Dev Academy
Yamunanagar (Haryana)

Comprehensive Notes

Electrochemistry

Class
12

CHEMISTRY

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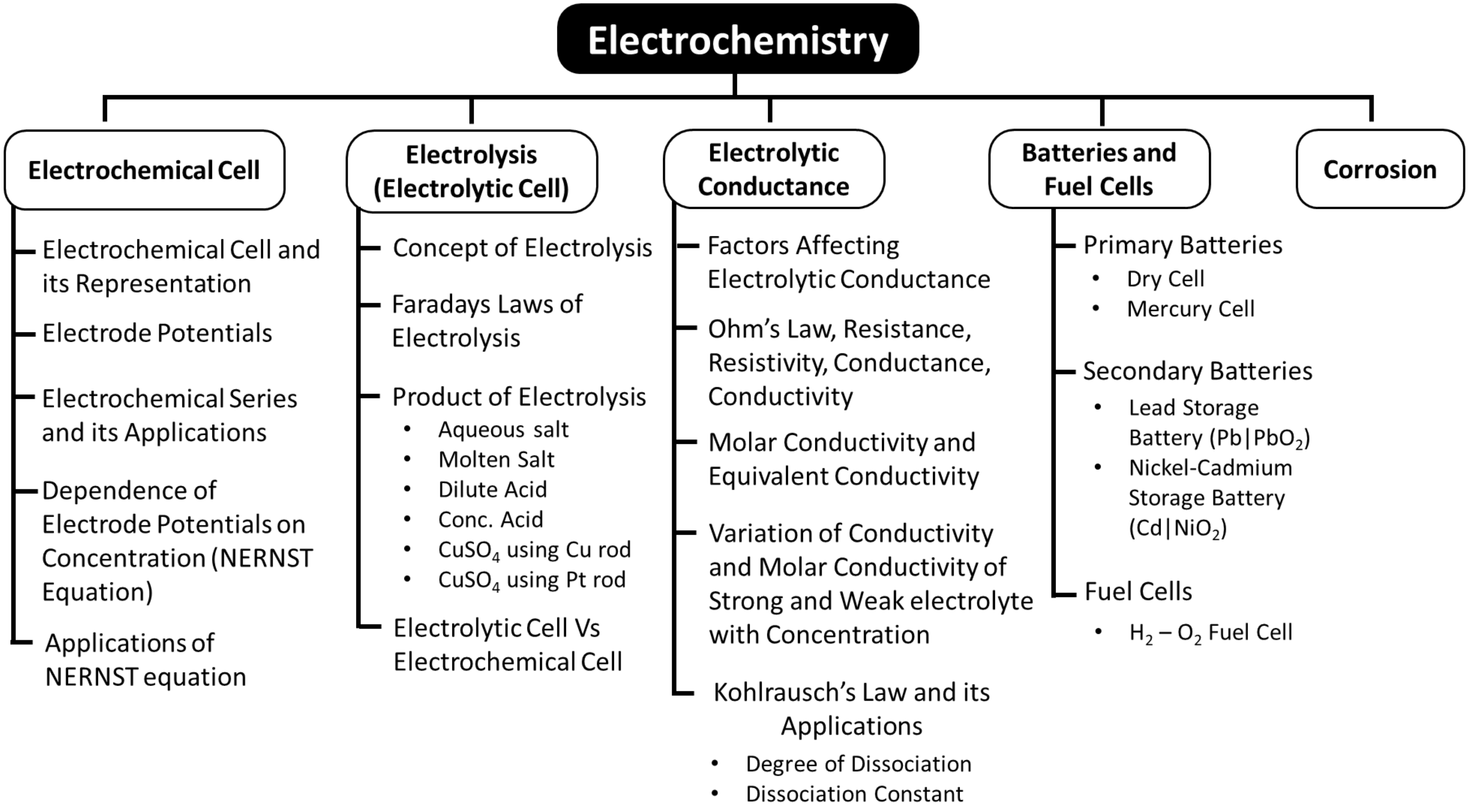

Electrochemistry

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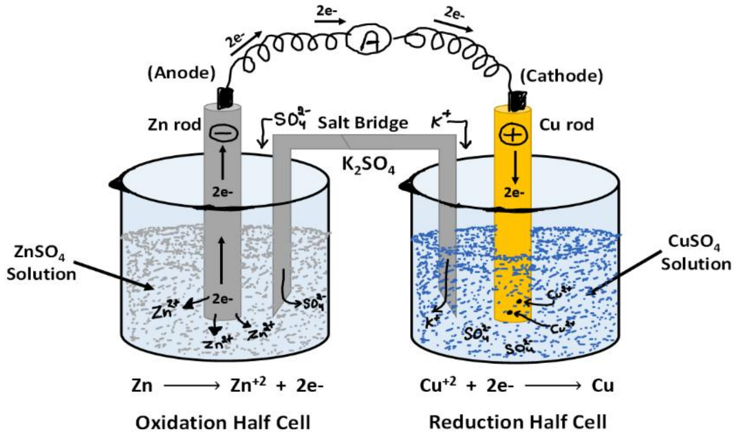
Electrochemical Cell – Galvanic Cell or Voltaic Cell

- An electrochemical cell is a device used to convert the **chemical energy** of a spontaneous redox reaction into **electrical energy**.
- These cells are also called **Galvanic cells** or **Voltaic cells**, named after **Luigi Galvani** and **Alessandro Volta**.

A Daniell Cell (Zn-$CuSO_4$ Cell)

Construction

- **Setup:**
  Two separate beakers are used. One beaker contains a **1M zinc sulphate** ($ZnSO_4$) solution with a **zinc (Zn) rod** immersed in it. Second beaker contains a **1M copper sulphate** ($CuSO_4$) solution with a **copper (Cu) rod**.
- **External Circuit:**
  The zinc and copper rods (electrodes) are connected by a wire through a voltmeter or ammeter.
- **Internal Circuit:**
  The two solutions are connected by a **salt bridge**, which allows electrical contact between the two solutions without letting them intermix.



Reactions in the Half-Cells

- **Left Beaker (Anode/Oxidation Half-Cell):**
  - The zinc rod acts as the **anode** (negative pole).
  - At the anode, zinc atoms are **oxidized** to zinc ions (Zn^{2+}), **releasing two electrons**.
  - The released electrons then travel through the external wire to the copper electrode.
    - **Oxidation Half Reaction:** $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
  - As a result of this oxidation, the **zinc rod progressively dissolves**, and the concentration of Zn^{2+} ions in the $ZnSO_4$ solution increases.
- **Right Beaker (Cathode/Reduction Half-Cell):**
  - The copper rod acts as the **cathode** (positive pole).
  - The electrons arriving from the anode are **gained by copper ions** (Cu^{2+}) from the solution.
  - These ions are **reduced** to metallic copper, which gets **deposited on the copper rod**. Consequently, the concentration of the $CuSO_4$ solution decreases.
    - **Reduction Half Reaction:** $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$
- **Overall-Cell Reaction:** The net reaction is the sum of the two half-reactions.
  - **Reaction:** $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

The Salt Bridge

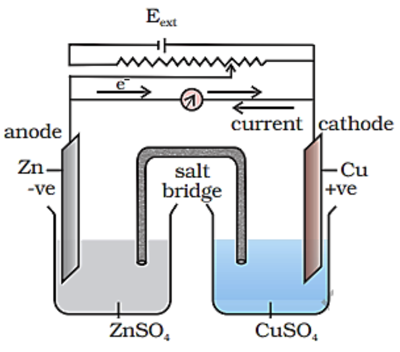
- A salt bridge is an **inverted U-shaped glass tube** filled with a saturated solution of an **inert electrolyte** (e.g., KCl, KNO_3, K_2SO_4) mixed with a gelling agent like **agar-agar** or **gelatin**.

Functions of a Salt Bridge

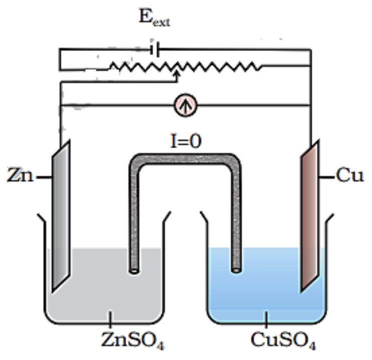
- It **completes the electrical circuit** by allowing ions to move between the two half-cells.
- It **maintains the electrical neutrality** of the solutions in both half-cells by supplying counter-ions.
- It **prevents the two solutions from mixing**.

Daniell Cell Functioning with Applied External Voltage (E_{ext})

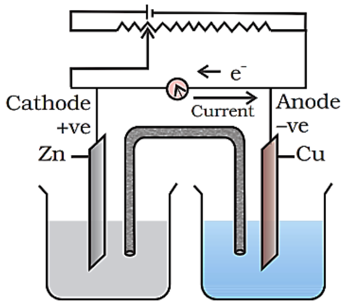
- The standard cell potential ($\mathbf{E^0_{cell}}$) of a Daniell cell is **1.1 V**.
- When external applied voltage is **smaller** than standard cell potential (**$E_{ext} < 1.1$ V**)
    - Electrons flow from **Zn rod to Cu rod**, hence, current flows from Cu to Zn.
    - Zn dissolves at anode and copper deposits at cathode.
- When external applied voltage is **equal** to standard cell potential (**$E_{ext} = 1.1$ V**)
    - No flow of electrons or current.
    - No chemical reaction.
- When external applied voltage is **greater** than standard cell potential (**$E_{ext} > 1.1$ V**)
    - Electrons flow from **Cu rod to Zn rod** and current flows from Zn to Cu.
    - Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.



When $E_{ext} < 1.1$ V



When $E_{ext} = 1.1$ V



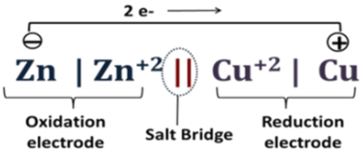
When $E_{ext} > 1.1$ V

Features of an Electrochemical Cell

- **Anode:** Oxidation occurs at the anode, which acts as the **negative pole**. The mass of the anode rod decreases as the cell operates.
- **Cathode:** Reduction occurs at the cathode, which acts as the **positive pole**. The mass of the cathode rod increases.
- **Flow of Charge:** Electrons flow from the anode to the cathode in the external circuit. Conventional current flows in the opposite direction, from the cathode to the anode.
- **Simultaneity:** The two half-reactions (oxidation and reduction) always occur simultaneously.
- **Circuit:** A salt bridge or porous membrane completes the inner electrical circuit and maintains electrolyte neutrality.

Electrochemical Cell Representation (Cell Notation)

- **General Form of Representation:**
  - Metal (Anode) | Ion (Anode) || Ion (Cathode) | Metal (Cathode)



- **Salt Bridge:** It is indicated by a double-parallel line (||)
- **Phase Interfaces:** It is indicated by a Single vertical line (|)

- **Left Side (Anode - Oxidation):** $Zn \longrightarrow Zn^{+2} + 2e^-$
  - Written as: Metal | Metal Ion
  - Example: $Zn_{(s)} | Zn^{2+}_{(aq.)}$

- **Right Side (Cathode - Reduction):** $Cu^{+2} + 2e^- \longrightarrow Cu$
  - Written as: Metal Ion | Metal
  - Example: $Cu^{2+}_{(aq.)} | Cu_{(s)}$

- **Examples:**
  - $Cu | Cu^{2+} || Ag^{+} | Ag$
  - $Zn | Zn^{2+} || Ag^{+} | Ag$
  - $Fe | Fe^{2+} || Cu^{2+} | Cu$

Standard Electrode Potential (E°)

Definition:

The potential difference that develops between **metal electrode** and **its own ions** in a solution of **1M** concentration at 298 K temperature.

OR

Standard electrode potential (E°) is the **tendency of an electrode** to **gain** (reduction potential) or **lose** (oxidation potential) **electrons** when it is in equilibrium with its own ionic solution. This value is measured under standard conditions, (i.e., concentration of **1 M** for the ionic solution, a temperature of **298 K** (25 °C), and a pressure of 1 bar (if gases are involved)).

$$Cu_{(s)} \rightleftharpoons Cu^{+2}_{(aq)} + 2e^-$$

Underlying Mechanism:

- When a **metal rod is immersed in its own ionic solution**, two opposing reactions occur simultaneously:
  - (i) **Oxidation:** Metal atoms lose electrons and go into solution as ions.

$$M_{(s)} \longrightarrow M^{+n}_{(aq)} + ne^-$$

  - (ii) **Reduction:** Metal ions gain electrons and are deposited on the rod.

$$M^{+n}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

- **Equilibrium:** A dynamic equilibrium is established between these two processes.

$$M_{(s)} \rightleftharpoons M^{+n}_{(aq)} + ne^-$$

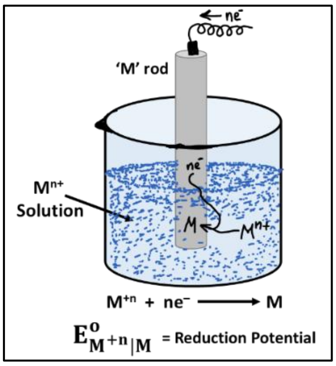
- **Electric Double Layer:** The resulting charge separation at the **metal – solution interface** creates an "electric double layer," and the potential difference across this layer is **the electrode potential**.

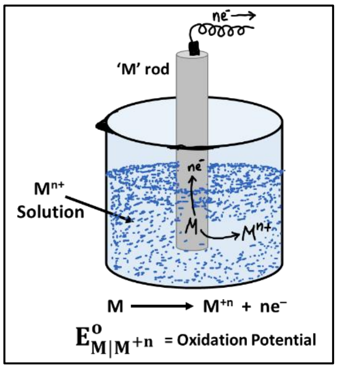
Types of Standard Electrode Potential

1. **Standard Oxidation Electrode Potential:**
   - The tendency of an electrode to **lose electrons** (under standard conditions).
   - Examples: $Zn \longrightarrow Zn^{+2} + 2e^-$ or $E^\circ_{Zn|Zn^{+2}}$

     $Fe \longrightarrow Fe^{+2} + 2e^-$ or $E^\circ_{Fe|Fe^{+2}}$
2. **Standard Reduction Electrode Potential:**
   - The tendency of an electrode to **gain electrons** (under standard conditions).
   - Examples: $Cu^{+2} + 2e^- \longrightarrow Cu$ or $E^\circ_{Cu^{+2}|Cu}$

     $Ag^{+1} + 1e^- \longrightarrow Ag$ or $E^\circ_{Ag^+|Ag}$





Key Relationship:

- Oxidation potential (O.P.) and reduction potential (R.P.) for the same half-reaction have **equal magnitude but opposite signs**.
  - $+E^\circ_{\text{Redution potential}} = -E^\circ_{\text{Oxidation potential}}$
- Example: If $E^\circ_{Ag^+|Ag}$ (**R.P.**) is **+0.80 V**, then $E^\circ_{Ag|Ag^+}$ (**O.P.**) is $-$**0.80 V**.

Factors Affecting the Electrode Potential:

- Nature of the metal and its ions
- Concentration of the ions in the solution
- Temperature

Therefore, standard electrode potentials are generally measured under standard conditions such as **1M** ionic concentration, a temperature of **298 K** and a pressure of **1 bar** (if gases are involved).

Measurement of Standard Electrode Potential (E°)

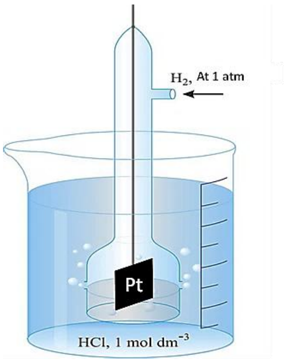
The standard electrode potentials of different elements have to be measured against standard hydrogen electrode (**SHE**) or normal hydrogen electrode (**NHE**).

Standard Hydrogen Electrode (SHE) or Reference Electrode

Construction

The SHE is a reference electrode built under standard conditions:

- A **platinized platinum electrode** fitted in glass tube and is dipped in **1M solution of H^+ ions** (e.g., 1M HCl).
- **Pure hydrogen gas** at **1 atm pressure** is bubbled over the electrode.
- The temperature is maintained at **298 K**.



Working Principle

- The electrode potential of the SHE is arbitrarily defined as **0.00V**.
- The platinum electrode facilitates the reversible half-reaction: $H_{2(g)} \rightleftharpoons 2H^+_{(aq)} + 2e^-$
- It can act as either an **anode** (oxidation) or a **cathode** (reduction) depending on the other half-cell.

To determine the electrode potential of any electrode, an **electrochemical cell is set up** using one electrode of a Standard Hydrogen Electrode (**S.H.E.**) and a second electrode of the element whose potential is to be measured.

The **Electromotive Force (E.M.F.)** of the cell is the **sum** of the oxidation potential of the anode and the reduction potential of the cathode. Since the standard hydrogen electrode has a **zero**-electrode potential, the E.M.F. of the cell will directly give the electrode potential of the electrode under investigation.

E.M.F. = Oxidation potential of anode + Reduction potential of cathode

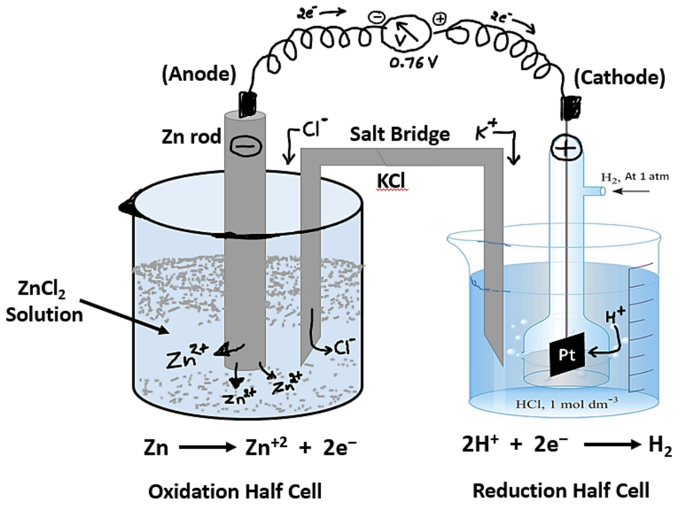
Determination of Standard electrode potential of Zn electrode ($E^\circ_{Zn^{+2}|Zn}$)

- An electrochemical cell is **set up** using one zinc electrode (Zn rod immersed in a 1M $ZnCl_2$ solution) and a second electrode of the S.H.E.
- The E.M.F. of the cell is found to be **0.76 V**.
- Furthermore, the **direction of electron flow** indicates that **oxidation takes place at the zinc electrode**. Hence, **+0.76 V is the standard oxidation potential** of the **zinc electrode**.
  - E.M.F. = Oxidation Potential of Zinc electrode + Reduction Potential of S.H.E.
    +0.76 V = Oxidation Potential of Zinc electrode + 0.00 V
    +0.76 V = Oxidation Potential of Zinc electrode

- It is important to note that it is common practice to express all electrode potentials as **reduction potentials**.
- We know that the reduction half-reaction is simply **the reverse** of the oxidation half-reaction. Therefore, the reduction potential is **obtained from** the oxidation potential by simply **changing the sign**.

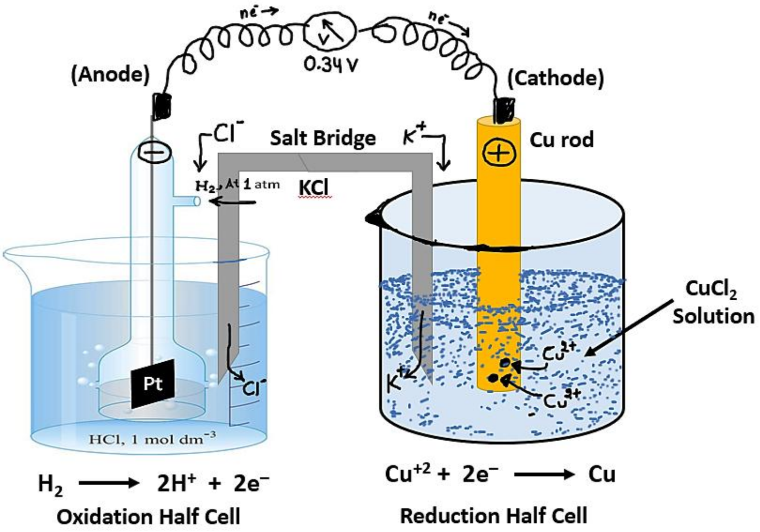
+RP = −OP OR −RP = +OP

- Thus, for the zinc electrode, the **Standard Reduction Potential** is **–0.76 V**.



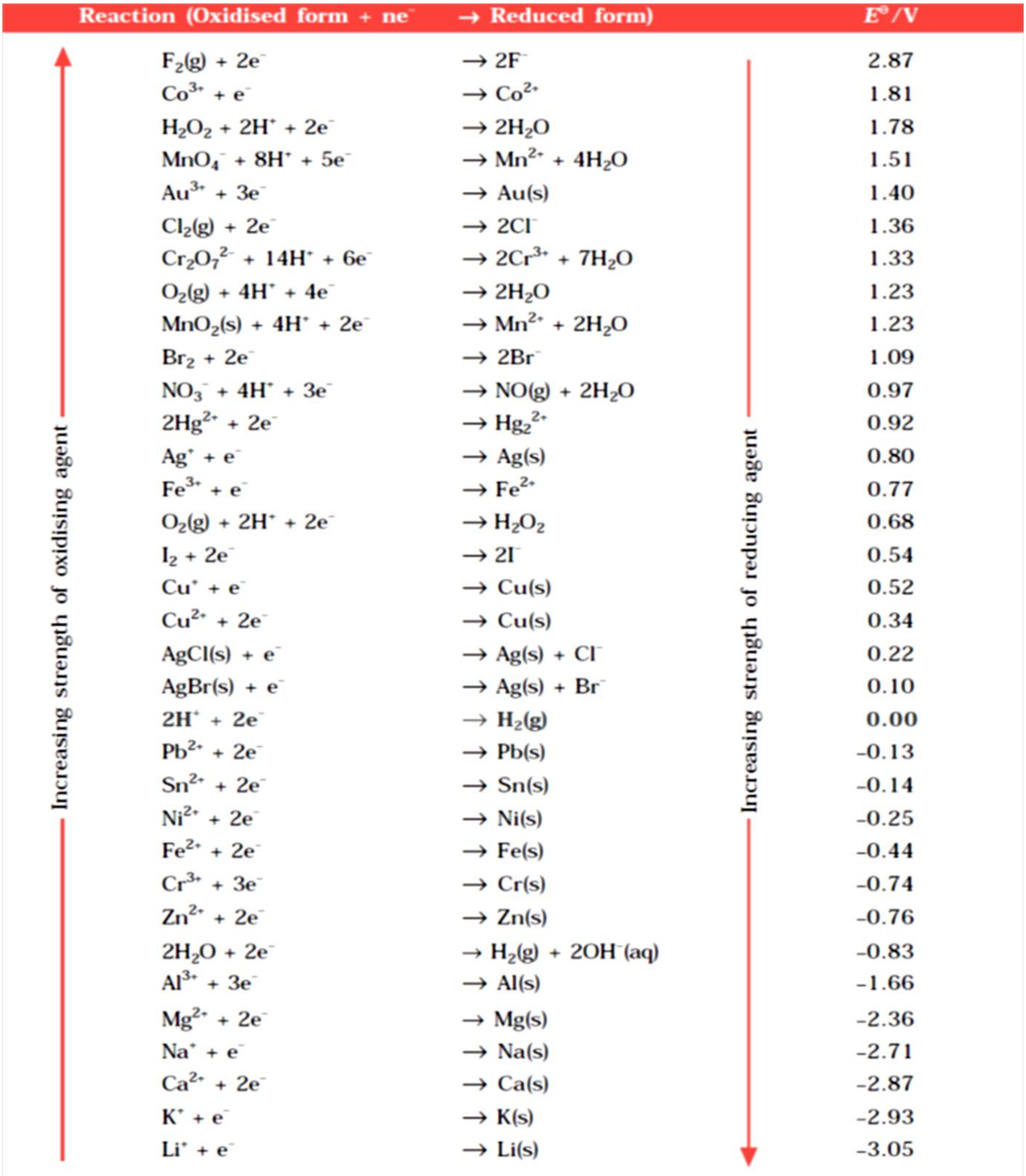
Determination of Standard electrode potential of Cu electrode – $E^\circ_{Cu^{+2}|Cu}$

- An electrochemical cell is **set up** using one zinc electrode (Cu rod immersed in a 1M $CuCl_2$ solution) and a second electrode of the S.H.E.
- The E.M.F. of the cell is found to be **0.34 V**.
- Furthermore, the **direction of electron flow** indicates that **reduction takes place at the copper electrode**. Hence, **+0.76 V is the standard reduction potential** of the **copper electrode**.
    - E.M.F. = Oxidation Potential of S.H.E. + Reduction Potential of copper electrode
      +0.34 V = 0.00 V + Reduction Potential of copper electrode
      +0.34 V = Reduction Potential of copper electrode
- Thus, for the copper electrode, the Standard Reduction Potential is **+0.34 V**.



Electrochemical Series or Electromotive Series

The standard electrode potentials for a number of electrodes, measured at **1M** ionic concentration and **298 K**, are arranged in a series. **As we move down the series** (from positive potential values to negative potential values), the **reducing agent character increases** and the **oxidizing agent character decreases**.



Reaction (Oxidised form + ne$^-$	→ Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	-0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	-2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
$K^+ + e^-$	$\rightarrow K(s)$	-2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

Applications of the Electrochemical Series

1. To Compare Relative Oxidizing and Reducing Strength

- The standard electrode potentials in the electrochemical series are all **reduction potentials**.
- This means that a **more positive** electrode potential indicates that a substance is **more easily reduced**, and therefore, it behaves as a **stronger oxidizing agent**.
- Conversely, a **more negative potential** indicates that the substance is **more easily oxidized**, making it a **stronger reducing agent**.

2. To Compare the Relative Reactivity of Metals

- The **reactivity of a metal increases** as its **tendency to be oxidized increases**. This corresponds to a more negative standard reduction potential.
- Therefore, the **reactivity of a metal increases** with a **decrease in the value of its standard electrode potential** in the series.
- Example:

Example:	Mg	>	Zn	>	Fe	>	Cu	>	Ag
$E^\circ_{R.P.}$(V):	-2.37	>	-0.76	>	-0.44	>	+0.34	>	+0.80

3. To Calculate the Standard E.M.F. of an Electrochemical Cell

- An electrochemical cell is composed of **two half-cells**, one with a **higher** reduction potential (undergoing in reduction) and one with a **lower** reduction potential (undergoing in oxidation).
- The **difference between standard reduction potentials (E°)** of the two half-cells undergoing in reduction and oxidation is the **standard cell potential or E.M.F.** (when no current is drawn).
- Formula used: $\mathbf{E^\circ_{cell} = (O.P)_{anode} + (R.P.)_{cathode}}$

  Since, $+\text{O.P.} = -\text{R.P.}$

  Therefore, $\mathbf{E^\circ_{cell} = (-R.P)_{anode} + (R.P.)_{cathode}}$

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

  Or

  $\mathbf{E^\circ_{cell} = E^\circ_{reduction} - E^\circ_{oxidation}}$

- For example, consider a **Daniell cell**: Zn | Zn^{2+} || Cu^{+2} | Cu
  - The **standard reduction potentials** of Zn electrode and Cu electrode are:

    $$E^0_{Zn^{+2}|Zn} = -\,0.76\ \text{V} \quad \text{and} \quad E^0_{Cu^{+2}|\,Cu} = +0.34\ \text{V}$$

  - **Zinc** has lower reduction potential, so it will **oxidise.** In contrast, **copper** has a higher reduction potential, so it will undergo in **reduction**. Therefore, the standard E.M.F. of the cell will be:

    $$\mathbf{E^\circ_{cell} = E^\circ_{reduction} - E^\circ_{oxidation}}$$
    $$\mathbf{E^\circ_{cell} = (+0.34\ V) - (-0.76\ V)}$$
    $$\mathbf{E^\circ_{cell} = +1.10\ V}$$

- **Factors Affecting the E.M.F. of a Cell**

  The Electromotive Force (E.M.F.) of an electrochemical cell is influenced by the following factors:
  - The nature of the electrodes and the electrolytes used.
  - The concentration of the solution in each half-cell.
  - The temperature of the system.

- **Difference between E.M.F. and Potential Difference**

E.M.F. (Electromotive Force)	Potential Difference
The potential difference between the two electrodes of a cell when **no current** is flowing (in an **open circuit**).	The potential difference between the two electrodes of a cell when **current** is flowing (in a **closed circuit**).
It can be measured using a **potentiometric method**.	It is measured using a **simple voltmeter**.
It represents the **maximum voltage** obtainable from the cell.	Its value is always **less than the E.M.F.** due to the voltage drop across the cell's internal resistance.
The magnitude of E.M.F. is a **constant value** for a given set of conditions.	The magnitude of the potential difference **varies**, as it depends on the current being drawn.
It is **independent** of the internal resistance of the circuit.	It **depends on** the internal and external resistance of the circuit.

4. To Predict Whether a Metal Will React with an Acid to Produce Hydrogen Gas (H_2)

- Acids contain **H^+ ions**, which can gain electrons from metal atoms to produce **H_2 gas**.
- Any metal with a standard reduction potential **more negative** than that of hydrogen (i.e., $E^\circ < 0$ V) will spontaneously react with an acid to liberate H_2 gas. Examples include **Mg**, **Fe**, and **Zn**.
- Conversely, metals with **a positive** standard reduction potential, such as **Cu**, **Ag**, and **Au**, will not react with acids to liberate hydrogen (H_2).

5. To Predict the Spontaneity of a Redox Reaction

- The spontaneity of a redox reaction is directly determined by the **E.M.F.** of the cell.
- For a reaction to be spontaneous in the forward direction, the calculated **E.M.F.** of the cell must be **positive** ($E^\circ_{cell} > 0$).
- If the E.M.F. is **negative** ($E^\circ_{cell} < 0$), the forward reaction is non-spontaneous, but the reverse reaction is spontaneous.

6. To Predict the Minimum Voltage Required for Electrolysis

- Electrolysis forces a non-spontaneous reaction to occur by applying an external voltage. The minimum voltage required to initiate this chemical change must be **equal to or greater than** the absolute value of the spontaneous cell's **E.M.F.**
- Minimum voltage required = $[\ E^\circ_{spontaneous}\ ]$

7. To Predict the Thermal Stability of Metal Oxides

- The thermal stability of a metal oxide is related to the metal's **tendency to lose electrons**.
- The **more negative** the reduction potential of a metal, the **more easily** it loses electrons, and the **more stable** its oxide is.
- For example:
  - Metals like **Ca**, **Na**, and **Mg** have **negative** reduction potentials, so their oxides (**CaO**, **Na_2O**, **MgO**) are **very stable**.
  - In contrast, metals like **Ag** and **Hg** have **positive** reduction potentials, making their oxides (**Ag_2O**, **HgO**) **less stable** and easier to decompose with heat.

The NERNST Equation : Effect of Concentration and Temperature on Electrode Potential

- The electrode potential, is **not** a fixed value but is influenced by several factors. The two most significant are the **temperature** and the **concentration of the electrolyte solution** in which the electrode is immersed.
- For this reason, a standard reference point is used: the **standard electrode potential (E°)**.
- The mathematical relationship that describes how electrode potential varies with concentration and temperature is given by the **Nernst Equation**.

Derivation and Application

- Consider a generalized half-reaction for a metal ion being **reduced to its solid metal** form:

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

- The NERNST equation for this **reduction half-reaction** is:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{RT}{nF} \ln Q$$

- Where, **Q is the reaction quotient**, which for this reaction is defined as:

$$Q = \frac{[M]}{[M^{n+}]}$$

- Now the NERNST equation can be written as:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

- For pure solids, liquids, and gases at 1 atm, their activity is considered to be **unity**. Therefore, **$[M_{(s)}] = 1$**. The equation simplifies to:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

- By changing the **natural logarithm (ln)** to the **common logarithm ($\log_{10}$)**, we use formula $\ln x = 2.303 \log_{10} x$. This gives us the more commonly used form of the Nernst equation:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{2.303\,RT}{nF} \log_{10} \frac{1}{[M^{n+}]}$$

  Where,
  - $E_{M^{n+}|M}$ = Electrode potential under the specific non-standard conditions (i.e., at any conc. and temp.).
  - $E^{\circ}_{M^{n+}|M}$ = Standard electrode potential, measured at 298 K and 1 M concentration.
  - **R** = Ideal gas constant, 8.314 $J \cdot K^{-1} \cdot mol^{-1}$.
  - **T** = Temperature in Kelvin.
  - **n** = Number of moles of electrons (e−) transferred in the balanced half-reaction.
  - **F** = Faraday constant, (charge on 1 mole of electrons, approx. 96,485 $C \cdot mol^{-1}$ (rounded off to 96,500 C)).

The Nernst Equation at Standard Temperature (298 K)

- A simplified version of the NERNST equation is often used for calculations at standard temperature (**298 K** or 25 ˚C). By substituting the constant values for R, T, and F:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log_{10} \frac{1}{[M^{n+}]}$$

- This simplifies to:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{0.0592}{n} \log_{10} \frac{1}{[M^{n+}]}$$

Note:

- When applying the NERNST equation, it is crucial to consistently use the **reduction potential** for all half-reactions, regardless of whether the half-reaction is an oxidation or a reduction in the overall cell.

The NERNST Equation and the EMF of an Electrochemical Cell

- The NERNST equation can be extended to calculate the total electromotive force (EMF) or cell potential (E_{cell}) of **an electrochemical cell** under non-standard conditions.
- Let us consider a classic example, the **Daniell cell**, which consists of a zinc electrode and a copper electrode.
  - The overall spontaneous cell reaction is:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

  - The cell is typically represented as:

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

In this cell, **reduction** occurs at **Cu electrode** (cathode), and **oxidation** occurs at **Zn electrode** (anode).

  - The EMF is the **difference in reduction potential** between the cathode and the anode.

$$\mathbf{EMF\ or\ E_{cell} = E_{cathode} - E_{anode}}$$

Applying the NERNST Equation to Each Electrode

- For the **cathode** (reduction of copper):

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$\mathbf{E_{Cu^{2+}|Cu} = E^{\circ}_{Cu^{2+}|Cu} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}]}}$$

- For the **anode** (oxidation of zinc, but we use the reduction potential form):

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$\mathbf{E_{Zn^{2+}|Zn} = E^{\circ}_{Zn^{2+}|Zn} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}]}}$$

Calculating the Cell Potential (E_{cell})

- As we know, $\mathbf{E_{cell} = E_{cathode} - E_{anode}}$
- Therefore,

$$E_{cell} = \left(E^{\circ}_{Cu^{2+}|Cu} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}]}\right) - \left(E^{\circ}_{Zn^{2+}|Zn} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}]}\right)$$

$$E_{cell} = \left(E^{\circ}_{Cu^{2+}|Cu} - E^{\circ}_{Zn^{2+}|Zn}\right) - \frac{RT}{2F}\left(\ln \frac{1}{[Cu^{2+}]} - \ln \frac{1}{[Zn^{2+}]}\right)$$

- The term $\left(E^{\circ}_{Cu^{2+}|Cu} - E^{\circ}_{Zn^{2+}|Zn}\right)$ is the standard cell potential, $\mathbf{E^{\circ}_{Cell}}$.
- We can simplify the logarithmic terms using the property; $\left(\ln x - \ln y = \ln \frac{x}{y}\right)$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F}\left(\ln \frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

- Converting to the common logarithm ($\log_{10}$), we use formula ; $\ln x = 2.303 \log_{10} x$.

$$\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{2.303\,RT}{2F} \log_{10} \frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Note 1:

  - The term $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ is the **reaction quotient** (**Q**), for the overall cell reaction.

Note 2:

- In general, if the cell reaction is $aA + bB \longrightarrow qQ + rR$
- Then applying NERNST equation, we have : $E_{cell} = E^{\circ}_{Cell} - \frac{2.303\,R\,T}{n\,F} \log \frac{[Q]^q\,[R]^r}{[A]^a\,[B]^b}$
- The term term $\frac{[Q]^q\,[R]^r}{[A]^a\,[B]^b}$ is the **reaction quotient** (**Q**), for the overall cell reaction.
- Therefore, NERNST Equation at standard temperature 25 °°C

$$E_{cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Q]^q\,[R]^r}{[A]^a\,[B]^b} \quad \text{at } 25\ ^{\circ}C$$

OR

$$E_{cell} = E^0_{Cell} - \frac{0.0591}{n} \log Q \quad \text{at } 25\ ^{\circ}C$$

Practice Problems

1. Represent the cell in which the following reaction takes place :

   $Mg + 2\,Ag^+_{(0.001\,M)} \longrightarrow Mg^{+2}_{(0.1\,M)} + 2\,Ag$

   Calculate the E_{cell}. (Given that $E^0_{Mg^{+2}|Mg}$ = -2.37 V and $E^0_{Ag^+|Ag}$ = +0.80 V)

2. Calculate the electrode potential of zinc electrode in which the zinc ion activity is 0.01M.
   (Given $E^0_{Zn^{+2}|Zn}$ = -0.76 V, R = 8.314 $JK^{-1}mol^{-1}$, F = 96500 C mol^{-1})

3. Calculate emf of the following cell: $Zn \mid Zn^{2+}_{(0.1\,M)} \parallel Sn^{2+}_{(0.001\,M)} \mid Sn$
   Given: $E^0_{Sn^{+2}|Sn}$ = –0.14 V and $E^0_{Zn^{+2}|Zn}$ = –0.76 V

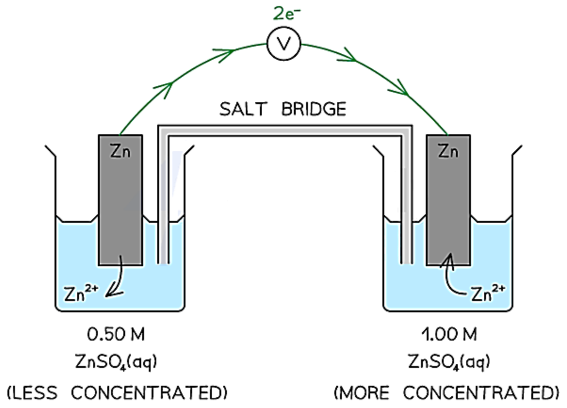
4. Represent the cell in which the following reaction takes place :

   $Zn + Pb^{+2}_{(0.02\,M)} \longrightarrow Zn^{+2}_{(0.1\,M)} + Pb$

   Calculate the emf of the cell. (Given that $E^0_{Zn^{+2}|Zn}$ = –0.76 V and $E^0_{Pb^{+2}|Pb}$ = –0.13 V)

Concentration Cells

- A **concentration cell** is a special type of electrochemical cell **with identical electrodes and electrolytes** in both half-cells, but with **different electrolyte concentrations** (C_1 and C_2).
- A concentration cell tends to **equalise the concentrations of the electrolyte** in the two half-cells.



Example: A Zinc Concentration Cell

- Consider a concentration cell composed of **two zinc electrodes**, each immersed in a **zinc sulphate** ($ZnSO_4$) solution. The two solutions have **different molar concentrations**, C_1 and C_2.
- Let us assume that $\mathbf{C_2 > C_1}$.
- **Oxidation occurs** in the half-cell with the **lower concentration** (C_1, the anode), and **reduction occurs** in the half-cell with the **higher concentration** (C_2, the cathode).
- The cell can be represented as:

$$Zn_{(s)} \mid Zn^{2+}_{(C1)} \parallel Zn^{2+}_{(C2)} \mid Zn_{(s)}$$

- At anode (oxidation): $Zn \longrightarrow Zn^{+2}_{(C1)} + 2e^-$
- At cathode (reduction): $Zn^{+2}_{(C2)} + 2e^- \longrightarrow Zn$

Overall reaction: $Zn^{+2}_{(C2)} \longrightarrow Zn^{+2}_{(C1)}$

- The net process involved is the **transfer of Zn^{2+} ions** from its **higher concentration** to **lower concentration**.
- The standard cell potential (E^0_{Cell}) for a concentration cell is **always zero** because the electrodes and electrolytes in both half-cells are identical.
- Therefore, the Nernst equation simplifies significantly.

$$E_{cell} = 0 - \frac{0.0591}{n} \log_{10} Q \quad \text{at } 25\ ^\circ C$$

- For the overall cell reaction, the **reaction quotient 'Q'** is ; $Q = \frac{[Zn^{2+}]_{oxi}}{[Zn^{2+}]_{red}}$
- Hence, $E_{cell} = 0 - \frac{0.0591}{n} \log_{10} \frac{[Zn^{2+}]_{oxi}}{[Zn^{2+}]_{red}}$ at 25 °C
- Since, n = 2 , $[Zn^{+2}]_{oxi} = C_1$, and $[Zn^{+2}]_{red} = C_2$ for the zinc reaction:

$$E_{cell} = 0 - \frac{0.0591}{2} \log_{10} \frac{C_1}{C_2} \quad \text{at } 25\ ^\circ C$$

- Using the property of logarithms, $\log\left(\frac{a}{b}\right) = -\log\left(\frac{b}{a}\right)$, the equation can be written as:

$$E_{cell} = \frac{0.0591}{2} \log_{10} \frac{C_2}{C_1} \quad \text{at } 25\ ^\circ C$$

- A concentration cell will continue to generate an emf or a potential until the concentrations of the electrolyte in both half-cells become equal ($\mathbf{C_1 = C_2}$). At this point, the reaction quotient **Q = 1**, and since $\mathbf{\log_{10}(1) = 0}$, the **cell potential** (E_{cell}) becomes **zero**. The cell has reached **equilibrium** and **stops working**.

Liquid – Junction Potential

- The **liquid-junction potential** is a potential difference that arises at **the interface or junction** between two electrolyte solutions with **different concentrations** (connecting through a **porous membrane**).
  - **Cause:**
    Ions tend to diffuse from a region of **higher** concentration to **lower** concentration. If the anions and cations have **different diffusion rates** (mobilities), a **charge separation** occurs at the junction.
  - **Mechanism:**
    For instance, if anions diffuse faster than cations, anions will move more quickly into the dilute solution, creating a net negative charge there. The slower cations accumulate in the concentrated solution, creating a net positive charge. This charge separation forms **an electrical double layer**, which results in a potential difference.

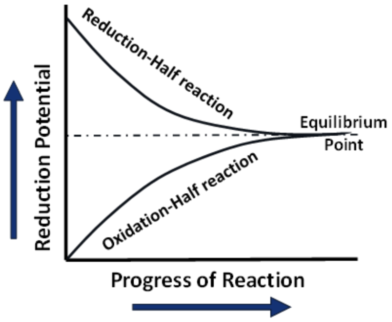
- **Effect on Cell EMF:**
  The liquid-junction potential opposes the cell's potential, thereby **reducing** the overall EMF.
  - To **minimize or eliminate** the liquid-junction potential, a **salt bridge** is used. A salt bridge contains a concentrated solution of an electrolyte whose ions (e.g., K^+ and Cl^- in KCl) have nearly equal mobilities. This ensures that both cations and anions diffuse at a similar rate, preventing the buildup of a significant charge separation at the junction.

Deriving the Equilibrium Constant (K_C) from the NERNST Equation

- An electrochemical cell, such as the **Daniell cell** ($Zn \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu$), generates an electromotive force (**EMF**) as long as the cell reaction proceeds. The overall spontaneous reaction is:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

- As the reaction progresses, the concentration of the reactants **decreases**, and the concentration of the products **increases**. Specifically, **$[Cu^{2+}]$ decreases** and **$[Zn^{2+}]$ increases**.
- Since, the electrode potential of each half-cell is **concentration-dependent**, as described by the **NERNST equation**. Consequently, the **cell potential (E_{cell})** also changes. Over time, the cell's EMF gradually **decreases**. Eventually, a **state of equilibrium is reached** where the forward and reverse reaction rates become equal.



- At **equilibrium**, three key conditions are met:
  (i) The reduction electrode potentials of both half-cells become **equal**.
  (ii) The net **current flow stops**, which means the cell potential, **Ecell**, becomes **zero**.
  (iii) The ratio of the product concentrations to the reactant concentrations becomes constant, defining the **equilibrium constant, Kc**.
- For the Daniell cell, the **reaction quotient**, **Q**, at any point is: $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$.
- At equilibrium, this ratio becomes the **equilibrium constant (K_C)**: $K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$
- Now, let us apply the Nernst equation for the cell potential:

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\,R\,T}{n\,F}\log_{10} Q$$

- At equilibrium, we have **E_{cell} = 0** and **Q = Kc**. Substituting these values into the equation:

$$0 = E^{\circ}_{cell} - \frac{2.303\,R\,T}{n\,F}\log_{10} K_C$$

- Rearranging the equation gives the relationship between the standard cell potential (E°_{cell}) and the equilibrium constant (Kc):

$$\mathbf{E^{\circ}_{cell} = \frac{2.303\,R\,T}{n\,F}\log_{10} K_C}$$

- At a standard temperature of 298 K, this simplifies to:

$$E^{\circ}_{cell} = \frac{0.0592}{n} \log_{10} K_C$$

- This equation can be rearranged to solve for Kc:

$$\frac{\mathbf{n\,E^{\circ}_{cell}}}{\mathbf{0.0592}} = \mathbf{\log_{10} K_C}$$

Significance of the Equilibrium Constant (Kc)

The value of Kc provides crucial information about **the extent** to which a reaction proceeds. A larger Kc indicates a greater tendency for the reaction to favour product formation.

- **$Kc > 10^3$** : At equilibrium, the concentration of products is significantly higher than that of reactants.
- **$Kc < 10^{-3}$** : At equilibrium, the concentration of reactants is much higher than that of products.
- **$10^{-3} < Kc < 10^3$** : At equilibrium, there are significant concentrations of both reactants and products.

Question : Calculate the equilibrium constant for the reaction : **$Cu + 2Ag^{+1} \rightleftharpoons Cu^{+2} + 2Ag$**
Given that $E^0_{Ag^+|Ag}$ = +0.80 V and $E^0_{Cu^{+2}|Cu}$ = +0.34 V

Gibbs Free Energy and Cell Potential

- In an electrochemical cell, the spontaneity of a redox reaction is directly related to the change in Gibbs free energy (ΔG). Gibbs free energy represents the **maximum amount of non-expansion work** that can be done by a system at constant temperature and pressure.
- In an electrochemical cell, this **work is the electrical energy** produced.

Relationship between Electrical Work and Gibbs Free Energy

- For a spontaneous process (like in a galvanic cell), the **system performs work** on its surroundings, leading to a **decrease in its free energy**. Therefore, the **decrease in Gibbs free energy** is equal to the **electrical work done** by the cell.
- **Electrical work ($W_{electrical}$)** is the product of the total **electric charge (Q)** that flows through the circuit and the **cell potential (E_{cell}).**

$$W_{electrical} = Q \cdot E_{cell}$$

- The total charge transferred is determined by the **number of moles of electrons (n)** involved in the reaction and **the Faraday constant (F)**, which is the charge on one mole of electrons (F ≈ 96,500 C/mol).

$$Q = nF$$

- So, the electrical work done is: $W_{electrical} = n\,F\,E_{cell}$
- The change in Gibbs free energy (ΔG) is the **negative** of the maximum electrical work done by the cell:

$$\Delta G = -W_{electrical}$$

- Therefore, the fundamental relationship between Gibbs free energy and cell potential is:

$$\Delta G = -\,n\,F\,E_{cell}$$

Where:

- **ΔG =** Gibbs free energy change (in Joules or Kilojoules).

- **n =** number of moles of electrons transferred in the balanced redox reaction.
- **F =** Faraday constant (96,485C/mol).
- **E_{cell} =** cell potential (in Volts).

Standard Gibbs Free Energy (ΔG°) and Standard Cell Potential (E°_{cell})

- When the reactants and products are in their standard states (1 M concentration, 1 atm pressure, 298 K), the relationship is between the standard Gibbs free energy change (ΔG°) and the standard cell potential (E°_{cell}) :

$$\Delta G^\circ = - n F E^\circ_{cell}$$

- This equation is particularly useful because standard potentials are readily available in tables.

Relationship with the Equilibrium Constant (Kc)

- We know from thermodynamics that the standard Gibbs free energy change (ΔG°) is also related to the equilibrium constant (Kc) by the equation:

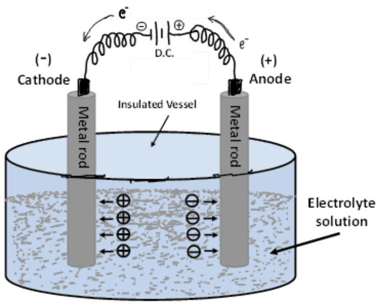
$$\Delta G^\circ = - n F \frac{2.303\,R\,T}{n\,F} \log_{10} K_C = \mathbf{-2.303\,RT\log_{10} Kc}$$

Question: Determine the values of equilibrium constant (K_C) and $\Delta^\circ G$ for the following reaction :

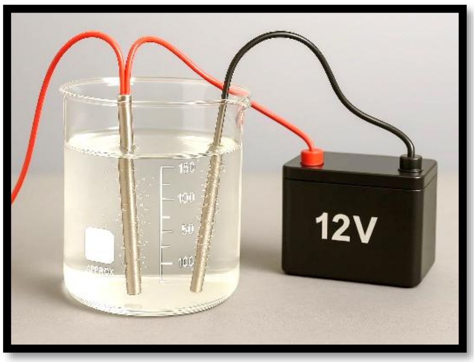
$$\mathbf{Ni + 2Ag^{+} \longrightarrow Ni^{+2} + 2Ag} \qquad (E^\circ_{cell} = 1.05\ V)$$

Electrolytic Cell and Electrolysis

Electrolysis is a process of decomposition of an electrolyte by the passage of electricity through its molten or aqueous state. In electrolysis a non-spontaneous redox reaction is forced to occur with the help of electrical energy.



Electrolytic Cell



Apparatus (Electrolytic Cell)

- ☐ Consists of a vessel containing the electrolyte.
- ☐ Two metal rods (electrodes) are dipped into the electrolyte.
- ☐ The electrodes are connected to a DC power source.
- ☐ **Anode (oxidation occurs):** The electrode connected to the *positive* terminal.
- ☐ **Cathode (reduction occurs):** The electrode connected to the *negative* terminal.

Mechanism of Electrolysis

- ❑ It can be easily explained on the basis of **ionization theory**.
- ❑ According to this theory, when an electrolyte is dissolved or melted, it dissociates into positively charged ions (**cations**) and negatively charged ions (**anions**).
- ❑ On passing an electric current (DC):
    - ➢ Cations move towards the cathode (negative electrode), gain electrons, and are reduced.
    - ➢ Anions move towards the anode (positive electrode), lose electrons, and are oxidized.
- ❑ At the electrodes, ions are converted into neutral species. This initial process of neutralization at the electrode is called the **primary change**.
- ❑ The product formed as a result of primary change may be collected as such or it may undergo a subsequent reaction to form the final, stable product. This further reaction is known as a **secondary change**.

- ❑ **Example: Electrolysis of Molten NaCl**
    - Ionisation: $\mathbf{NaCl \rightleftharpoons Na^+ + Cl^-}$
    - On passing electricity, Na^+ ions move toward cathode while Cl^- ions move towards anode.
    - Na^+ ions gain electrons and start depositing at cathode while Cl^- ions lose electrons and become neutral chlorine atoms.
    - Since chlorine atoms are unstable, they undergo secondary change to form Cl_2 gas molecules and start liberating at the anode.

At Cathode : $2\,Na^+ + 2e^- \longrightarrow 2Na$ (Reduction, primary change)

At Anode : $2\,Cl^- \longrightarrow 2Cl + 2e^-$ (Oxidation, primary change)

$Cl + Cl \longrightarrow Cl_2$ (secondary change)

Overall $\mathbf{2NaCl \longrightarrow 2Na + Cl_2}$

Difference between Electrochemical Cell and Electrolytic Cell

Electrochemical Cell	Electrolytic Cell
It is a device that converts chemical energy into electrical energy.	It is a device that converts electrical energy into chemical energy.
The redox reaction is spontaneous.	The redox reaction is non-spontaneous.
The two electrodes are dipped in different electrolytes, which are in different beakers.	Both electrodes are placed in a solution or molten electrolyte in the same beaker.
The anode is negative, while the cathode is positive.	The anode is positive, while the cathode is negative.
Both electrodes are typically made of different materials.	The electrodes can be made of the same or different materials.
A salt bridge or porous pot is used to separate the two half-cells.	A salt bridge or porous pot is not needed.

Faraday's Laws of Electrolysis

Faraday's First Law of Electrolysis

According to this law, the amount of substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$W \propto Q$ (W = Weight of substance deposited or liberated, Q = Quantity of Electricity in coulombs)

$W = Z\,Q$ (Z = Electrochemical equivalent constant or Proportionality constant)

As we know,

$Q = I \times T$ (I = Current in amperes, T = time in second)

Then,

$$W = Z \times I \times T$$

If, 1 ampere current is passed for 1 second (or 1 coulomb of electricity is passed), then,

$$W = Z \times 1\ \text{amp} \times 1\ \text{sec}$$

$$W = Z$$

Therefore, **electrochemical equivalent (Z)** of a substance may be defined as the mass of the substance deposited when a current of 1 ampere is passed for 1 second (i.e., a quantity of electricity is equal to 1 coulomb).

Note

1. Equivalent weight of a substance may be defined as the mass of substance deposited or liberated at any electrode when 1F or 96500 Coulombs of electricity is passed).

   $$\text{Equivalent weight} = Z \times 1F = Z \times 96500\ \text{C}$$

2. Charge on **1 mole electrons** $= 6.022 \times 10^{23} \times 1.602 \times 10^{-19}\ \text{C} = 96472\ \text{C} \approx 96500\ \text{C} = 1\ \text{F}$
3. **Atomic mass** of a substance = **Equivalent weight × 'n' factor**
4. **'n' factor** is electronic factor, (i.e., total number of electrons gain or lose by a substance).
5. **Electric Energy (E) = V × Q** (V = Potential differences in volts, Q = Quantity of electricity in coulombs)
6. **Power (P) = V × I** (V = Potential differences in volts, I = Current in amperes)
7. **Current Efficiency** $= \dfrac{Q\,(\text{required}) \times 100}{Q\,(\text{passed})}$

Formula Sheet

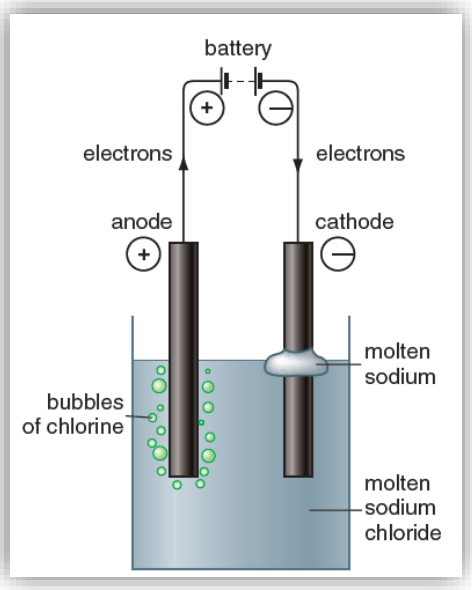
$$W = Z\,Q$$

$$W = Z \times I \times T$$

$$W = \frac{\text{Equivalent weight}}{96500} \times I \times T$$

$$W = \frac{\text{Atomic mass}}{\text{'n' factor} \times 96500} \times I \times T$$

$Q = I \times T$
Equivalent weight $= Z \times 1F$
Equivalent weight $= Z \times 96500$ C
Atomic mass = Equivalent weight × 'n' factor



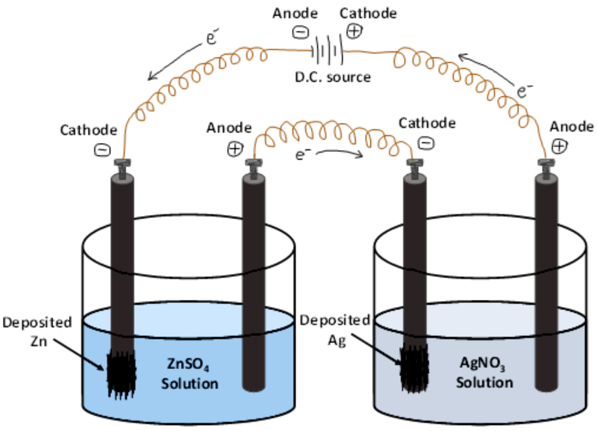
Faraday's Second Law of Electrolysis

When the same quantity of electricity passes through different electrolyte solutions connected in series, the masses of the substances deposited or liberated at electrodes are directly proportional to their equivalent weights.

OR

If the same amount of electricity is passed through various electrolyte solutions in series, the weights of the substances deposited or liberated at the electrodes are in the same ratio as their equivalent weights.

$$\frac{\text{Mass deposited of element A}}{\text{Mass deposited of element B}} = \frac{\text{Equivalent weight of element A}}{\text{Equivalent weight of element B}}$$



This law can also be derived from first law as follows :

- According to Faraday's first law of electrolysis : **W = Z × Q**
- In case of first electrolyte : $W_1 = Z_1 \times Q_1$
  In case of second electrolyte : $W_2 = Z_2 \times Q_2$
- If same quantity of electricity is passed through solution of both electrolytes, then, $\mathbf{Q_1 = Q_2 = Q}$
- On dividing, $\frac{W_1}{W_2} = \frac{Z_1 \times Q}{Z_2 \times Q} = \frac{Z_1}{Z_2}$ As we know : $Z = \frac{\text{Equivalent weight}}{96500} = \frac{E}{96500}$
- Thus, $\boxed{\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1 \times 96500}{96500 \times E_2} = \frac{E_1}{E_2}}$

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Exercises

1. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at cathode ? (Atomic mass of Cu is 63.5 gm/mol)
2. A current of 1.5 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The mass of silver deposited at cathode was 1.5 gm. How long did the current flow ? (At. Wt. of Ag is 108 gm/mol)

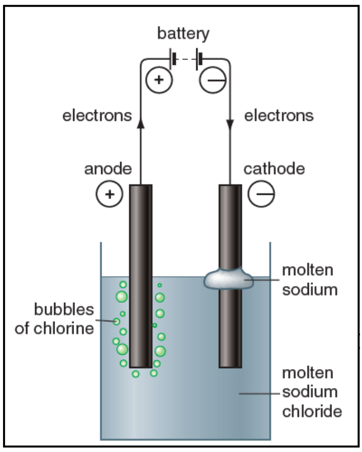
3. Calculate the quantity of electricity that would be required to reduce 12 gm of Al_2O_3 to Al, if current efficiency for the process is 70%. If the potential drop across the cell is 3 volt, How much energy will be consumed ?
4. A current of 4 ampere was passed for 2 hours through a solution of $CuSO_4$ when 3.2 gm of copper was deposited. Calculate current efficiency.
5. Silver is electro-deposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.2 A for 4 hours. Calculate the thickness of silver deposited. Given the density of Ag as 10.47 gm/cc.
6. Calculate the charge in coulombs required for the reduction of 1 mole of $Cr_2O_7^{-2}$ to Cr^{+3}.
7. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 A was passed through them till 1.078 gm of Ag were deposited. How long did the current flow ? What weight of copper will be deposited ? (At. Wt. of Cu and Ag are 63.5 and 107.8 gm/mol respectively)
8. How many coulombs of electricity arere required for
   a. complete oxidation of 90 gm of water.
   b. complete reduction of 100 ml of 0.1 M $KMnO_4$ solution.
9. Two electrolytic cells connecting silver nitrate solution and dilute sulfuric acid solution were connected in series. A steady current of 2.5 amperes was passed through them till 1.078 gm of silver was deposited.
   a. How much electricity was consumed ?
   b. What was the weight of oxygen gas liberated ?
10. How many grams of chlorine can be produced by electrolysis of molten NaCl with a current of 1 A for 15 minutes ? Also calculate the number of chlorine molecules liberated.
11. Calculate the time to deposit 1.27 grams of copper at cathode when a current of 2 A was passed through the solution of copper sulphate (Given, Atomic mass of Cu = 63.5 gm/mol).
12. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 A for 20 minutes. What mass of Ni will be deposed at cathode. (Given, Atomic mass of Ni is 58.7 gm/mol).
13. How much electricity in terms of Faraday's is required to produce 20 grams of calcium from molten calcium chloride ($CaCl_2$).
14. When a steady current of 2A was passed through two electrolytic cells, A and B containing electrolytes, zinc sulphate and copper sulphate connected in series, 2 gm of copper were deposed at the cathode of cell 'B'. How long did the current flow? What mass of zinc was deposited at cathode of cell 'A'. (Given, Atomic mass of Cu = 63.5 gm/mol, and Atomic mass of Zn = 65 gm/mol).
15. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation. $CrO_3 + 6H^+ + 6e^- \longrightarrow Cr + 3H_2O$
    Calculate how many grams of chromium will be electroplated by 24,000 coulombs.
    How long will it take to electroplate 1.5 gm of Cr using 12.5 A current. (At.wt. of Cr = 52 gm/mol)
16. How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours?
17. A steady current of 2A was passed through two electrolytic cells, X and Y, connected in series containing electrolytes, $FeSO_4$ and $ZnSO_4$, until 2.8 gm of Fe deposed at the cathode of cell 'X'. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell 'Y'. (Given, Atomic mass of Fe = 56 gm/mol, and Atomic mass of Zn = 65.3 gm/mol).
18. Aq. solution of $CuSO_4$ and $AgNO_3$ are electrolysed by 1A current for 10 min in separate electrolytic cells. Will the mass of Cu and Ag deposited on cathode be same or different? Explain your answer.

Product of Electrolysis

The products of electrolysis depend on several factors, such as:

- The nature of the electrolyte
- The type of electrodes (**attackable** and **non-attackable**)
    - The attackable electrodes (e.g., copper or carbon) take part in the chemical reactions and influence the nature of the products.
    - The non-attackable electrodes, also called **inert electrodes** (e.g., platinum or gold), simply act as carriers of electrons.
- The oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.

1. Electrolysis of Molten NaCl



- Ionisation: **$NaCl \rightleftharpoons Na^+ + Cl^-$**
- On passing electricity, Na^+ ions move toward cathode while Cl^- ions move towards anode.
- Na^+ ions gain electrons and start depositing at cathode while Cl^- ions lose electrons and become neutral chlorine atoms.
- Since chlorine atoms are unstable, they undergo secondary change to form Cl_2 gas molecules and start liberating at the anode.

At Cathode : $2\,Na^+ + 2e^- \longrightarrow 2Na$ (Reduction, primary change)

At Anode : $2\,Cl^- \longrightarrow 2Cl + 2e^-$ (Oxidation, primary

e)

$Cl + Cl \longrightarrow Cl_2$ (secondary change)

$2NaCl \longrightarrow 2Na + Cl_2$ **Overall Reaction**

2. Electrolysis of Aqueous NaCl

- Ionisation: **$NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$**
- **At Cathode:**

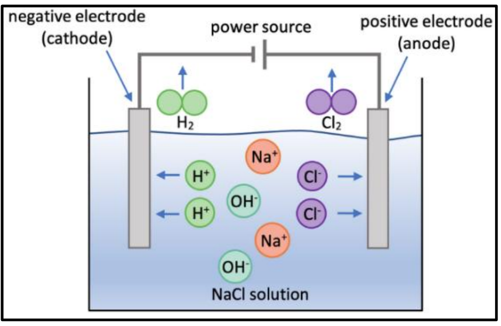
  There is a competition between **Na^+** and **H_2O** for reduction:

  $Na^+_{(aq)} + e^- \longrightarrow Na_{(l)}$ $E° = -2.71$ V

  $2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(aq)}$ $E° = -0.83$ V

  Here, the reaction with **higher reduction potential value is preferred.** Since water has a higher (less negative) reduction potential, **H_2O is preferentially reduced**, liberating **H_2 gas**:

  $2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(aq)}$



- **At the Anode:**

  There is a competition between **Cl^-** and **H_2O** for oxidation:

  $2Cl^-_{(aq)} \longrightarrow Cl_{2\,(g)} + 2e^-$ $E° = +1.36$ V

  $2H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4H^+ + 4e^-$ $E° = +1.23$ V

  Here, the reaction with **lower reduction potential value is preferred.**

  Since, H_2O and Cl^- have almost the same reduction potential, so both can be oxidised at the anode. **We may expect a mixture of O_2 and Cl_2 gases**. But actually, **Cl_2 gas is released at the anode**.

This is because forming O_2 from H_2O needs extra voltage (called **overpotential**). The **pH of the solution also increases** during the reaction, which makes it harder to release O_2.

Theoretically, **1.23 V** is enough to get O_2 from H_2O, but in real conditions it may need up to **2.2 V**. So, Cl^- gets oxidised more easily, and **Cl_2 gas is formed at the anode**.

$$\mathbf{2Cl^-_{(aq)} \longrightarrow Cl_{2\,(g)} + 2e^-}$$

Thus, the net reaction may be represented as :

$$2\,NaCl_{(aq)} \xrightarrow{H_2O} 2\,Na^+_{(aq)} + 2\,Cl^-_{(aq)}$$

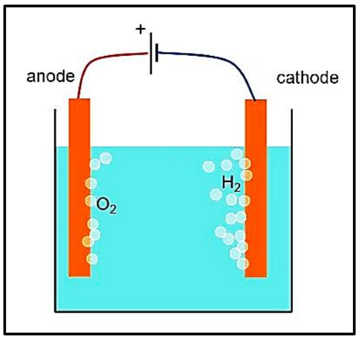
At cathode: $2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(aq)}$

At anode: $2Cl^-_{(aq)} \longrightarrow Cl_{2\,(g)} + 2e^-$

$$NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2\,(g)} + Cl_{2\,(g)}$$

Thus, we may sum up that during electrolysis of aqueous NaCl, Hydrogen gas is evolved at cathode and Chlorine gas is evolved at anode. The solution contains both **Na^+** ions and **OH^-** ions. The electrolysis of aqueous NaCl is called **Chlor-alkali process**.

3. Electrolysis of Acidulated Water (or dilute H_2SO_4)



- Pure water is a **poor conductor of electricity** because it is **very weakly ionised**, producing very few ions. Due to the extremely low concentration of these ions, current does not pass effectively.

  $$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

- When a small amount of **sulphuric acid (H_2SO_4)** is added to water, it increases the **ion concentration** significantly, making the solution a good conductor.

  Sulphuric acid ionizes completely as:

  $$H_2SO_{4\,(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

- Thus, the solution now contains three types of ions:
  - H^+ , OH^- , SO_4^{2-}

- **Reaction at Cathode (reduction occurs):**

  Hydrogen ions migrate towards the cathode (-) and are reduced to form hydrogen gas.

  $$\mathbf{2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2}$$

- **Reaction at Anode (oxidation occurs):**

  Both OH^- and SO_4^{2-} ions migrate towards anode.
  - SO_4^{2-} ions discharge as:

    $$2\,SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_8^{2-} + 2e^- \qquad E^o_{red} = +1.96\ V$$

  - OH^- ions discharge as:

    $$4\,OH^- \longrightarrow 2\,H_2O + O_2 + 4e^-$$

    Since, OH^- ions are formed by H_2O molecules, so the above equation can be written as:

    $$2\,H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^- \qquad E^o_{red} = +1.23\ V$$

  Here, the reaction with **lower reduction potential value is preferred.** Hence, **OH^- ions are discharged** in preference to SO_4^{2-}.

  $$\mathbf{2\,H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^-}$$

- **Thus, the net reaction may be represented as :**

  At cathode: $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_{2\,(g)}$] × 2

  At anode: $2\,H_2O_{\,(l)} \longrightarrow 4H^+_{(aq)} + O_{2\,(g)} + 4e^-$

  Net reaction: $2\,H_2O_{\,(l)} \longrightarrow 2H_{2\,(g)} + O_{2\,(g)}$

4. Electrolysis of Concentrated H_2SO_4

- **Ionisation:**

  $$H_2O_{\,(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$$
  $$H_2SO_{4\,(aq)} \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

- There are three ions in concentrated sulphuric acid ; H^+ , OH^- , SO_4^{2-}
- On passing electricity, H^+ ions move toward cathode while OH^- and SO_4^{2-} ions move towards anode.
- **Reaction at Cathode (reduction occurs):**

  Hydrogen ions migrate towards the cathode (-) and are reduced to form hydrogen gas.

  $$\mathbf{2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2}$$

- **Reaction at Anode (oxidation occurs):**

  Both OH^- and SO_4^{2-} ions migrate towards anode.

  - SO_4^{2-} ions discharge as:

    $$2\,SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_8^{2-} + 2e^- \qquad E^o_{red} = +1.96\text{ V}$$

  - OH^- ions discharge as:

    $$4\,OH^- \longrightarrow 2\,H_2O + O_2 + 4e^-$$

    Since, OH^- ions are formed by H_2O molecules, so the above equation can be written as:

    $$2\,H_2O_{\,(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^- \qquad E^o_{red} = +1.23\text{ V}$$

  Here, the reaction with **lower reduction potential value is preferred**, but due low pH and high conc. of SO_4^{2-} ions, the **overpotential** of oxygen comes into act. Hence, **oxidation of SO_4^{2-} ions will take place** at anode.

  $$\mathbf{2\,SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_8^{2-} + 2e^-}$$

- **Thus, the net reaction may be represented as :**

  At cathode: $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_{2\,(g)}$

  At anode: $2\,SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_8^{2-} + 2e^-$

  Net reaction: $H_2SO_4 + SO_4^{2-} \longrightarrow H_{2\,(g)} + S_2O_8^{2-}$

  Or

  $2\,H_2SO_4 \longrightarrow H_{2\,(g)} + H_2S_2O_8$

  $H_2S_2O_8$ is Peroxy-disulphuric acid (also called **Marshall's acid** after its inventor Professor Hugh Marshall).

5. Electrolysis of Aqueous $CuSO_4$ (Using inert electrodes, i.e., Pt or Au)

- **Ionisation:**

  $$CuSO_{4\,(aq)} \longrightarrow Cu^{+2}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

- **Reaction at Cathode (Reduction occurs):**

  Both H_2O and Cu^{+2} ions migrate towards cathode for reduction.

  $$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{\,(s)} \qquad E^o = +0.34\text{ V}$$
  $$2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^- \qquad E^o = -0.83\text{ V}$$

  Here, the reaction with **higher reduction potential value is preferred.** So, it is much **easier to reduce $Cu^{+2}_{(aq)}$** ion into metallic copper. Hence, Copper will deposit at cathode.

  $$\mathbf{Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{\,(s)}}$$

- **Reaction at Anode (Oxidation occurs):**
  Both H_2O and SO_4^{2-} ions migrate towards anode for oxidation.

  $2\ SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_8^{2-} + 2e^-$ $\qquad E^o_{red} = +1.96\ V$

  $2\ H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^-$ $\qquad E^o_{red} = +1.23\ V$

  Here, the reaction with **lower reduction potential value is preferred**. So that, SO_4^{2-} ions remain in solution and water molecule will oxidise as:

  $$\mathbf{2\ H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^-}$$

- **Thus, the net reaction may be represented as :**
  At cathode: $Cu^{+2} + 2e^- \longrightarrow Cu_{(s)}\ ] \times 2$
  At anode: $2\ H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_2 + 4e^-$
  Net reaction: $2\ Cu^{+2}_{(aq)} + 2\ H_2O_{(l)} \longrightarrow 2\ Cu_{(s)} + 4H^+_{(aq)} + O_{2\,(g)}$

  Thus, as a result of electrolysis of aqueous copper sulphate, **copper is deposited on the cathode** while **oxygen is liberated at the anode**. The solution contains H_2SO_4 and is, therefore, acidic in nature.

6. Electrolysis of Aqueous $CuSO_4$ (Using attacking electrodes | Cu electrodes)

- **Ionisation:**

  $$CuSO_{4\,(aq)} \longrightarrow Cu^{+2}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

- **Reaction at Cathode (Reduction occurs):**
  There is competition for reduction between Cu^{+2} ions and H_2O molecules.

  $Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $\qquad E^o = +0.34\ V$

  $2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-$ $\qquad E^o = -0.83\ V$

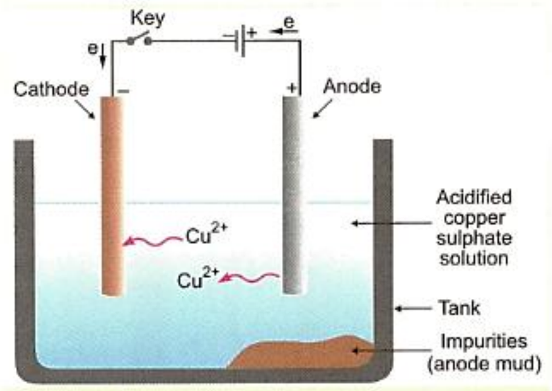
  Here, the reaction with **higher reduction potential value is preferred.** So, it is much **easier to reduce $Cu^{+2}_{(aq)}$** ion into metallic copper. Hence, **Copper will deposit at cathode**.

  $$\mathbf{Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}}$$

- **Reaction at Anode (Oxidation occurs):**
  Neither H_2O and nor SO_4^{2-} ions migrate. Copper atoms from the anode are oxidised to Cu^{+2} ions.

  $$\mathbf{Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^-}$$

  Thus, the net result of electrolysis is that from the solution **Cu^{+2} ions are deposited on the cathode as Cu** while an equivalent amount of **Cu from the anode goes into the solution**.



NOTE: This method is used in **electrolytic refining** of various metals like copper, silver, lead, zinc etc. The impure metal is taken at anode and pure metal is taken at cathode in an electrolytic cell containing solution of same metal ions. On passing electric current, metal ions from the solution reduced to metal atom at cathode. Simultaneously, equivalent amount of pure metal from anode gets oxidised to metal ions. The impurities left behind as anode mud. **Electroplating** is also based upon this mode of electrolysis.

Electrolytic Conductance

The **movement of the ions** of the electrolyte **towards the oppositely charged electrodes** under the influence of electric field is called electrolytic conduction.

Conductors

Conductors are materials that **allow electric current to pass through them**. They are divided into two main types:

- **Metallic Conductors (Class I):** These substances (like metals and graphite) conduct electricity **without undergoing any chemical change**. The flow of electricity is due to the **movement of electrons**.
- **Electrolytic Conductors (Class II):** Also known as ionic conductors, these substances conduct electricity through the **movement of ions**, which **results in a chemical change** (decomposition). Examples include ionic compounds in a molten state or dissolved in a polar solvent like water.

Strong and Weak Electrolytes

Electrolytes can be further classified based on how well they dissociate into ions in a solution:

- **Strong Electrolytes:** These substances **completely or almost completely ionize** in their aqueous solution, leading to **high electrical conductivity**.
  - **Examples:** NaCl, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3, HCl, H_2SO_4, HNO_3, NaOH, KOH etc.
- **Weak Electrolytes:** These substances **only partially dissociate into ions**, resulting in **low electrical conductivity**. The extent of their dissociation is represented by the degree of dissociation ($\propto$)
  - **Examples:** $HgCl_2$, HCN, CH_3COOH, H_2CO_3, NH_4OH, H_3BO_3, H_3PO_4 etc.

Factors Affecting the Electrical Conductivity of Solutions

Several factors can influence how well an electrolytic solution conducts electricity:

- **Interionic Attractions (Solute-Solute Interaction):** Stronger attractions between the ions of the solute lead to lower dissociation and, therefore, lower conductivity. Diluting the solution decreases these attractions, which is why the conductivity of weak electrolytes increases significantly upon dilution.
- **Solvation of Ions (Solute-Solvent Interaction):** When ions are solvated (surrounded by solvent molecules), their effective size increases, slowing them down and decreasing conductivity. Smaller ions tend to be more heavily solvated. For instance, a Li^+ ion is smaller than a Na^+ ion but is more solvated, making its effective size larger and its migration slower.
- **Viscosity of Solvent (Solvent-Solvent Interaction):** Higher viscosity (thicker solvent) suppresses (or hinders) the movement of ions, thus decreasing conductivity.
- **Temperature:** Increasing the temperature boosts electrolytic conductance. This is because higher temperatures decrease interionic attractions, solvation, and solvent viscosity, while increasing the kinetic energy of the ions.
- **Concentration of Electrolyte:** Generally, higher concentration of solution lead to stronger interionic interactions, which decreases electrolytic conduction. Therefore, conductivity often increases with dilution.

Factors Affecting the Electrical Conductivity of Metals

- **Nature and structure of metal:** Metals with a more regular and uniform crystal lattice structure generally offer less resistance to electron flow, resulting in higher conductivity. Impurities or defects in the crystal structure disrupt this regularity, scattering the electrons and decreasing conductivity.
- **Number of valence electrons per atom:** A higher number of valence electrons per atom generally leads to higher electrical conductivity.
- **Temperature:** As the temperature of a metal increases, the positive ions in the crystal lattice vibrate more vigorously. These increased vibrations cause more resistance to electron flow leads to a decrease in electrical conductivity.

Understanding Conductance and Conductivity

Fundamental Concepts

- **Ohm's Law:** It states that the **potential difference (V)** across a conductor is **directly proportional** to the **current (I)** flowing through it.

$$V \propto I$$

$$V = I\,R$$

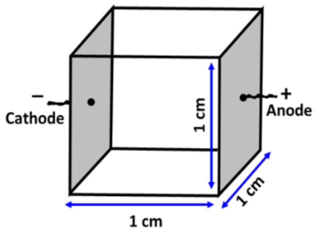
Where, **R** is proportionality constant called **resistance**. Resistance of a conductor can be measured with the help of a **Wheatstone bridge**.

- **Resistance (R):** It is the opposition to the flow of electric current. Resistance is **directly proportional to the length (l)** and **inversely proportional to the cross-sectional area (a)** of the conductor. Its unit is the **ohm (Ω)**. In SI based units, **ohm** is equal to **kg m^2 Sec^{-3} A^{-2}**.

$$R \propto l \quad \text{-------(i)} \qquad \text{and} \qquad R \propto \frac{1}{a} \quad \text{--------(ii)}$$

By combining the equations (i) and (ii), we get:

$$R \propto \frac{l}{a} \qquad \text{or} \qquad R = \rho\frac{l}{a} \quad \text{---------(iii)}$$



Here, ρ is known as **specific resistance or resistivity**.

By rearranging the equation (iii), we get: $\rho = R\frac{a}{l}$

Therefore, **specific resistance or resistivity** (ρ) is defined as **the resistance** of that conductor having its **length equal to 1 cm** and **area of cross-section equal to 1 cm^2**.

$$\rho = R\frac{1\ \text{cm}^2}{1\ \text{cm}} \qquad \text{Units: } \Omega\ \text{cm}$$

- **Conductance (G):** The ease with which electric current flows through a material. It is the reciprocal of resistance (R).

$$G = \frac{1}{R} \qquad \textbf{Units:}\quad G = \frac{1}{\Omega} = \Omega^{-1} \text{ or } S$$

Written as : **ohm^{-1}** or **mho** or **Siemen (S)**

- **Specific conductance or conductivity (κ):** It is reciprocal of the resistivity (ρ). It is denoted by the Greek symbol, kappa 'κ'.

$$\kappa = \frac{1}{\rho} \qquad \textbf{Units:}\quad \kappa = \frac{1}{\Omega\ \text{cm}} = \Omega^{-1}\ \text{cm}^{-1} \text{ or } S\ \text{cm}^{-1}$$

Written as : **ohm^{-1} cm^{-1}** or **mho cm^{-1}**

- **Understanding the Specific conductance or Conductivity (κ) of electrolytic solutions:**

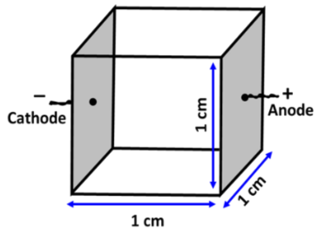
As we know, $\kappa = \frac{1}{\rho}$ --------- (i) and $\rho = R\frac{a}{l}$ --------- (ii)

Substituting the value of equation (ii) in equation (i), we get: $\kappa = \frac{1}{R} \times \frac{l}{a}$ ----------(iii)

As we know: $G = \frac{1}{R}$ --------(iv)

Substituting the value of equation (iv) in equation (iii), we get:

$$\kappa = G \times \frac{l}{a} \quad \text{-----------(v)}$$



Now, if l = 1 cm and **a** = 1 cm^2, then: $\kappa = G \times \frac{1\ \text{cm}}{1\ \text{cm}^2}$

Therefore, **conductivity (κ)** is defined as the **conductance (G)** of an electrolyte solution placed between two electrodes that are **1 cm apart** and each have a **cross-sectional area of 1 cm²**.
Simply, conductivity (κ) is the conductance (G) of 1 cm^3 (or 1ml) of the electrolytic solution.

Measurement of the Conductivity of Electrolytic or Ionic Solutions

- We have studied that the **conductivity (κ)** of an electrolyte is calculated using the equation:

$$\kappa = \frac{1}{R} \times \frac{l}{a} \qquad \text{where, } \frac{l}{a} = G^* \text{ (cell constant)}$$

Thus, the **conductivity (κ)** of an electrolyte can be determined if the **resistance (R)** of the electrolyte and the **cell constant (G*)** are known.

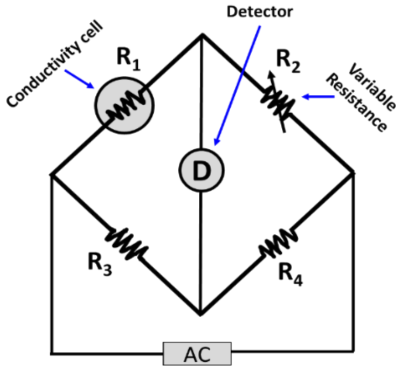
Measurement of Resistance (R) and Cell Constant (G*):

Accurate measurement of an **unknown resistance** can be performed using a **Wheatstone bridge**. However, when dealing with electrolytic solutions, **two major problems arise**:

(a) **Change in Composition**: On passing direct current (DC) through the solution alters its composition due to electrolysis.
(b) **Connection Issue**: Electrolytic solutions cannot be connected to a Wheatstone bridge in the same way as a metallic wire.

The **first problem** is resolved by using alternating current (AC) instead of DC. The **second problem** is addressed by using a specially designed vessel known as a **conductivity cell**.

1.) Measurement of Resistance (R) using modified Wheatstone bridge:



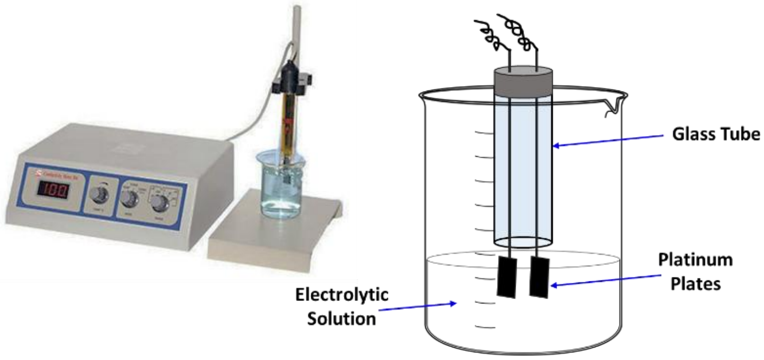
- The setup consists of:
    - Two fixed resistors: **R_3** and **R_4**
    - One variable resistor: **R_2**
    - The conductivity cell: **R_1** (unknown resistance)
- Under balanced conditions: $\frac{R_1}{R_2} = \frac{R_3}{R_4}$

Then, Unknown resistance : $R_1 = \frac{R_2 R_3}{R_4}$

- The bridge is powered using **AC current** (typically in the frequency range of 550 to 5000 Hz) to prevent electrolysis.
- Since a standard galvanometer cannot detect the null point in AC circuits, it is replaced by a suitable AC detector, such as a **headphone or earphone**. The bridge is considered balanced when no sound is heard in the detector, indicating that no current flows through it.

Conductivity Cell

A conductivity cell consists of two platinum electrodes with a cross-sectional area ‘**a**’, separated by a distance ‘l’. Hence, the solution between the electrodes forms a column of length ‘l’ and cross-sectional area ‘**a**’.



- Irrespective of the nature of the electrolytic solution filled inside the conductivity cell, the **length and cross-sectional area of the electrodes remain unchanged**.
- As the experimental determination of ‘l’ and ‘**a**’ is inconvenient and often unreliable. Therefore, the ratio of length to the cross-sectional area is determined experimentally. This is referred to as the **cell constant (G*).**

2.) Measurement of Cell Constant (G*):

- The cell constant can be determined by measuring the **conductance (G)** of a standard solution with a known **conductivity (κ)**.

  As we know, $\kappa = G \times \frac{l}{a}$ where, $\frac{l}{a}$ = **G*** (cell constant)

  Therefore, $\kappa = G \times G^*$ **Conductivity = Conductance × Cell constant**

  By rearranging the above equation, we get: $G^* = \frac{\kappa}{G}$
- A common standard solution is **potassium chloride (KCl)**, whose conductivity is well-documented at various concentrations and temperatures.

Concentration of KCl solution (mol/L)	Conductivity of KCl solution (S/cm)
1.00 M	0.1113
0.10 M	0.0129
0.01 M	0.00141

  - To prepare the electrolyte solution, **conductivity water** is used. This is a specially purified form of water with extremely low conductance.
  - Now we can determine **cell constant (G*)** by using formula;

$$G^* = \frac{\kappa}{G} = \frac{\textbf{Conductivity } (\kappa) \textbf{ of KCl solution}}{\textbf{Measured conductance } (G) \textbf{ of KCl solution at 298.15 K}}$$

For example: The conductivity of 1 Molar KCl solution at 298.15 K is 0.1113 $\Omega^{-1}cm^{-1}$.

$$G^* = \frac{0.1113 \text{ S } cm^{-1}}{\text{Measured conductance (G)of 1 Molar KCl solution at 298.15 K}}$$

- ○ Once the cell constant is determined, we can use it to measure the conductivity of another solution. The standardized conductivity cell has to be filled with that solution and used.

NOTE:

The **specific conductivity (κ)** of different electrolyte solutions (in the same solvent and at a given temperature) varies depending on:

- The **size and charge** of the ions produced during dissociation.
- The **ease with which these ions move** under a potential gradient.
- The **ion concentration**.

Therefore, it is necessary to define more physically meaningful quantities, such as **molar conductivity** and **equivalent conductivity**.

Molar Conductivity and Equivalent Conductivity

Molar Conductivity (λ_m)

Molar conductivity (λ_m) is defined as **the conductance of all the ions** present in an electrolytic solution containing **1 mole** of the electrolyte. It is denoted by the Greek letter lambda (λ_m).

$$\lambda_m = \kappa \times V \quad \text{---------- (i)}$$

Where:

- ○ **κ** = specific conductivity (conductivity of 1 cm^3 or 1 mL of solution)
- ○ **V** = volume of the solution (in mL) that contains 1 mole of the electrolyte

- We know that **increasing the volume** of a 1 molar electrolyte solution by adding water **decreases its concentration**. Thus, the volume of a solution is **the reciprocal** of its molar concentration.

$$V = \frac{1}{C} \quad \text{-----------(ii)}$$

Where:

- ○ **C =** Concentration or **Molarity (M)**

- From equations (i) and (ii), we get:

$$\lambda_m = \frac{\kappa}{C} = \frac{\kappa}{M} \quad \text{--------- (iii)}$$

- Depending on the units of specific conductivity (κ), the equation (iii), can be expressed as:
  - ○ If the unit of specific conductivity (κ) is **Ω^{-1} cm^{-1} :**

$$\lambda_m = \frac{\kappa}{M} = \frac{\text{S cm}^{-1}}{\frac{\text{mol}}{\text{L}}} = \frac{\text{S cm}^{-1}\text{ L}}{\text{mol}} = \frac{\text{S cm}^{-1}\text{ dm}^3}{\text{mol}} = \frac{\text{S cm}^{-1}\text{ }10^3\text{ cm}^3}{\text{mol}}$$

Units = S cm^2 mol^{-1}

According to this, the equation (iii) can be modified as:

$$\boxed{\lambda_m = \frac{\kappa \times 10^3}{M}}$$

- If the unit of specific conductivity (κ) is **$\Omega^{-1}\,m^{-1}$:**

$$\lambda_m = \frac{\kappa}{M} = \frac{S\,m^{-1}}{\frac{mol}{L}} = \frac{S\,m^{-1}\,L}{mol} = \frac{S\,m^{-1}\,dm^3}{mol} = \frac{S\,m^{-1}\,10^{-3}\,cm^3}{mol}$$

Units = $S\,m^2\,mol^{-1}$

According to this, the equation (iii) can be modified as:

$$\boxed{\lambda_m = \frac{\kappa \times 10^{-3}}{M}}$$

- Conversion between the units of molar conductivity (λ_m)

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

Equivalent Conductivity (λ_{eq})

Equivalent conductivity (λeq) is defined as **the conductance** of all the ions present in an electrolytic solution containing **1 gram equivalent** of the electrolyte. It is denoted by the Greek letter lambda (λeq).

$$\lambda_{eq} = \kappa \times V \quad \text{---------- (i)}$$

Where:

- **κ** = specific conductivity (conductivity of 1 cm^3 or 1 mL of solution)
- **V** = volume of the solution (in mL) that contains 1-gram equivalent of the electrolyte

- We know that **increasing the volume** of a 1-gram equivalent electrolyte solution by adding water **decreases its concentration**. Thus, the volume of a solution is **the reciprocal** of its molar concentration.

$$V = \frac{1}{C} \quad \text{-----------(ii)}$$

Where:

- **C =** Concentration or **Normality (N)**

- From equations (i) and (ii), we get:

$$\lambda_{eq} = \frac{\kappa}{C} = \frac{\kappa}{N} \quad \text{--------- (iii)}$$

- Depending on the units of specific conductivity (κ), the equation (iii), can be expressed as:
  - If the unit of specific conductivity (κ) is **$\Omega^{-1}\,cm^{-1}$:**

$$\lambda_{eq} = \frac{\kappa}{N} = \frac{S\,cm^{-1}}{\frac{gm.eq.}{L}} = \frac{S\,cm^{-1}\,L}{gm.eq.} = \frac{S\,cm^{-1}\,dm^3}{gm.eq.} = \frac{S\,cm^{-1}\,10^3\,cm^3}{gm.eq.}$$

Units = $S\,cm^2\,(gm.eq.)^{-1}$

According to this, the equation (iii) can be modified as:

$$\boxed{\lambda_{eq} = \frac{\kappa \times 10^3}{N}}$$

- If the unit of specific conductivity (κ) is **$\Omega^{-1}\,m^{-1}$:**

$$\lambda_{eq} = \frac{\kappa}{N} = \frac{S\,m^{-1}}{\frac{gm.eq.}{L}} = \frac{S\,m^{-1}\,L}{gm.eq.} = \frac{S\,m^{-1}\,dm^3}{gm.eq.} = \frac{S\,m^{-1}\,10^{-3}\,cm^3}{gm.eq.}$$

Units = $S\,m^2\,(gm.eq.)^{-1}$

According to this, the equation (iii) can be modified as:

$$\boxed{\lambda_{eq} = \frac{\kappa \times 10^{-3}}{N}}$$

- Conversion between the units of equivalent conductivity (λ_{eq})

  1 S m^2 (gm.eq.)$^{-1}$ = **10^4** S cm^2 (gm.eq.)$^{-1}$

- **Relationship between Molar conductivity (λ_m) and Equivalent conductivity (λ_{eq})**

$$\lambda_{eq} = \frac{\kappa \times 10^{-3}}{N} = \frac{\kappa \times 10^{-3}}{M \times \text{nfactor}} = \frac{\lambda m}{\text{nfactor}}$$

Exercises

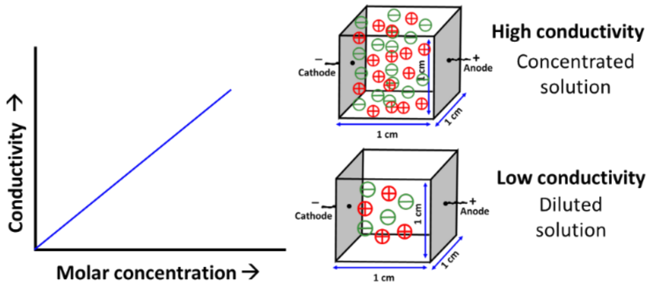
1. Electrolytic conductivity of 0.30 M solution of KCl at 298 K is 3.72 × 10^2 S cm^{-1}. Calculate its molar conductivity.
2. Calculate the specific resistance of a 0.02 N solution of an electrolyte having equivalent conductance 104 S cm^2 (gm.eq)$^{-1}$.
3. The measured resistance of a conductivity cell containing 7.5 × 10^{-3} M solution of KCl at 298 K was 1005 ohms. Calculate (a) specific conductance (b) Molar conductance (Given cell constant = 125 cm^{-1})
4. Electrolytic conductivity of 0.20 M solution of KCl at 298 K is 2.48 × 10^{-2} S cm^{-1}. Calculate its molar conductivity.
5. A 0.05 M NaOH solution offered a resistance of 31.6 ohms in a conductivity cell at 298 K. If the cell constant of the conductivity cell is 0.367 cm^{-1}, find out the specific and molar conductance of the NaOH solution.
6. A 0.1 M NaOH solution offered a resistance of 63 ohms in a conductivity cell at 298 K. If the area of the plates of conductivity cell is 3.8 cm^2 and the distance between them is 1.4 cm, calculate the molar conductivity of NaOH solution.
7. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3 ohm. Calculate the resistivity, conductivity, and molar conductivity.
8. Calculate the equivalent conductivity of 1 M H_2SO_4 solution whose conductivity is 26 × 10^{-2} S cm^{-1}.
9. The electrical resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 100 ohm. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.125 × 10^{-3} Ω^{-1} cm^{-1} ?
10. The resistance of 0.05 M CH_3COOH solution is found to be 100 ohm. If the cell constant is 0.0354 cm^{-1}, calculate the molar conductivity of the acetic acid solution.

Variation of Conductivity (κ) and Molar Conductivity (λ_m) with Concentration

Variation of Conductivity (κ) with Concentration

Conductivity (κ ; also called specific conductance) **decreases with dilution** for both strong and weak electrolytes. This is because the **number of ions per unit volume decreases** as the solution becomes more diluted.

- **Strong Electrolytes** (e.g., NaCl, KCl) are almost fully ionized in solution, so they have high conductivity.
- **Weak Electrolytes** (e.g., CH_3COOH, NH_4OH) are only partially ionized, so their conductivity is lower.



Variation of Molar Conductivity (λ_m) with Concentration

Molar conductivity (λ_m) **increases with dilution** for both strong and weak electrolytes. However, **strong electrolyte shows small increase** in molar conductivity whereas **weak electrolyte shows sharp increase** in molar conductivity with dilution. Let us discuss these two one by one;

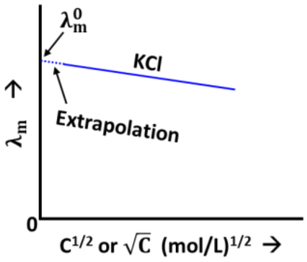
In case of Strong Electrolytes :

- Strong electrolytes (e.g., NaCl, KCl etc.) **ionize almost completely** in aqueous solution. Therefore, they have **high molar conductivity at room temperature**.
- Molar conductivity **increases slightly with dilution** due to **reduced inter-ionic attractions** and **greater ionic mobility**.
- On further dilution, a point is reached where no further increase occurs—this is called the **limiting molar conductivity**, denoted as λ_m^∞ or λ_m^0 (molar conductance at infinite dilution or at nearly zero concentration of solution). The value of λ_m^∞ or λ_m^0 **can be obtained by extrapolation**.
- Mathematical relationship between the **molar conductivity at any concentration** and **the molar conductivity at infinite dilution** is known as **Debye-Hückel–Onsager Equation**.

$$\lambda_m = \lambda_m^0 - A\sqrt{C}$$

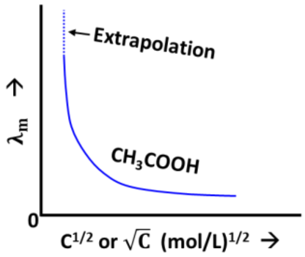
Where:

- λ_m= Molar conductivity at concentration C
- λ_m^∞ or λ_m^0 = Molar conductivity at infinite dilution
- A = Constant depending on solvent and temperature
- C = Concentration of electrolyte



In case of Weak Electrolytes :

- Weak electrolytes (e.g., CH_3COOH, NH_4OH etc.) **ionize partially** in aqueous solution. Therefore, they have **low molar conductivity at room temperature**.
- Molar conductivity **increases sharply with dilution** due to **increased ionization**.
- Therefore, their λ_m vs $\sqrt{C}$ curve is not linear, so λ_m^∞ or λ_m^0 **cannot be determined by extrapolation**. To solve this, we use **Kohlrausch's Law**.



Kohlrausch's Law

At infinite dilution (when the dissociation of an electrolyte is complete), **each ion** of an electrolyte **contributes independently** to the **total molar conductivity** of an electrolyte, **regardless of the other ion** present in the solution.

$$\lambda_{electrolyte}^0 = \lambda_{cation}^0 + \lambda_{anion}^0$$

Therefore, the **total molar conductivity** of an electrolyte is **the sum of the ionic conductivities of all the ions** present in the solution. The **contribution of each ion** to the total molar conductivity is called its **ionic conductivity**.

- **Example:**
  If an electrolyte is $Al_2(SO_4)_3$, then, the molar conductivity (λ_m^0) of the salt at infinite dilution is expressed as:

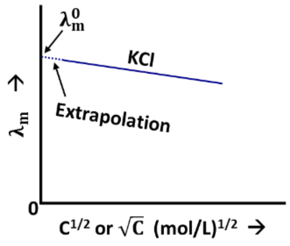
$$\lambda_m^0 = \lambda^0_{Al_2(SO_4)_3} = 2\lambda^0_{Al^{+3}} + 3\lambda^0_{SO_4^{-2}}$$

- The Kohlrausch's law can be confirmed by taking example of strong electrolytes having common cations or anions.
  - **Pair of Strong electrolytes having common anions: (KCl:NaCl and KBr:NaBr)**
    - $\boldsymbol{\lambda^0_{KCl} - \lambda^0_{NaCl}} = (\lambda^0_{K^+} + \lambda^0_{Cl^-}) - (\lambda^0_{Na^+} + \lambda^0_{Cl^-}) = \boldsymbol{\lambda^0_{K^+} - \lambda^0_{Na^+}}$
      $\lambda^0_{KCl} - \lambda^0_{NaCl} = 149.86 - 126.45 = \mathbf{23.41}$
    - $\boldsymbol{\lambda^0_{KBr} - \lambda^0_{NaBr}} = (\lambda^0_{K^+} + \lambda^0_{Br^-}) - (\lambda^0_{Na^+} + \lambda^0_{Br^-}) = \boldsymbol{\lambda^0_{K^+} - \lambda^0_{Na^+}}$
      $\lambda^0_{KBr} - \lambda^0_{NaBr} = 151.92 - 128.51 = \mathbf{23.41}$
  - **Pair of Strong electrolytes having common cations: (KCl:KBr and NaCl:NaBr)**
    - $\boldsymbol{\lambda^0_{KBr} - \lambda^0_{KCl}} = (\lambda^0_{K^+} + \lambda^0_{Br^-}) - (\lambda^0_{K^+} + \lambda^0_{Cl^-}) = \boldsymbol{\lambda^0_{Br^-} - \lambda^0_{Cl^-}}$
      $\lambda^0_{KBr} - \lambda^0_{KCl} = 151.92 - 149.86 = \mathbf{2.06}$
    - $\boldsymbol{\lambda^0_{NaBr} - \lambda^0_{NaCl}} = (\lambda^0_{Na^+} + \lambda^0_{Br^-}) - (\lambda^0_{Na^+} + \lambda^0_{Cl^-}) = \boldsymbol{\lambda^0_{Br^-} - \lambda^0_{Cl^-}}$
      $\lambda^0_{NaBr} - \lambda^0_{NaCl} = 128.51 - 126.45 = \mathbf{2.06}$

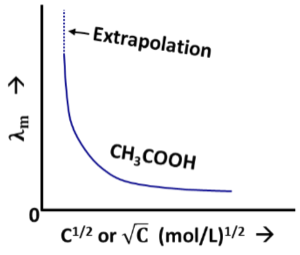
Applications of Kohlrausch's Law

(a) Determination of λ_m^∞ or λ_m^0 for Weak Electrolytes :

- As discussed earlier, the **molar conductivity of strong electrolytes** at infinite dilution **can be determined graphically by extrapolating** the λ_m vs $\sqrt{C}$ curve. However, this method **does not work for weak electrolytes** because their dissociation remains incomplete even at very low concentrations. Therefore, their λ_m vs $\sqrt{C}$ curve is not linear, so **λ_m^0 cannot be determined by extrapolation**. To solve this, we use **Kohlrausch's Law**.



For Strong Electrolyte



For Weak Electrolyte

- **Example:**
  The molar conductivity of Acetic acid (CH_3COOH) can be found if the molar conductivities at infinite dilution of strong electrolytes (HCl, CH_3COONa and NaCl) are known.

$$\lambda^0_{CH_3COOH} = \lambda^0_{CH_3COONa} + \lambda^0_{HCl} - \lambda^0_{NaCl}$$

OR

$$\lambda^0_{CH_3COO^-} + \lambda^0_{H^+} = (\lambda^0_{CH_3COO^-} + \lambda^0_{Na^+}) + (\lambda^0_{H^+} + \lambda^0_{Cl^-}) - (\lambda^0_{Na^+} + \lambda^0_{Cl^-})$$

(b) Determination of Degree of Dissociation (α) for Weak Electrolyte :

- Molar conductivity of a weak electrolyte depends on its degree of dissociation (α : extent of ionisation).
- Higher the degree of dissociation means greater the number of ions in the solution, and hence, the higher the molar conductivity.
- Thus, Degree of dissociation (α) = $\dfrac{\text{Molar conductivity at given concentration } (\lambda^c_m)}{\text{Molar conductivity at infinite dilution } (\lambda^0_m \text{ or } \lambda^\infty_m)}$

(c) Determination of Dissociation Constant (K_d) for Weak Electrolyte :

- Dissociation constant (K_d) at given molar concentration (C), for weak electrolyte 'AB' can be calculated from the degree of dissociation, as follow :

	AB	⇌	**A^+**	**+**	**B^-**
Initial Concentration (mol/L):	C		0		0
Final Concentration (mol/L):	C-Cα		Cα		Cα

$$K_d = \frac{[A^+]\,[B^-]}{[AB]} = \frac{C\alpha\ .\ C\alpha}{C-C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \mathbf{\frac{C\alpha^2}{1-\alpha}}$$

- If an electrolyte dissociates into **'n' number of ions**, then ;

$$K_d = \frac{C^n\alpha^n}{C(1-\alpha)} = \mathbf{\frac{C^{n-1}\alpha^n}{1-\alpha}}$$

(d) Molar Solubility of Sparingly Soluble Salts :

- Salts like $BaSO_4$, $PbSO_4$, AgCl, AgBr, AgI etc., do not dissolve to a large extent in water are called sparingly soluble salts. The solubility of these salts can be determined by conductance measurement.
- By finding specific conductance ($\boldsymbol{\kappa}$) and molar conductivity at infinite dilution ($\boldsymbol{\lambda^0_m}$), molar solubility can be calculated as follows:

$$\lambda^0_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility (in mol/L)}}$$

- Therefore, Solubility (in mol/L) = $\dfrac{\kappa \times 1000}{\lambda^0_m}$

(e) Calculation of Absolute Ionic Mobilities (μ^0_{ion}) :

- It is the speed of an ion at infinite dilution under potential gradient of 1 volt/cm. It can be calculated as:

$$\text{Absolute ionic mobility } (\mu^0_{ion}) = \frac{\text{Speed of ion at infinite dilution}}{\text{Potential gradient}}$$

- As we know, Potential gradient = $\dfrac{\text{Applied EMF}}{\text{Distance between the electrodes}}$
- Therefore, Absolute ionic mobility (μ^0_{ion}) = $\dfrac{\text{Speed of ion at infinite dilution} \times \text{Distance between the electrodes}}{\text{Applied EMF}}$
- **Units of** μ^0_{ion} = $\dfrac{cm\ sec^{-1} \times \text{cm}}{\text{volt}}$ = $\mathbf{cm^2\ sec^{-1}\ volt^{-1}}$

- It has been established that the ionic conductivity ($\lambda^0_{m\,(ion)}$) at infinite dilution is directly proportional to the absolute ionic mobility (μ^0_{ion}) :

$$\boldsymbol{\lambda^0_{m\,(ion)} \propto \mu^0_{ion}} \qquad \text{OR} \qquad \boldsymbol{\lambda^0_{m\,(ion)} = F \times \mu^0_{ion}} \qquad [1F = 96500\ C]$$

Exercises

1. At 291 K the molar conductance values at infinite dilution of NH_4Cl, NaOH and NaCl are 129.1, 217.4 and 108.3 S cm^2 mol^{-1} respectively. Calculate the molar conductance of NH_4OH at infinite dilution.
2. The value of molar conductance at infinite dilution for HCl, NaCl, CH_3COONa are 426.1, 126.5 and 91.0 S cm^2 mol^{-1} respectively. Calculate the value of molar conductance at infinite dilution for Acetic acid (CH_3COOH).
3. At 298 K, the specific conductivity of a saturated solution of AgCl in water is 2.3×10^{-6} S cm^{-1}. Calculate its solubility in gm/L at 298 K. Given molar conductance at infinite dilution for silver ion and chloride ion are 61.9 and 76.3 S cm^2 mol^{-1} respectively.
4. For a saturated solution of $BaSO_4$ at 291 K, conductivity is 3.648×10^{-6} S cm^{-1} and that of water used for preparing the solution was 1.25×10^{-6} S cm^{-1}. Calculate the solubility of $BaSO_4$ at 291 K. Given molar conductivity at infinite dilution for Barium ion and Sulphate ion are 110 and 136.6 S cm^2 mol^{-1} respectively.
5. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If molar conductivity at infinite dilution for acetic acid is 390.5 S cm^2 mol^{-1} what is its dissociation constant?
6. The conductivity of 0.001028 M acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if λ^0_m for acetic acid is 390.5 S cm^2 mol^{-1}.
7. The molar conductivity of 0.025 M methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate is degree of dissociation and dissociation constant. Given $\lambda^0_m(H^+)$ = 349.6 S cm^2 mol^{-1} and, $\lambda^0_m(HCOO^{-1})$ = 54.6 S cm^2 mol^{-1}.
8. The molar conductivity at infinite dilution for Al_2SO_4 is 858 S cm^2 mol^{-1}. What will be the molar ionic conductivity of Al^{+3} ion if molar ionic conductivity of sulphate ion is 160 S cm^2 mol^{-1} ?
9. The molar conductivities of Ag^+ and NO_3^{-1} ions are 54.14 and 61.27 S cm^2 mol^{-1} at infinite dilution. Calculate the ionic mobility of these ions at infinite dilution.
10. Calculate the ionic mobility of K^+ ion at infinite dilution if molar ionic conductivity of K^+ ion in KCl solution is 64.35 S cm^2 mol^{-1}.
11. A conductivity cell gives a resistance of 100 Ω when filled with a 0.1 mol L^{-1} potassium chloride (KCl) solution. The conductivity of this solution is 1.29 S/m. When the same cell is filled with a 0.02 mol L^{-1} KCl solution, its resistance is 520 Ω. Calculate the conductivity and molar conductivity of the 0.02 mol L^{-1} KCl solution.
12. A column containing a 0.05 M sodium hydroxide (NaOH) solution has a length of 50 cm and a diameter of 1 cm. The measured electrical resistance of this solution is 5.55×10^3 Ω. Calculate resistivity, conductivity, molar conductivity of the solution.
13. The molar conductivity of a 0.025 M methanoic acid solution is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. (Given: λ^0_m (H+)=349.6 S cm^2 mol^{-1} & λ^0_m(HCOO−) = 54.6 S cm^2 mol^{-1}).
14. The conductivity of 0.0025 M CH_3COOH is 5.25×10^{-5} $\Omega^{-1}cm^{-1}$. Calculate its degree of dissociation if λ^0_m for acetic acid is 390 $\Omega^{-1}cm^2$ mol^{-1}.
15. The electrical resistance of a column of 0.001 M CH_3COOH solution of diameter 1 cm and length 50 cm is 12.8×10^5 ohm. Calculate the degree of dissociation and dissociation constant for 0.001 M CH_3COOH solution, if the molar conductance at infinite dilution for HCl, NaCl, CH_3COONa are 426.1, 126.5 and 91.0 S cm^2 mol^{-1} respectively.

Batteries and Fuel Cells

Batteries

A battery is an electrochemical cell (or a set of cells) that acts as a source of electrical energy.
For a battery to be sold and used commercially, it should meet three main conditions:

- **Light and Compact:** It should not be too heavy or take up too much space.
- **Stable Voltage:** Its power output should remain fairly constant and not drop significantly while it is being used.
- **Long Life:** It needs to be durable and last for a reasonable amount of time.

There are mainly two types of batteries: (a) Primary batteries, and (b) Secondary batteries

1. Primary Batteries

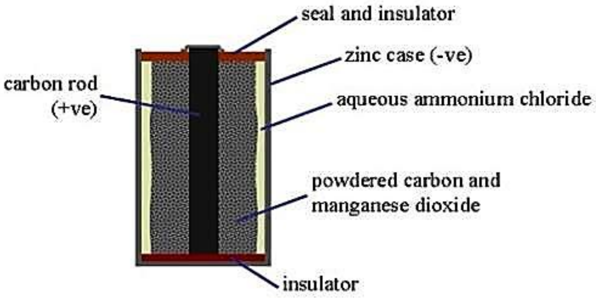
- A **primary battery** is a type of **single-use**, **non-rechargeable** battery.
- In these batteries, the electrochemical reaction **occurs only once** and **cannot be reversed**.
- After the reactants are consumed over a period of use, the battery becomes "dead" and must be discarded.
- Two common examples of primary batteries are the **dry cell** and the **mercury cell**.

(a) Dry Cell (Leclanché Cell)

The dry cell is one of the most familiar types of commercial batteries, commonly used to power devices like torches, toys, and transistors.

Construction

- A dry cell consists of a cylindrical **zinc container** that acts as the negative electrode **(anode)**.
- This cylinder is filled with moist electrolyte paste made of **NH_4Cl** (ammonium chloride) and small amount of **$ZnCl_2$** (zinc chloride).
- At the center of the cell is a **carbon (graphite) rod** that serves as the positive electrode **(cathode)**.
- This rod is surrounded by a black paste of powdered **MnO_2 (manganese dioxide)** and **carbon powder**.
- The cell is sealed at the top to prevent leakage.



Chemical Reactions :

At Anode : $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$

At Cathode : $2NH_4Cl + 2MnO_{2\,(s)} + 2e^- \longrightarrow \overbrace{Mn_2O_{3\,(s)} + H_2O}^{2\,MnO(OH)} + 2NH_3 + 2Cl^{-1}$

Overall Recⁿ : $Zn_{(s)} + 2NH_4Cl + 2MnO_{2\,(s)} \longrightarrow Mn_2O_{3\,(s)} + H_2O + 2NH_3 + ZnCl_2$

The ammonia (**NH_3**) produced at the cathode reacts with the zinc ions (**Zn^{2+}**) from the anode to form a stable complex ion, **$[Zn(NH_3)_4]^{2+}$**. This prevents the buildup of ammonia gas, which would otherwise disrupt the current flow.

$$Zn^{+2}_{(aq)} + 2NH_{3\,(aq)} \longrightarrow [Zn(NH_3)_2]^{+2}_{(aq)}$$

Voltage and Lifespan

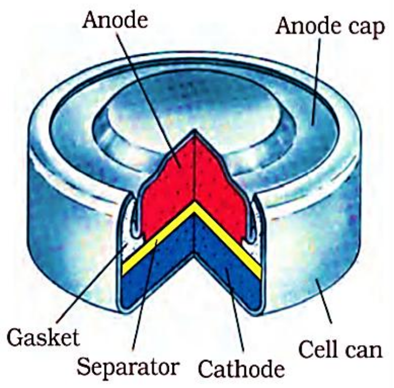
A dry cell produces a voltage of about **1.25 V to 1.5 V**. Over time, the zinc casing gets consumed, and the acidic ammonium chloride can corrode the zinc even when the cell is not being used. This can cause the battery to leak, which is why modern cells are often designed to be "**leak-proof**."

(b) Mercury Cell (Ruben-Mallory Cell)

The mercury cell is another type of primary battery, **ideal for low-current devices** like watches, hearing aids, and cameras due to its **stable voltage** and compact size.

Construction

- The **anode**, or the negative electrode, is made of a **zinc-mercury amalgam** (a mixture of zinc and mercury, denoted as Zn/Hg).
- The **cathode**, or the positive electrode, consists of a paste made from **mercuric oxide (HgO)** mixed with **carbon powder** to improve electrical conductivity.
- A moist paste of **potassium hydroxide (KOH)** and **zinc oxide (ZnO)** serves as the **electrolyte**. This paste fills the space between the electrodes.
- To prevent the electrodes from touching each other and causing a short circuit, a **porous separator** (often made of paper or a similar absorbent material) soaked in the electrolyte is placed between the anode and the cathode.



Chemical Reactions

At Anode : $Zn(Hg)_{(s)} + 2OH^{-1}_{(aq)} \longrightarrow ZnO_{(s)} + Hg + H_2O + 2e^-$

At Cathode : $HgO_{(s)} + H_2O + 2e^- \longrightarrow Hg_{(l)} + 2OH^{-1}_{(aq)}$

Overall reac^n : $Zn_{(s)} + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

Voltage

The mercury cell provides a very constant voltage of **1.35 V** throughout its life.

This stability is because the overall reaction does not involve any ions whose concentration changes as the battery is used.

2. Secondary Batteries

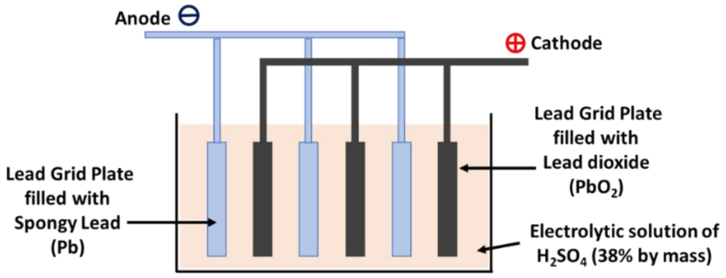
- Secondary batteries are the electrochemical cells in which the redox reaction can be **reversed by passing an electric current** through the cell.
- Therefore, these batteries are **rechargeable** and can undergo multiple charging and discharging cycles.
- Two common examples of secondary batteries are the **lead-acid storage battery** and **the nickel-cadmium (Ni-Cd) battery.**

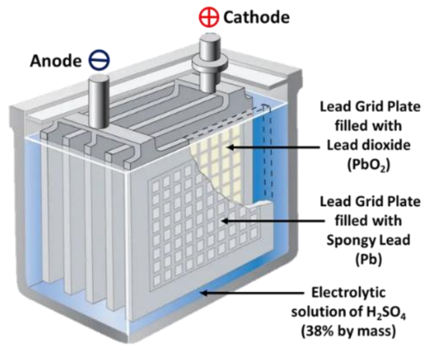
(a) Lead-Acid Storage Battery :

The **lead storage battery** is one of the most widely used secondary or rechargeable batteries, commonly found in **automobiles, inverters**, and other power backup systems. As the voltage of individual cell is only **2 volts**, therefore, 3 or 6 such cells are joined in series to get a **6-volt or 12-volt battery**.

Construction

- **Anode (-):** Grids is made of lead packed with **spongy lead (Pb)**.
- **Cathode (+):** Grids is made of lead packed with **lead dioxide (PbO_2)**.
- **Electrolyte:** A solution of approximately **38% sulfuric acid (H_2SO_4)** having **density 1.31 gm/ml** is filled between the electrodes.
- **Separators:** The anode and cathode plates are arranged alternately and are separated by thin, porous sheets of plastic or fiberglass to prevent **short circuits**. The entire assembly is immersed in the electrolyte within a hard plastic container.





Chemical Reactions : (During Discharging or working)

At anode : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4\,(s)} + 2e^-$

At Cathode : $PbO_{2\,(s)} + H_2SO_{4\,(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4\,(s)} + 2H_2O$

Overall reac^n : $Pb_{(s)} + PbO_{2\,(s)} + 2H_2SO_{4\,(aq)} \longrightarrow 2PbSO_{4\,(s)} + 2H_2O$

From the above reaction it is clear that during working of the cell, **$PbSO_4$ is formed** and **H_2SO_4 is used up**. Therefore, the density of H_2SO_4 falls. The battery **needs to be charged** when the **density of H_2SO_4 falls below 1.2 gm/mL**.

During Recharging :

Recharge is done by applying an **external direct current (DC) source**. Since **$PbSO_4$ formed during discharge** is a solid and sticks to the electrodes, it is **converted back into spongy lead and lead dioxide**.

Chemical Reactions : (During Recharging)

At anode (oxidation) : $PbSO_{4\,(s)} + 2H_2O \longrightarrow PbO_{2\,(s)} + H_2SO_{4\,(aq)} + 2H^+_{(aq)} + 2e^-$

At Cathode (reduction) : $PbSO_{4\,(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$

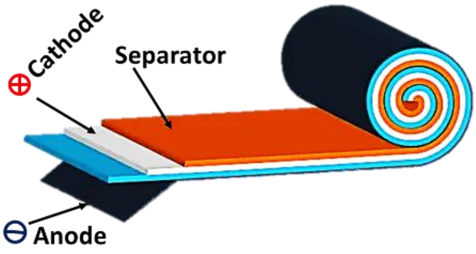
Overall reaction : $2PbSO_{4\,(s)} + 2H_2O \longrightarrow Pb_{(s)} + PbO_{2\,(s)} + 2H_2SO_{4\,(aq)}$

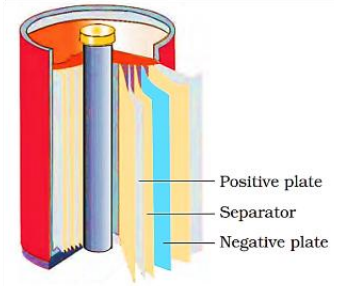
(b) Nickel-Cadmium (Ni-Cd) Battery :

The **Ni-Cd battery** generally has a longer lifespan than a lead-acid battery but is more expensive. It is used in devices like calculators, cameras, and cordless power tools. However, its use has declined due to the environmental toxicity of cadmium. The battery produces a **voltage of about 1.4V**.

Construction

- **Anode (-): Cadmium (Cd)** metal.
- **Cathode (+):** A metal grid containing **nickel(IV) oxide (NiO_2)**.
- **Electrolyte:** A solution of **potassium hydroxide (KOH)**.





Chemical Reactions : (During Discharging or working)

At anode : $Cd_{(s)} + 2OH^{-1}{}_{(aq)} \longrightarrow Cd(OH)_{2\,(s)} + 2e^-$

At Cathode : $NiO_{2\,(s)} + 2H_2O + 2e^- \longrightarrow Ni(OH)_{2\,(s)} + 2OH^{-1}$

Overall reaction : $Cd_{(s)} + NiO_{2\,(s)} + 2H_2O \longrightarrow Cd(OH)_{2\,(s)} + Ni(OH)_{2\,(s)}$

During Recharging :

The solid products, cadmium hydroxide and nickel(II) hydroxide, stick to the electrodes, allowing the reaction to be easily reversed.

Chemical Reactions : (During Recharging)

At anode (oxi) : $Ni(OH)_{2\,(s)} + 2OH^{-1} \longrightarrow NiO_{2\,(s)} + 2H_2O + 2e^-$

At Cathode (Red) : $Cd(OH)_{2\,(s)} + 2e^- \longrightarrow Cd_{(s)} + 2OH^{-1}{}_{(aq)}$

Overall reaction : $Cd(OH)_{2\,(s)} + Ni(OH)_{2\,(s)} \longrightarrow Cd_{(s)} + NiO_{2\,(s)} + 2H_2O$

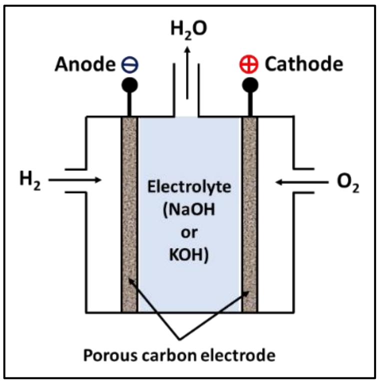
Fuel Cells

Fuel cells are **electrochemical devices** that designed to directly convert the **chemical energy** from the combustion of fuels (like **hydrogen** or **hydrocarbons**) into **electrical energy**.

Hydrogen-Oxygen (H_2-O_2) Fuel Cell – Bacon Cell

Construction :

- **Electrodes and Electrolytes:** Hydrogen (**H_2**) and oxygen (**O_2**) gases are bubbled through porous carbon electrodes into a concentrated aqueous solution of **KOH** or **NaOH**.
- **Catalysts:** To accelerate the reactions, catalysts such as Platinum (Pt), Palladium (Pd), Silver (Ag), or Cobalt(II) Oxide (CoO) are incorporated into the electrodes.
- **Operating Conditions:** The cell works continuously as long as H_2 and O_2 gases are supplied. It typically operates at a temperature of 525 K and a pressure of 50 atm.



Chemical Reactions :

At anode : $2H_{2\,(g)} + 4OH^{-1}_{(aq)} \longrightarrow 4H_2O + 4e^-$

At Cathode : $O_{2\,(g)} + 2H_2O + 4e^- \longrightarrow 4OH^{-1}_{(aq)}$

Overall reac^n : $2H_{2\,(g)} + O_{2\,(g)} \longrightarrow 2H_2O$

Efficiency (η) of a Fuel Cell :

The efficiency of a fuel cell is the ratio of the useful **electrical energy produced** (**ΔG**, Gibbs Free Energy) to the total **heat released** by the fuel's combustion (**ΔH**, Enthalpy).

The efficiency of a fuel cell is given by $\eta = \frac{\Delta G}{\Delta H} \times 100$

ΔG for H_2-O_2 fuel cell = —nFE = —2 × 96500 ×1.23 V = —237390 = —237.39 kJ/mol

ΔH for H_2-O_2 fuel cell = —285.8 kJ/mol

Therefore, $\eta = \frac{\Delta G}{\Delta H} \times 100 = \frac{-237.39\ \text{kJ/mol}}{-285.8\ \text{kJ/mol}} \times 100 \approx 83\ \%$

83% is the theoretical value of efficiency, but the **actual efficiency of the fuel cell is 60-70%**. It is still regarded better in term of efficiency of thermal power plants whose efficiency is about 40%.

Advantages of a Fuel Cell :

- Since, fuel cells convert chemical energy of a fuel directly into electricity, making them more efficient than conventional methods like thermal power plants or nuclear power plants etc.
- The cell has been used in the **Apollo program**. Because the water formed during the reaction is used by the astronauts for drinking.
- These cells are environmental-friendly and do not cause any pollution problem.

Corrosion

Corrosion is a natural process in which metals, when exposed to **air and moisture**, undergo a chemical change on their surfaces forming **ore-like compounds** such as: (i) Metal **oxides**, (ii) Metal **carbonates**, and (iii) Metal **sulphides**. These compounds slowly **eat away the metal**, degrading its strength and appearance.

Examples of Corrosion:

- **Rusting of Iron:** It is the most familiar example of corrosion, where **iron (Fe)** forms a **flaky, brown layer** (called **rust**) of hydrated ferric oxide (**$Fe_2O_3.xH_2O$**) over its surface, when exposed to air and moisture.

- **Tarnishing of Silver:** It is the formation of a **dark black coating** of **silver sulphide (Ag_2S)** on the surface of silver articles. This occurs due to a reaction between silver and **sulphur compounds** (like hydrogen sulphide, H_2S) present in the air.

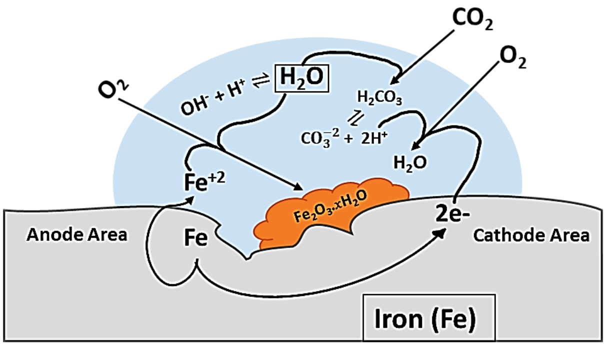
- **Patina on Copper or Bronze:** It refers to the **formation of a green coating** on the surface of **copper** or **bronze** over time due to prolonged exposure to **moist air** and **pollutants** like carbon dioxide **(CO_2),** oxygen **(O_2),** and sulphur compounds **(SO_2, H_2S)**. This green layer is mainly a mixture of **$Cu(OH)_2.CuCO_3$** (basic copper carbonate) and **$Cu(OH)_2.CuSO_4$** (basic copper sulphate), commonly known as **patina**.

Factors responsible for Corrosion:

- **Reactivity of Metal:**
  More reactive metals, like iron, tend to corrode more easily than less reactive metals, like gold.
- **Presence of Air and Moisture:**
  Atmospheric gases such as carbon dioxide (**CO_2**) and sulphur dioxide (**SO_2**) can dissolve in water to form acidic solutions, which act as electrolytes and accelerate corrosion.
- **Presence of Impurities:**
  Impurities with **higher reduction potential** create tiny electrochemical cells, accelerating corrosion.
- **Presence of Electrolytes:**
  Electrolytes (like salts) in water speed up corrosion. Example: **Iron corrodes faster in seawater** than in distilled water.
- **Uneven metal surface:**
  Scratches, dents, or other depressions on a metal's surface can trap moisture and create areas where corrosion is more likely to start.

Mechanism of Corrosion (Rusting of Iron) :

- The actual mechanism of rusting is in fact a complicated process which is not fully understood. Several theories have been proposed, one of these is the **electrochemical theory**.
- It suggests that the **uneven surface** of iron behaves like **small electrochemical cell** in the presence of water.
- Gases like **CO_2** and **O_2** dissolved in water and this water serves as the electrolytic solution.



Chemical Reactions :

At anode : $\mathrm{Fe}_{(s)} \longrightarrow \mathrm{Fe}^{+2}_{(aq)} + 2e^- \quad] \times 2 \qquad E^0_{\mathrm{Fe}^{+2}|\mathrm{Fe}} = -0.44\ \mathrm{V}$

Due to the accumulation of these electrons, the rest of the metal behave as cathode.

Electrolytes in water: $H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$

$H_2O \rightleftharpoons H^+ + OH^{-1}$

At cathode : $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad E^0_{H^+|O_2|H_2O} = 1.23\ \mathrm{V}$

Overall reaction : $2Fe + 4H^+ + O_2 \longrightarrow 2\,Fe^{+2} + 2H_2O \qquad E^0_{cell} = 1.67\ \mathrm{V}$

The **Fe^{+2} ions** formed in reaction is further **oxidized** by atmospheric oxygen **to form rust** and H^+ ion.

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

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$$

The hydrated ferric oxide once formed acts as a catalyst for further oxidation of the fresh metal.

Net reaction of rusting : $4Fe + 3O_2 + 2(xH_2O) \longrightarrow 2Fe_2O_3.xH_2O$

How to Prevent Corrosion ?

There are several effective methods to protect metals from corrosion.

(a) Barrier Protection

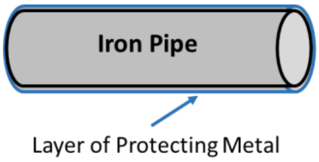
This is the simplest method, which works by **creating a physical barrier** to stop the metal surface from coming into contact with environmental agents like oxygen (O_2), moisture, or carbon dioxide (CO_2).
This can be achieved by:

- **Painting** the surface of the metal.
- Coating the metal with a thin film of **oil, grease, or bisphenol**.
- **Electroplating** the metal with a layer of a non-corrosive metal like Nickel (Ni), Chromium (Cr), or Tin (Sn).

(b) Sacrificial Protection

In this method, the iron object is covered with a protective layer of a **more reactive (more electropositive) metal**, such as Zinc (**Zn**) or Magnesium (**Mg**). This more reactive metal corrodes first, thereby "sacrificing" itself to protect the iron.

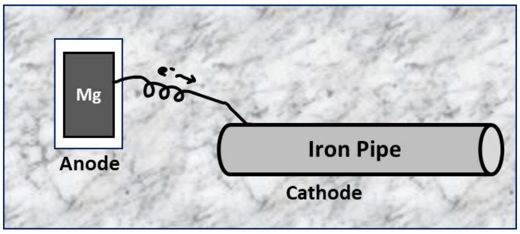
- **Example: Galvanization**
  The most common example is **galvanization**, where iron is coated with **zinc**. The zinc layer reacts with O_2 and CO_2 in the air to form a tough, protective, invisible layer of **basic zinc carbonate** ($ZnCO_3 \cdot Zn(OH)_2$), which shields the underlying iron from corrosion.



(c) Electrical Protection (Cathodic Protection)

This method is commonly used to protect large, submerged iron structures like underground pipelines, storage tanks, and ship hulls.

- **How it works:**
  The **iron object** is connected by a wire to a block of a **more electropositive metal** (e.g., Magnesium, Aluminium, or Zinc). This creates an electrochemical cell where **the iron** is forced to act as the **cathode** (and is thus protected from corrosion), while the **more reactive metal block** acts as the **anode** and corrodes instead.



NOTE: Anodising

Anodising is a widely used electrochemical process that **enhances the corrosion resistance of metals** by forming a **protective oxide layer on their surface**. This technique is especially valuable for **non-ferrous metals**, such as **aluminium**, **magnesium**, and **titanium**, which are commonly used in construction, aerospace, electronics, and consumer goods.

Process of Anodising:

i. The **metal object (e.g., Aluminium)** is made the **anode** in an electrolytic cell.
ii. It is **immersed in an acidic electrolyte** (e.g., sulphuric acid).
iii. When **electric current** is passed:
    - **Oxide ions (O^{2-})** are generated from the electrolyte.
    - These ions **react with the metal atoms** at the anode.
    - A **thick, protective layer of metal oxide** forms on the surface.

Advantages of Anodising

- **Corrosion Resistance**:
  The oxide layer shields the metal from moisture, oxygen, and environmental pollutants.
- **Improved Surface Hardness**:
  Increases wear resistance, making the surface harder and more durable.
- **Electrical Insulation**: The oxide layer acts as an insulator in electronic components.

NCERT : Intext Questions

1. How would you determine the standard electrode potential of the system $Mg^{2+}|Mg$?
2. Can you store copper sulphate solutions in a zinc pot?
3. Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.
4. Represent the cell in which the following reaction takes place:
   $Mg_{(s)} + 2Ag^+ (0.0001M) \longrightarrow Mg^{2+}(0.130M) + 2Ag(s)$
   Calculate its E_{cell} if E^0_{cell} is 3.17 V.
5. Calculate the equilibrium constant of the reaction: $Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$ if E^0_{cell} is 0.46 V.
6. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.
7. Calculate the emf of the cell in which the following reaction takes place:
   $Ni_{(s)} + 2Ag^+ (0.002\ M) \longrightarrow Ni^{2+} (0.160\ M) + 2Ag_{(s)}$
   Given that E^0_{cell} is 1.05 V.
8. The cell in which the following reaction occurs: $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2\,(s)}$ has E^0_{cell} = 0.236 V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.
9. A conductivity cell gives a resistance of 100 Ω when filled with a 0.1 mol L^{-1} potassium chloride (KCl) solution. The conductivity of this solution is 1.29 S/m. When the same cell is filled with a 0.02 mol L^{-1} KCl solution, its resistance is 520 Ω. Calculate the conductivity and molar conductivity of the 0.02 mol L^{-1} KCl solution.
10. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate the resistivity, conductivity, and molar conductivity.

11. The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

$C^{1/2}$ / (mol $L^{-1})^{1/2}$	λ_m / S cm^2 mol^{-1}
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between λ_m and $C^{1/2}$ is a straight line. Determine the values of λ_m^0 and A for KCl.

12. Calculate λ_m^0 for $CaCl_2$ and $MgSO_4$ if the ionic conductivity at infinity dilution are as follows:
$\lambda^0 Ca^{+2}$ = 119.0 , $\lambda^0 Mg^{+2}$ = 106.0 , $\lambda^0 Cl^{-1}$ = 76.3 , and $\lambda^0 SO_4^{-2}$ = 160.0
13. λ_m^0 for NaCl, HCl and NaAc are 126.4, 425.9, and 91.0 S cm^2 mol^{-1} respectively. Calculate λ_m^0 for HAc.
14. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}.
15. Why does the conductivity of a solution decrease with dilution ?
16. Suggest a way to determine the λ_m^0 value of water.
17. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given λ_m^0 (H^+) = 349.6 Scm^2mol^{-1} and λ_m^0 ($HCOO^-$) = 54.6 Scm^2mol^{-1}.
18. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?
19. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?
20. Suggest a list of metals that are extracted electrolytically.
21. Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$. What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?
22. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.
23. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.
24. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

NCERT : Exercise Questions

1. Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn.
2. Given standard electrode potentials, $K^+|K = -2.93$ V, $Ag^+|Ag = 0.80$ V, $Hg^{2+}|Hg = 0.79$ V $Mg^{2+}|Mg = -2.37$ V, and $Cr^{3+}|Cr = -0.74$ V. Arrange these metals in their increasing order of reducing power.
3. Depict the galvanic cell in which the reaction; $Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show:
    (i) Which of the electrode is negatively charged?
    (ii) The carriers of the current in the cell.
    (iii) Individual reaction at each electrode.
4. Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
    (i) $2Cr_{(s)} + 3Cd^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Cd$
    (ii) $Fe^{2+}_{(aq)} + Ag^+_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$

    Calculate the ΔG^0 and equilibrium constant of the reactions.

5. Write the Nernst equation and emf of the following cells at 298 K:
   - (i) $Mg_{(s)}|Mg^{2+}(0.001M)||Cu^{2+}(0.0001\ M)|Cu_{(s)}$
   - (ii) $Fe_{(s)}|Fe^{2+}(0.001M)||H^{+}\ (1M)|H_2\ _{(g)(1bar)}|\ Pt_{(s)}$
   - (iii) $Sn_{(s)}|Sn^{2+}(0.050\ M)||H^{+}\ (0.020\ M)|H_2\ _{(g)\ (1\ bar)}|Pt_{(s)}$
   - (iv) $Pt_{(s)}|Br^{-}\ (0.010\ M)|Br_2\ _{(l)}||H^{+}\ (0.030\ M)|\ H_2\ _{(g)\ (1\ bar)}|Pt_{(s)}$.

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

   $$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^{-}_{(aq)}$$

   Determine ΔG^0 and E_{cell} for the reaction.

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

8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

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

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

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

   Calculate λ_m for all concentrations and draw a plot between λ_m and c½. Find the value of λ_m^0.

11. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If λ_m^0 for acetic acid is 390.5 Scm^2mol^{-1}, what is its dissociation constant?

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

13. How much electricity in terms of Faraday is required to produce
   - (i) 20.0 g of Ca from molten $CaCl_2$?
   - (ii) 40.0 g of Al from molten Al_2O_3 ?

14. How much electricity is required in coulomb for the oxidation of
   - (i) 1 mol of H_2O to O_2 ?
   - (ii) 1 mol of FeO to Fe_2O_3 ?

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

16. Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

17. Using the standard electrode potentials given in electrochemical series, predict if the reaction between the following is feasible:
   - (i) $Fe^{3+}_{(aq)}$ and $I^{-1}_{(aq)}$
   - (ii) $Ag^{+}_{(aq)}$ and $Cu_{(s)}$
   - (iii) $Fe^{3+}_{(aq)}$ and $Br^{-1}_{(aq)}$
   - (iv) $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$
   - (v) $Br_{2\ (aq)}$ and $Fe^{2+}_{(aq)}$.

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

NCERT : Examplar

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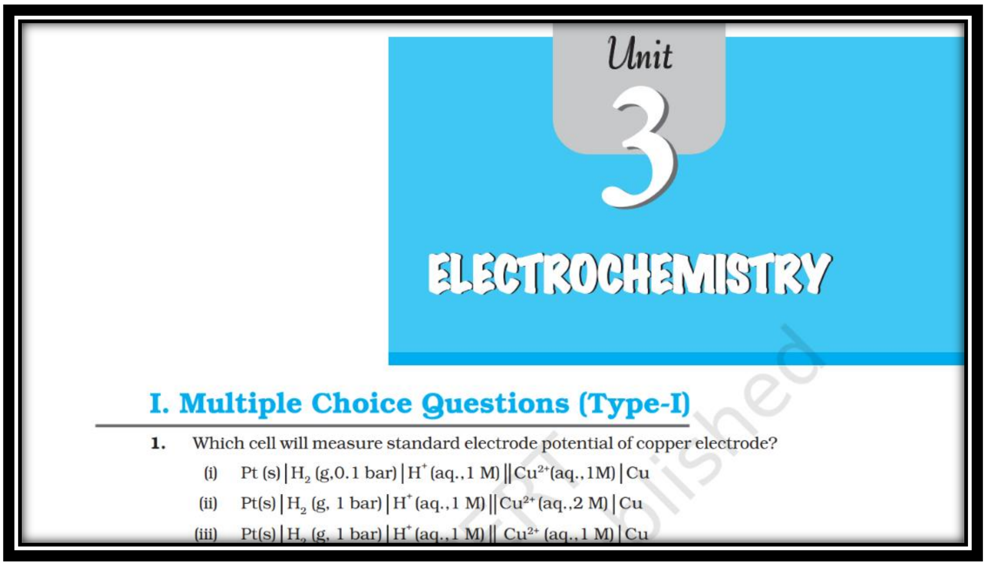

Unit
3
ELECTROCHEMISTRY

I. Multiple Choice Questions (Type-I)

1. Which cell will measure standard electrode potential of copper electrode?
   - (i) $Pt(s)|H_2(g, 0.1\ bar)|H^+(aq., 1\ M)||Cu^{2+}(aq., 1M)|Cu$
   - (ii) $Pt(s)|H_2(g, 1\ bar)|H^+(aq., 1\ M)||Cu^{2+}(aq., 2\ M)|Cu$
   - (iii) $Pt(s)|H_2(g, 1\ bar)|H^+(aq., 1\ M)||Cu^{2+}(aq., 1\ M)|Cu$

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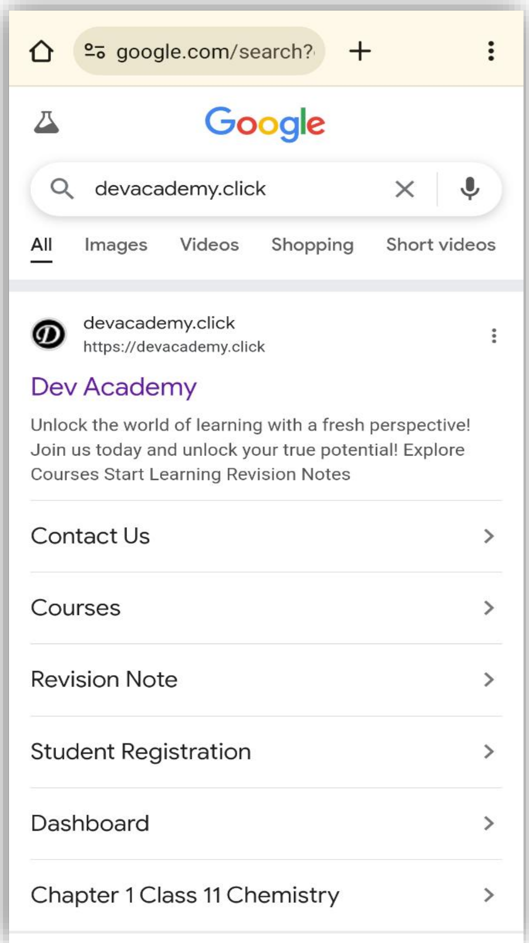

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