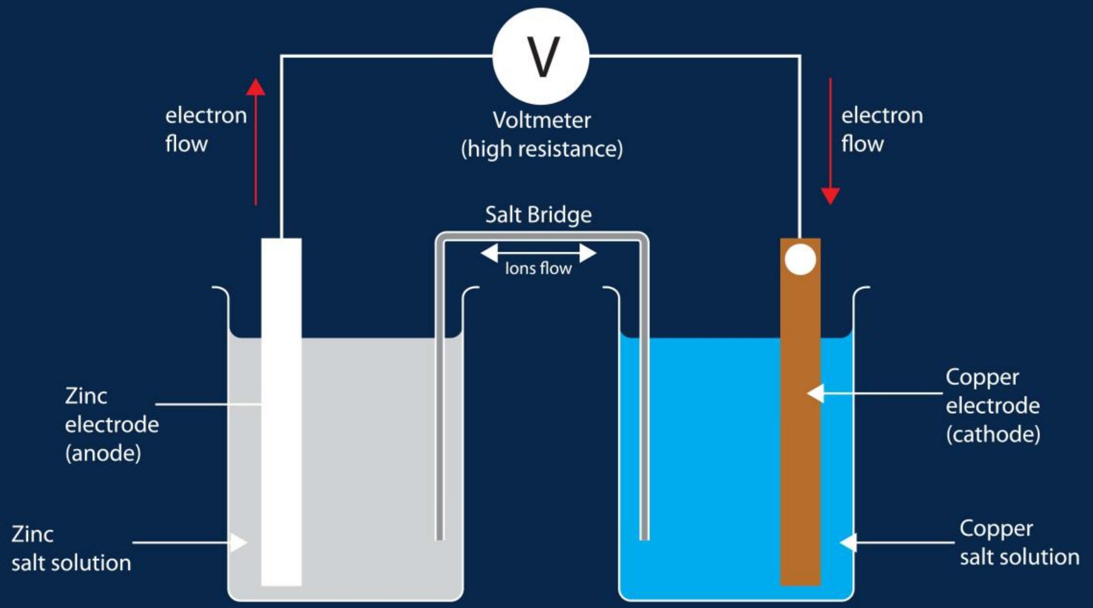
ELECTROCHEMISTRY- L4



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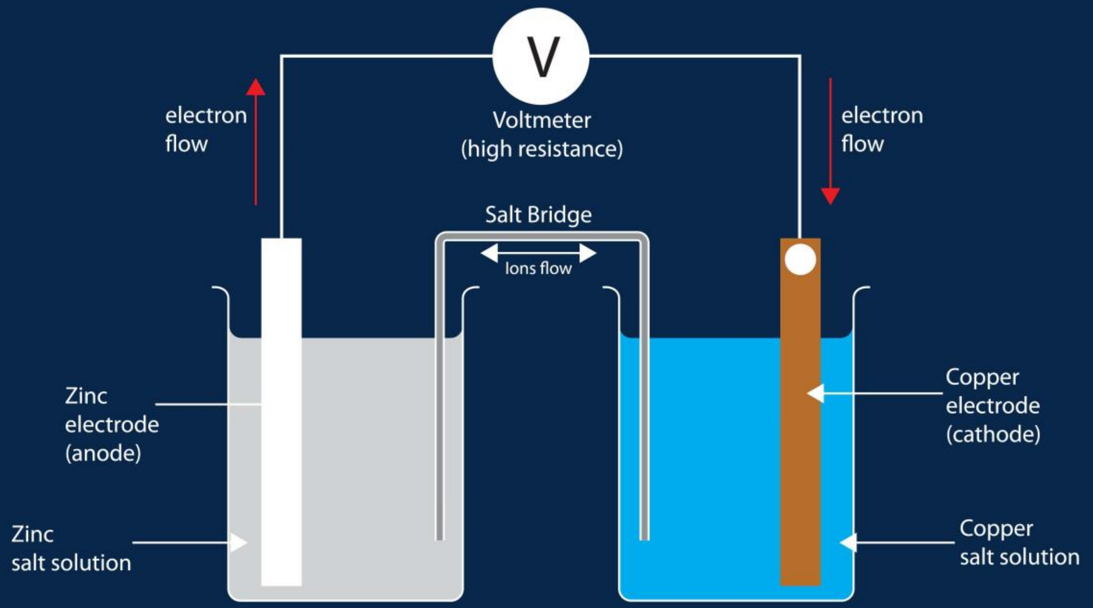

CHEMISTRY

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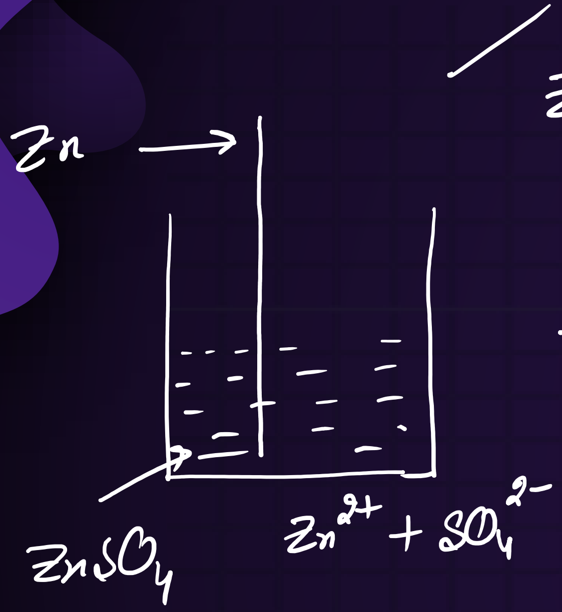
Electrochemical Cell



$Zn^{2+}_{aq} + \underset{\substack{\uparrow \\ \text{from rod}}}{2e^-} \longrightarrow Zn_{(s)}$

Reduction → rod gets positive charge
solution will have excess negative

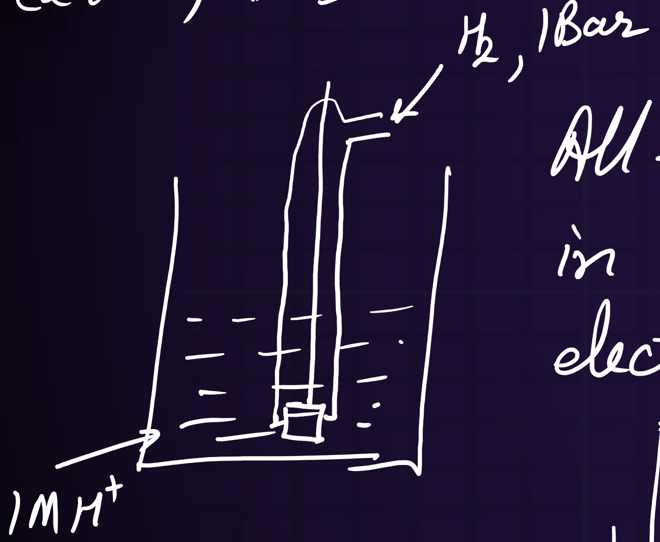
$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + \underset{\substack{\uparrow \\ \text{to rod}}}{2e^-}$

Oxidation → Rod gets negative charge
solution will be positive.

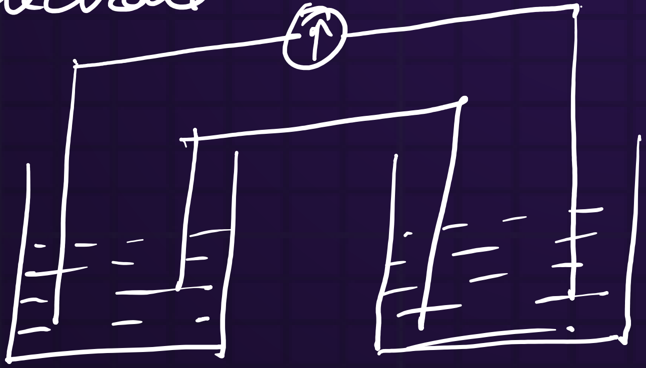
The potential difference created when an electrode is dipped in an electrolyte solution is termed electrode potential. It is at equilibrium so no actual current flows due to this potential. The absolute value of this potential cannot be determined. It can only be compared

Electrochemical Cell

- For comparison, the electrode used is called standard hydrogen electrode SHE. It is a platinised platinum electrode dipped in 1 molar H^+ solution. under a constant 1Bar H_2 pressure maintained at a constant temperature (298K). It has been arbitrarily given an electrode potential of 0 Volts for all temperatures



All electrode potentials are determined in comparison to standard hydrogen electrode.



If an electrode shows oxidation, that is
SHE has negative charge compared to H-electrode

That electrode has a negative electrode potential

Electrochemical Cell

Electrode potential or cell potential is not of any element, compound or solution. It is of a reaction. redox reaction.

half reaction → reduction or oxidation

If a substance can show more than one reaction, it will have more than one potentials.

For comparisons, we always consider reduction reactions.

$H^+_{aq} + e^- \longrightarrow \frac{1}{2}H_2(g)$, Reduction ✓

$\frac{1}{2}H_2(g) \longrightarrow H^+_{(aq)} + e^-$ Oxidation

Electrochemical Cell

Salt bridge → saturated solution of a strong electrolyte (salt) supported on an inert medium (agar agar, silica gel, gelatin)

1. Ions of electrolyte must not react with any electrolyte in half cell.
2. The ions must have similar mobility.

cation	anion
K^+	Cl^-
NH_4^+	NO_3^-
	SO_4^{2}

6 salts

Functions of salt bridge

1. Completes the circuit

Electrochemical Cell

2. Maintains electroneutrality of solutions by providing opposite charged ions.
3. Prevents mixing of electrolytes.

Electrochemical Cell

standard electrode potential → E° → Potential of an electrode compared to standard hydrogen electrode when concentration of each reacting ion is 1 molar and the partial pressure of each reacting gas is 1 Bar at 298 K.

Reduction potential can be positive or negative.

E° positive → The substance is easier to reduce compared to H^+. So it is a stronger oxidizing agent than H^+

More positive is the reduction potential, stronger oxidising agent is the substance.

Electrochemical Cell

Negative reduction potential means the substance is more difficult to reduce compared to H^+. This means the reduced specie is easier to oxidise compared to H_2

$$\underset{\uparrow \text{ difficult to reduce}}{Zn^{2+}_{(aq)}} + 2e^- \longrightarrow \underset{\uparrow \text{ is easier to oxidize}}{\underline{\underline{Zn_{(s)}}}} \qquad E^0_{Zn^{2+}/Zn} = -0.76\,V$$

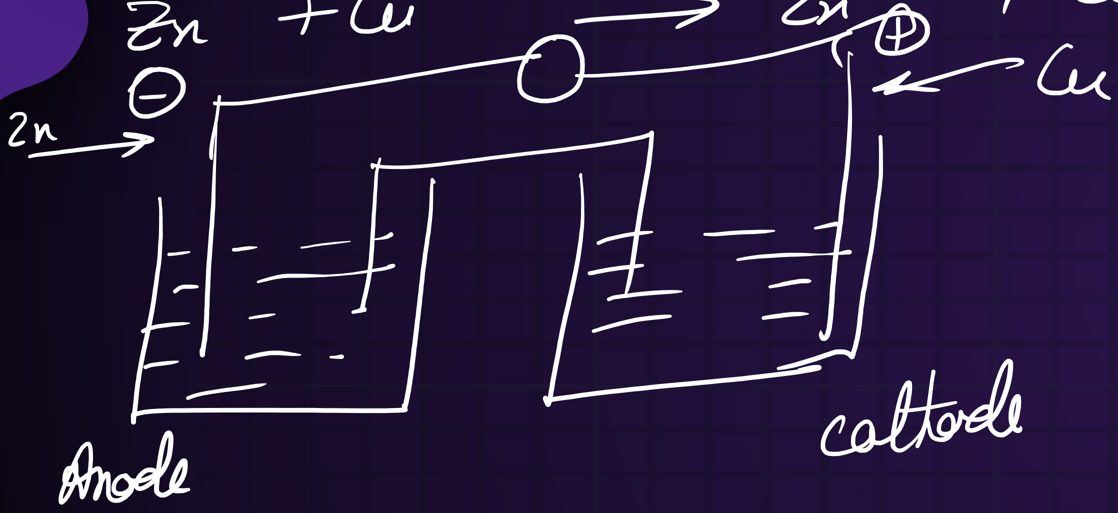
So the reduced specie is a stronger reducing agent.

Electrochemical Cell

cell reaction → actual reaction taking place in the cell

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

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



Cell representation gives flow of positive charge through the cell.

The electrode where oxidation takes place is called Anode and is always placed on left. In electrochemical cells anode is negative.

Electrochemical Cell

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

$$= E^\circ_{Right} - E^\circ_{left}$$

Electrochemical Cell

An electrochemical cell consists of **two electrodes** or **metallic conductors** in contact with an **electrolyte**, which is an **ionic conductor** (a solution, liquid, or solid).

Electrochemical Cell

An electrode and its electrolyte comprise an **electrode compartment** (half-cell).

The two electrodes may share the **same compartment.**

Galvanic Cell

Galvanic Cell

Spontaneous redox reaction is used here to produce **electricity**.

Example	**Daniel cell**

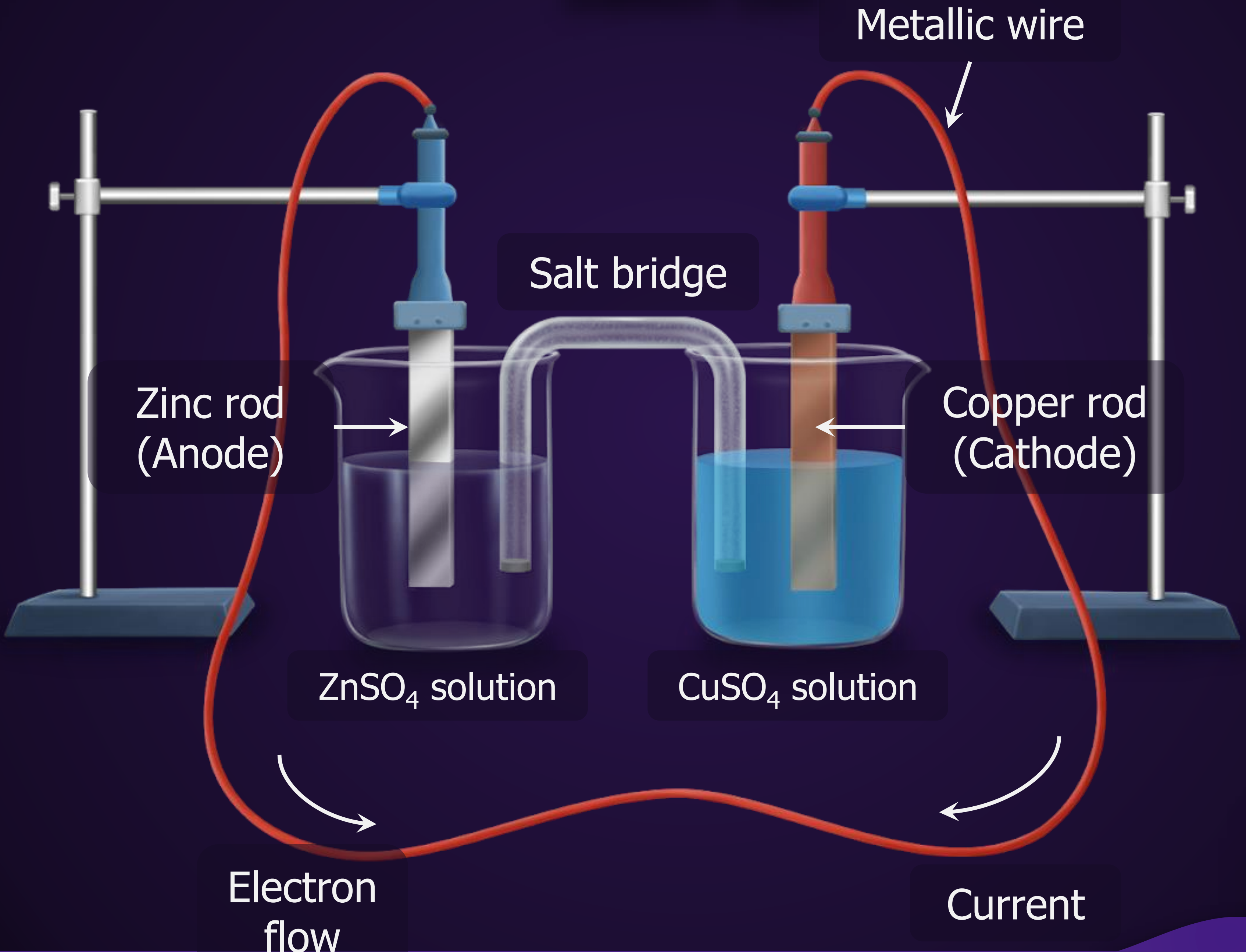
Daniell Cell

It is built using **two electrodes**

Zn rod dipped in **$ZnSO_4$** solution.

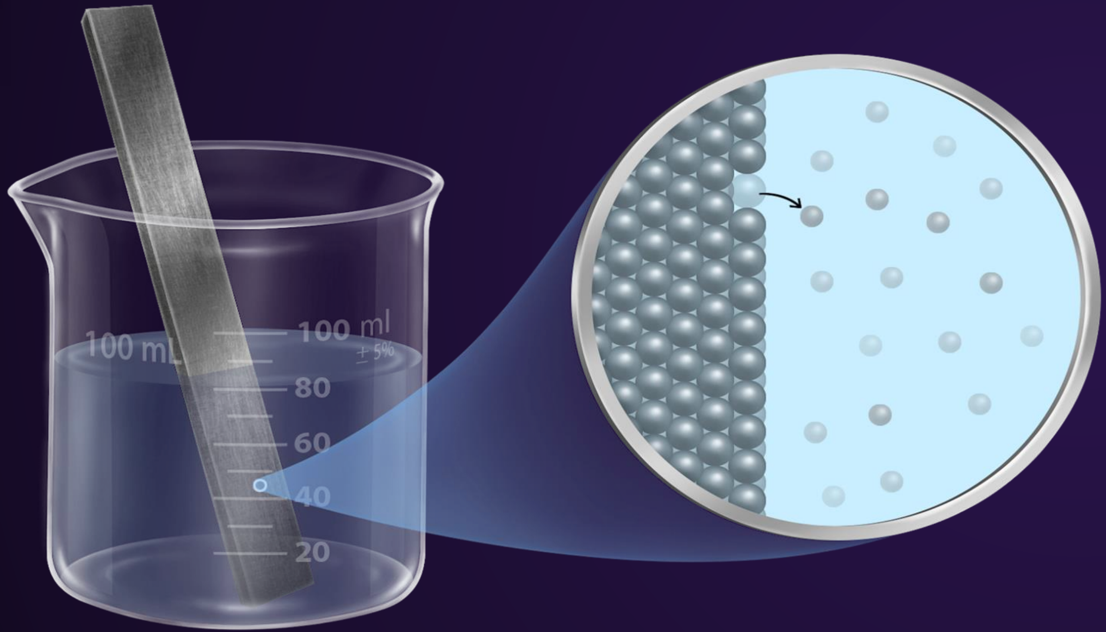
Cu rod dipped in **$CuSO_4$** solution.

Daniell Cell



Daniel Cell

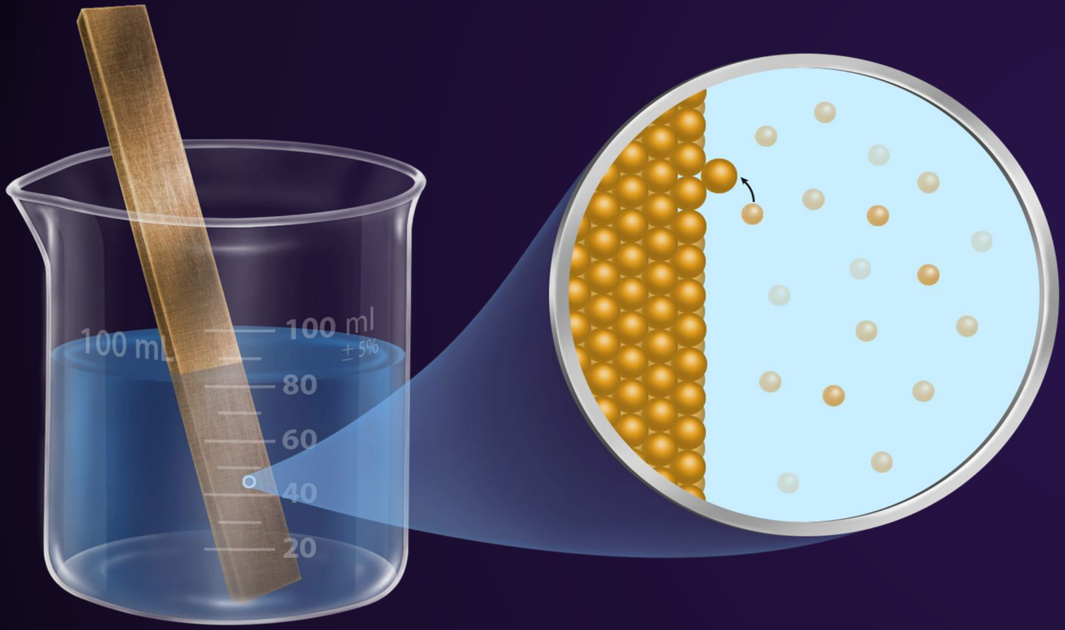
Zn atoms will move in the solution to form **Zn^{2+} ions**



$$Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^{-}$$

Daniell Cell

Cu^{2+} ions will get deposited to form **Cu atoms**



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

Daniell Cell

An **electrical double layer** is developed in the system and hence, a potential difference is created between the rod and the solution.

Known as **electrode potential**

Characteristics of Anode in Daniel Cell

Oxidation takes place at **anode**.

It acts as a **source of electrons**.

It has **negative polarity**.

The electrode potential is **represented** by → $E_{Zn/Zn^{2+}}$

Characteristics of Cathode in Daniel Cell

Reduction takes place at **cathode**.

It acts as a **sink of electrons**.

It has **positive polarity**.

The electrode potential is **represented** by → $E_{Cu^{2+}/Cu}$

Daniel Cell

On joining the metal strips through a **wire** (of negligible resistance)

The **current flows** as long as the potential difference exists between the metal phase and the liquid phase.

Why?

The **current** is generated,
but it is **not sustainable.**

Anode

Zn atoms will move in the solution to form **Zn^{2+} ions**

After some time, an **equilibrium** will be established

$$Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2e^{-}$$

Anode

Accumulation of extra **positive charge** in the solution

Will **not allow** extra **Zn^{2+} ions to move** in the solution

The solution will be **saturated** with Zn^{2+} ions

Cathode

Cu^{2+} ions will get deposited on the electrode to form **Cu atoms**

After some time, an **equilibrium** is established

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

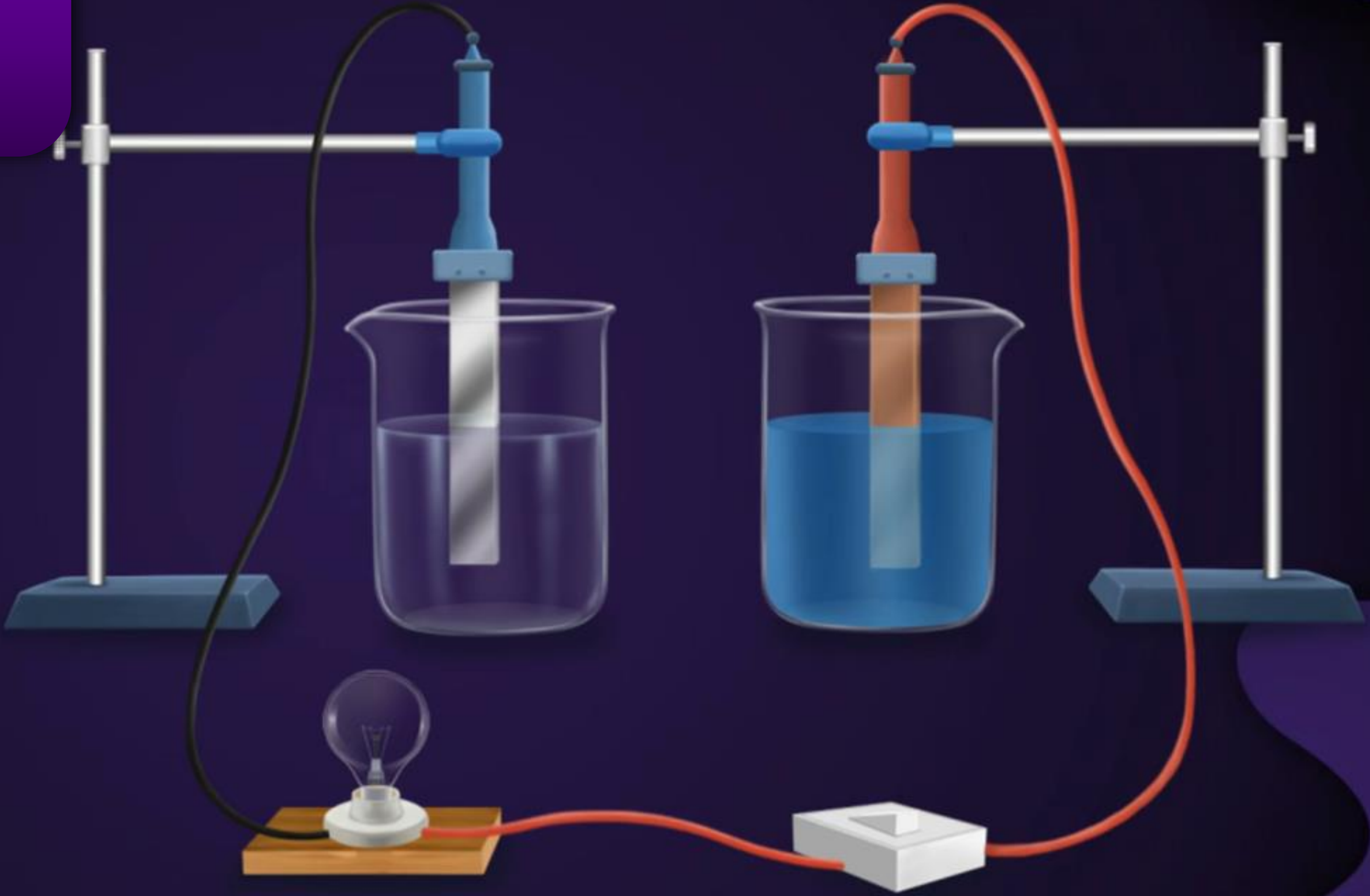
Cathode

Accumulation of sufficient **positive charge** on the rod

↓

Will **not allow** extra Cu^{2+} ions to get deposited

How can we get sustainable current?



Salt Bridge

U-shaped inverted tube that contains **a gel** permeated with an **inert electrolyte** (E.g.: potassium chloride in agar jelly).

Functions of Salt Bridge

1 It **connects** the solution of two half-cells to complete the circuit.

2 It maintains the **electrical neutrality** of the solution in order to give a **continuous** flow or generation of current.

3 It ensures that the two electrolytic solutions **do not mix,** but a **slight diffusion** of ions from one electrode to another is **possible**.

Functions of Salt Bridge

The **simultaneous electrical neutrality** of the anodic oxidation chamber and cathodic reduction chamber is due to:

The **same ionic mobility** or velocity of K^+ and $N\bar{O}_3$ ions taken into the salt bridge

Note

Salt bridge is **not required** for a galvanic cell in which a common electrolyte of anode half and cathode half is present.

Example **Concentration cell**

In a galvanic cell, the salt bridge:

a Does not participate chemically in the cell reaction

b Stops the diffusion of ions from one electrode to another

c Is necessary for the occurrence of the cell reaction

d Ensures mixing of the two electrolytic solutions

Electrode Potential

Whenever a **metal strip** is put in an electrolyte

A potential difference is developed between the **metal electrode** and **its ions** in solution.

Electrode Potential

Oxidation Potential (O.P.)

$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^{-}$ $\quad E_{Zn/Zn^{2+}}$

Greater the O.P., greater will be the tendency to get **oxidised**.

Electrode Potential

Reduction Potential (R.P.)

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $\quad E_{Cu^{2+}/Cu}$

Greater the R.P., greater will be the tendency to get **reduced**.

Note

The **potential difference** developed between the **metal electrodes** and the **solution of its ions** at **1 M concentration** and **1 bar pressure** at a particular temperature is known as **standard electrode potential (E^0).**

Standard Electrode Potential

Electrode reaction in standard conditions	Representation
Reduction: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	$E^0_{Zn^{2+}/Zn}$ (SRP)
Oxidation: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$	$E^0_{Zn/Zn^{2+}}$ (SOP)

Cell Potential

The driving force that pushes the electrons away from the anode and pulls them towards the cathode is an electrical potential called electromotive force, also known as **cell potential** or **the cell voltage.**

Unit: Volt

Did You Know?

Electromotive force of a cell is equal to the **potential difference** between its terminals when **no current** is passing through the circuit.

Calculation of E_{cell}

	Electrode reaction	**$\Delta_r G$**
1	**Anode**: $A\,(s) \rightarrow A^{n+}\,(aq) + ne^-$	$\Delta_r G_1 = -nFE_{A/A^{n+}}$
2	**Cathode**: $B^{m+}\,(aq) + me^- \rightarrow B\,(s)$	$\Delta_r G_2 = -mFE_{B^{m+}/B}$

Multiply eq. (1) by **m**, & eq. (2) by **n,** and then add both the equations.

Calculation of E_{cell}

Cell reaction	**Δ_rG**
$mA\,(s) + nB^{m+}\,(aq) \xrightarrow[(s)]{} mA^{n+}\,(aq) + nB$	Δ_rG_3

$$\Delta_rG_3 = m\,\Delta_rG_1 + n\,\Delta_rG_2$$

Calculation of E_{cell}

$$\Delta_r G_3 = m\,\Delta_r G_1 + n\,\Delta_r G_2$$

$$-nmFE_{cell} = -nmFE_{A/A^{n+}} - nmFE_{B^{m+}/B}$$

$$E_{cell} = E_{A/A^{n+}} + E_{B^{m+}/B}$$

Calculation of E_{cell}

When **reduction potential** of both electrodes are taken into account:

E_{cell} = Reduction potential of cathode – Reduction potential of anode

$$E_{cell} = E_{red}\,(\text{cathode}) - E_{red}\,(\text{anode})$$

Calculation of E_{cell}

$$\Delta_r G_3 = m\,\Delta_r G_1 + n\,\Delta_r G_2$$

$$-nmFE_{cell} = -nmFE_{A/A^{n+}} - nmFE_{B^{m+}/B}$$

$$E_{cell} = E_{A/A^{n+}} + E_{B^{m+}/B}$$

Calculation of E_{cell}

When **reduction potential** of both electrodes are taken into account:

E_{cell} = Reduction potential of cathode – Reduction potential of anode

$$E_{cell} = E_{red}\,(\text{cathode}) - E_{red}\,(\text{anode})$$

E_{cell} of Daniell Cell

$$E_{cell} = E_{Cu^{2+}/Cu} + E_{Zn/Zn^{2+}}$$

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

E_{cell} of Daniell Cell

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$$

$$E^0_{cell} = 0.34\ V - (-0.76\ V)$$

$$E^0_{cell} = \mathbf{1.1\ V}$$

Given: $E^0_{(Cu^{2+}/Cu)} = 0.337$ V and $E^0_{(Sn^{2+}/Sn)} = -0.136$ V. Which of the following statements is correct?

- a Cu^{2+} can be reduced by H_2 (g)
- b Cu can be oxidised by H$^+$
- c Sn^{2+} can be reduced by H_2 (g)
- d Cu can reduce Sn^{2+}

Given:

(i) $Cu^{2+} + 2e^- \longrightarrow Cu$; $E^0 = 0.337$ V

(ii) $Cu^{2+} + e^- \longrightarrow Cu^+$; $E^0 = 0.153$ V

The electrode potential, E^0 for the reaction,

$Cu^+ + e^- \longrightarrow Cu$, will be:

(NEET 2009)

a 0.90 V	b 0.30 V
c 0.38 V	d 0.52 V

A button cell used in watches functions as following:

$Zn\ (s) + Ag_2O\ (s) + H_2O\ (\ell) \rightleftharpoons 2Ag\ (s) + Zn^{2+}\ (aq) + 2OH^-\ (aq)$

If half cell potentials are:

$Zn^{2+}\ (aq) + 2e^- \longrightarrow Zn\ (s);\ E^0 = -0.76\ V$

$Ag_2O\ (s) + H_2O\ (\ell) + 2e^- \longrightarrow 2Ag\ (s) + 2OH^-\ (aq);\ E^0 = 0.34\ V$

The cell potential will be:

(NEET 2013)

a 0.84 V

b 1.34 V

c 1.10 V

d 0.42 V

“Stay Positive, Work Hard. Make It Happen!”

THANK YOU