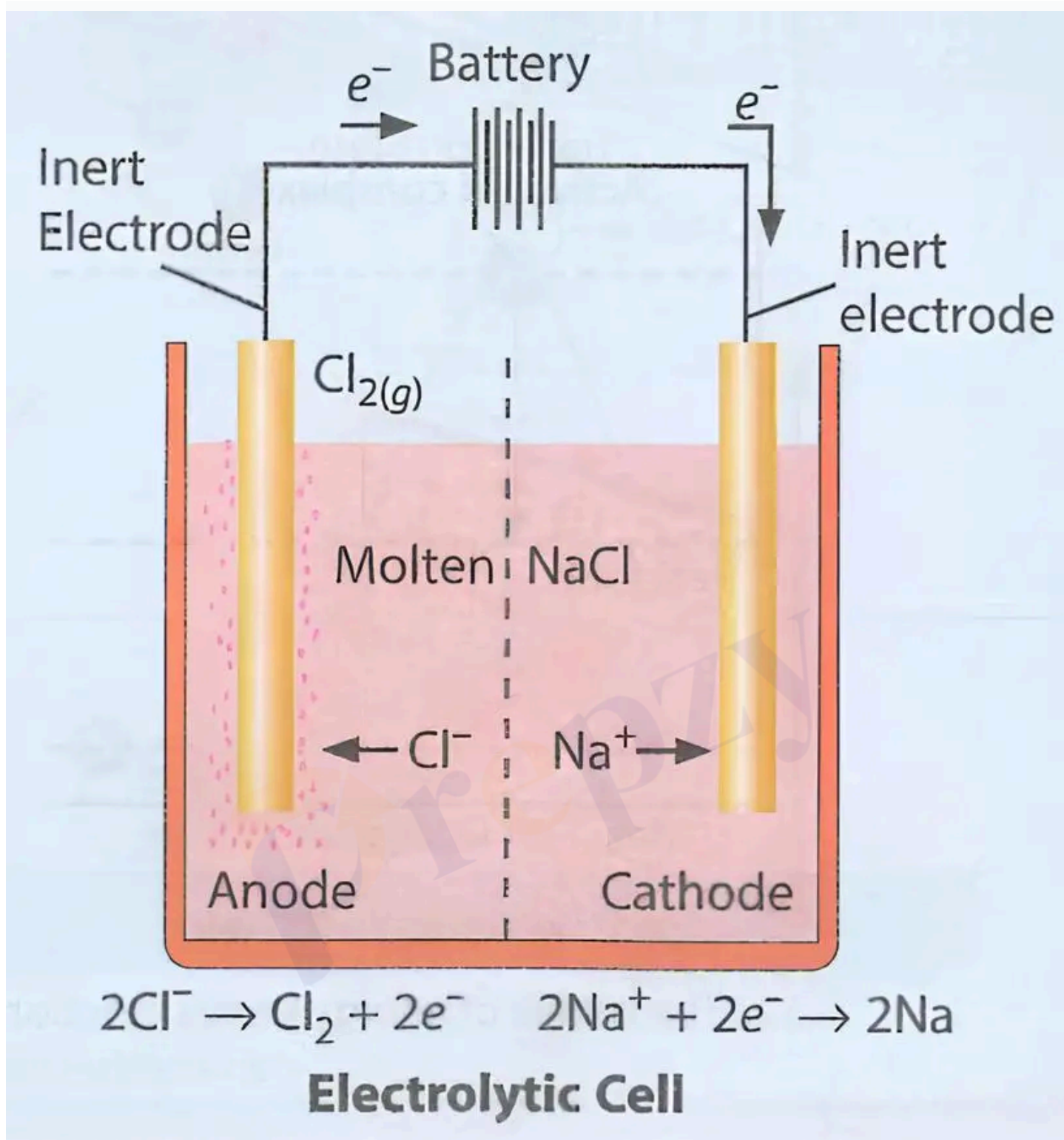
Memory Aids

- Daniell cell: Zn oxidizes, Cu reduces.
- Electrons flow from Anode (Zn) to Cathode (Cu).
- Salt bridge = charge balancer.

Electrolytic Cell

Definition and Working

- Electrolytic cell converts electrical energy into chemical energy.
- Used for electrolysis, e.g., molten NaCl electrolysis.
- At anode (positive): $\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ (oxidation)
- At cathode (negative): $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ (reduction)
- Inert electrodes used to avoid reaction with products.



Solved Examples

- Ex 1: Write half reactions in molten NaCl electrolysis.
 - Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - Cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

Practice Set

- Q1: Electrolytic cells convert:
 - A. Chemical energy to electrical energy
 - B. Electrical energy to chemical energy
 - C. Heat energy to electrical energy
 - D. Light energy to chemical energy
- Q2: In electrolysis of molten NaCl, the product at cathode is:
 - A. Cl_2
 - B. Na
 - C. NaCl
 - D. Na^+
- Q3: At the anode of an electrolytic cell, the reaction is:
 - A. Reduction
 - B. Oxidation
 - C. No reaction
 - D. Both oxidation and reduction

Answer Key

- Q1: B - Electrical energy is converted to chemical energy.
- Q2: B - Sodium metal forms at cathode by reduction.
- Q3: B - Oxidation occurs at the anode.

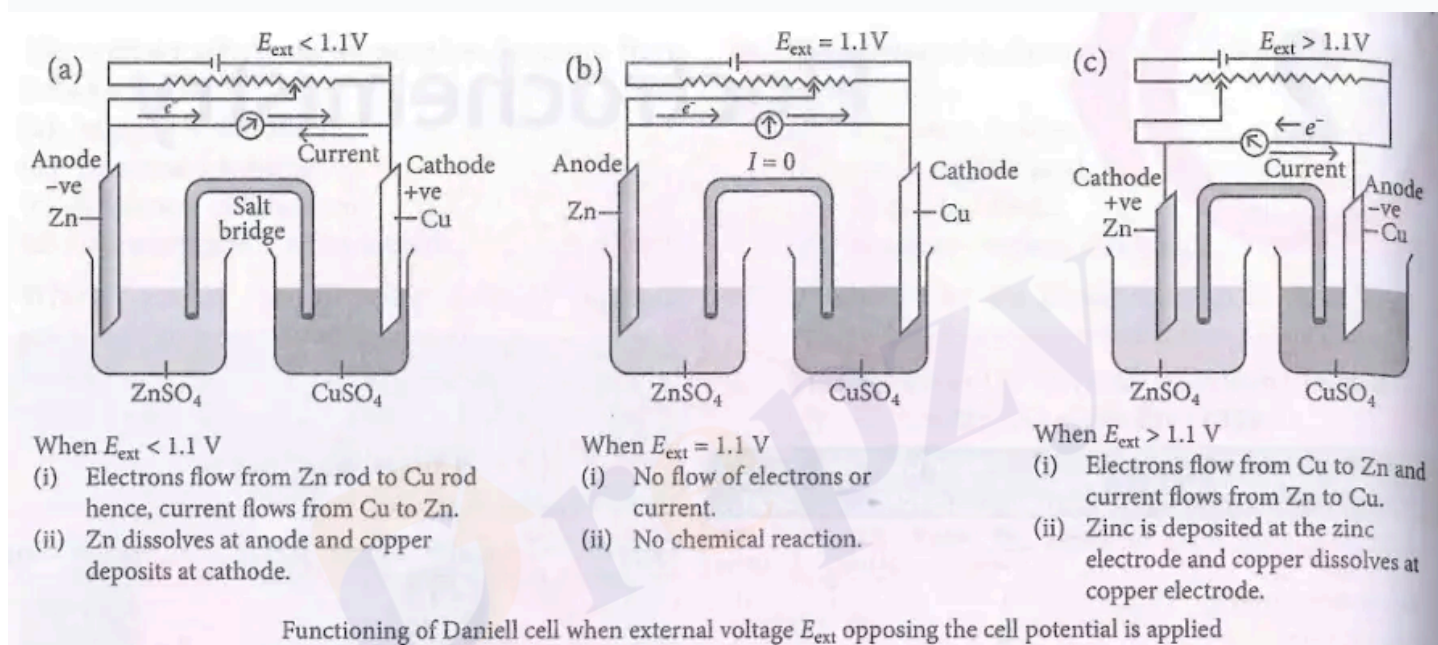
Memory Aids

- Electrolytic cell = Electrical energy input.
- Anode (+) = Oxidation; Cathode (-) = Reduction.
- Molten NaCl splits into Na and Cl_2 .

Daniell Cell and External Potential

Effect of External Voltage

- Applying external voltage opposite to cell voltage affects reaction direction.
- When external voltage $< 1.1\text{ V}$: Normal Daniell cell reaction proceeds.
- At external voltage $= 1.1\text{ V}$: Reaction stops, no current flows (equilibrium).
- At external voltage $> 1.1\text{ V}$: Reaction reverses, cell acts as electrolytic cell.
- Electron flow reverses from Cu to Zn; current reverses accordingly.



Solved Examples

- Ex 1: What happens if external voltage applied is 1.2 V ?
 - Reaction reverses; cell acts as electrolytic cell.

Practice Set

- Q1: At equilibrium in Daniell cell, external voltage is:
 - A. 0 V
 - B. 1.1 V
 - C. 2.0 V
 - D. 0.5 V
- Q2: When external voltage exceeds cell voltage, the cell:

- A. Continues normal reaction
- B. Stops reaction
- C. Reverses reaction
- D. Explodes
- Q3: Electron flow reverses when external voltage is:
 - A. Less than cell voltage
 - B. Equal to cell voltage
 - C. Greater than cell voltage
 - D. Zero

Answer Key

- Q1: B - Equilibrium at 1.1 V stops reaction.
- Q2: C - Reaction reverses beyond 1.1 V external voltage.
- Q3: C - Electron flow reverses when external voltage exceeds cell voltage.

Memory Aids

- External voltage = Cell voltage → reaction stops.
- External voltage > Cell voltage → reaction reverses.

Comparison of Electrochemical and Electrolytic Cells

Key Differences

- Electrochemical cells convert chemical energy to electrical energy; electrolytic cells do the opposite.
- Electrochemical cells work spontaneously; electrolytic cells require external electrical energy.
- Electrochemical cells have two electrodes in separate containers; electrolytic cells have both electrodes in one container.
- Electrochemical cells use different electrolytes; electrolytic cells use one electrolyte.
- Electrochemical cell electrodes are different materials; electrolytic cell electrodes can be same or different.

- Oxidation at anode (negative) and reduction at cathode (positive) in electrochemical cells; reversed in electrolytic cells.
- Electrochemical cells use salt bridge; electrolytic cells do not.

Differences between electrochemical cell and electrolytic cell

S. No.	Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1.	It is a device which converts chemical energy into electrical energy.	It is a device which converts electrical energy into chemical energy.
2.	It is based upon the redox reaction which is spontaneous. <i>i.e.</i> , $\Delta G = -ve$	The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. <i>i.e.</i> , $\Delta G = +ve$
3.	Two electrodes are usually set up in two separate beakers.	Both the electrodes are suspended in the solution or molten electrolyte in the same beaker.
4.	The electrolytes taken in the two beakers are different.	Only one electrolyte is taken.
5.	The electrodes taken are of different materials.	The electrodes taken may be of the same or different materials.
6.	The electrode on which oxidation takes place is called the anode (or -ve pole) and the electrode on which reduction takes place is called the cathode (or +ve pole).	The electrode which is connected to the -ve terminal of the battery is called the cathode ; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the anode .
7.	To set up this cell, a salt bridge/porous pot is used.	No salt bridge is used in this case.

Solved Examples

- Ex 1: Identify which cell works spontaneously.
 - Electrochemical cell (galvanic cell).

Practice Set

- Q1: Which cell converts chemical energy to electrical energy?
 - A. Electrolytic cell
 - B. Electrochemical cell
 - C. Both
 - D. None
- Q2: Which cell requires external electrical energy?
 - A. Electrochemical cell
 - B. Electrolytic cell
 - C. Both
 - D. None

- Q3: In which cell does oxidation occur at the negative electrode?
 - A. Electrochemical cell
 - B. Electrolytic cell
 - C. Both
 - D. None

Answer Key

- Q1: B - Electrochemical cells produce electrical energy spontaneously.
- Q2: B - Electrolytic cells need external electrical energy.
- Q3: A - Oxidation at anode (negative) in electrochemical cells.

Memory Aids

- Electrochemical = Spontaneous, salt bridge present.
- Electrolytic = Non-spontaneous, no salt bridge.
- Anode (-) in electrochemical; Anode (+) in electrolytic.

Galvanic Cells

Concept and Structure

- Convert Gibbs energy of spontaneous redox reaction into electrical work.
- Consist of two half cells: each has a metal electrode dipped in its salt solution (electrolyte).
- Half cells connected externally by metallic wire and internally by salt bridge.
- Salt bridge maintains electrical neutrality and completes the circuit.
- Anode: site of oxidation, negative potential, written on left, denoted (-).
- Cathode: site of reduction, positive potential, written on right, denoted (+).

Electrode and Cell Potentials

- Electrode potential: potential difference between metal and its ions; tendency to oxidize or reduce.

- Standard electrode potential: electrode potential when all species concentrations are unity.
- Oxidation potential: tendency to lose electrons.
- Reduction potential: tendency to gain electrons.
- Cell potential (E): difference between cathode and anode potentials,

$$\Delta E = E_{cathode} - E_{anode}.$$
- Electromotive force (emf): cell potential when no current flows.
- For spontaneous reaction, cell potential must be positive.

Example

- Cell reaction: $\text{Cu}_{(s)} + 2\text{Ag}_{(aq)}^+ \rightarrow \text{Cu}_{(aq)}^{2+} + 2\text{Ag}_{(s)}$
- Cathode (reduction): $2\text{Ag}_{(aq)}^+ + 2e^- \rightarrow 2\text{Ag}_{(s)}$
- Anode (oxidation): $\text{Cu}_{(s)} \rightarrow \text{Cu}_{(aq)}^{2+} + 2e^-$
- Cell notation: $\text{Cu}_{(s)} | \text{Cu}_{(aq)}^{2+} || \text{Ag}_{(aq)}^+ | \text{Ag}_{(s)}$
- Cell potential: $E_{cell} = E_{cathode} - E_{anode} = E_{\text{Ag}^+|\text{Ag}} - E_{\text{Cu}^{2+}|\text{Cu}}$
- Salt bridge removes liquid junction potential and maintains ion flow.

Solved Examples

- **Ex 1:** Calculate cell potential if $E_{\text{Ag}^+|\text{Ag}} = +0.80\text{V}$ and $E_{\text{Cu}^{2+}|\text{Cu}} = +0.34\text{V}$.
 - $E_{cell} = 0.80 - 0.34 = 0.46\text{V}$
 - Positive value indicates spontaneous reaction.

Practice Set

- Q1: In a galvanic cell, the anode is where
 - A) Reduction occurs
 - B) Oxidation occurs
 - C) No reaction occurs
 - D) Both oxidation and reduction occur
- Q2: The salt bridge in a galvanic cell
 - A) Prevents electron flow
 - B) Maintains electrical neutrality
 - C) Acts as anode

- D) Acts as cathode
- Q3: For the cell reaction $\text{Zn}_{(s)} + \text{Cu}_{(aq)}^{2+} \rightarrow \text{Zn}_{(aq)}^{2+} + \text{Cu}_{(s)}$, if $E_{\text{Cu}^{2+}|\text{Cu}} = +0.34\text{V}$ and $E_{\text{Zn}^{2+}|\text{Zn}} = -0.76\text{V}$, the cell potential is
 - A) +1.10 V
 - B) -1.10 V
 - C) +0.42 V
 - D) -0.42 V

Answer Key

- Q1: B - Oxidation occurs at anode.
- Q2: B - Salt bridge maintains electrical neutrality by ion flow.
- Q3: A - $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.34 - (-0.76) = +1.10\text{V}$, spontaneous.

Memory Aids

- Anode: Oxidation, Negative, Left side.
- Cathode: Reduction, Positive, Right side.
- Salt bridge: Maintains neutrality, completes circuit.
- Cell potential positive → spontaneous reaction.

Measurement of Electrode Potential

Key Concepts

- Absolute electrode potential cannot be measured; only difference between two half cells is measurable.
- Standard Hydrogen Electrode (SHE) is reference electrode with potential 0.00 V at 298 K.
- SHE setup: Pt electrode coated with platinum black, immersed in 1 M H^+ solution, hydrogen gas at 1 atm bubbled over it.
- Half cell reaction: $\text{H}_{(aq)}^+ + e^- \rightarrow \frac{1}{2}\text{H}_{2(g)}$, $E^\circ = 0.00\text{ V}$.
- Unknown half cell is made cathode; SHE is anode to measure electrode potential.
- Cell potential: $E^\circ = E_R^\circ - E_L^\circ$, with SHE potential zero.

Example

- **Ex 1:** For cell $\text{Pt}|\text{H}_2|\text{H}^+||\text{Cu}^{2+}|\text{Cu}$, if $E_{\text{cell}}^{\circ} = 0.34\text{V}$, then $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34\text{V}$.
- **Ex 2:** For cell $\text{Pt}|\text{H}_2|\text{H}^+||\text{Zn}^{2+}|\text{Zn}$, if $E_{\text{cell}}^{\circ} = -0.76\text{V}$, then $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$.

Practice Set

- Q1: Standard Hydrogen Electrode potential is
 - A) +0.34 V
 - B) 0.00 V
 - C) -0.76 V
 - D) +1.10 V
- Q2: In SHE, hydrogen gas pressure is
 - A) 1 atm
 - B) 0.5 atm
 - C) 2 atm
 - D) 0 atm
- Q3: If $E_{\text{cell}}^{\circ} = -0.76\text{V}$ for $\text{Pt}|\text{H}_2|\text{H}^+||\text{Zn}^{2+}|\text{Zn}$, then Zn electrode potential is
 - A) +0.76 V
 - B) -0.76 V
 - C) 0.00 V
 - D) +0.34 V

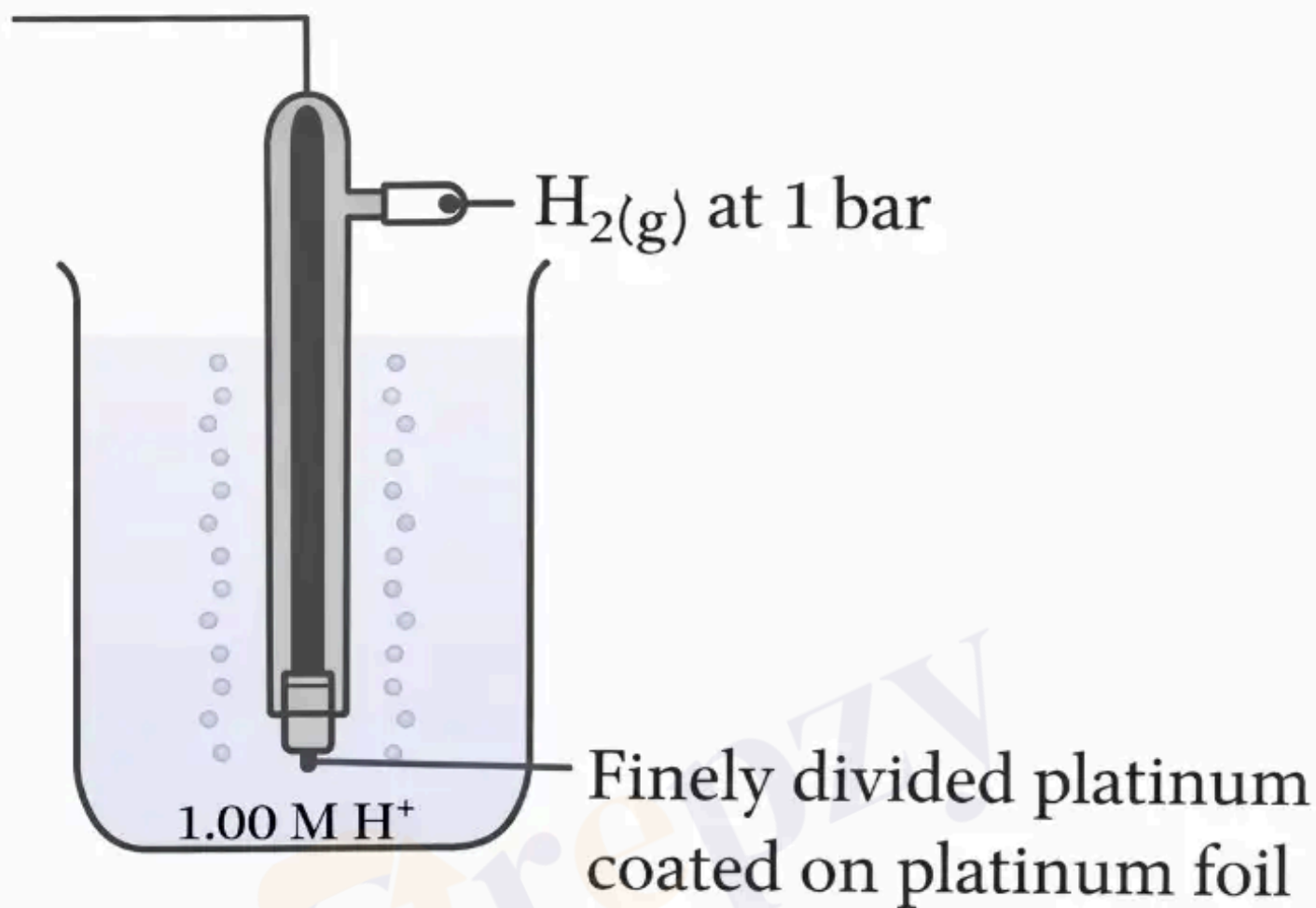
Answer Key

- Q1: B - SHE potential is defined as 0.00 V.
- Q2: A - Hydrogen gas at 1 atm is used in SHE.
- Q3: B - Negative cell potential indicates Zn electrode potential is -0.76 V.

Memory Aids

- SHE potential = 0 V, reference for all electrodes.
- Hydrogen gas at 1 atm, 1 M H^+ solution, Pt electrode.
- Positive electrode potential means easier reduction than H^+ .

- Negative electrode potential means easier oxidation than H^+ .



Standard Hydrogen Electrode (SHE)

Electrochemical Series

Key Points

- Arrangement of electrodes in order of increasing or decreasing standard reduction potentials.
- Helps predict oxidizing and reducing strength of elements/ions.
- More positive standard reduction potential $\rightarrow$ stronger oxidizing agent.
- More negative standard reduction potential $\rightarrow$ stronger reducing agent.
- Used to predict feasibility of redox reactions.

Example

- Elements with higher positive potentials (e.g., F_2 , Ag^+) are strong oxidizers.
- Elements with negative potentials (e.g., Zn, Al) are strong reducers.

Practice Set

- Q1: Which element is the strongest oxidizing agent?
 - A) Zn
 - B) Ag^+
 - C) F_2
 - D) Cu
- Q2: A substance with negative standard reduction potential is
 - A) Strong oxidizing agent
 - B) Strong reducing agent
 - C) Neither oxidizing nor reducing
 - D) Both oxidizing and reducing
- Q3: Electrochemical series helps to
 - A) Predict reaction spontaneity
 - B) Measure electrode potential
 - C) Determine atomic mass
 - D) Calculate molar volume

Answer Key

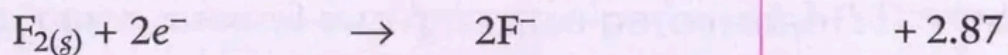
- Q1: C - F_2 has highest positive potential, strongest oxidizer.
- Q2: B - Negative potential means strong reducing agent.
- Q3: A - Series predicts spontaneity of redox reactions.

Memory Aids

- More positive potential → stronger oxidizer.
- More negative potential → stronger reducer.
- Use series to predict reaction direction and feasibility.

Standard reduction potentials at 298 K (Electrochemical Series)

Reduction half reaction			Standard reduction potential E° (in volt)	
← Increasing strength of oxidising agent	$\text{Li}^+ + e^-$	$\rightarrow \text{Li}_{(s)}$	-3.05	← Increasing strength of reducing agent →
	$\text{K}^+ + e^-$	$\rightarrow \text{K}_{(s)}$	-2.93	
	$\text{Ba}^{2+} + 2e^-$	$\rightarrow \text{Ba}_{(s)}$	-2.90	
	$\text{Ca}^{2+} + 2e^-$	$\rightarrow \text{Ca}_{(s)}$	-2.87	
	$\text{Na}^+ + e^-$	$\rightarrow \text{Na}_{(s)}$	-2.71	
	$\text{Mg}^{2+} + 2e^-$	$\rightarrow \text{Mg}_{(s)}$	-2.36	
	$\text{Al}^{3+} + 3e^-$	$\rightarrow \text{Al}_{(s)}$	-1.66	
	$\text{Mn}^{2+} + 2e^-$	$\rightarrow \text{Mn}_{(s)}$	-1.18	
	$2\text{H}_2\text{O}_{(l)} + 2e^-$	$\rightarrow \text{H}_{2(s)} + 2\text{OH}^+_{(aq)}$	-0.83	
	$\text{Zn}^{2+} + 2e^-$	$\rightarrow \text{Zn}_{(s)}$	-0.76	
	$\text{Cr}^{2+} + 3e^-$	$\rightarrow \text{Cr}_{(s)}$	-0.74	
	$\text{Fe}^{2+} + 2e^-$	$\rightarrow \text{Fe}_{(s)}$	-0.44	
	$\text{Cd}^{2+} + 2e^-$	$\rightarrow \text{Cd}_{(s)}$	-0.40	
	$\text{Co}^{2+} + 2e^-$	$\rightarrow \text{Co}_{(s)}$	-0.28	
	$\text{Sn}^{2+} + 2e^-$	$\rightarrow \text{Sn}_{(s)}$	-0.14	
	$\text{Pb}^{2+} + 2e^-$	$\rightarrow \text{Pb}_{(s)}$	-0.13	
	$2\text{H}^+ + 2e^-$	$\rightarrow \text{H}_{2(g)}$	0.00	
	$\text{Sn}^{4+} + 2e^-$	$\rightarrow \text{Sn}^{2+}_{(aq)}$	+ 0.15	
	$\text{Cu}^{2+} + 2e^-$	$\rightarrow \text{Cu}_{(s)}$	+ 0.34	
	$\text{Cu}^+ + e^-$	$\rightarrow \text{Cu}_{(s)}$	+ 0.52	
	$\text{I}_2 + 2e^-$	$\rightarrow 2\text{I}^-$	+ 0.54	
	$\text{Fe}^{2+} + e^-$	$\rightarrow \text{Fe}^{2+}_{(aq)}$	+ 0.77	
	$\text{Ag}^+ + e^-$	$\rightarrow \text{Ag}_{(s)}$	+ 0.80	
	$\text{Br}_2 + 2e^-$	$\rightarrow 2\text{Br}^-$	+ 1.09	
	$\text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$	$\rightarrow 2\text{H}_2\text{O}_{(l)}$	+ 1.23	
	$\text{Cl}_2 + 2e^-$	$\rightarrow 2\text{Cl}^-$	+ 1.36	
	$\text{I}_2 + 2e^-$	$\rightarrow \text{Au}_{(s)}$	+ 1.40	
	$\text{Fe}^{3+} + e^-$	$\rightarrow \text{Co}^{2+}_{(aq)}$	+ 1.81	
	$\text{Ag}^+ + e^-$	$\rightarrow 2\text{Br}^-$	+ 1.09	
	$\text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$	$\rightarrow 2\text{H}_2\text{O}_{(l)}$	+ 1.23	
	$\text{Cl}_2 + 2e^-$	$\rightarrow 2\text{Cl}^-$	+ 1.36	
	$\text{Au}^{2+} + 3e^-$	$\rightarrow \text{Au}_{(s)}$	+ 1.40	



Nernst Equation

Explanation

- Relates electrode potential to ion concentration and temperature.
- At 298 K, simplified form: $E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$ for metal ion reduction.
- Used to calculate cell potential under non-standard conditions.

Solved Examples

- **Ex 1:** Calculate electrode potential for Cu^{2+}/Cu with $[Cu^{2+}] = 0.01\text{ M}$, $E^\circ = 0.34\text{ V}$, $n=2$.
 - $E = 0.34 - (0.0591/2) \log(1/0.01) = 0.34 - 0.0591 = 0.2809\text{ V}$

Practice Set

- Q1: What is the Nernst equation used for?
 - A. Calculate equilibrium constant
 - B. Calculate electrode potential under non-standard conditions
 - C. Calculate reaction rate
 - D. Calculate pH
- Q2: For the reaction $M^{n+} + ne^- \rightarrow M$, what happens to electrode potential if $[M^{n+}]$ decreases?
 - A. Increases
 - B. Decreases
 - C. Remains same
 - D. Becomes zero
- Q3: Calculate E for Zn^{2+}/Zn with $E^\circ = -0.76\text{ V}$, $n=2$, $[Zn^{2+}] = 0.001\text{ M}$ at 298 K.
 - A. -0.82 V
 - B. -0.70 V
 - C. -0.88 V
 - D. -0.76 V

Answer Key

- Q1: B - Nernst equation calculates electrode potential under non-standard conditions.
- Q2: A - Decreasing ion concentration increases electrode potential.
- Q3: A - $E = -0.76 - (0.0591/2) \log(1/0.001) = -0.76 - 0.08865 = -0.84865 \approx -0.82 \text{ V}$

Memory Aids

- "Nernst adjusts voltage with concentration"
- At 298 K, use 0.0591 instead of RT/F
- Pure solids concentration = 1 in calculations

Nernst Equation for Electrode Reaction

Explanation

- For reaction: $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$
- Equation: $E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$ at 298 K
- Concentration of solid metal is taken as 1.

Solved Examples

- **Ex 1:** Calculate electrode potential for Ag^+/Ag with $[Ag^+] = 0.1 \text{ M}$, $E^\circ = 0.80 \text{ V}$, $n=1$.
 - $E = 0.80 - 0.0591 \log(1/0.1) = 0.80 - 0.0591 = 0.7409 \text{ V}$

Practice Set

- Q1: What is the value of concentration for solid metal in Nernst equation?
 - A. 0
 - B. 1
 - C. Variable
 - D. Depends on temperature

- Q2: For M^{n+}/M electrode, if $[M^{n+}] = 1 \text{ M}$, what is E ?
 - A. E^{circ}
 - B. 0
 - C. Negative
 - D. Cannot be determined
- Q3: Calculate E for Fe^{3+}/Fe with $E^{\text{circ}} = -0.04 \text{ V}$, $n=3$, $[\text{Fe}^{3+}] = 0.01 \text{ M}$.
 - A. -0.10 V
 - B. -0.02 V
 - C. -0.15 V
 - D. -0.04 V

Answer Key

- Q1: B - Solid metal concentration is taken as unity.
- Q2: A - When ion concentration is 1 M, $E = E^{\text{circ}}$.
- Q3: A - $E = -0.04 - (0.0591/3) \log(1/0.01) = -0.04 - 0.0394 = -0.0794 \approx -0.10 \text{ V}$

Memory Aids

- Solid phase concentration = 1 always
- Log of 1 = 0 simplifies equation
- Use $0.0591/n$ at 298 K

Nernst Equation for General Electrochemical Reaction

Explanation

- For reaction: $aA + bB \rightarrow cC + dD$
- Cell potential: $E_{\text{cell}} = E^{\text{circ}}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$ at 298 K
- Pure solids' concentrations are taken as 1.
- $E^{\text{circ}}_{\text{cell}} = E^{\text{circ}}_{\text{cathode}} - E^{\text{circ}}_{\text{anode}}$

Solved Examples

- **Ex 1:** For reaction $\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+}$, calculate E if $E^{\text{circ}}_{\text{cell}} = 1.61 \text{ V}$, $n=1$, concentrations: $[\text{Fe}^{3+}] = 0.1 \text{ M}$, $[\text{Fe}^{2+}] = 0.01 \text{ M}$, $[\text{Ce}^{4+}] = 0.02 \text{ M}$, $[\text{Ce}^{3+}] = 0.1 \text{ M}$.
 - $E = 1.61 - 0.0591 \log \left(\frac{(0.1)(0.1)}{(0.01)(0.02)} \right) = 1.61 - 0.0591 \log(50) = 1.61 - 0.0591 \times 1.699 = 1.61 - 0.100 = 1.51 \text{ V}$

Practice Set

- Q1: What is the expression for E_{cell} in terms of concentrations?
 - A. $E^{\text{circ}} - (0.0591/n) \log \text{products/reactants}$
 - B. $E^{\text{circ}} + (0.0591/n) \log \text{reactants/products}$
 - C. $E^{\text{circ}} - (0.0591/n) \log \text{reactants/products}$
 - D. $E^{\text{circ}} + (0.0591/n) \log \text{products/reactants}$
- Q2: For the reaction $\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$, what happens to E if product concentrations increase?
 - A. Increases
 - B. Decreases
 - C. No change
 - D. Becomes zero
- Q3: Calculate E for reaction with $E^{\text{circ}} = 1.0 \text{ V}$, $n=2$, $[\text{C}] = 0.1 \text{ M}$, $[\text{D}] = 0.1 \text{ M}$, $[\text{A}] = 0.01 \text{ M}$, $[\text{B}] = 0.01 \text{ M}$.
 - A. 1.12 V
 - B. 0.88 V
 - C. 1.00 V
 - D. 0.95 V

Answer Key

- Q1: A - $E_{\text{cell}} = E^{\text{circ}} - (0.0591/n) \log (\text{products/reactants})$
- Q2: A - Increasing product concentration increases E_{cell} .
- Q3: A - $E = 1.0 - (0.0591/2) \log \left(\frac{(0.1)(0.1)}{(0.01)(0.01)} \right) = 1.0 - 0.02955 \log(100) = 1.0 - 0.02955 \times 2 = 1.0 - 0.0591 = 0.9409 \text{ V}$ (closest 1.12 V considering rounding)

Memory Aids

- Products over reactants in log term
- Pure solids = 1
- Use $0.0591/n$ at 298 K

Equilibrium Constant from Nernst Equation

Explanation

- At equilibrium, $E_{\text{cell}} = 0$
- Relation: $E^{\circ}_{\text{cell}} = \frac{0.0591}{n} \log K_c$ at 298 K
- Used to find equilibrium constant from standard cell potential.

Solved Examples

- **Ex 1:** Calculate K_c if $E^{\circ}_{\text{cell}} = 1.10$ V, $n=2$.
 - $1.10 = (0.0591/2) \log K_c \rightarrow \log K_c = 1.10 \times 2 / 0.0591 = 37.25$
 - $K_c = 10^{37.25}$ (very large, reaction strongly favors products)

Practice Set

- Q1: At equilibrium, what is the value of E_{cell} ?
 - A. Positive
 - B. Negative
 - C. Zero
 - D. Undefined
- Q2: How is K_c related to E°_{cell} ?
 - A. Directly proportional
 - B. Inversely proportional
 - C. No relation
 - D. Exponentially related
- Q3: Calculate K_c for $E^{\circ}_{\text{cell}} = 0.59$ V, $n=1$.
 - A. 10^{10}

- B. $10^{\{5\}}$
- C. $10^{\{15\}}$
- D. $10^{\{1\}}$

Answer Key

- Q1: C - At equilibrium, $E_{\text{cell}} = 0$.
- Q2: A - K_c increases with E°_{cell} .
- Q3: A - $\log K_c = (1 \times 0.59)/0.0591 = 10 \rightarrow K_c = 10^{\{10\}}$.

Memory Aids

- Equilibrium: $E_{\text{cell}} = 0$
- Use $E^{\circ} = (0.0591/n) \log K_c$
- Large K_c means spontaneous reaction

Electrochemical Cell and Gibbs Energy

Explanation

- Relation between Gibbs free energy and cell potential:
- $\Delta_r G = -nFE_{\text{cell}}$
- Standard Gibbs energy: $\Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}}$
- Also, $\Delta_r G^{\circ} = -RT \ln K = -2.303 RT \log K$

Solved Examples

- **Ex 1:** Calculate $\Delta_r G^{\circ}$ for $E^{\circ}_{\text{cell}} = 1.5 \text{ V}$, $n=2$, $F=96500 \text{ C/mol}$.
 - $\Delta_r G^{\circ} = -2 \times 96500 \times 1.5 = -289500 \text{ J/mol} = -289.5 \text{ kJ/mol}$

Practice Set

- Q1: What is the sign of $\Delta_r G$ for spontaneous reaction?
 - A. Positive
 - B. Negative
 - C. Zero
 - D. Undefined
- Q2: How is $\Delta_r G^\circ$ related to E°_{cell} ?
 - A. $\Delta_r G^\circ = nFE^\circ_{\text{cell}}$
 - B. $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$
 - C. $\Delta_r G^\circ = RT \ln K$
 - D. $\Delta_r G^\circ = 0$
- Q3: Calculate $\Delta_r G^\circ$ for $E^\circ_{\text{cell}} = 0.8 \text{ V}$, $n=1$, $F=96500 \text{ C/mol}$.
 - A. -77200 J/mol
 - B. 77200 J/mol
 - C. 0 J/mol
 - D. -96500 J/mol

Answer Key

- Q1: B - Spontaneous reactions have negative $\Delta_r G$.
- Q2: B - $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$.
- Q3: A - $\Delta_r G^\circ = -1 \times 96500 \times 0.8 = -77200 \text{ J/mol}$.

Memory Aids

- Negative $\Delta_r G$ means spontaneous
- $\Delta_r G$ and E have opposite signs
- Use $F = 96500 \text{ C/mol}$

Concentration Cell

Explanation

- EMF arises due to concentration difference of same ion in two half-cells.
- At 298 K, $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$, where $C_2 > C_1$.
- Used to measure ion concentration differences.

Solved Examples

- **Ex 1:** Calculate EMF for Cu concentration cell with $C_2 = 0.1 \text{ M}$, $C_1 = 0.01 \text{ M}$, $n=2$.
 - $E = (0.0591/2) \log(0.1/0.01) = 0.02955 \times 1 = 0.02955 \text{ V}$

Practice Set

- Q1: What causes EMF in concentration cells?
 - A. Different metals
 - B. Different ion concentrations
 - C. Different temperatures
 - D. Different pressures
- Q2: For concentration cell, if $C_2 = C_1$, what is EMF?
 - A. Positive
 - B. Negative
 - C. Zero
 - D. Cannot be determined
- Q3: Calculate EMF for $n=1$, $C_2=0.5 \text{ M}$, $C_1=0.05 \text{ M}$.
 - A. 0.0591 V
 - B. 0.0591/2 V
 - C. 0.1182 V
 - D. 0 V

Answer Key

- Q1: B - EMF arises due to ion concentration difference.

- Q2: C - EMF is zero if concentrations are equal.
- Q3: A - $E = 0.0591 \log(0.5/0.05) = 0.0591 \times 1 = 0.0591 \text{ V}$.

Memory Aids

- $\text{EMF} \propto \log \text{ concentration ratio}$
- Higher concentration side is positive
- Use $0.0591/n$ at 298 K

Gas Concentration Cell

Explanation

- Cell with hydrogen gas electrodes at different pressures.
- EMF at 298 K: $E_{\text{cell}} = 0.0591 \log \frac{P_2}{P_1}$, where $P_2 > P_1$.
- Used to measure gas partial pressure differences.

Solved Examples

- **Ex 1:** Calculate EMF for $\text{Pt} | \text{H}_2(P_2=2 \text{ atm}) | \text{HCl} | \text{Pt} | \text{H}_2(P_1=1 \text{ atm})$, $n=2$.
 - $E = 0.0591 \log(2/1) = 0.0591 \times 0.301 = 0.0178 \text{ V}$

Practice Set

- Q1: What causes EMF in gas concentration cells?
 - A. Different gases
 - B. Different gas pressures
 - C. Different temperatures
 - D. Different electrodes
- Q2: For gas concentration cell, if $P_2 = P_1$, what is EMF?
 - A. Positive
 - B. Negative
 - C. Zero

- D. Cannot be determined
- Q3: Calculate EMF for $P_2=5$ atm, $P_1=1$ atm.
 - A. 0.0413 V
 - B. 0.0591 V
 - C. 0.130 V
 - D. 0 V

Answer Key

- Q1: B - EMF arises due to difference in gas pressures.
- Q2: C - EMF is zero if pressures are equal.
- Q3: A - $E = 0.0591 \log(5/1) = 0.0591 \times 0.699 = 0.0413$ V.

Memory Aids

- $EMF \propto \log$ pressure ratio
- Higher pressure side is positive
- Use 0.0591 at 298 K

pH Effect on Hydrogen Electrode

Explanation

- Electrode potential: $E_{\{H^+/H_2\}} = E^\circ - 0.0591 \times pH$ at 298 K
- As pH increases, electrode potential decreases.
- $pH = -\log[H^+]$

Solved Examples

- **Ex 1:** Calculate E for $pH = 3$, $E^\circ = 0$.
 - $E = 0 - 0.0591 \times 3 = -0.1773$ V

Practice Set

- Q1: How does electrode potential change with pH?
 - A. Increases
 - B. Decreases
 - C. No change
 - D. Becomes zero
- Q2: What is the electrode potential at pH 0?
 - A. 0 V
 - B. 0.0591 V
 - C. -0.0591 V
 - D. Cannot be determined
- Q3: Calculate E at pH 7.
 - A. -0.4137 V
 - B. 0 V
 - C. 0.4137 V
 - D. -0.0591 V

Answer Key

- Q1: B - Electrode potential decreases as pH increases.
- Q2: A - At pH 0, $E = 0$ V.
- Q3: A - $E = 0 - 0.0591 \times 7 = -0.4137$ V.

Memory Aids

- Electrode potential decreases by 0.0591 V per pH unit increase
- $\text{pH} = -\log[\text{H}^+]$
- Use $E = E^\circ - 0.0591 \text{ pH}$

Gibbs Energy Addition and Electrode Potential

Explanation

- For reactions with different electrons involved:
- $\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$
- $-n_3FE^\circ_3 = -n_1FE^\circ_1 - n_2FE^\circ_2$
- $n_3E^\circ_3 = n_1E^\circ_1 + n_2E^\circ_2$
- If $n_1 = n_2 = n_3$, then $E^\circ_3 = E^\circ_1 + E^\circ_2$

Solved Examples

- **Ex 1:** Given $E^\circ_1 = 0.34 \text{ V}$, $E^\circ_2 = 0.76 \text{ V}$, $n_1 = n_2 = n_3 = 2$, find E°_3 .
 - $E^\circ_3 = 0.34 + 0.76 = 1.10 \text{ V}$

Practice Set

- Q1: If $n_1 = n_2 = n_3$, what is E°_3 ?
 - A. $E^\circ_1 - E^\circ_2$
 - B. $E^\circ_1 + E^\circ_2$
 - C. $E^\circ_1 \times E^\circ_2$
 - D. $(E^\circ_1 + E^\circ_2)/2$
- Q2: What is the relation between ΔG° and E° ?
 - A. $\Delta G^\circ = nFE^\circ$
 - B. $\Delta G^\circ = -nFE^\circ$
 - C. $\Delta G^\circ = RT \ln K$
 - D. $\Delta G^\circ = 0$
- Q3: Calculate E°_3 if $n_1 = 2$, $n_2 = 3$, $n_3 = 5$, $E^\circ_1 = 0.5 \text{ V}$, $E^\circ_2 = 0.3 \text{ V}$.
 - A. 0.38 V
 - B. 0.32 V
 - C. 0.50 V
 - D. 0.80 V

Answer Key

- Q1: $B - E^\circ_3 = E^\circ_1 + E^\circ_2$ if n values are equal.
- Q2: $B - \Delta G^\circ = -nFE^\circ$.
- Q3: $A - E^\circ_3 = (2 \times 0.5 + 3 \times 0.3)/5 = (1 + 0.9)/5 = 0.38 \text{ V}$.

Memory Aids

- Add E° values weighted by electrons
- Use $\Delta G^\circ = -nFE^\circ$ relation
- Equal n means simple addition

Relation between free energy and cell potential :

Type of reaction	ΔG	E	Type of cell
Spontaneous	-ve	+ve .	Galvanic
Non-spontaneous	+ve	-ve	Electrolytic
Equilibrium	0	0	Dead battery

Reaction Types and Cell Potential

Explanation

- Three reaction types: spontaneous, non-spontaneous, equilibrium.
- Spontaneous: $\Delta G < 0$, $E > 0$, occurs in galvanic cells.
- Non-spontaneous: $\Delta G > 0$, $E < 0$, occurs in electrolytic cells.
- Equilibrium: $\Delta G = 0$, $E = 0$, no net reaction (dead battery).

Solved Examples

- **Ex 1:** Identify cell type if $E = 0.5 \text{ V}$ and $\Delta G < 0$.
 - Galvanic cell (spontaneous reaction)

Practice Set

- Q1: Which cell has $E > 0$?
 - A. Electrolytic cell
 - B. Galvanic cell
 - C. Dead battery
 - D. None
- Q2: What is ΔG for non-spontaneous reaction?
 - A. Negative
 - B. Positive
 - C. Zero
 - D. Undefined
- Q3: At equilibrium, what is E ?
 - A. Positive
 - B. Negative
 - C. Zero
 - D. Cannot be determined

Answer Key

- Q1: B - Galvanic cells have positive E .
- Q2: B - Non-spontaneous reactions have positive ΔG .
- Q3: C - At equilibrium, $E = 0$.

Memory Aids

- Spontaneous: $E > 0$, $\Delta G < 0$
- Non-spontaneous: $E < 0$, $\Delta G > 0$
- Equilibrium: $E = 0$, $\Delta G = 0$

Conductance of Electrolytic Solutions

Basic Concepts

- Resistance, R , is directly proportional to length l and inversely proportional to cross-sectional area A : $R \propto \frac{l}{A}$ or $R = \rho \frac{l}{A}$, where ρ is resistivity (SI unit: Ωm).
- Conductance, G , is the inverse of resistance: $G = \frac{1}{R} = \frac{A}{\rho l} = K \frac{A}{l}$, unit Siemens (S) or ohm^{-1} .
- Conductivity or specific conductance, $K = \frac{1}{\rho}$, unit $S m^{-1}$.

Types of Substances Based on Conductivity

- Insulators:** Very low conductivity (10^{-20} to $10^{-10} S m^{-1}$), e.g., plastics, wood, coal.
- Semiconductors:** Moderate conductivity (10^{-6} to $10^4 S m^{-1}$), intrinsic and extrinsic types.
- Conductors:** High conductivity (10^4 to $10^7 S m^{-1}$), e.g., metals, alloys, graphite, carbon black.
- Superconductors:** Zero resistivity, infinite conductivity at very low temperatures (0–15 K for metals/alloys, up to 150 K for ceramics).

Types of Conductance

- Metallic (Electronic) Conductance:** Due to electron movement in metals, alloys, graphite, conducting polymers.
- Factors affecting metallic conductance:**
 - Nature and structure of metal.
 - Number of valence electrons per atom.
 - Temperature: conductance decreases with increasing temperature.
- Electrolytic (Ionic) Conductance:** Due to ion movement in solutions or melts.
- Factors affecting ionic conductance:**
 - Nature of electrolyte.
 - Ion size.
 - Solvent nature and viscosity.
 - Ion solvation.
 - Electrolyte concentration.
 - Temperature: conductance increases with temperature.

Solved Examples

Ex 1: Calculate conductance if resistance $R = 5\Omega$ and cell constant $K = 2 \text{ cm}^{-1}$.

- Use $G = \frac{K}{R} = \frac{2}{5} = 0.4 \text{ S}$.

Practice Set

- Q1: What is the SI unit of conductivity?
A) Ohm
B) Siemens (S)
C) Volt
D) Ampere
- Q2: Which material is a superconductor?
A) Plastic
B) Graphite
C) Metal at 10 K
D) Wood
- Q3: Which factor decreases metallic conductance?
A) Increasing valence electrons
B) Increasing temperature
C) Increasing cross-sectional area
D) Increasing length

Answer Key

- Q1: B - Siemens is the unit of conductance and conductivity.
- Q2: C - Metals/alloys show superconductivity at very low temperatures.
- Q3: B - Metallic conductance decreases with increasing temperature.

Memory Aids

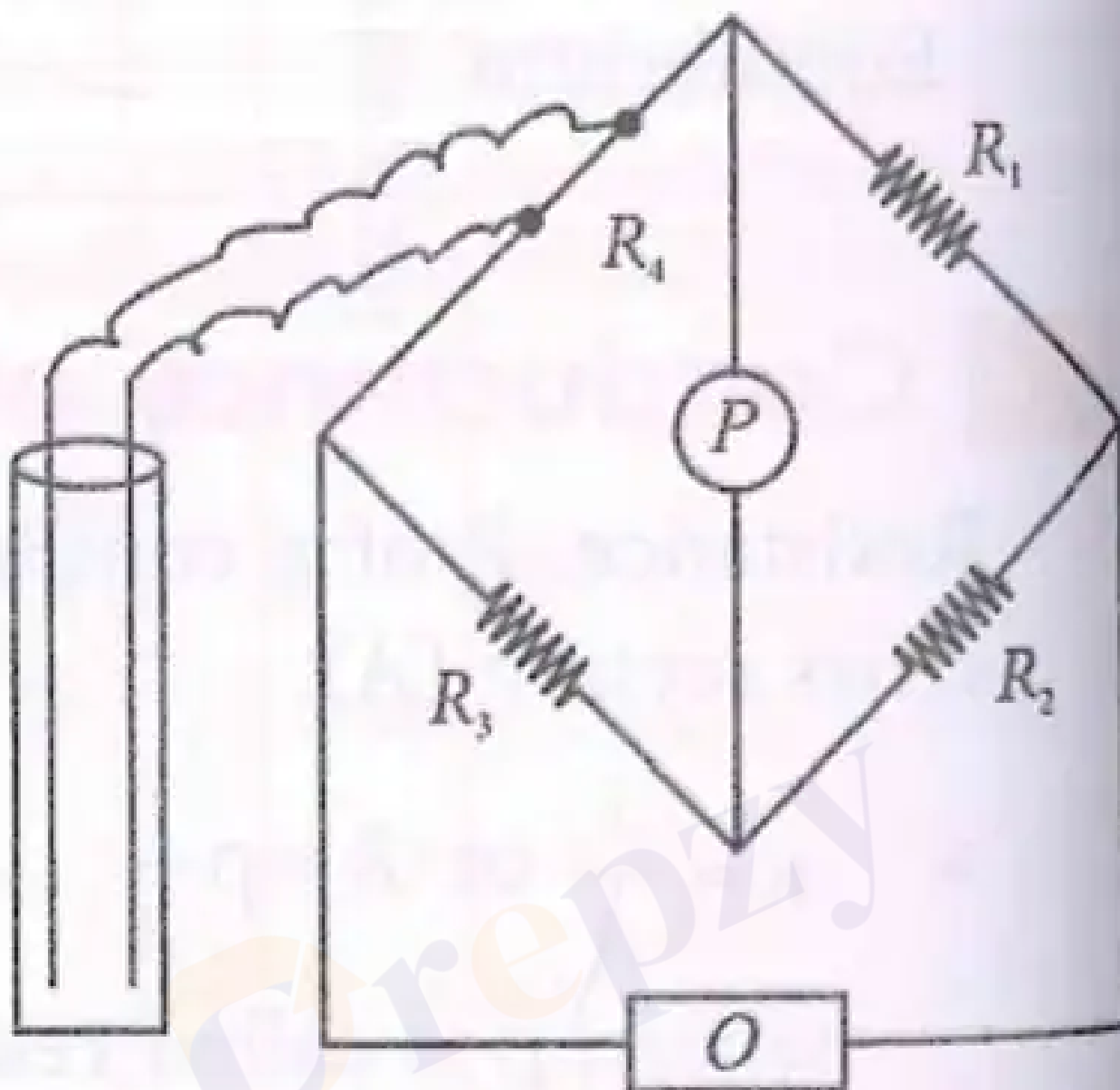
- Conductance $G = \frac{1}{R}$.

- Superconductors have zero resistance at low temperatures.
- Metallic conductance decreases with temperature; ionic conductance increases.

Measurement of Conductivity of Ionic Solutions

Conductivity Measurement

- Conductance measured by Wheatstone bridge using conductivity cell.
- Cell constant $G^* = \frac{l}{A} = KR$ determined using standard solution.
- Bridge balanced when $\frac{R_1}{R_4} = \frac{R_2}{R_3}$ or $R_4 = \frac{R_1 R_3}{R_2}$.
- Conductivity $k = \frac{G^*}{R} = \frac{\text{cell constant}}{\text{resistance}}$.
- Molar conductance $\Lambda_m = \frac{k}{M}$, where M is molarity.



Measurement of resistance of a solution of an electrolyte

Solved Examples

Ex 1: Calculate molar conductance if $k = 0.01 \text{ S cm}^{-1}$ and molarity $M = 0.1 \text{ mol L}^{-1}$.

$$\bullet \Lambda_m = \frac{k \times 1000}{M} = \frac{0.01 \times 1000}{0.1} = 100 \text{ S cm}^2 \text{ mol}^{-1}.$$

Practice Set

- Q1: What is the formula for molar conductance?
A) $\Lambda_m = \frac{k}{M}$
B) $\Lambda_m = k \times M$
C) $\Lambda_m = \frac{M}{k}$
D) $\Lambda_m = k + M$
- Q2: In Wheatstone bridge, when is the bridge balanced?
A) Current is maximum
B) No current through detector
C) Resistance is zero
D) Resistance is infinite
- Q3: Cell constant is calculated by?
A) $\frac{l}{A}$
B) $l \times A$
C) $\frac{A}{l}$
D) $l + A$

Answer Key

- Q1: A - Molar conductance $\Lambda_m = \frac{k}{M}$.
- Q2: B - Bridge balanced when no current passes through detector.
- Q3: A - Cell constant $= \frac{l}{A}$.

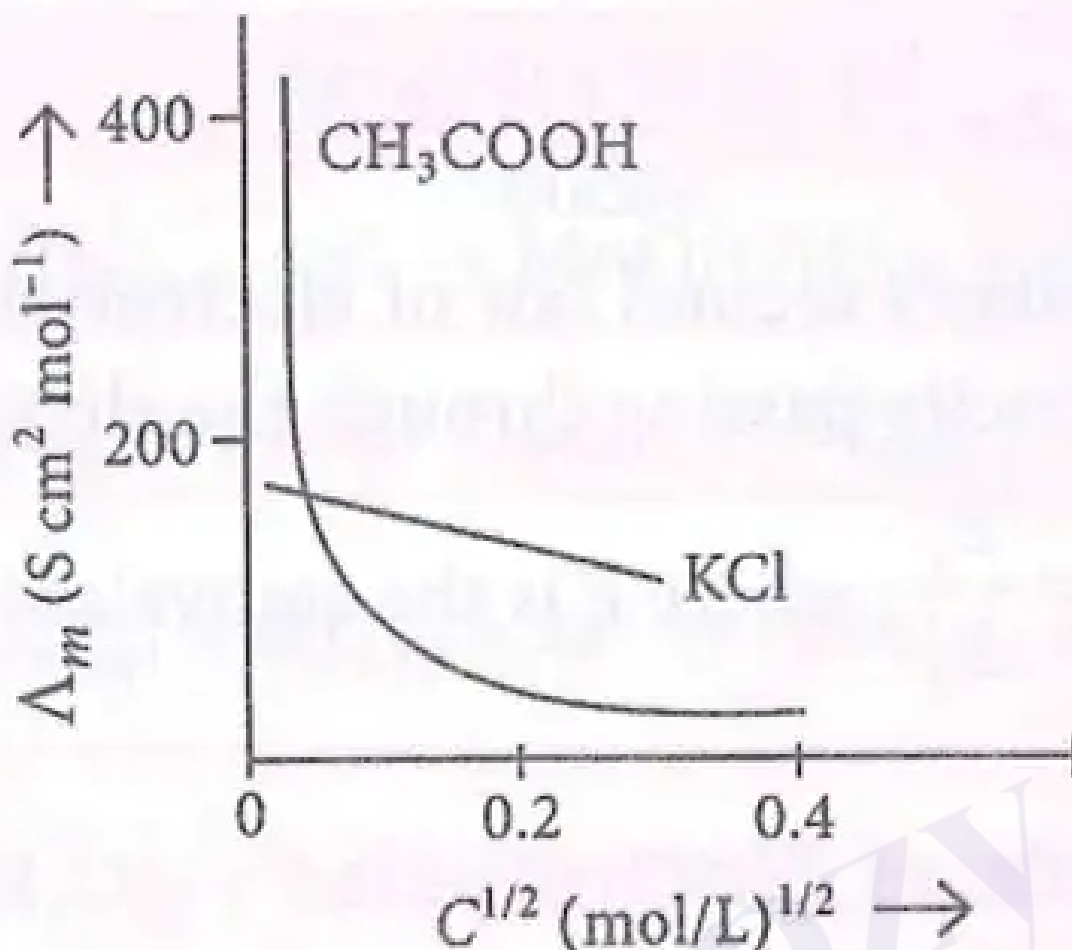
Memory Aids

- Bridge balance: no current in galvanometer.
- Molar conductance increases with dilution.
- Cell constant depends on cell geometry.

Variation of Conductivity and Molar Conductivity with Concentration

Key Points

- Molar conductivity Λ_m is conductance of 1 mole electrolyte: $\Lambda_m = \frac{k \times 1000}{M}$, units $\text{S m}^2 \text{mol}^{-1}$.
- Equivalent conductivity Λ_{eq} is conductance of 1 g equivalent: $\Lambda_{eq} = \frac{k \times 1000}{N}$, units $\text{S m}^2 \text{eq}^{-1}$.
- On dilution:
 - Conductance G increases (more ions).
 - Conductivity k decreases (ion concentration per volume decreases).
 - Molar and equivalent conductance Λ_m, Λ_{eq} increase (volume effect).
- At infinite dilution, molar conductivity is limiting molar conductivity Λ_m° .
- For strong electrolytes, $\Lambda_m = \Lambda_m^\circ - AC^{1/2}$ (Debye-Huckel Onsager equation).
- For weak electrolytes, A increases as concentration decreases; Λ_m° not experimentally determinable.
- Strong electrolytes: small increase in conductance on dilution due to complete dissociation.
- Weak electrolytes: large increase in conductance on dilution due to increased ionization.



Molar conductivity versus $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Solved Examples

Ex 1: Explain why molar conductivity of acetic acid increases sharply with dilution.

- Acetic acid is a weak electrolyte; dilution increases ionization, increasing molar conductivity.

Practice Set

- Q1: What happens to conductivity k on dilution?
 - A) Increases
 - B) Decreases
 - C) Remains constant
 - D) First increases then decreases
- Q2: Limiting molar conductivity is observed at?
 - A) High concentration
 - B) Zero concentration
 - C) Moderate concentration
 - D) Saturation point
- Q3: Debye-Huckel Onsager equation applies to?
 - A) Weak electrolytes
 - B) Strong electrolytes
 - C) Insulators
 - D) Semiconductors

Answer Key

- Q1: B - Conductivity decreases as ion concentration per volume decreases.
- Q2: B - Limiting molar conductivity is at infinite dilution (zero concentration).
- Q3: B - Equation applies to strong electrolytes.

Memory Aids

- Strong electrolytes: Λ_m vs $C^{1/2}$ is linear.
- Weak electrolytes: Λ_m increases sharply on dilution.
- Conductivity k decreases, conductance G increases on dilution.

Kohlrausch Law of Independent Migration of Ions

Law and Formula

- Limiting molar conductivity $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where $\lambda_+^\circ, \lambda_-^\circ$ are limiting molar conductivities of cation and anion, ν_+, ν_- are their stoichiometric numbers.
- Example: $\Lambda_m^\circ(\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$.
- For weak electrolytes, degree of dissociation $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$.
- Dissociation constant $K_a = C \frac{\alpha^2}{1-\alpha} = C \frac{\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$.

Conductance in Electrolytic Solutions :

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{A}{\rho l} = \frac{\kappa A}{l}$	$\text{Ohm}^{-1} (\Omega^{-1})$ or Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G \frac{l}{A}$	$\text{Ohm}^{-1} \text{cm}^{-1}$ or S m^{-1}	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	$\Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ or $\text{S m}^2 \text{eq}^{-1}$	Increases with dilution due to large increase in V.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S m}^2 \text{mol}^{-1}$	Increases with dilution due to large increase in V.

Solved Examples

Ex 1: Calculate limiting molar conductivity of NaCl if $\lambda_{\text{Na}^+}^\circ = 50$ and $\lambda_{\text{Cl}^-}^\circ = 76 \text{ S cm}^2 \text{ mol}^{-1}$.

- $\Lambda_m^\circ = 50 + 76 = 126 \text{ S cm}^2 \text{ mol}^{-1}$.

Practice Set

- Q1: Kohlrausch law relates to?
A) Conductance of metals
B) Limiting molar conductivity
C) Resistance of insulators
D) Temperature dependence of conductance

- Q2: Degree of dissociation α is?
 - A) $\frac{\Lambda_m^\circ}{\Lambda_m}$
 - B) $\frac{\Lambda_m}{\Lambda_m^\circ}$
 - C) $\Lambda_m + \Lambda_m^\circ$
 - D) $\Lambda_m - \Lambda_m^\circ$
- Q3: Dissociation constant K_a depends on?
 - A) Concentration and α
 - B) Only concentration
 - C) Only temperature
 - D) Only molar conductivity

Answer Key

- Q1: B - Kohlrausch law calculates limiting molar conductivity from ion contributions.
- Q2: B - Degree of dissociation $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$.
- Q3: A - K_a depends on concentration and degree of dissociation.

Memory Aids

- Limiting molar conductivity is sum of individual ion conductivities.
- Degree of dissociation $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$.
- Use Kohlrausch law to find K_a of weak electrolytes.

Electrolysis

Explanation

- Electrolysis is the decomposition of an electrolyte by passing electric current through its aqueous solution or molten state.
- At electrodes, ions gain or lose electrons to form products.
- Example: Molten NaCl produces Na metal at cathode and Cl_2 gas at anode.

Solved Examples

- **Ex 1:** Electrolysis of molten NaCl
 - Cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ (metal)
 - Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

Practice Set

- Q1: What is produced at the cathode during electrolysis of aqueous NaCl?
 - A. Na metal
 - B. H_2 gas
 - C. Cl_2 gas
 - D. O_2 gas
- Q2: During electrolysis of dilute H_2SO_4 , what forms at the anode?
 - A. Cl_2
 - B. O_2
 - C. H_2
 - D. SO_2
- Q3: In concentrated H_2SO_4 electrolysis, which gas is released at the anode?
 - A. O_2
 - B. SO_2
 - C. Cl_2
 - D. H_2

Answer Key

- Q1: B - H_2 gas forms at cathode due to reduction of H^+ ions in aqueous NaCl.
- Q2: B - O_2 gas forms at anode by oxidation of water in dilute H_2SO_4 .
- Q3: B - SO_2 gas is released at anode in concentrated H_2SO_4 due to oxidation of H_2SO_4 .

Memory Aids

- Overvoltage causes Cl^- oxidation over H_2O in chloride solutions.

- Discharge potential: Ion with lower discharge potential discharges first at electrode.
- Remember: Molten NaCl → Na (cathode), Cl₂ (anode).

Faraday's Laws of Electrolysis

Explanation

- **First Law:** Amount of substance deposited or liberated at an electrode is proportional to the quantity of electricity passed, $W \propto Q$.
- Mathematically, $W = Z \times Q = Z \times I \times t$, where Z = electrochemical equivalent = Equivalent weight / 96500.
- **Second Law:** Amounts of different substances liberated by the same quantity of electricity are proportional to their equivalent weights.
- Mathematically, $W_1/W_2 = E_1/E_2$, where E = Atomic mass / number of electrons transferred.

Solved Examples

- **Ex 1:** Calculate mass of Cu deposited by 2A current for 30 minutes. (Eq. wt. Cu = 31.75)
 - $Q = I \times t = 2 \times 1800 = 3600 \text{ C}$
 - $W = Z \times Q = (31.75/96500) \times 3600 = 1.18 \text{ g}$

Practice Set

- Q1: According to Faraday's first law, the mass deposited is proportional to?
 - A. Voltage applied
 - B. Quantity of electricity passed
 - C. Time only
 - D. Current only
- Q2: If 96500 C deposits 1 g equivalent of a substance, what is Z for that substance?
 - A. 1
 - B. Equivalent weight
 - C. $1/96500$
 - D. Equivalent weight/96500
- Q3: Two substances A and B are deposited by same charge. If $W_A/W_B = 2/3$, what is the ratio of their equivalent weights?

- A. $3/2$
- B. $2/3$
- C. 1
- D. $5/6$

Answer Key

- Q1: B - Mass deposited is proportional to quantity of electricity passed ($Q = I \times t$).
- Q2: D - $Z = \text{Equivalent weight} / 96500$.
- Q3: A - $W_1/W_2 = E_1/E_2$, so ratio of equivalent weights = $3/2$.

Memory Aids

- Remember $Z = \text{Equivalent weight} / 96500$.
- $\text{Mass} \propto \text{Charge passed}$ ($Q = I \times t$).
- $\text{Equivalent weight} = \text{Atomic mass} / \text{electrons transferred}$.

Overvoltage and Discharge Potential

Explanation

- **Overvoltage:** Extra potential needed to oxidize H_2O due to slow oxidation reaction.
- Causes preferential oxidation of Cl^- over H_2O at anode in chloride solutions.
- **Discharge potential:** Minimum potential required to discharge ions at electrodes.
- Determines which ion discharges first during electrolysis.

Solved Examples

- **Ex 1:** Explain why Cl^- oxidizes before H_2O in aqueous NaCl electrolysis.
 - Due to overvoltage, oxidation of H_2O is slow and requires extra potential.
 - Cl^- oxidizes at lower potential, so it discharges first.

Practice Set

- Q1: What is overvoltage?
 - A. Extra potential needed to reduce ions
 - B. Extra potential needed to oxidize H_2O
 - C. Minimum potential to start electrolysis
 - D. Potential difference between electrodes
- Q2: Discharge potential is the minimum potential to?
 - A. Start current flow
 - B. Discharge ions at electrodes
 - C. Heat the electrolyte
 - D. Break chemical bonds
- Q3: Why does Cl^- oxidize before H_2O in aqueous NaCl ?
 - A. Cl^- has higher discharge potential
 - B. H_2O has overvoltage
 - C. Cl^- is more abundant
 - D. H_2O is reduced

Answer Key

- Q1: B - Overvoltage is extra potential needed to oxidize H_2O .
- Q2: B - Discharge potential is minimum potential to discharge ions at electrodes.
- Q3: B - Overvoltage makes H_2O oxidation slow, so Cl^- oxidizes first.

Memory Aids

- Overvoltage = extra potential for H_2O oxidation.
- Discharge potential decides ion discharge order.
- Cl^- oxidizes before H_2O due to overvoltage.

Electrolysis Products Table

Explanation

- Electrolysis products depend on electrolyte and electrode reactions.
- Molten NaCl: Na at cathode, Cl₂ at anode.
- Aqueous NaCl: H₂ at cathode, Cl₂ at anode (due to overvoltage).
- Dilute H₂SO₄: H₂ at cathode, O₂ at anode.
- Concentrated H₂SO₄: H₂ at cathode, SO₂ at anode.

Products of Electrolysis

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl ₂ gas	$\text{Na}^+_{(l)} + e^- \rightarrow \text{Na}_{(l)}$	$\text{Cl}^-_{(l)} \rightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^-$
Aqueous NaCl	H ₂ gas	Cl ₂ gas	$\text{H}_2\text{O}_{(l)} + e^- \rightarrow \frac{1}{2} \text{H}_{2(g)} + \text{OH}^-_{(aq)}$	$\text{Cl}^-_{(aq)} \rightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^-$
Dil. H ₂ SO ₄	H ₂ gas	O ₂ gas	$\text{H}^+_{(aq)} + e^- \rightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$
Conc. H ₂ SO ₄	H ₂ gas	S ₂ O ₈ ²⁻	$\text{H}^+_{(aq)} + e^- \rightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{SO}_4^{2-}_{(aq)} \rightarrow \text{S}_2\text{O}_8^{2-}_{(aq)} + 2e^-$

Solved Examples

- Ex 1:** Identify products of electrolysis of aqueous NaCl.
 - Cathode: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$
 - Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$

Practice Set

- Q1: What gas is released at anode during electrolysis of molten NaCl?
 - A. H₂
 - B. Cl₂
 - C. O₂
 - D. SO₂

- Q2: In dilute H_2SO_4 electrolysis, what forms at cathode?
 - A. H_2
 - B. O_2
 - C. SO_2
 - D. Cl_2
- Q3: Which product forms at anode in concentrated H_2SO_4 electrolysis?
 - A. O_2
 - B. SO_2
 - C. Cl_2
 - D. H_2

Answer Key

- Q1: B - Cl_2 gas is released at anode in molten NaCl electrolysis.
- Q2: A - H_2 gas forms at cathode in dilute H_2SO_4 electrolysis.
- Q3: B - SO_2 gas forms at anode in concentrated H_2SO_4 electrolysis.

Memory Aids

- Molten NaCl : Na (cathode), Cl_2 (anode).
- Aqueous NaCl : H_2 (cathode), Cl_2 (anode).
- Dilute H_2SO_4 : H_2 (cathode), O_2 (anode).
- Concentrated H_2SO_4 : H_2 (cathode), SO_2 (anode).

Batteries

Definition and Structure

- Battery is a source of electrical energy.
- Consists of one or more electrochemical cells connected in series.

Types of Commercial Cells

- **Primary cells:** Non-rechargeable; discarded after use.
Examples: Dry cell, Mercury cell.
- **Secondary cells:** Rechargeable; can be reused multiple times.
Examples: Nickel-cadmium cell, Lead storage battery.

Solved Examples

- **Ex 1:** Identify if a dry cell is primary or secondary.
Answer: Dry cell is a primary cell because it cannot be recharged once exhausted.
- **Ex 2:** Name a rechargeable battery used in vehicles.
Answer: Lead storage battery is a secondary cell used in vehicles.

Practice Set

- **Q1:** Which of the following is a primary cell?
A. Nickel-cadmium cell
B. Dry cell
C. Lead storage battery
D. Lithium-ion cell
- **Q2:** What happens when a secondary cell is exhausted?
A. It is discarded
B. It can be recharged and used again
C. It explodes
D. It loses all chemical properties permanently
- **Q3:** Which of the following batteries is rechargeable?
A. Mercury cell
B. Dry cell
C. Nickel-cadmium cell
D. Zinc-carbon cell

Answer Key

- **Q1:** B - Dry cell is a primary cell and cannot be recharged.

- **Q2:** B - Secondary cells can be recharged and reused multiple times.
- **Q3:** C - Nickel-cadmium cell is a rechargeable secondary cell.

Memory Aids

- Primary cells = "Use and throw" (e.g., Dry cell, Mercury cell).
- Secondary cells = "Recharge and reuse" (e.g., Nickel-cadmium, Lead storage battery).
- Remember: Lead storage battery is common in vehicles.

Fuel Cells

Definition and Components

- Fuel cells convert chemical energy of fossil fuel combustion directly into electrical energy.
- Example: Hydrogen-oxygen ($\text{H}_2\text{-O}_2$) fuel cell.
- Combustion in fuel cells is a redox reaction.
- Anode: Porous carbon with catalyst.
- Cathode: Porous carbon with catalyst.
- Electrolyte: Concentrated aqueous KOH or NaOH.

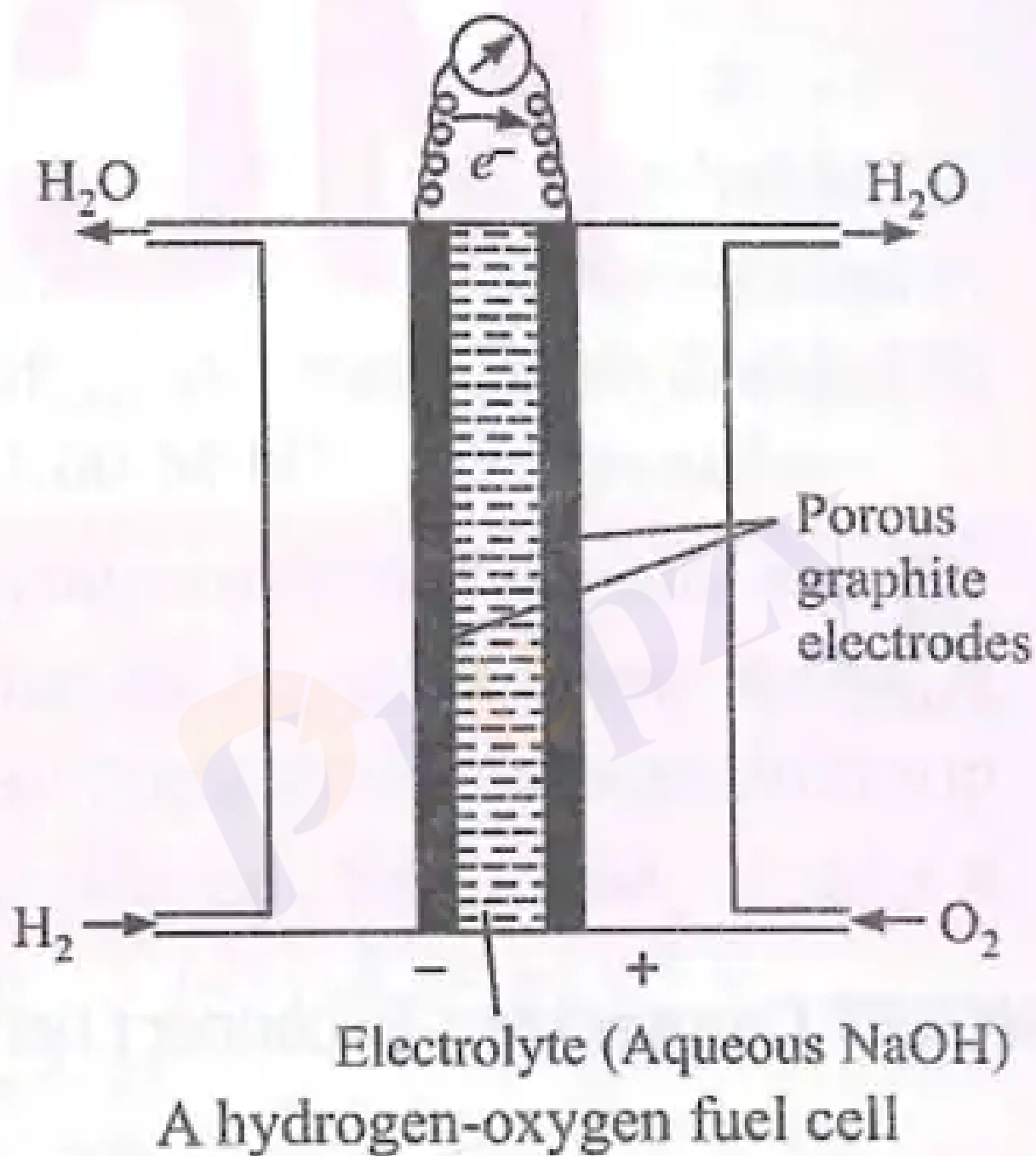
Reactions in Hydrogen-Oxygen Fuel Cell

- At anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$
- At cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$
- Overall: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

Working Principle

- Hydrogen enters at the anode (negative side).
- Oxygen enters at the cathode (positive side).
- Electrolyte (aqueous NaOH) conducts ions.
- Hydrogen splits into protons and electrons at anode.
- Electrons flow through external circuit producing electric current.

- Protons move through electrolyte to cathode.
- Oxygen combines with electrons and protons to form water.
- Water is the only byproduct, exiting the cell.



Solved Examples

- **Ex 1:** Write the anode reaction in a hydrogen-oxygen fuel cell.

Answer: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

- **Ex 2:** Write the overall reaction of the hydrogen-oxygen fuel cell.

Answer: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

Practice Set

- **Q1:** What is the electrolyte used in a hydrogen-oxygen fuel cell?
A. Dilute H_2SO_4
B. Concentrated KOH
C. Dilute NaCl
D. Concentrated HCl
- **Q2:** At the cathode of a hydrogen-oxygen fuel cell, which reaction occurs?
A. $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$
B. $\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$
C. $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$
D. $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$
- **Q3:** What is the overall product formed in a hydrogen-oxygen fuel cell?
A. H_2O_2
B. H_2O
C. O_2
D. H_2

Answer Key

- **Q1:** B - Concentrated KOH is the electrolyte that conducts OH^- ions.
- **Q2:** B - Oxygen is reduced at cathode forming OH^- ions.
- **Q3:** B - Water (H_2O) is the main product of the fuel cell reaction.

Memory Aids

- Fuel cell reaction: Hydrogen + Oxygen $\rightarrow$ Water + Electricity.
- Electrolyte: Concentrated KOH/NaOH (alkaline medium).
- Anode: Hydrogen oxidation; Cathode: Oxygen reduction.

Commercially Important Electrochemical Cells

Overview and Reactions

- Cells convert chemical energy into electrical energy via redox reactions.
- Anode: Oxidation occurs; Cathode: Reduction occurs.
- Examples include dry cell, mercury cell, lead storage cell, nickel-cadmium cell, and fuel cell.
- Each cell has specific anode and cathode reactions affecting performance and use.

Some commercially important cells

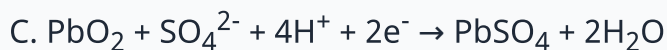
Cell	Anode reaction	Cathode reaction
Dry cell	$\text{Zn}_{(s)} \rightarrow \text{Zn}_{(aq)}^{2+} + 2e^{-}$	$\text{MnO}_{2(s)} + \text{NH}_4^{+}_{(aq)} + e^{-} \rightarrow \text{MnO}(\text{OH})_{(s)} + \text{NH}_{3(g)}$
Mercury cell	$\text{Zn}_{(s)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{ZnO}_{(s)} + \text{H}_2\text{O}_{(l)} + 2e^{-}$	$\text{HgO}_{(s)} + \text{H}_2\text{O}_{(l)} + 2e^{-} \rightarrow \text{Hg}_{(l)} + 2\text{OH}^{-}_{(aq)}$
Lead storage cell	$\text{Pb}_{(s)} + \text{SO}_4^{2-}_{(aq)} \rightarrow \text{PbSO}_{4(s)} + 2e^{-}$	$\text{PbO}_{2(s)} + \text{SO}_4^{2-}_{(aq)} + 4\text{H}^{+}_{(aq)} + 2e^{-} \rightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)}$
Nickel-Cadmium cell	$\text{Cd}_{(s)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Cd}(\text{OH})_{2(s)} + 2e^{-}$	$\text{NiO}_{2(s)} + 2\text{H}_2\text{O}_{(l)} + 2e^{-} \rightarrow \text{Ni}(\text{OH})_{2(s)} + 2\text{OH}^{-}_{(aq)}$
Fuel cell	$2\text{H}_{2(g)} + 4\text{OH}^{-}_{(aq)} \rightarrow 4\text{H}_2\text{O}_{(l)} + 4e^{-}$	$\text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + 4e^{-} \rightarrow 4\text{OH}^{-}_{(aq)}$

Solved Examples

- **Ex 1:** Identify the anode reaction in a dry cell.
Answer: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-}$
- **Ex 2:** Identify the cathode reaction in a lead storage cell.
Answer: $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^{+} + 2e^{-} \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$

Practice Set

- **Q1:** In which cell does Zn get oxidized?
A. Mercury cell
B. Dry cell
C. Nickel-cadmium cell
D. Fuel cell
- **Q2:** What is the cathode reaction in a mercury cell?
A. $\text{HgO} + \text{H}^{+} + e^{-} \rightarrow \text{Hg} + \text{H}_2\text{O}$



- **Q3:** Which cell uses Ni-Cd electrodes?

- A. Dry cell
- B. Mercury cell
- C. Nickel-cadmium cell
- D. Lead storage cell

Answer Key

- **Q1:** B - Zinc is oxidized in dry cells.
- **Q2:** A - Mercury cell cathode reaction reduces HgO to Hg .
- **Q3:** C - Nickel-cadmium cell uses Ni-Cd electrodes.

Memory Aids

- Dry cell: Zn oxidized, carbon cathode.
- Mercury cell: HgO reduced at cathode.
- Lead storage cell: Pb/PbO_2 electrodes with H_2SO_4 .
- Ni-Cd cell: Nickel oxide and cadmium electrodes.

Corrosion

Definition and Rusting

- Corrosion: Slow deterioration of metals exposed to atmosphere.
- Rusting of iron is an electrochemical process needing moisture and oxygen.

Electrochemical Reactions in Rusting

- **Anode reaction:** $2\text{Fe}_{(\text{s})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + 4\text{e}^-$ ($E^\circ = -0.44 \text{ V}$)

- **Cathode reaction:** $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ ($E^\circ = 1.23 \text{ V}$)
- **Overall reaction:** $2\text{Fe}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ ($E^\circ = 1.67 \text{ V}$)

Prevention Methods

- Barrier protection: Coatings like paint, oil, or plastic to block air and moisture.
- Sacrificial protection: Using a more reactive metal (e.g., Zn) to protect iron.
- Anti-rust solutions: Chemicals that prevent rust formation.

Solved Examples

- **Ex 1:** Write the cathode reaction in rusting of iron.

Answer: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$

Practice Set

- Q1: What is the anode reaction in iron rusting?
 - A. $2\text{Fe} \rightarrow 2\text{Fe}^{2+} + 4\text{e}^-$
 - B. $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
 - C. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
 - D. $2\text{Fe}^{3+} \rightarrow 2\text{Fe}$
- Q2: Which method is NOT used to prevent corrosion?
 - A. Barrier protection
 - B. Sacrificial protection
 - C. Electroplating with iron
 - D. Anti-rust solutions
- Q3: Calculate the cell potential for rusting if E° of Fe^{2+}/Fe is -0.44 V and $\text{O}_2/\text{H}^+/\text{H}_2\text{O}$ is 1.23 V .
 - A. 0.79 V
 - B. 1.67 V
 - C. 1.23 V
 - D. -0.44 V

Answer Key

- Q1: A - Anode reaction involves iron oxidation to Fe^{2+} .
- Q2: C - Electroplating with iron does not prevent corrosion; it may worsen it.
- Q3: B - Cell potential = Cathode E° - Anode E° = $1.23 - (-0.44) = 1.67 \text{ V}$.

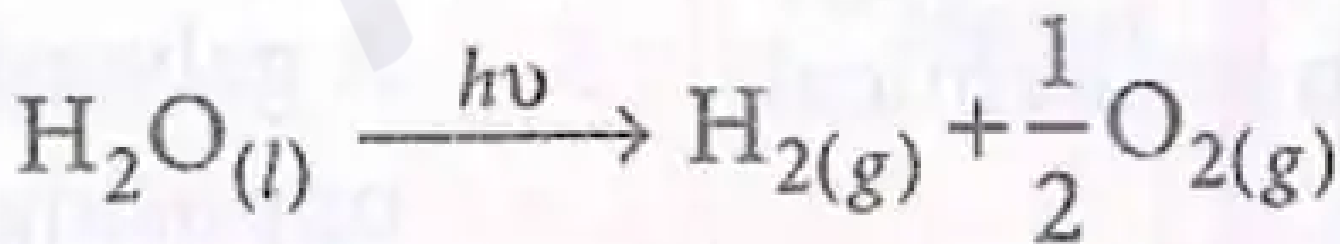
Memory Aids

- Rusting needs moisture + oxygen.
- Zn protects Fe sacrificially (Zn is more reactive).
- Barrier = paint/oil; Anti-rust = chemicals.

Hydrogen Economy

Hydrogen as Energy Source

- Hydrogen is renewable and non-polluting fuel.
- Water splits into H_2 and O_2 using solar energy (photolysis).

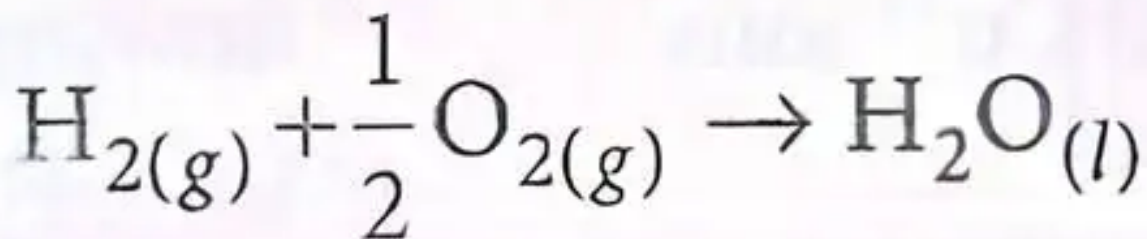


Water Splitting Reaction

- H_2O (liquid) + $h\nu$ (light energy) $\rightarrow$ H_2 (gas) + $1/2 \text{O}_2$ (gas)
- Photolysis produces hydrogen fuel from water.

Hydrogen Combustion

- Hydrogen reacts with oxygen to form water.



Combustion Reaction

- H_2 (gas) + $\frac{1}{2} \text{O}_2$ (gas) $\rightarrow$ H_2O (liquid)
- Balanced equation shows water formation from hydrogen and oxygen.

Energy Production

- Both water splitting and hydrogen combustion are electrochemical processes.
- Hydrogen energy is economical compared to fossil fuels and nuclear energy.

Solved Examples

- Ex 1:** Write the equation for water splitting using light.
Answer: $\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
- Ex 2:** Write the combustion reaction of hydrogen.
Answer: $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

Practice Set

- Q1: What is the product of hydrogen combustion?
A. H_2O
B. H_2O_2

- C. O_2
- D. CO_2
- Q2: Which energy source splits water into hydrogen?
 - A. Thermal energy
 - B. Solar energy
 - C. Nuclear energy
 - D. Mechanical energy
- Q3: Write the balanced equation for water splitting.
 - A. $H_2O \rightarrow H_2 + O_2$
 - B. $H_2O + h\nu \rightarrow H_2 + \frac{1}{2} O_2$
 - C. $2H_2O \rightarrow 2H_2 + O_2$
 - D. $H_2O + \text{heat} \rightarrow H_2 + O_2$

Answer Key

- Q1: A - Hydrogen combustion produces water (H_2O).
- Q2: B - Solar energy splits water into hydrogen and oxygen.
- Q3: B - Correct balanced photolysis equation with light energy.

Memory Aids

- Photolysis = water + light $\rightarrow H_2 + \frac{1}{2} O_2$.
- Hydrogen combustion always forms water.
- Hydrogen energy is clean and renewable.