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Aakash + BYJU'S LIVE

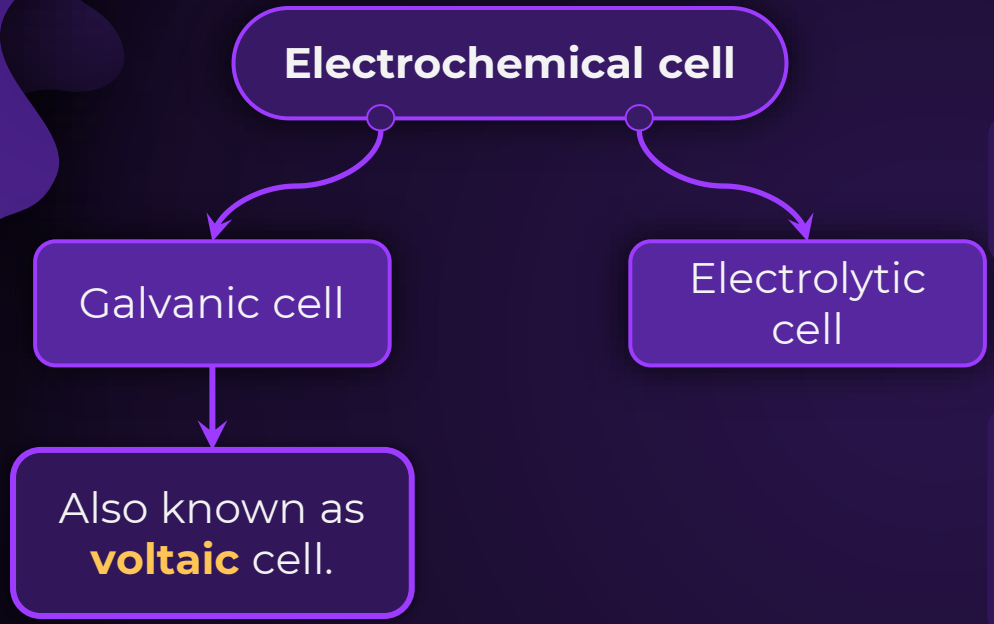
Electrochemistry

Electrochemistry

The area of chemistry concerned with the **interconversion** of chemical energy and electrical energy.

Electrochemical Cell

The devices which **convert electrical energy into chemical energy** or **vice versa.**



Example

A **battery** is an electrochemical cell

It takes the energy released by a **spontaneous** chemical reaction and uses it to **produce electricity**.

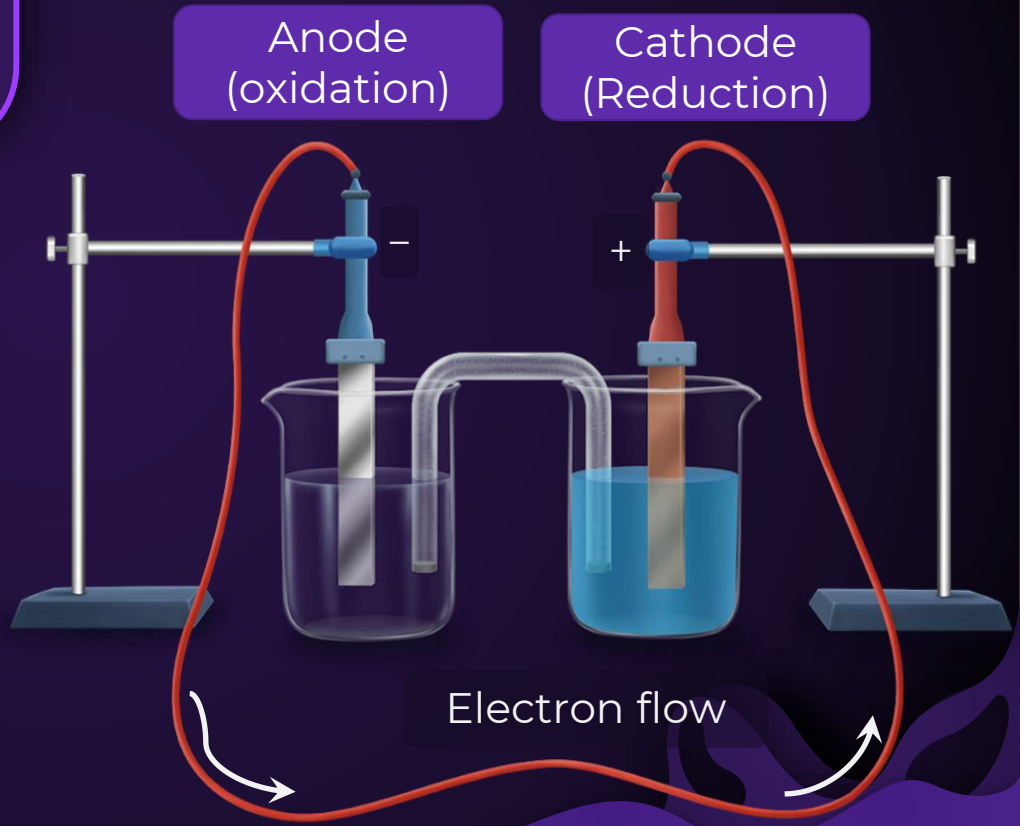
Galvanic Cell

A galvanic cell is an **electrochemical cell** that produces **electricity** as a result of the **spontaneous reaction** occurring inside it.

$\Delta_r G < 0$

Example	**Daniel cell**

Chemical energy is converted into **electrical energy**.

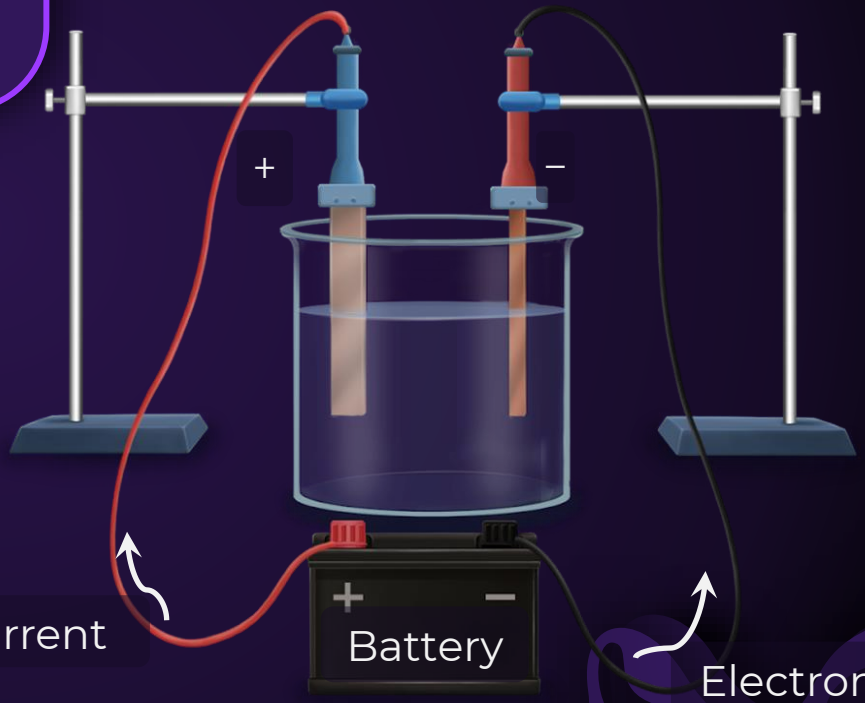


Electrolytic Cell

An electrolytic cell is an electrochemical cell in which a **non-spontaneous reaction** is driven by an **external source** of current.

$\Delta_r G > 0$

Electrical energy is converted into **chemical energy**.



Important Points

1. Galvanic and electrolytic cells are **reverse** of each other.

2. **Redox reactions** are involved in both cells.

Redox Couple

Any redox reaction may be expressed as the **difference of two half-reactions,** which are conceptual reactions showing **gain and loss of electrons**, i.e., reduction and oxidation, respectively.

The reduced and oxidised species in a half-reaction form a **redox couple.**

Reduction

Redox couple	Half-reaction
M^+/M	$M^+ (aq) + e^- \longrightarrow M (s)$

Oxidation

Redox couple	Half-reaction
M/M^+	$M (s) \longrightarrow M^+ (aq) + e^-$

Electrochemical Cell

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

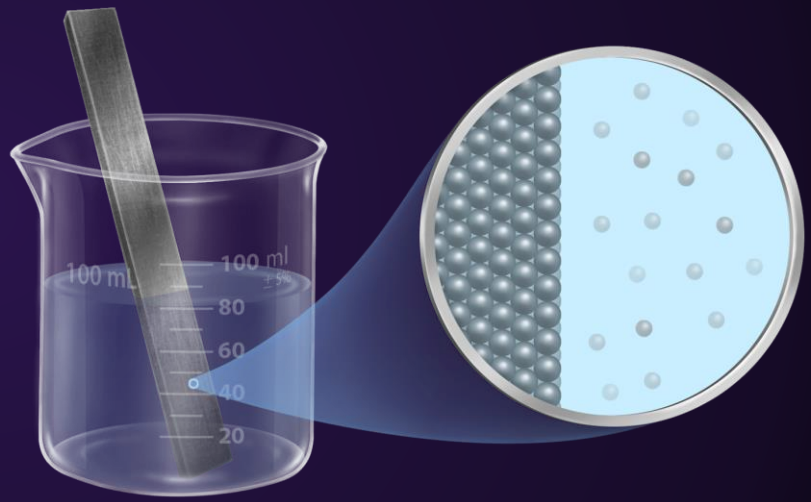
An electrode and its electrolyte comprise an **electrode compartment** (half cell).The two electrodes may share the **same compartment.**

Half Cell

Whenever a **metal strip** is put in an electrolyte, the process of **oxidation or reduction** takes place within the system.

Some reactive metals have a tendency to go into the **solution phase,** when placed in contact with their ions or their salt solution, it is called **oxidation.**

Example



Zn rod in $ZnSO_4$ solution

Electrode Potential

Electrode Potential:

Whenever a **metal strip** is put in an electrolyte, a **potential difference** developed between **metal electrode** and **its ions** in solution.

Oxidation Potential (O.P.)

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

Electrode potential can be either **oxidation potential** or **reduction potential.**

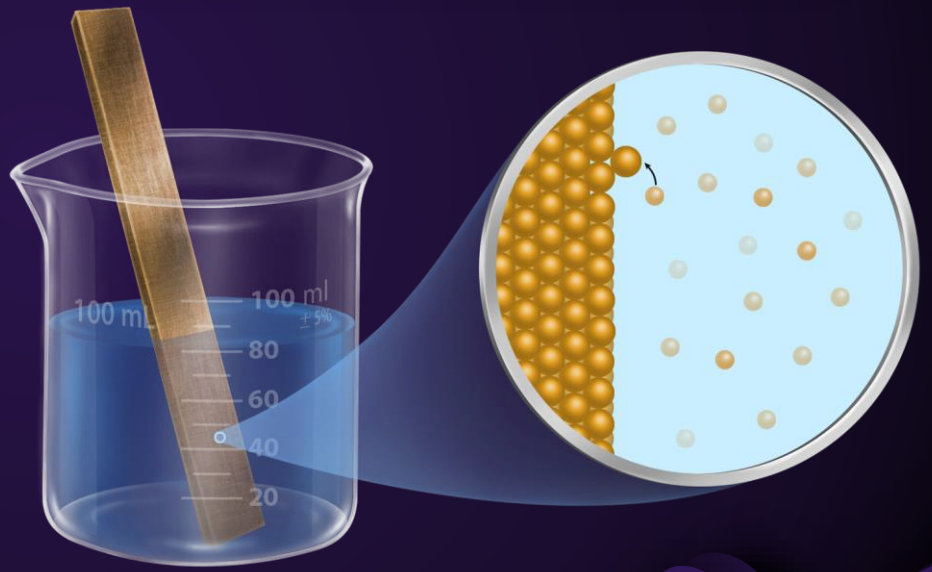
Greater the O.P., greater will be the tendency to get **oxidised**.

Electrode Potential

Some metals (Cu, Ag, Au, etc.) when in contact with their ions in the solution have a tendency to get **deposited** on the **metal rod.**

Reduction

Cu rod in $CuSO_4$ solution



Electrode Potential

Reduction Potential (R.P.)

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

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

Standard Electrode Potential

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

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

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

Cell Potential

E^{0}_{cell} = SRP of substance reduced − SRP of substance oxidised

SRP stands for standard reduction potential which measures the tendency for a given chemical species to be reduced.

E^{0}_{cell} is a positive number

The sign of the cell potential tells us the direction in which the reaction must shift to reach equilibrium.

Cell Potential

Reactions for which E° cell is positive.

Have equilibrium constants that favor the formation of the products of the reaction.

Occurs naturally and referred to as **spontaneous** reaction.

The magnitude of the cell potential

is a measure of the driving force behind a reaction. The larger the value of the cell potential.

The farther is the reaction from **equilibrium.**

Relation between $\Delta_r G$ and E_{cell}

From thermodynamics

$$dG = dW_{non\text{-}exp} + VdP - SdT$$

Maximum non-expansion (electrical) work that a system (the cell) can do is equal to decrease in Gibbs free energy

At constant T & P

$$\int dG = \int dW_{non\text{-}exp}$$

$$W_{e,\,max} = |\Delta G|$$

$$|\Delta G| = W_{non\text{-}exp,\,max.}$$

ΔG identified with the Gibbs energy of the cell reaction, $\Delta_r G$

Relation between $\Delta_r G$ and E_{cell}

Maximum electrical work obtained from a cell = $|\Delta_r G|$

1 F = Charge present on 1 mole of electron

$\Delta_r G$ = $-q \times V$ = **$-nFE$**

= 96,485 C/mol

≈ 96,500 C/mol

where, F is Faraday's constant
n = Number of moles of electron
E = Electrode potential or cell EMF
$\Delta_r G$ = Change in Gibbs energy for half-cell or cell

Relation between $\Delta_r G$ and E_{cell}

By knowing the $\Delta_r G$ at a specified composition, the **cell emf** at that composition can be stated.

Spontaneous cell reaction	$\Delta_r G < 0$	$E_{cell} > 0$
Non-spontaneous cell reaction	$\Delta_r G > 0$	$E_{cell} < 0$

Calculation of E_{cell}

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

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

$mA(s) + nB^{m+}(aq) \longrightarrow mA^{n+}(aq) + nB(s)$	$\Delta_r G_3$

Cell reaction	$\Delta_r G$

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

Calculation of E_{cell}

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

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

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

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

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

E_{cell} = **E_{red} (cathode)** − **E_{red} (anode)**

The **difference** in electrode potentials of the two half-cell reactions (oxidation half-cell and reduction half-cell) is known as **emf of the cell** or **cell potential**.

Electrode potential **depends** on:

1. **Concentration** of solution
2. Nature of **metal**
3. Nature of the **electrolyte**
4. **Pressure, temperature** conditions

Electrode potential or cell potential are **intensive** properties and **does not depend** on:

1. **Amount** of solution
2. **Thickness** of metal rod/plate/wire, etc.
3. Stoichiometric variation of a given cell reaction

$A^{2+}(aq) + 2e^- \longrightarrow A(s)$, E = x volt

$2A^{2+}(aq) + 4e^- \longrightarrow 2A(s)$, E = x volt

Electrode Potential

The potential of a **single electrode** **cannot** be determined. But the potential difference between **two electrodes** can be **measured accurately**.

The potential of an electrode is calculated using a **reference electrode**.

An electrode is chosen as a **reference** with respect to which all other electrodes are valued.

Standard Hydrogen Electrode (**SHE**) is taken as standard reference electrode.

Its electrode potential is arbitrarily assumed to be **0.00 volt**.

Electrode Potential

Electrode potential of SHE at

Anode

$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

O.P. = E_{H_2/H^+}

Under **standard state,**

S.O.P. = $E^0_{H_2/H^+}$

Cathode

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

R.P. = E_{H^+/H_2}

Under **standard state,**

S.R.P. = $E^0_{H^+/H_2}$

Reference Potential

Electrode potential of **SHE** is taken to be **zero** at all temperature.

S.O.P. = -S.R.P. = **0**

Calculation of Standard Electrode Potential

(at 298 K experimentally)

To calculate standard potential of any other electrode, it is **coupled with SHE**

Its **potential is measured** and that gives the value of standard electrode potential of that electrode.

Example

Construct a cell

Anode	**Zinc electrode**	Cathode	**SHE**

E^{0}_{cell} = 0.76 V

Example

$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$

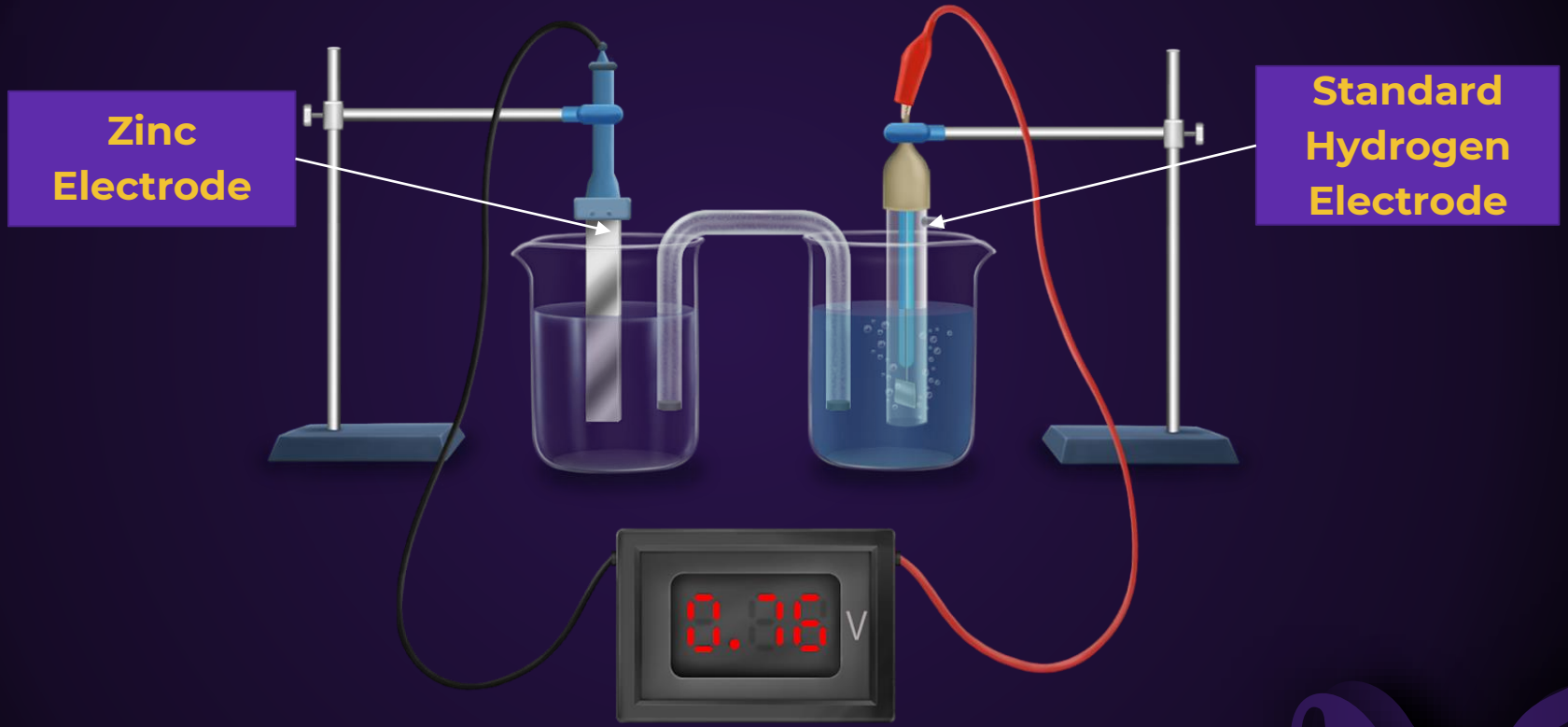
$0.76 = 0 - E^0_{Zn^{2+}/Zn}$

$E^0_{Zn^{2+}/Zn} = -0.76\ V$

$E^0_{Zn/Zn^{2+}} = 0.76\ V$

W.r.t. H_2, Zn has greater tendency to get **oxidised**.

Measuring SRP of Zinc Electrode



Standard Electrode Potential

Similarly, **SRP** (at 298 K) for many other electrodes are calculated.

They are arranged in an decreasing order series known as **electrochemical series.**

Electrochemical Series

Standard reduction potentials (**SRP**) for various half-cells are measured at 25℃ **w.r.t. SHE**

These SRP are arranged in an **decreasing order**

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	2.87 V
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	1.81 V
$H_2O_2(l) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	1.78 V
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	1.40 V
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	1.36 V
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33 V
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	1.23 V
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.23 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	1.09 V
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	0.97 V
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	0.92 V
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80 V
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2$	0.68 V
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	0.54 V
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	0.52 V
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	0.34 V
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	0.22 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$AgBr\ (s) + e^- \longrightarrow Ag\ (s) + Br^-\ (aq)$	0.10 V
$2H^+\ (aq) + 2e^- \longrightarrow H_2\ (g)$	**0.00 V**
$Pb^{2+}\ (aq) + 2e^- \longrightarrow Pb\ (s)$	−0.13 V
$Sn^{2+}\ (aq) + 2e^- \longrightarrow Sn\ (s)$	−0.14 V
$Ni^{2+}\ (aq) + 2e^- \longrightarrow Ni\ (s)$	−0.25 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44 V
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74 V
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76 V
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83 V
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66 V

Electrochemical Series

Half-reaction	SRP, E^0 (at 298 K)
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.36 V
$Na^{+}(aq) + e^- \longrightarrow Na(s)$	−2.71 V
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87 V
$K^{+}(aq) + e^- \longrightarrow K(s)$	−2.93 V
$Li^{+}(aq) + e^- \longrightarrow Li(s)$	−3.05 V

Application of Electrochemical Series

(i) Species (particularly metals) having **highly negative SRP** are powerful **reducing agents**.

Examples | Li, Na, Ca etc.

(ii) Species having **highly +ve SRP** are powerful **oxidising agents**.

Examples | F_2, MnO_4^- etc.

Application of Electrochemical Series

(iii) **More active** metals can **displace less active** metals from their salt solution

$CuSO_4$ (aq) + Zn (s) ⟶ Cu (s) + $ZnSO_4$ (aq)

$ZnSO_4$ (aq) + Cu (s) ⟶ No reaction

(iv) **Oxides** of **active** metals are **thermally stable**.

Examples: Na_2O, Al_2O_3, CaO

Application of Electrochemical Series

(v) **Oxides** of **less active** metals are **thermally less stable**.

$$Ag_2O\,(s) \xrightarrow{\Delta} 2Ag\,(s) + \frac{1}{2}O_2\,(g)\uparrow$$

$$HgO\,(s) \xrightarrow{\Delta} Hg\,(l) + \frac{1}{2}O_2\,(g)\uparrow$$

Galvanic Cell

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

Example | **Daniell cell**

Daniell cell

It is built by **two electrodes**

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

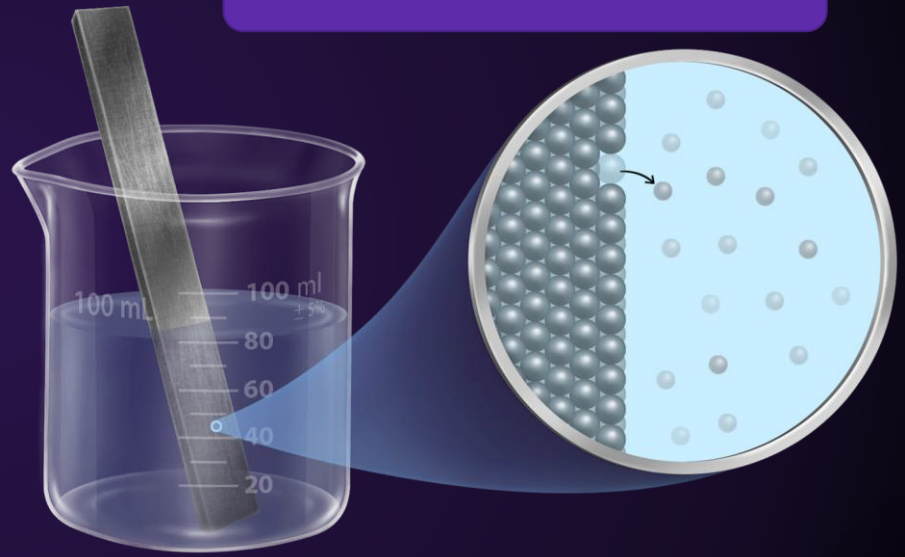
Cu rod dipped in **$CuSO_4$** solution

Daniell Cell

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

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

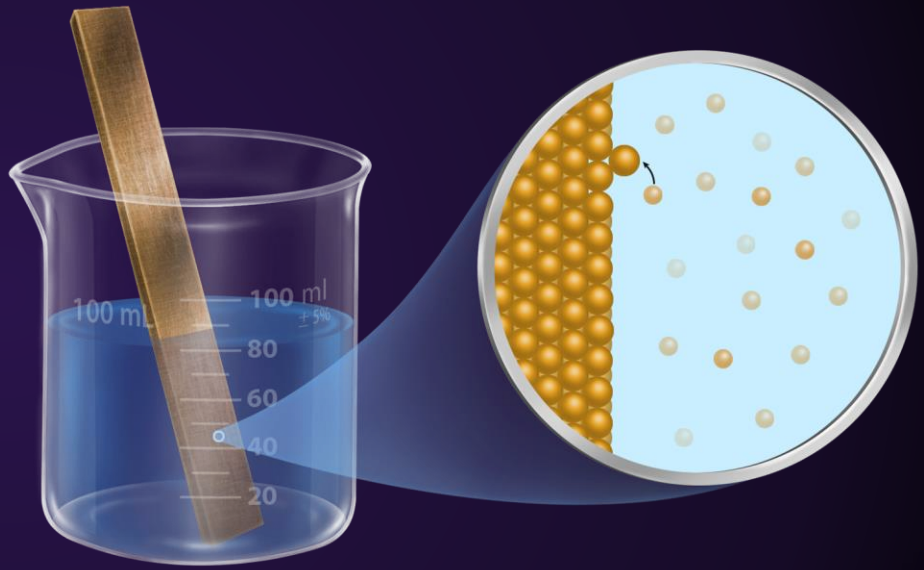
Zn rod in $ZnSO_4$ solutions



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

Daniell Cell

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



Cu^{2+} (aq) + $2e^-$ → Cu (s)

Daniell Cell

From electrochemical series,

$E^0_{Cu^{2+}/Cu} > E^0_{Zn^{2+}/Zn}$

Construct a cell

- Anode — **Zn half-cell**
- Cathode — **Cu half-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.

Anode

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

After some time, **equilibrium** is established

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

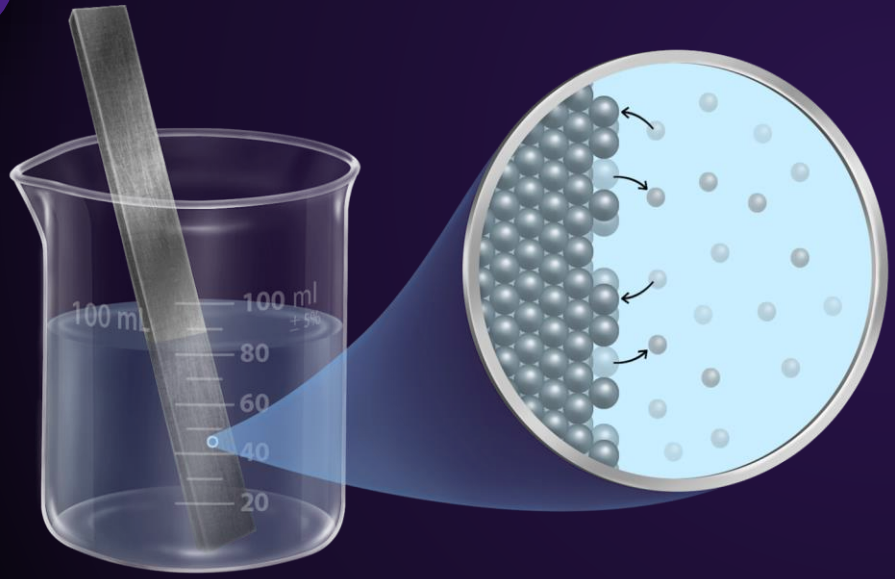
Accumulation of extra **positive charge** in the solution

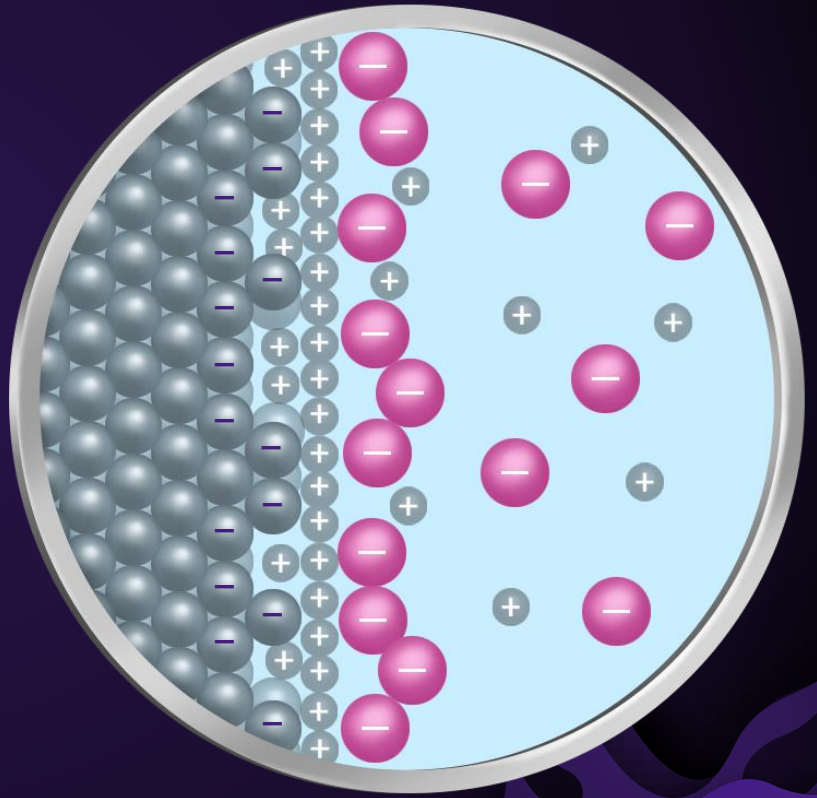
Will **not allow** extra **zinc ions to move** in the solution.

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

Anode

Dynamic equilibrium





Cathode

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

After some time, **equilibrium** is established

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

Accumulation of sufficient **positive charge** on the rod will **not allow** extra copper ions to get deposited.

Anode

Oxidation takes place at **anode**.

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

It has **negative polarity**.

The electrode potential is **represented** by

$E_{Zn/Zn^{2+}}$

Cathode

Reduction takes place at **cathode**.

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

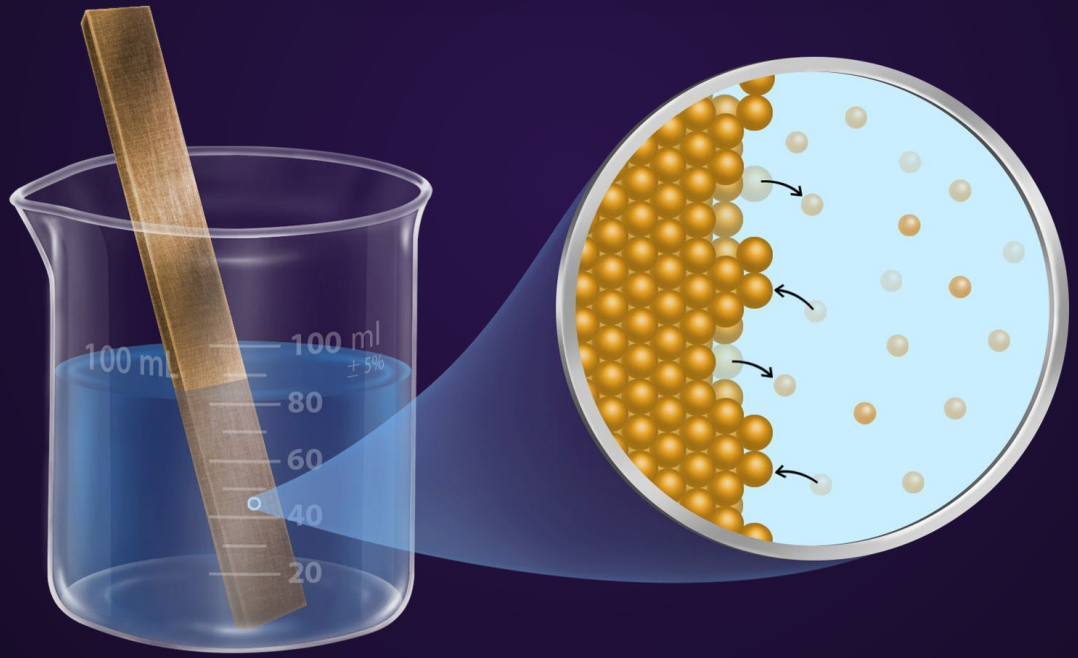
It has **positive polarity**.

The electrode potential is **represented** by

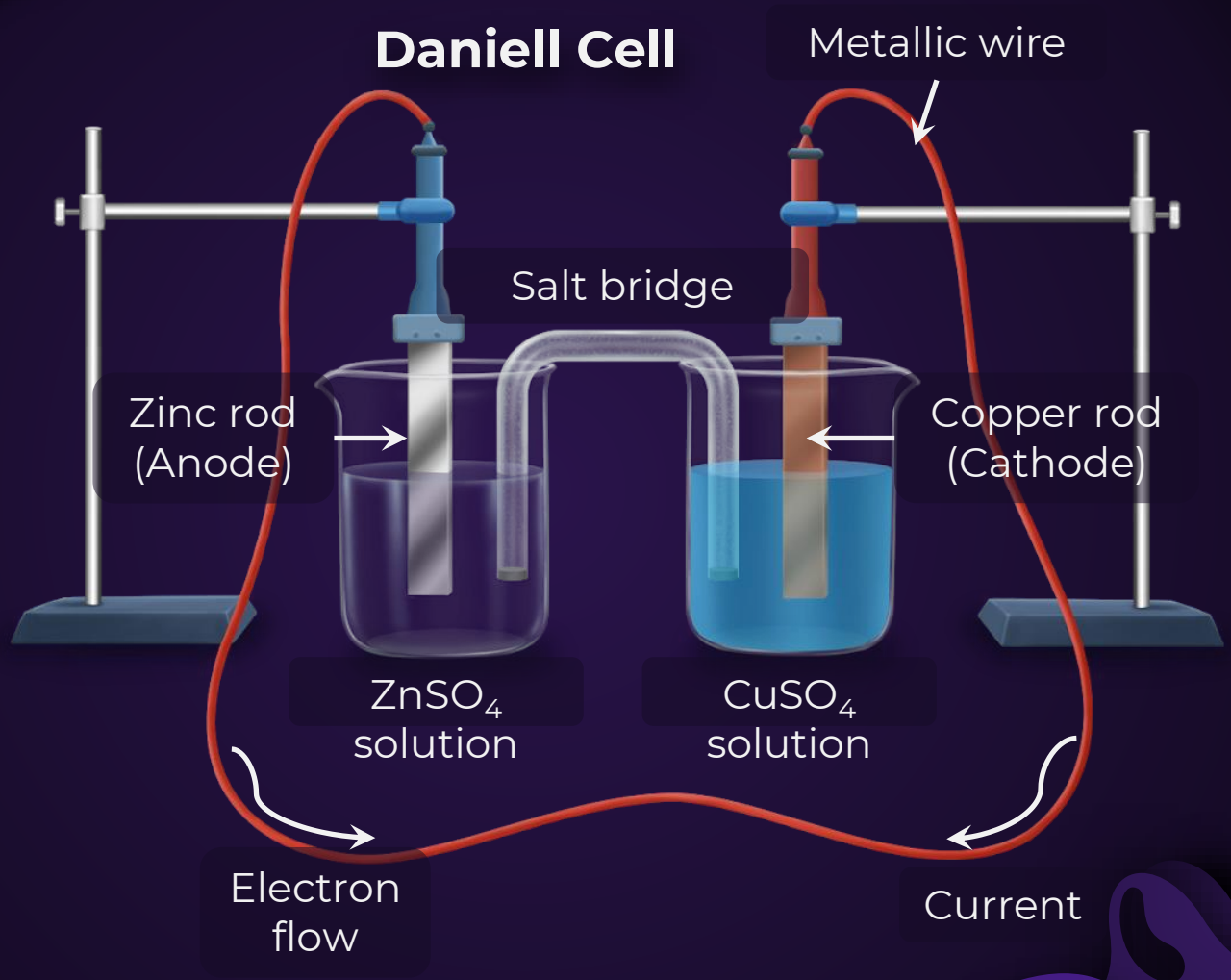
$E_{Cu^{2+}/Cu}$

Cathode

Dynamic equilibrium



Daniell Cell



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 **minimises** the **liquid junction potential**.

Liquid Junction Potential

In a cell, if two electrolytic solutions of **different concentrations** are in contact with each other,

↓

A **potential difference** develops across the boundary of the two solutions.

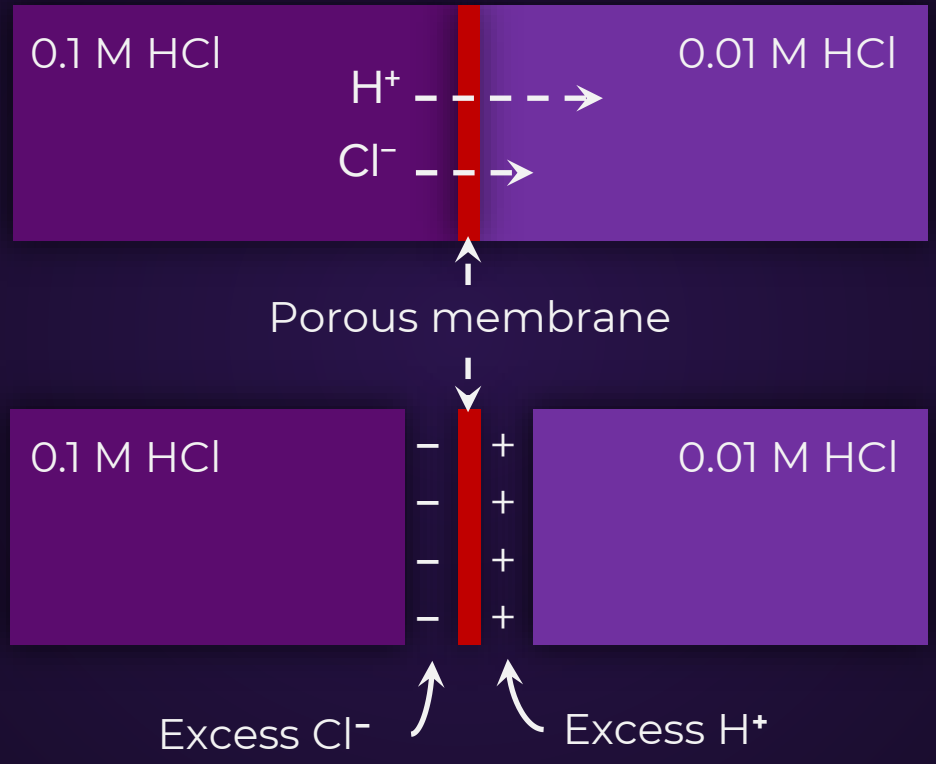
↓

This potential difference is known as the **liquid junction potential**.

It arises because of the **difference in the rates of diffusion** of positive and negative ions from more concentrated solution to less concentrated solution.

Ions of salt bridge electrolyte diffuse through the gel-like solution and **minimise** the liquid junction potential.

Example


0.1 M HCl
0.01 M HCl
H+
Cl−
Porous membrane
0.1 M HCl
0.01 M HCl
Excess Cl-
Excess H+

Functions of Salt Bridge

3

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

4

Ensures that the two electrolytic solutions **do not mix** but **slight diffusion** of ions from one electrode to another is **possible**.

The **simultaneous electrical neutrality** of the anodic oxidation chamber and cathodic reduction chamber is due to the **same mobility** or velocity of K^+ and NO_3^- ions taken into salt bridge.

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

Selection of Electrolyte for Salt Bridge

Generally tube is filled with a paste of **agar-agar powder** with a natural electrolyte

Generally, **not common** to anodic/cathodic compartment with porous plugs at each mouth of tube.

The electrolyte in **salt bridge** should be such that, speed of its cation **equals to** the speed of its anion in electrical field.

The ions of the inert electrolyte **do not react** with other ion in the solution.

The ions are **not oxidised or reduced** at the electrodes.

Selection of Electrolyte for Salt Bridge

KCl is generally **preferred** but KNO_3 or NH_4NO_3 can also be used.

If **Ag^+, Hg_2^{2+}, Pb^{2+}, Tl^+** ions are present in a cell, then in salt bridge, **KCl is not used**

Because there can be **formation of precipitate** of AgCl, Hg_2Cl_2, $PbCl_2$ or TlCl at the mouth of the tube which will **prevent** the migration of ions and its functioning will stop.

E_{cell} of Daniell Cell

At Anode

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

$\Delta_r G_1 = -2 \times F \times E_{Zn/Zn^{2+}}$

At Cathode

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

$\Delta_r G_2 = -2 \times F \times E_{Cu^{2+}/Cu}$

E_{cell} of Daniell Cell

Cell reaction

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

$$\Delta_r G_3 = \Delta_r G_1 + \Delta_r G_2$$

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

E_{cell} of Daniell Cell

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

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

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

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

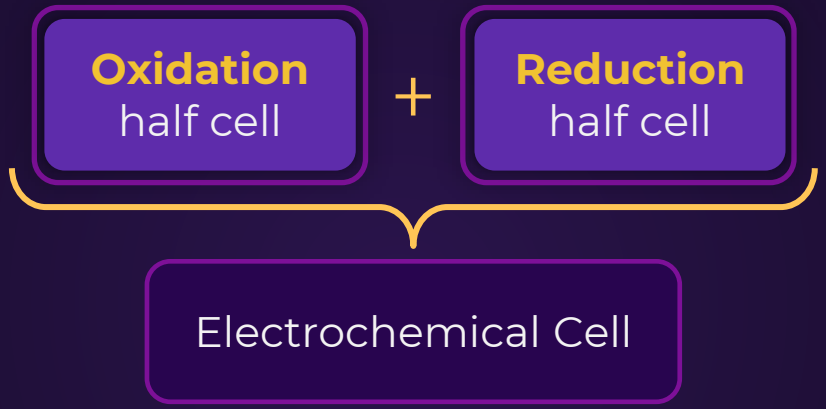
$$E^0_{cell} = 1.1\ V$$

Efficiency of Daniell Cell

$$\text{Efficiency } (\eta) = \frac{|\Delta_r G|}{|\Delta_r H|} \times 100$$

$$= \frac{\text{Maximum electrical work}}{\text{Heat released in reaction}} \times 100$$

Cell Representation



A cell can be **represented** using some universal conventions and notations.

Cell Representation

Rule 1

On the **left** side → **Anode** half cell

On the **right** side → **Cathode** half cell

Rule 2

The **separation** of two phases shown by single **vertical line (|)**

Cell Representation

Rule 3

Various materials present in the same phase are shown together with **comma (,)**

Example

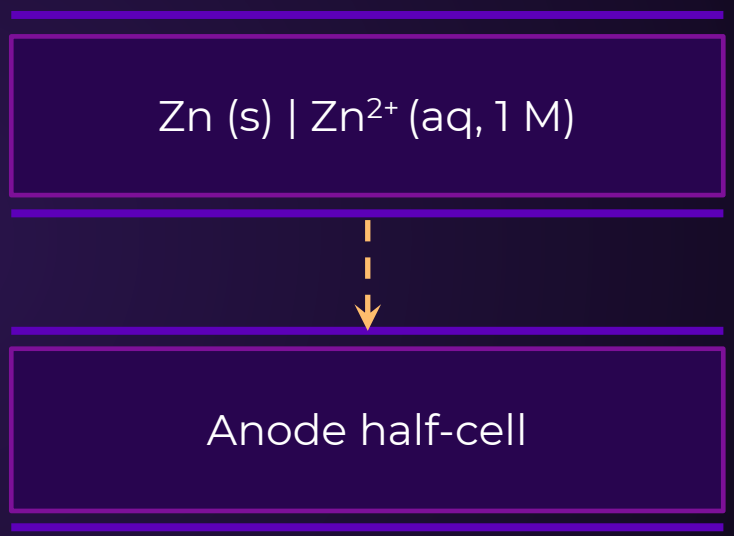
$Sn(s) \mid Sn^{2+}(aq), Sn^{4+}(aq)$

Anode half cell

Cell Representation

The **significant features** of the substance, like pressure of a gas, concentration of ions, etc. is indicated in **brackets** immediately after writing the substance.

Example

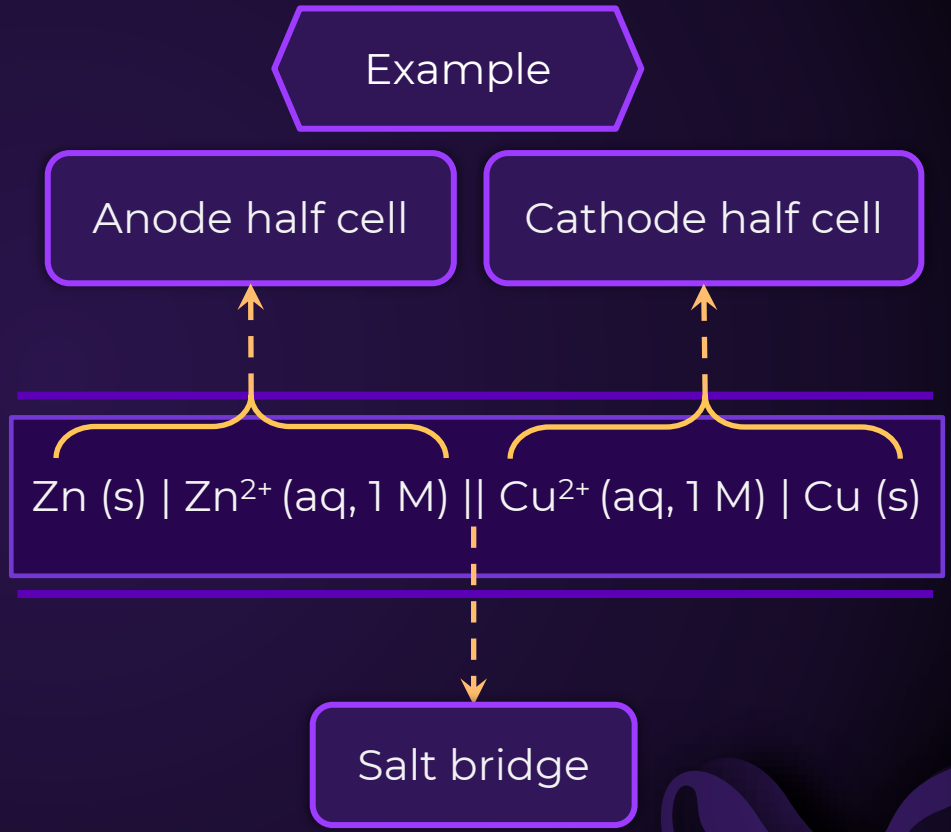


Cell Representation

Rule 4

The **salt bridge** is represented by **double slash (||)**

Example



Cell Representation

Rule 5

For gas electrode

Gas indicated **after** electrode

For **anode**

Gas indicated **before** electrode

For **cathode**

Example

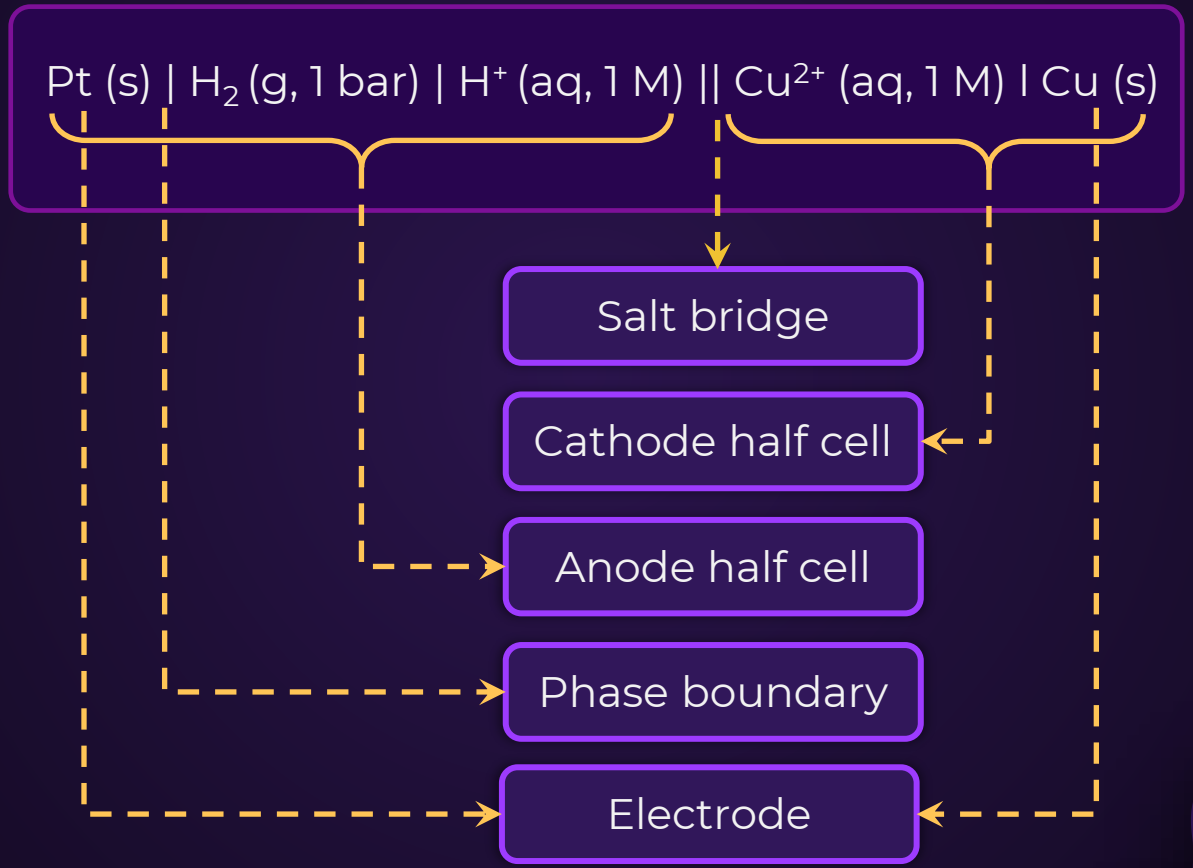
$Pt\ (s) \mid H_2\ (g) \mid H^+\ (aq)$

For **anode**

$H^+\ (aq) \mid H_2\ (g) \mid Pt\ (s)$

For **cathode**

Complete Cell Representation



Factor Affecting Cell Potential

(1) **Temperature**

(2) **Composition** of the reaction mixtures

(3) The **partial pressure** of the gas (if any)

Nernst Equation

The dependence of the concentration and pressure of the gas on the cell potential can be derived from **thermodynamics**.

For any reaction,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q$$

$$-nFE_{cell} = -nFE^0_{cell} + 2.303\ RT \log Q$$

Q - Reaction quotient

Reaction Quotient

For any reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \quad \ldots(1)$$

$$E_{cell} = E^0_{cell} - \frac{2.303\,RT}{nF}\log Q \quad \ldots(2)$$

Nernst equation

Where,
R = Universal gas constant
T = Temperature
n = Number of transferred electrons
F = Faraday's constant
Q = Reaction quotient

Nernst Equation

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log Q$$

$$= E^0_{cell} - \frac{0.059}{n} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

From thermodynamics,

$$\Delta_r G = \Delta_r G^0 + RT \ln Q$$

At **chemical equilibrium**,

$$\Delta_r G = 0$$

$$E_{cell} = 0$$

Cell will be of **no use**

Equilibrium in Electrochemical Cell

$$\Delta_r G^o = -RT \ln K_{eq}$$

$$-nFE^0_{cell} = -2.303\ RT \log (K_{eq})$$

$$E^0_{cell} = \frac{2.303\ RT}{nF} \log K_{eq}$$

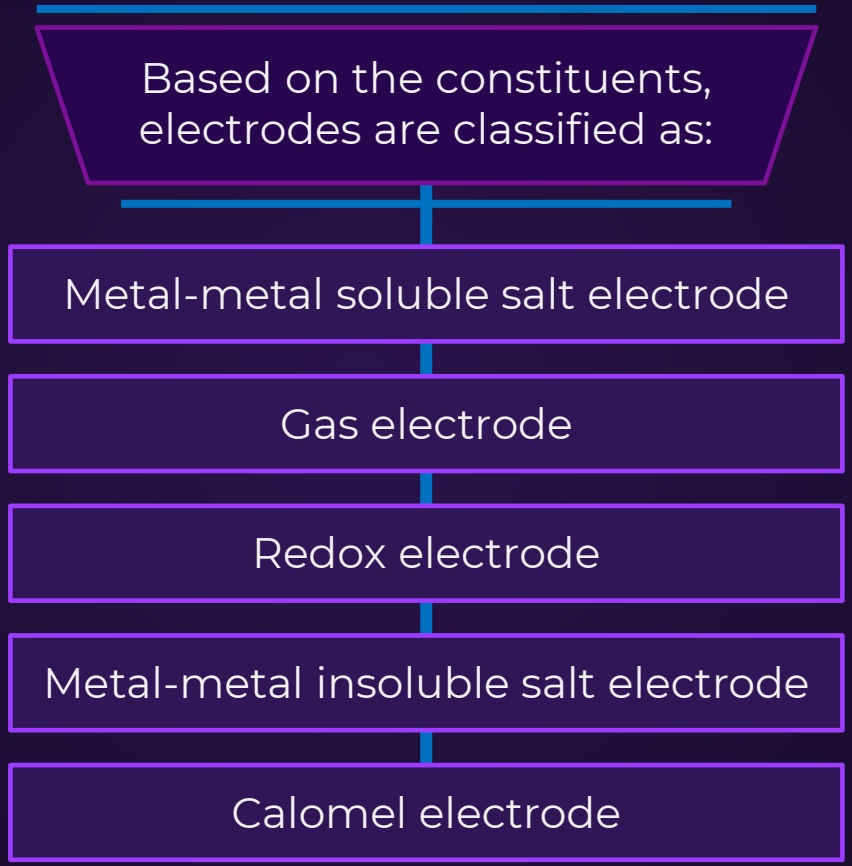
$$\log K_{eq} = \frac{nF}{2.303\ RT} E^0_{cell}$$

Take

T = 298 K,
R = 8.314 J/mol K,
F = 96500 C

$$\log K_{eq} = \frac{n}{0.059} E^0_{cell}$$

Nernst Equation for Different Types of Half-Cells



Metal–Metal Soluble Salt Electrode

Considering a half-cell reaction,

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

Cell representation

$M^{n+}(aq) \mid M(s)$

Nernst equation for the half-cell,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$= E^0_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

Metal–Metal Soluble Salt Electrode

Similarly for oxidation

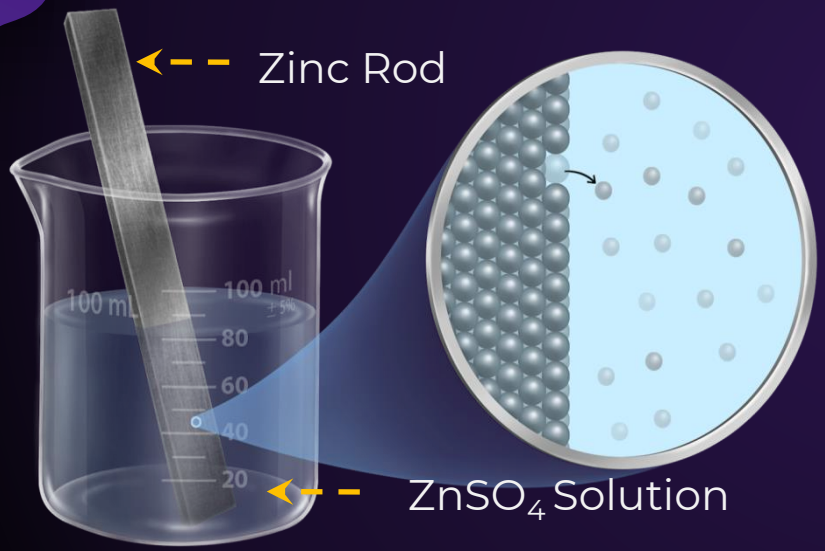
$$B(s) \longrightarrow B^{m+}(aq) + me^{-}$$

$$E_{B/B^{m+}} = E^{0}_{B/B^{m+}} - \frac{2.303RT}{mF} \log[B^{m+}(aq)]$$

Cell representation: **B (s) | B^{m+} (aq)**

Metal–Metal Soluble Salt Electrode

Example



Zinc half-cell,

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

Electrode potential

$$E_{Zn^{2+}/Zn} = E^{0}_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

Cell representation: **Zn^{2+} (aq) | Zn (s)**

Standard Hydrogen Electrode (SHE)

At 298 K

A **platinum foil** (platinum electrode coated with finely powdered Pt black).

Dipped in an **acidic solution of 1 M HCl.**

Pure hydrogen gas is bubbled at **1 bar** into the solution.

Pure H_2 gets **adsorbed** at Pt surface

↓

Which is in contact with H^+ ions in the solution

↓

Reduction or oxidation occurs on **Pt foil**.

Standard Hydrogen Electrode (SHE)

If it acts as **anode**,

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ **SOP = 0**

Cell representation

Pt (s) | H_2 (g, 1 bar) | H^+ (aq, 1 M)

If it acts as **cathode**,

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ **SRP=0**

Cell representation

H^+ (aq, 1 M) | H_2 (g, 1 bar) | Pt (s)

Gas Electrode

Example	**Cl_2 gas** electrode

If it acts as **cathode**

$Pt\ (s)\ |\ Cl_2\ (g)\ |\ Cl^-\ (aq)$

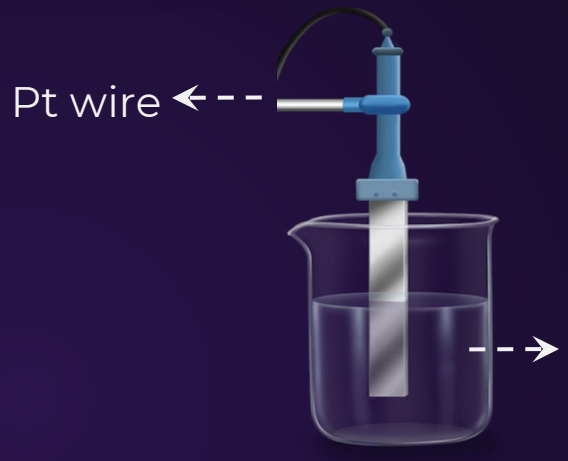
$Cl^-\ (aq)\ |\ Cl_2\ (g)\ |\ Pt\ (s)$

If it acts as **anode**

Redox Electrode

The electrode potential results due to the presence of ions of the **same substance** in **different oxidation states**.

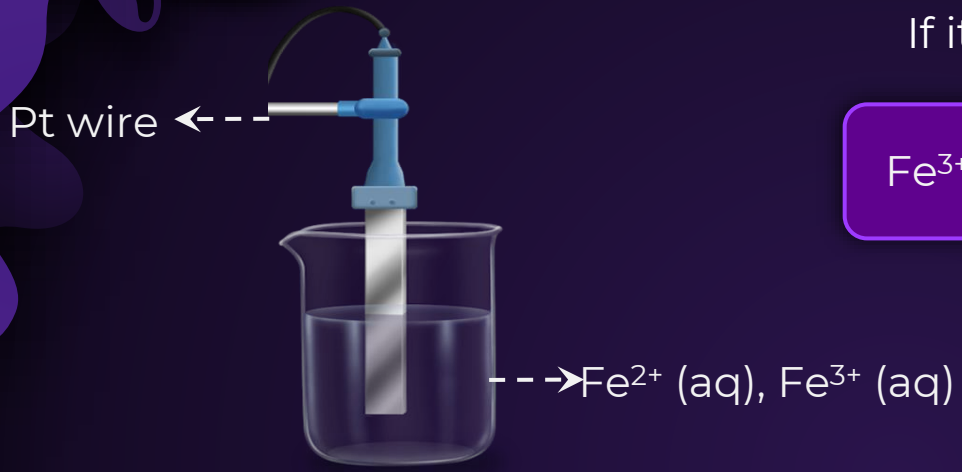
Pt wire is used as **electron carrier**.



If it acts as **anode**,

$$Fe^{2+}\,(aq) \longrightarrow Fe^{3+}\,(aq) + e^{-}$$

Pt (s) | Fe^{2+} (aq), Fe^{3+} (aq)



If it acts as **cathode**,

$$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$$

Fe^{3+} (aq), Fe^{2+} (aq) | Pt (s)

Example:

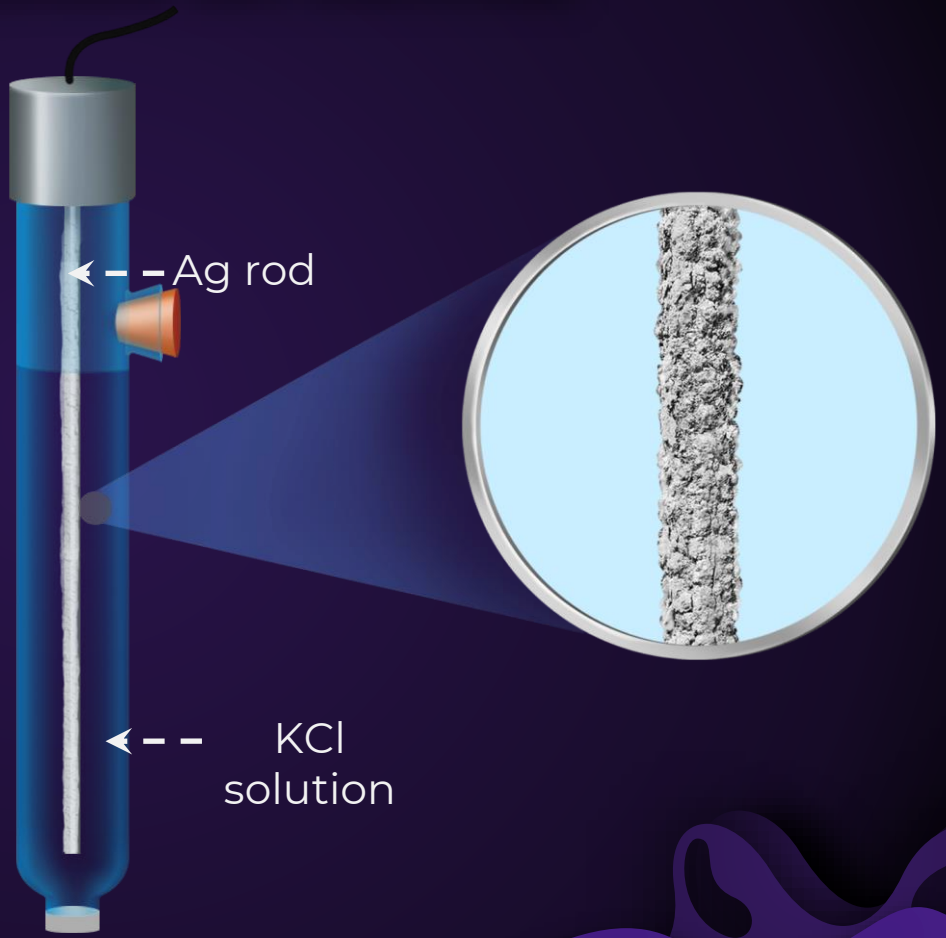
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$E_{MnO_4^-/Mn^{2+}} = E^0_{MnO_4^-/Mn^{2+}} - \frac{0.059}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Metal-Metal Insoluble Salt Electrode

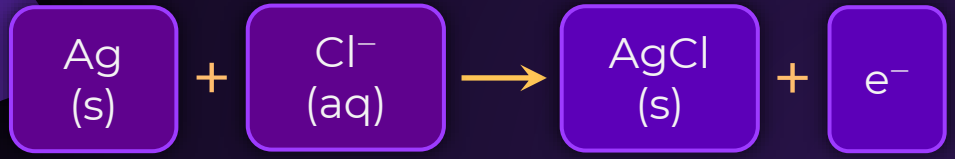
It consists of a **metal rod** coated with metal insoluble salt & dipped into an **aq. solution** containing anion of insoluble salt.

Example:
Ag (s) | AgCl (saturated) in KCl



Metal-Metal Insoluble Salt Electrode

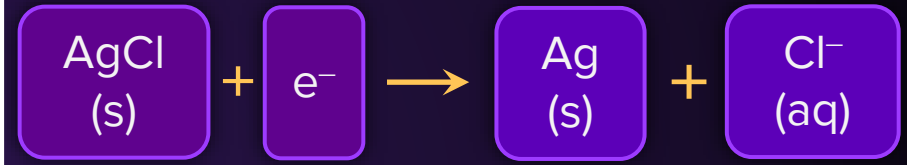
If it acts as **anode**,



Cell representation

Ag (s) | AgCl (s) | Cl^- (aq)

If it acts as **cathode**,



Cell representation

Cl^- (aq) | AgCl (s) | Ag (s)

Determination of E^0_{cell}

Half-cell: Cl^- (aq) | AgCl (s) | Ag (s)

Cell reaction:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad \ldots (1)$$

$$\Delta_r G^0_1 = -2.303RT \log K_{sp}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \quad . (2)$$

$$\Delta_r G^0_2 = -n \times F \times E^0_{Ag^+/Ag}$$

Determination of E^0_{cell}

$$AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-\,(aq) \quad \ldots (3)$$

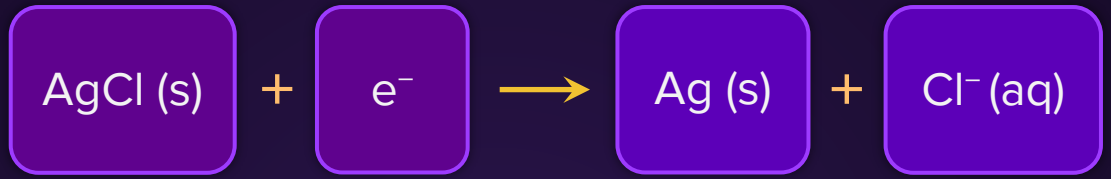
Eq. 3 = Eq. 1 + Eq. 2

Therefore,

$$\Delta_r G^0_3 = \Delta_r G^0_1 + \Delta_r G^0_2$$

$$-nFE^0_{Cl^-/AgCl/Ag} = -nFE^0_{Ag^+/Ag} + (-2.303RT \log K_{sp})$$

Metal-metal Insoluble Salt Electrode

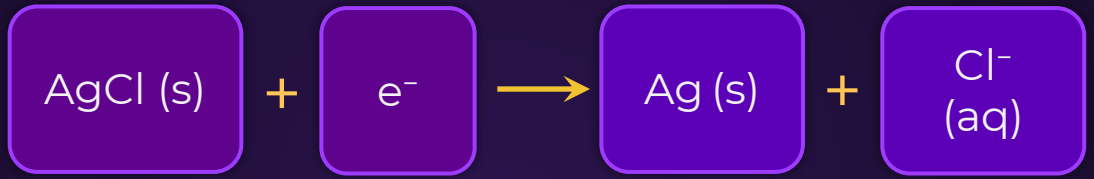


$$E^{0}_{Cl^-/AgCl/Ag} = E^{0}_{Ag^+/Ag} + \frac{2.303RT}{nF} \log K_{sp}$$

Standard half-cell potential of metal-metal insoluble salt half cell.

Determination of E_{cell}

Half-cell reaction



Applying Nernst equation

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - \frac{0.059}{n} \log [Cl^-]$$

Determination of E_{cell}

$$E_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.059}{n} \log K_{sp} - \frac{0.059}{n} \log [Cl^-]$$

$$E_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} - \frac{0.059}{n} \log \frac{[Cl^-]}{K_{sp}}$$

Determination of E_{cell}

Solution is **saturated** w.r.t. AgCl

$$[Ag^+] \times [Cl^-] = K_{sp}\ (AgCl)$$

$$\frac{[Cl^-]}{K_{sp}(AgCl)} = \frac{1}{[Ag^+]}$$

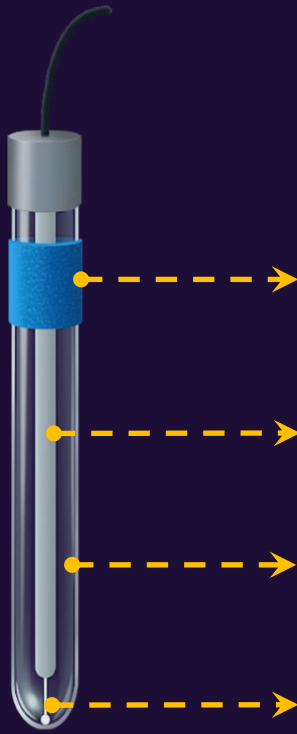
$$E_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} - \frac{0.059}{n} \log \frac{[Cl^-]}{K_{sp}}$$

$$E_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} - \frac{0.059}{n} \log \frac{1}{[Ag^+]}$$

Calomel Electrode

A calomel electrode consists of a **platinum electrode** dipped into **mercury** in contact with calomel (dimercury (I) chloride, **Hg_2Cl_2**) and **KCl** solution. Usually, the solution is saturated with KCl.

The cell has **E^0 = 0.28 V** (with respect of SHE) at 25°C



Calomel Electrode

If it acts as **anode**

$2Hg\ (l) + 2Cl^-\ (aq) \rightarrow Hg_2Cl_2\ (s) + 2e^-$

Cell representation

$Pt\ (s)\ |\ Hg\ (l)\ |\ Hg_2Cl_2(s)\ |\ Cl^-(aq)$

$E^0_{Hg/Hg_2Cl_2/Cl^-}$ = SOP

If it acts as **cathode**

$Hg_2Cl_2\ (s) + 2e^- \rightarrow 2Hg\ (l) + 2Cl^-\ (aq)$

Cell representation

$Cl^-\ (aq)\ |\ Hg_2Cl_2(s)\ |\ Hg\ (l)\ |\ Pt\ (s)$

$E^0_{Cl^-/Hg_2Cl_2/Hg}$ = SRP

Calomel Electrode

$$E_{Cl^-/Hg_2Cl_2/Hg} = E^0_{Cl^-/Hg_2Cl_2/Hg} - \frac{RT}{F} \ln [Cl^-]$$

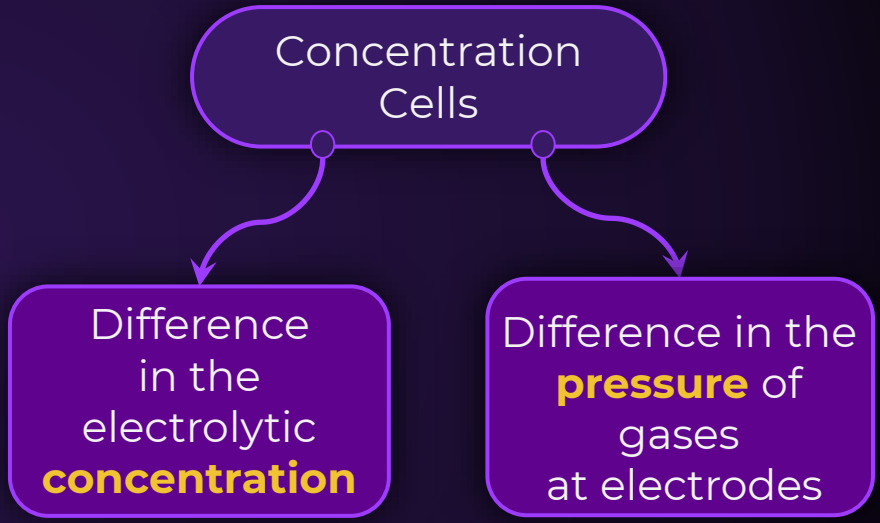
Standard (normal) calomel electrode

When $[Cl^-]$ = **1 M = 1 N**

Concentration Cells

A concentration cell consists of two electrodes of the **same material**, each electrode dipping in a solution of its **own ions**.

Current flows in the outer circuit due to **difference in concentration** of solution or partial pressure of the gases involved.



Concentration Cells

From Nernst equation,

$$E_{cell} = E^{0}_{cell} - \frac{0.059}{2} \log \frac{C_1}{C_2} \quad ...(1)$$

Here, n = 2, T = 298 K

Example

$Cu\ (s)\ |\ Cu^{2+}\ (aq.,\ C_1)\ ||\ Cu^{2+}\ (aq.,\ C_2)\ |\ Cu\ (s)$

Two copper electrodes having Cu^{2+} ions at **different concentrations**.

C_1 & C_2 are concentrations of Cu^{2+} ions of each half-cell.

Concentration Cells

Electrode	Half-reaction
Anode	$Cu\ (s) \rightarrow Cu^{2+}\ (aq, C_1) + 2e^-$
Cathode	$Cu^{2+}\ (aq, C_2) + 2e^- \rightarrow Cu\ (s)$

Same metal and its solution

As cathode and anode consist of **same electrode**.

Net cell reaction:

$Cu^{2+}\ (aq, C_2) \rightarrow Cu^{2+}\ (aq, C_1)$

$E^0_{Cathode} = E^0_{Anode}$

Concentration Cells

E^0_{cell} for all concentration cells

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{C_1}{C_2} \quad ...(1)$$

Putting values in eq. (1)

$$E^0_{Cell} = E^0_{Cathode} - E^0_{Anode}$$

$$E^0_{Cell} = 0.00 \text{ Volt}$$

$$E_{cell} = 0 - \frac{0.059}{2} \log \frac{C_1}{C_2}$$

$$E_{cell} = \frac{0.059}{2} \log \frac{C_2}{C_1}$$

Concentration Cells

$$E_{cell} = \frac{0.059}{2} \log \frac{C_2}{C_1}$$

For **spontaneous** reactions to take place,

$C_1 < C_2$

Concentration Cells

- Difference in the electrolytic concentration
- Difference in the **pressure** of gases at electrodes

Concentration Cells

Example

$Pt\ (s) \mid H_2\ (g, P_1) \mid HCl\ (x\ M) \mid H_2\ (g, P_2) \mid Pt\ (s)$

Electrode	Half-reaction
Anode	$H_2\ (g, P_1) \rightarrow 2H^+\ (aq, x\ M) + 2e^-$
Cathode	$2H^+\ (aq, x\ M) + 2e^- \rightarrow H_2\ (g, P_2)$

Two hydrogen electrodes having hydrogen gas at **different pressures**, dipped in the **same** electrolytic solution (x M HCl).

Net cell reaction:

$H_2\ (g, P_1) \rightarrow H_2\ (g, P_2)$

$E^0_{cell} = 0$ **Volt**

Concentration Cells

$H_2(P_1) \longrightarrow H_2(P_2)$

Putting values in eq. (1)

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{P_2}{P_1}$$

$$E_{cell} = 0 - \frac{0.059}{2} \log \frac{P_2}{P_1}$$

$$E_{cell} = \frac{0.059}{2} \log \frac{P_1}{P_2}$$

$$E_{cell} = \frac{0.059}{2} \log \frac{P_1}{P_2}$$

For **spontaneous** reactions to take place,

$$P_1 > P_2$$

Concentration Cells at Equilibrium

At equilibrium

$$E_{cell} = 0$$

At 298 K,

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log K_{eq}$$

$$0 = E^0_{cell} - \frac{0.059}{n} \log K_{eq}$$

$$E^0_{cell} = \frac{0.059}{n} \log K_{eq}$$

$$K_{eq} = 10^{\frac{nE^0_{cell}}{0.059}}$$

For concentration cell,

$$E^0_{cell} = 0$$

Concentration Cells at Equilibrium

$$K_{eq} = 10^0$$

$$K_{eq} = 1$$

For concentration cell at equilibrium,

$$E_{cell} = 0,\ E^0_{cell} = 0,\ K_{eq} = 1$$

Determination of Thermodynamic Functions

Cell reaction:

$$aA + bB \longrightarrow cC + dD \qquad E_{cell}$$

$$\Delta_r G = -nFE_{cell}$$

For a substance,

$$dG = VdP - SdT$$

For a chemical reaction,

$$d(\Delta_r G) = (\Delta V)\, dP - (\Delta_r S)\, dT$$

Determination of Thermodynamic Functions

$$\Delta_r S = -\frac{d}{dT}(-nFE_{cell})$$

$$\Delta_r S = nF\frac{dE_{cell}}{dT}$$

$\frac{dE_{cell}}{dT}$ Temp. coefficient of cell reaction

Unit: **V/K** or **V/°C**

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$$\Delta_r H = -nFE_{cell} + nFT\frac{dE_{cell}}{dT}$$

Electrolytic Cell

An electrolytic cell is an electrochemical cell in which a **non-spontaneous reaction** is driven by an external source of current.

Converts **electrical** energy into **chemical** energy.

Cell reaction:

$2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$ $E_{cell} = -1.23\ V$

The spontaneous process is actually the **reverse reaction** (i.e., formation of H_2O from H_2 and O_2)

For this at pH = 7, **E_{cell} = 1.23 V**

Construction of Electrolytic Cell

Source of current

External Battery

Cathode is attached to negative terminal of the battery

Reduction occurs at cathode

So, cathode acts as a **negative** electrode

Electrolysis

Electrolysis is a process of oxidation and reduction **due to current** in the electrolytic solution

Electrolyte is a combination of **cations and anions** which in fused state or in aqueous solution can conduct electricity.

Construction of Electrolytic Cell

Anode is attached to positive terminal of the battery

Oxidation occurs at anode

So, anode acts as a **positive** electrode

Electrode	Half-Reaction
Cathode	$Na^+ (l) + e^- \longrightarrow Na (l)$
Anode	$2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Overall reaction:

$$2Na^+ (l) + 2Cl^- (l) \longrightarrow 2Na (l) + Cl_2 (g)$$

$$E^0_{cell} < 0\ V$$

Electrolysis of Molten NaCl

Sodium metal and chlorine gas are called **product of electrolysis** of molten NaCl.

Product obtained during electrolysis depends on following factors:

1. Amount of charge passed into the electrolyte
2. Nature of the electrolyte
3. Concentration the of electrolyte
4. Nature of the electrode

Faraday's First Law

The **mass** deposited/ released/produced of any substance during electrolysis is proportional to the **amount of charge** passed into the electrolyte.

Faraday's First Law

$W \propto Q$

$W = ZQ$

If $Q = 1\,C$

$W = Z$

W: Mass deposited or liberated
Q: Amount of charge passed
Z: **Electrochemical equivalent** of the substance

Z

Mass deposited or liberated when **1 C** of charge is passed into the solution

Unit: **kg/C** or **g/C**

Equivalent Mass (E)

Mass of any substance produced when **1 mole of electrons** are passed through the solution during electrolysis.

$$E = \frac{\text{Molar mass}}{\text{No. of } e^- \text{ involved in oxidation/reduction}}$$

$$= \frac{M}{\textbf{n-factor}}$$

Calculating Equivalent Mass (E)

$$E = \frac{M}{1}$$

$$E = \frac{M}{3}$$

$$E = \frac{M}{2}$$

Faraday's First Law

We know,

1 mole of e^- = **1 F** of Charge

1 C charge flow = $\frac{E}{96500}$ **g** metal deposited

1 F = 96500 C

96500 C charge flow = **E gram** metal deposited or liberated

So, $Z = \frac{E}{96500}$

Z is the mass deposited or liberated when **1 C** of charge is passed into the solution.

Faraday's First Law

From Faraday's first law

$$W = ZQ$$

Substituting the value of Z

$$W = \frac{E}{96500} \times Q$$

$$W = \frac{EQ}{96500}$$

$$E = \frac{M}{\text{n-factor}}$$

$$Q = i \times t$$

$$W = \frac{\text{Molar mass}}{\text{n-factor}} \times \frac{i \times t}{96500}$$

Faraday's Second Law

If equal charge **(Q)** is passed through two electrolytic cells and cells are connected in the series

The mass deposited at electrode will be in the ratio of their **electrochemical equivalents** or in the ratio of the **equivalents masses.**

Faraday's Second Law

Considering two electrolytic cells, 1 & 2 connected in series

Applying 1st law,

$W_1 = Z_1 \times Q_1$ $\quad$ $W_2 = Z_2 \times Q_2$

For two cells

Since charge passed is same for both the cells,

$$Q_1 = Q_2$$

So, $$\frac{W_1}{W_2} = \frac{Z_1}{Z_2}$$

Faraday's Second Law

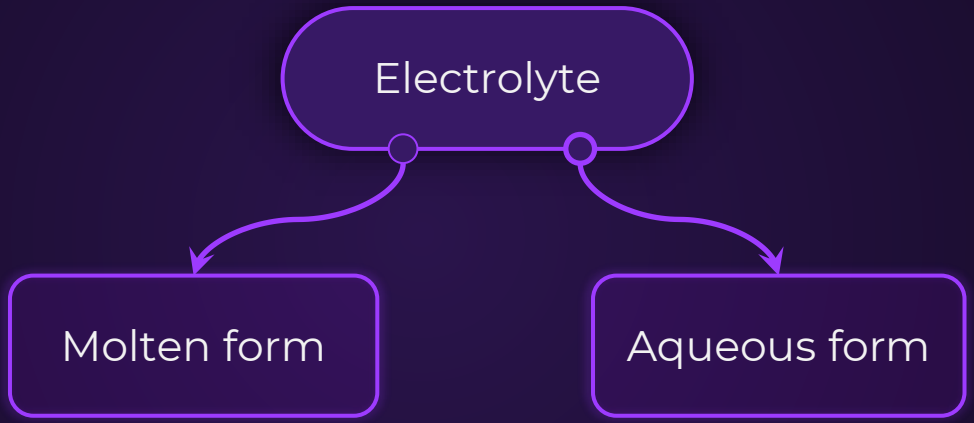
As, $Z = \frac{E}{96500}$

$Z_1 = \frac{E_1}{96500}$ & $Z_2 = \frac{E_2}{96500}$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Nature of the electrolyte



Aqueous Electrolyte

When **electrolysis** of aqueous solution of electrolyte is carried out, there may be **two or more species** present in the solution which may **compete** for reduction at cathode or oxidation at anode.

Aqueous Electrolyte

For species competing for reduction at cathode,

Higher is the **SRP,** greater will be its ease to undergo **reduction** at cathode.

For species competing for **oxidation** at **anode**,

Lower is the **SRP** (or higher in SOP) greater will be its ease to undergo **oxidation** at anode.

Molten Electrolyte

Electrolysis of **molten NaF** solution

Electrode	Half-reaction	E^0
Cathode	$Na^+ (l) + e^- \rightarrow Na (l)$	$E^0 = -2.71$ V
Anode	$2F^- \rightarrow F_2 + 2e^-$	$E^0 = -2.87$ V

Product of electrolysis:

Anode	F_2

Cathode	**Na**

Aqueous Electrolyte

Electrolysis of **aq. NaF** solution

Possibilities at cathode:

$Na^+ (aq) + e^- \longrightarrow Na (s)$	$E^0 = -2.71$ V
$2H_2O (l) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$	$E^0 = -0.83$ V

Product of electrolysis at **cathode**	**H_2**

Aqueous Electrolyte

Electrolysis of **aq. NaF** solution

Possibilities at anode:

$2F^-(aq) \longrightarrow F_2(g) + 2e^-$	$E^0_{ox} = -2.87\ V$
$2H_2O(l) \longrightarrow O_2 + 4H^+ + 4e^-$	$E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode**	**O_2**

Aqueous Electrolyte

Electrolysis of **aq. NaCl** solution

Possibilities at cathode:

$Na^+ (aq) + e^- \longrightarrow Na (s)$	$E^0 = -2.71$ V
$2H_2O (l) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$	$E^0 = -0.83$ V

Product of electrolysis at **cathode**	**H_2**

Aqueous Electrolyte

Electrolysis of **aq. NaCl** solution

Possibilities at anode:

$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$ $\quad E^0_{ox} = -1.36\ V$

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode**	Cl_2

Aqueous Electrolyte

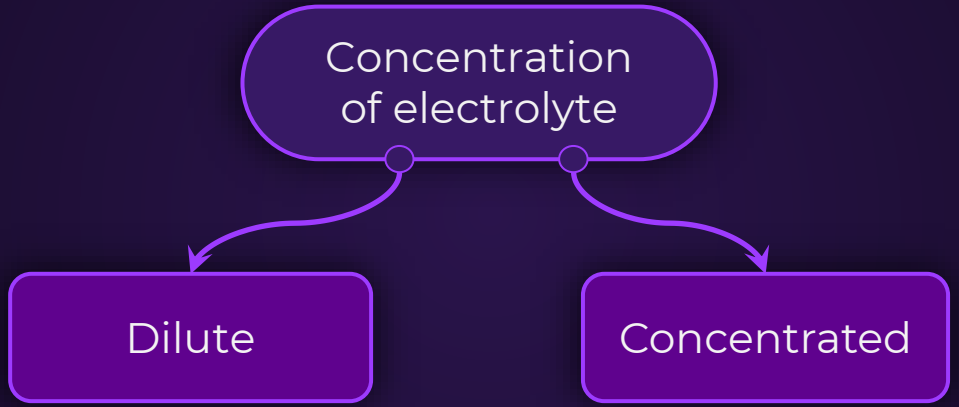
According to **thermodynamics**, oxidation of H_2O to produce O_2 should take place on **anode**.

However, **experimentally** the rate of oxidation of water is found to be **very slow**.

To **increase its rate**, the greater potential difference is applied known as **over voltage** or over potential

But because of this **oxidation of Cl^- ions** also become **feasible** and this takes place on anode.

Concentration of electrolyte



Dilute Electrolyte

Electrolysis of **aq. H_2SO_4** solution

Possibilities at cathode:

$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$	$E^0 = 0.00$ V
$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$	$E^0 = -0.83$ V

Product of electrolysis at **cathode**	**H_2**

Dilute Electrolyte

Electrolysis of **aq. H_2SO_4** solution

Possibilities at anode:

$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$	E^0_{ox} = -2.05 V
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	E^0_{ox} = -1.23 V

Product of electrolysis at **anode**	**O_2**

Concentrated Electrolyte

Electrolysis of **highly conc. aq H_2SO_4** solution

Possibilities at cathode:

$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$	$E^0 = 0.00$ V
$2H_2O (l) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$	$E^0 = -0.83$ V

Product of electrolysis at **cathode**	**H_2**

Concentrated Electrolyte

Electrolysis of **highly conc. aq H_2SO_4** solution

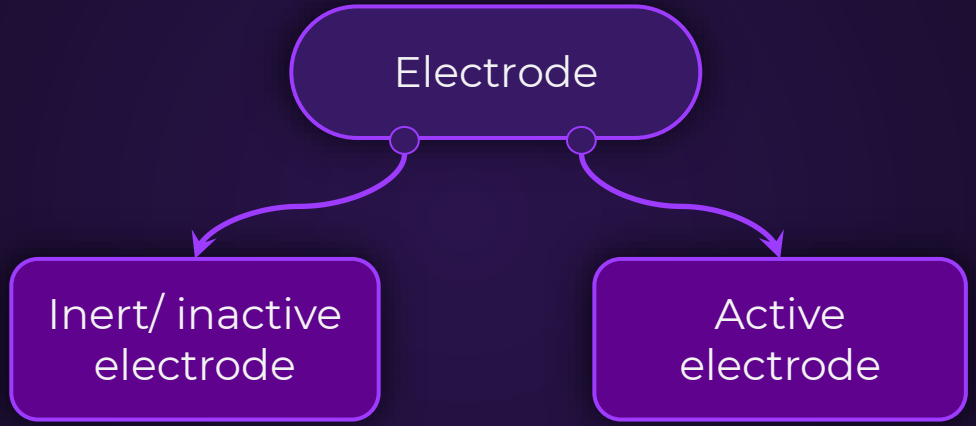
Possibilities at anode:

$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$ $\quad E^0_{ox} = -2.05\ V$

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode** $\quad$ **$S_2O_8^{2-}$**

Nature of the electrode



Inert Electrode

Electrode that **conduct electrons** into or out of the cell but cannot take part in the half-reactions.

e.g. Pt, graphite, etc.

Active Electrode

The metal electrodes in the cell that are **active**, because the metals themselves are **components** of the half reactions.

E.g. Cu, Ag etc.

Purification of Metals

Electrolytic cell can be used for the **purification of metals**.

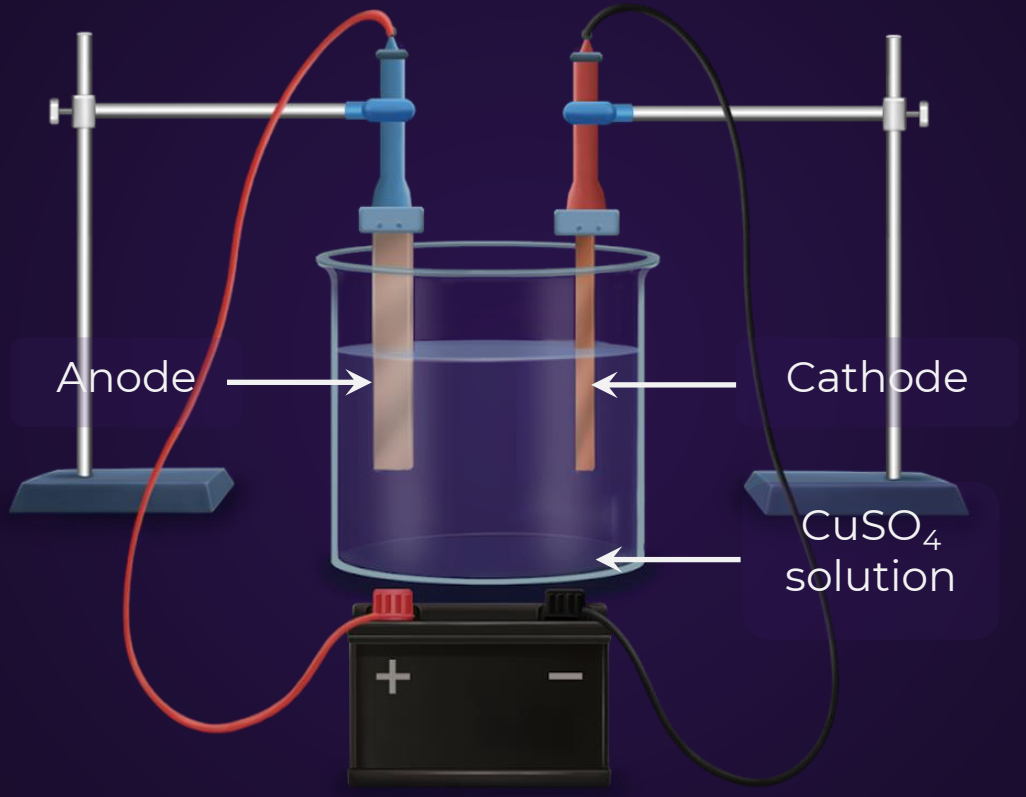
By taking **impure** metal → At **anode**

Pure metal → At **cathode**

Example

Purification of impure copper

Obtained by dipping **two Cu strips in aq. $CuSO_4$**


Anode
Cathode
$CuSO_4$ solution
+
−

Possibilities at anode

$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$ $\quad E^0_{ox} = -1.23\ V$

$2SO_4^{2-}\ (aq) \rightarrow S_2O_8^{2-}\ (aq) + 2e^-$ $\quad E^0_{ox} = -2.05\ V$

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$ $\quad E^0_{ox} = -0.34\ V$

At the **impure Cu anode**

Cu is oxidised along with the more easily oxidised metallic impurities such as Zn & Fe.

The less easily oxidised impurities such as **Ag, Au, and Pt fall to the bottom** of the cell as anode mud, which is **reprocessed** to recover the precious metals.

Possibilities at cathode

$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$

$E^0 = -0.83\ V$

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

$E^0 = 0.34\ V$

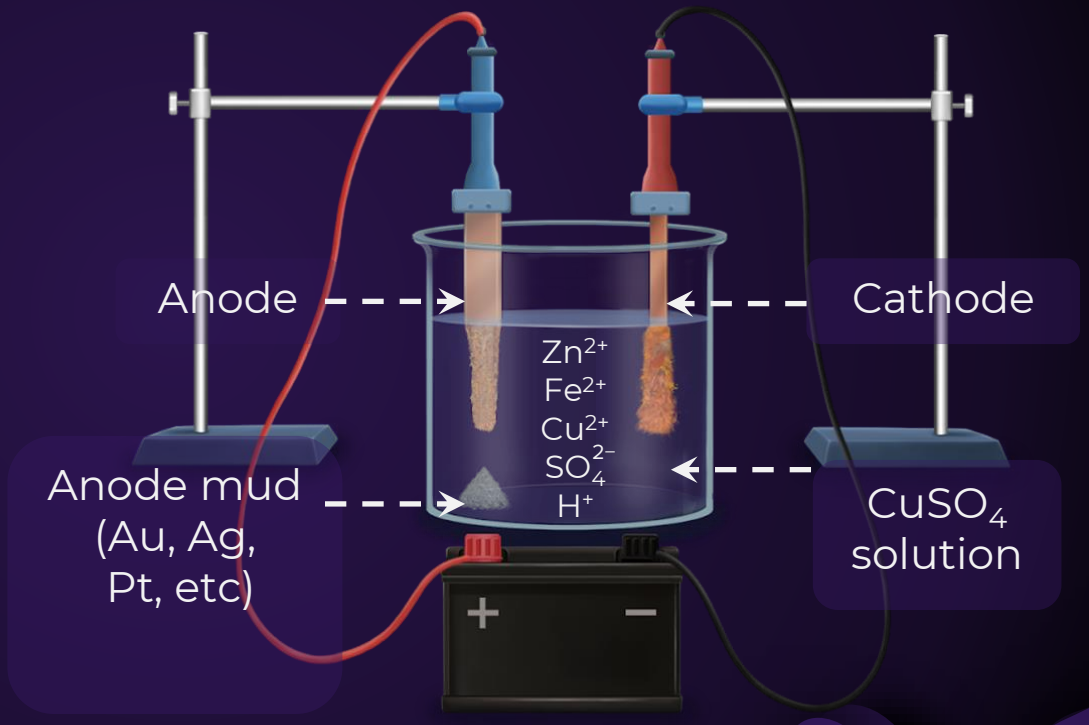
At the **pure Cu cathode**

Cu^{2+} ions get reduced to **pure copper** metal

However, the less easily reduced metal ions (Zn^{2+}, Fe^{2+} and so forth) **remain** in the solution.

The net cell reaction simply involves transfer of Cu metal from the **impure anode to the pure cathode**.

Cu obtained by this process is **99.95%** pure.



Electroplating

Electrolytic **deposition** of a thin **film of metal** on an object.

Object to be electroplated → **Cathode**

Aq. solution of a salt of the plating metal → **Electrolyte**

Electroplating

Metal is deposited on the **cathode** from ions in the electrolyte solution.

These cations are either **supplied by** the **added salt** or **from oxidation at anode**, which is made of plating metal

For **silver plating**,

Solution of silver salt → **Electrolyte**

Object to be electroplated → **Cathode**

So that **metal ions move to it** when current is switched on.

Cathode reaction

Ag^{+} (aq) + e^{-} → Ag (s)

Conductors

Metallic conductors	Electrolytic conductors
Charge carriers are **electrons**	Charge carriers are **ions**
No chemical changes	**Decomposition** of electrolyte takes place

Metallic conductors	Electrolytic conductors
No transfer of mass	**Transfer** of mass
Resistance is because of **collision of electrons** with fixed metal atom.	Resistance is because of **collision of ions** with solvent molecules & because of interionic force of attraction.

Conductors

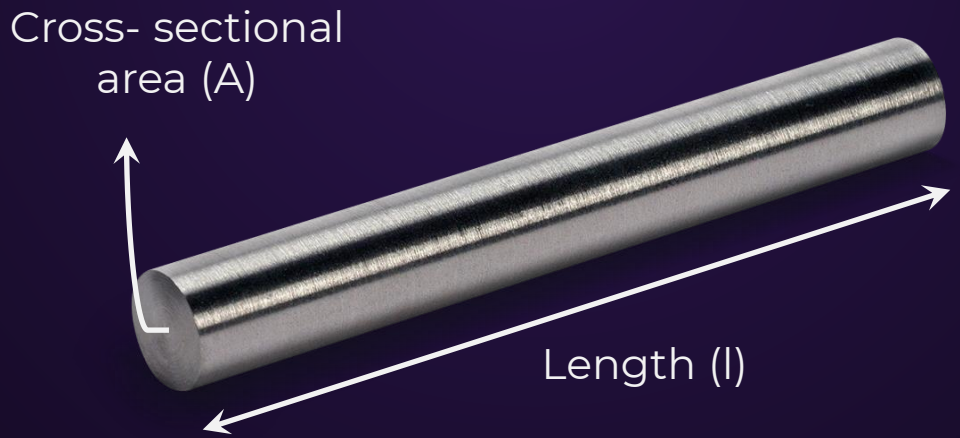
Metallic conductors	Electrolytic conductors
Metallic conduction depends on the **nature of metal** (e.g. no. of valence e^- per metal atom, crystal structure etc.), **temperature**, **length** & **area** of cross section.	Electrolytic conduction depends on the **nature of electrolyte** (strong/ weak), nature of **solvent and its viscosity**, **temperature** etc.

Metallic conductors	Electrolytic conductors
↑ T Electrolytic conduction ↓	↑ T Electrolytic conduction ↑

Electrical Resistance (R)

The electrical resistance of a conductor

- Directly proportional to its length (l)
- Inversely proportional to its area of cross section (A).



Electrical Resistance (R)

$$R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

Known as resistivity/specific resistance

Similarly for electrolytic conductors

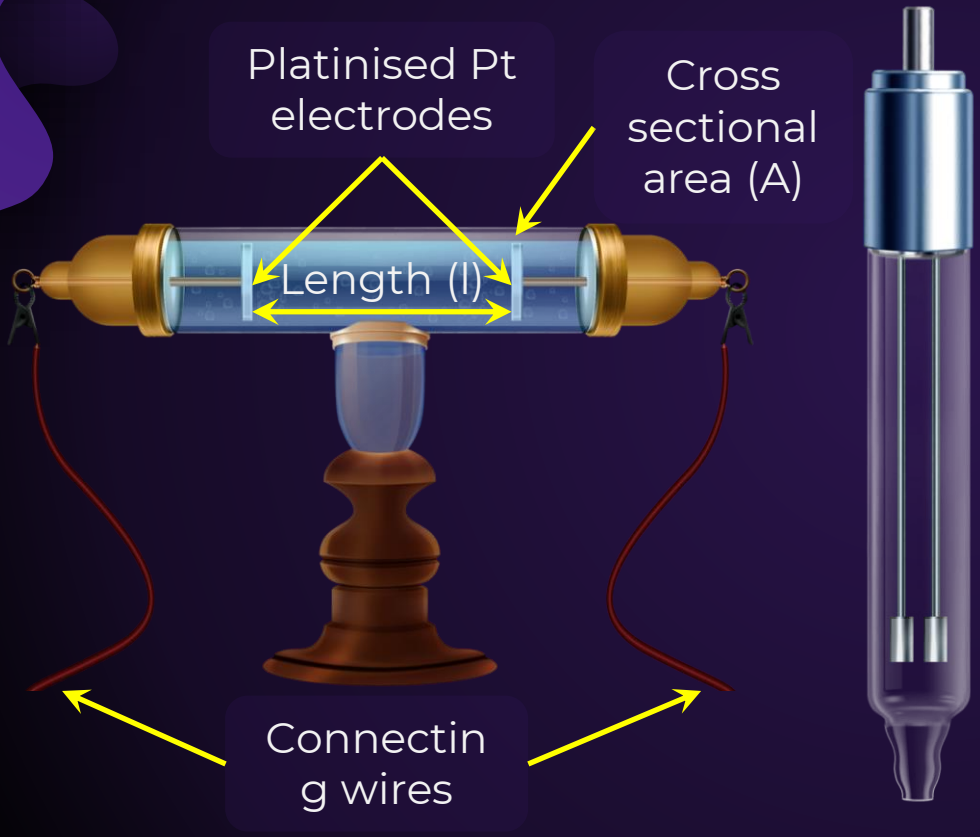
$$R = \rho \frac{l}{A}$$

$\frac{l}{A}$ Cell constant

l Separation between the electrodes

A Overlapping area of cross-section of electrodes dipped in the solution

Resistivity



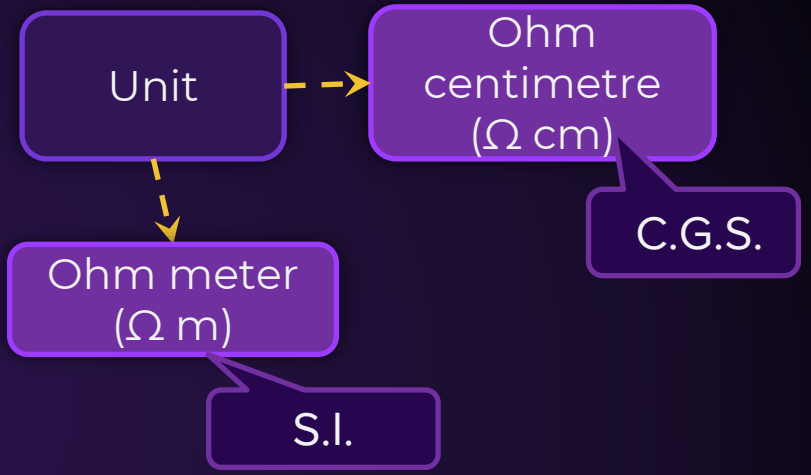
$$\rho = R\frac{A}{l}$$

When l = 1 cm,
A = 1 cm^2

$$\rho = R$$

Resistivity

Resistivity of a solution is defined as the **resistance of the solution** between the two electrodes of **1 cm²** area of cross-section and **1 cm** apart.



1 Ω m = 100 Ω cm

1 Ω cm = 0.01 Ω m

Conductance

The inverse of the resistance is known as **conductance.**It is represented by **G.**

$$G = \frac{1}{R}$$

$$R = \rho \frac{l}{A}$$

$$G = \frac{A}{l\rho}$$

Unit — mho or Ω^{-1} or S (siemens)

S.I.

Factors Affecting Conductance & Resistance

(i) **Solute-solute** interactions (Inter-Ionic force of attraction)

Greater the force of attraction, greater will be the resistance.

$$\text{Force} \propto \text{Charge}$$

(ii) **Solute-solvent interaction** (Hydration of ions)

Greater the solvation, greater will be resistance

$$\text{Solvation} \propto \text{Charge} \propto \frac{1}{\text{Size}}$$

Factors Affecting Conductance & Resistance

Li^+ – Hydrated **largest**

Hydrated **smallest** – Cs^+

(iii) **Solvent-solvent interaction** (Viscosity):

Greater the viscosity, greater will be resistance

Resistance of LiCl > Resistance of CsCl

(iv) **Temperature** ↑, Resistance ↓

Factors Affecting Conductance & Resistance

(v) **Nature of electrolyte**

Electrolyte	Conductance
Weak	Low
Strong	High

Conductivity (κ)

The inverse of resistivity is known as **conductivity/ specific conductance** (κ).

$$\kappa = \frac{1}{\rho}$$

$$G = \kappa \times \frac{A}{l}$$

$$G = \frac{1}{\rho} \times \frac{A}{l}$$

$$\kappa = \frac{G\,l}{A}$$

Units of Conductivity (κ)

Unit → $S\ cm^{-1} / \Omega^{-1} cm^{-1}$ — C.G.S.

Unit → $S\ m^{-1} / \Omega^{-1} m^{-1}$ — S.I.

$$\kappa = \frac{G\,l}{A} = \frac{G\,l}{A} \times \frac{l}{l} = \frac{G\,l^2}{V}$$

When $l = 1\ cm$, $V = 1\ cm^3$

$$\kappa = G$$

$$1\ S\ cm^{-1} = 100\ S\ m^{-1}$$

Conductivity (κ)

Conductivity is the **conductance** of **unit volume** of solution filled between two parallel electrodes at **unit distance**.

We know,

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

Accurate measurement of resistance (R) performed on a **Wheatstone bridge**

Conductivity is **computed** by measuring the **resistance (R)** of the electrolyte and cell constant.

Cell Constant (G*)

Value of **cell constant** is written in the description of cell.

Using **G*** and **R** of the solution, conductivity of the cell is determined.

$$\kappa = \frac{G^*}{R}$$

Note

1. **Conductance** is **extensive** property.
2. **Conductivity** is **intensive** property.
3. $\kappa \propto$ Number of ions
4. Conductivity is **additive** property when l/A is same.

Conductivity or resistivity of the solution is dependent on its **concentration.**

$$\kappa_{total} = \kappa_1 + \kappa_2 + \kappa_3 + ... + \kappa_{water}$$

$$G_{total} \times \frac{l}{A} = G_1 \times \frac{l}{A} + G_2 \times \frac{l}{A} + G_3 \times \frac{l}{A} + ... + G_{water} \times \frac{l}{A}$$

Note

$$G_{total} = G_1 + G_2 + G_3 + ... + G_{water}$$

$$\frac{1}{R_{total}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + ... + \frac{1}{R_{water}}$$

All electrolytes in solution are connected in **parallel.**

Molar Conductivity (Λ_m)

Conductance of a solution containing **1 mole** of an electrolyte between two electrodes which are **unit length** apart

$l = 1$, and solution contains 1 mol of electrolyte

$$\Lambda_m = G$$

$$\kappa = \frac{G\,l}{A}$$

$$\Lambda_m = \kappa \times V$$

$$G = \frac{\kappa A}{l} \times \frac{l}{l} = \frac{\kappa V}{l^2}$$

Volume of solution which contain 1 mol of electrolyte

In C.G.S. Unit

Molarity of a solution → C mol/L

C mol electrolyte dissolves in → 10^3 cm^3 solution

1 mol electrolyte will dissolve in → $\frac{1000}{C}$ cm^3 solution

$\Lambda_m = \kappa \times V$

$\Lambda_m\ (S\ cm^2\ mol^{-1}) = \frac{\kappa\ (S\ cm^{-1}) \times 1000}{\text{Molarity}}$

In S.I. Unit

Molarity of a solution	→	C mol/L	Λ_m =	$\kappa \times V$
C mol electrolyte dissolves in	→	10^{-3} m^3 solution	Λ_m **(S m^2 mol^{-1})** =	$\frac{\kappa\ (S\ m^{-1})}{1000 \times \text{Molarity}}$
1 mol electrolyte will dissolve in	→	$\frac{1}{1000\ C}$ m^3 solution	**1 S m^2 mol^{-1}** =	10^4 S cm^2 mol^{-1}
			1 S cm^2 mol^{-1} =	10^{-4} S m^2 mol^{-1}

Equivalent Conductivity (Λ_{eq})

The conductance of a solution containing **1 g-equivalent** of the electrolyte

Normality of a solution	N eq./L
N eq. electrolyte dissolves in	10^3 cm^3 solution
1 mol electrolyte will dissolve in	$\frac{1000}{N}$ cm^3 solution

Equivalent Conductivity (Λ_{eq})

$$\Lambda_{eq} = \kappa \times V$$

$$\Lambda_{eq}\ (S\ cm^2\ eq^{-1}) = \frac{\kappa\ (S\ cm^{-1}) \times 1000}{\text{Normality}}$$

$$\Lambda_{eq} = \kappa \times V$$

$$\Lambda_{eq}\ (S\ m^2\ eq^{-1}) = \frac{\kappa\ (S\ m^{-1})}{1000 \times \text{Normality}}$$

Normality of a solution → N eq./L

N eq. electrolyte dissolves in → 10^{-3} m^3 solution

1 eq. electrolyte will dissolve in → $\frac{1}{1000\ N}$ m^3 solution

Relation between Λ_{eq} and Λ_m

1 S m^2 eq^{-1} = 10^4 S cm^2 eq^{-1}

1 S cm^2 eq^{-1} = 10^{-4} S m^2 eq^{-1}

$$\Lambda_m \text{ (S cm}^2\text{ mol}^{-1}\text{)} = \frac{\kappa \text{ (S cm}^{-1}\text{)} \times 1000}{M} \quad \text{.....(eq. 1)}$$

$$\Lambda_{eq} \text{ (S cm}^2\text{ eq}^{-1}\text{)} = \frac{\kappa \text{ (S cm}^{-1}\text{)} \times 1000}{N} \quad \text{.....(eq. 2)}$$

Dividing (eq. 2) by (eq. 1)

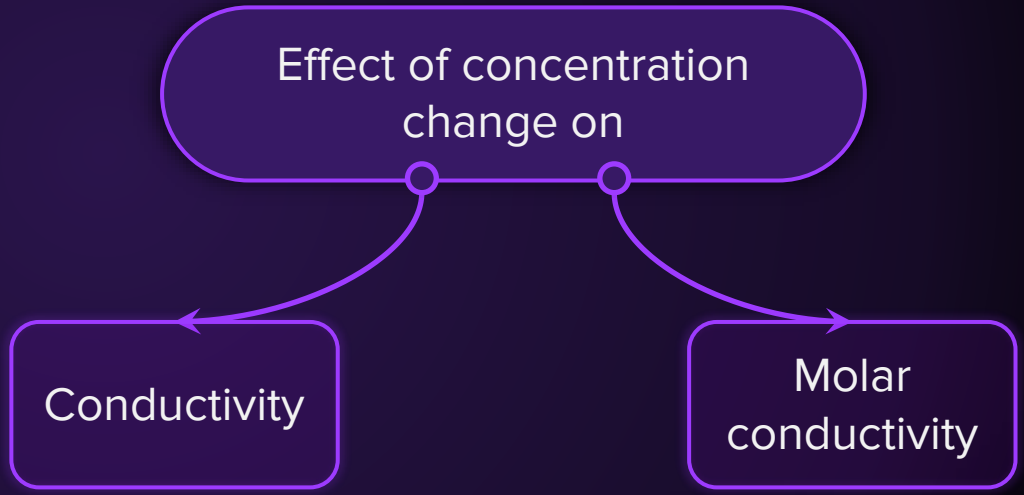
$$\frac{\Lambda_{eq}}{\Lambda_m} = \frac{M}{N}$$

$$N = M \times \text{n-factor}$$

$$\Lambda_{eq} = \frac{\Lambda_m}{\text{n-factor}}$$

Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity & molar conductivity **change with the concentration** of the electrolyte.



Variation of Conductivity (κ) with Concentration

Both for **weak** and **strong** electrolytes.

Concentration ↓ → Conductivity ↓

Dilution ↑

Since, conductivity is the **conductance per unit volume** of electrolytic solution.

On **dilution**, number of ions per unit volume decreases.

↓

Also, conductivity depends upon the number of ions per unit volume.

↓

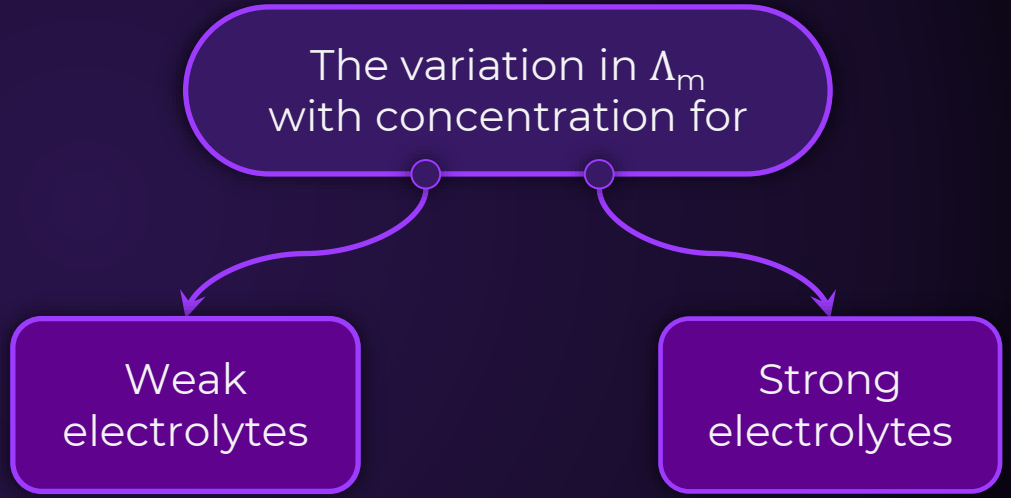
Conductivity decreases on dilution.

Variation of Molar Conductivity (Λ_m) with Concentration

Molar conductance **increases** upon dilution

Or **decreases** on increasing the concentration.

Reason is different for **strong** and **weak** electrolytes



The Variation in Λ_m for Weak Electrolyte

At higher concentration,

Weak electrolytes like acetic acid have **lower** degree of dissociation

With dilution of an ionic solution

The degree of dissociation (α) of the electrolyte increases

At infinite dilution, $\alpha \rightarrow 1$

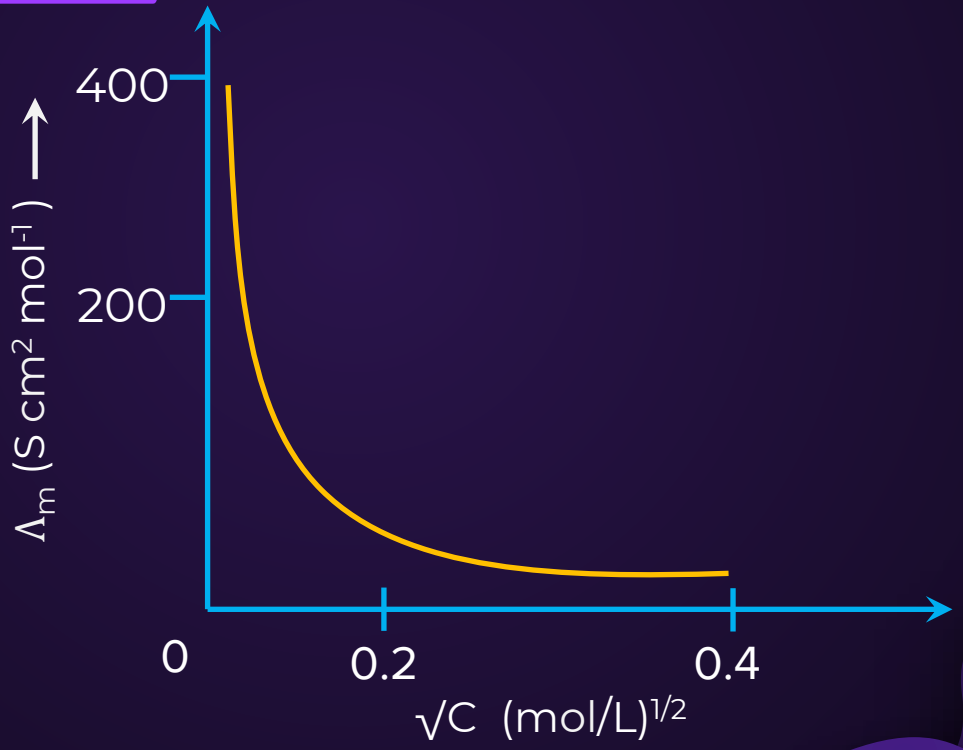
Near lower concentration

Steep increase in molar conductance

Increase in the number of ions in solution

Plot of Λ_m vs. $\sqrt{C}$

For CH_3COOH solution



The Variation in Λ_m for Strong Electrolytes

Λ_m **increases slowly** with dilution.

As strong electrolytes are mostly in **ionised state**

No abrupt change in the number of ions with dilution.

In **concentrated** solution

Strong attraction between oppositely charged ions

Slows down the movement of ions

The Variation in Λ_m for Strong Electrolytes

With **dilution**, distance between the ions increases

Decrease in interionic attractions

Influence of other ions on the movement of the ion decreases

Gradual increase in the molar conductivity of the solution

When concentration approaches **zero**

The molar conductivity is known as **limiting molar conductivity**

Molar conductivity at infinite dilution

Plot of Λ_m vs. $\sqrt{C}$

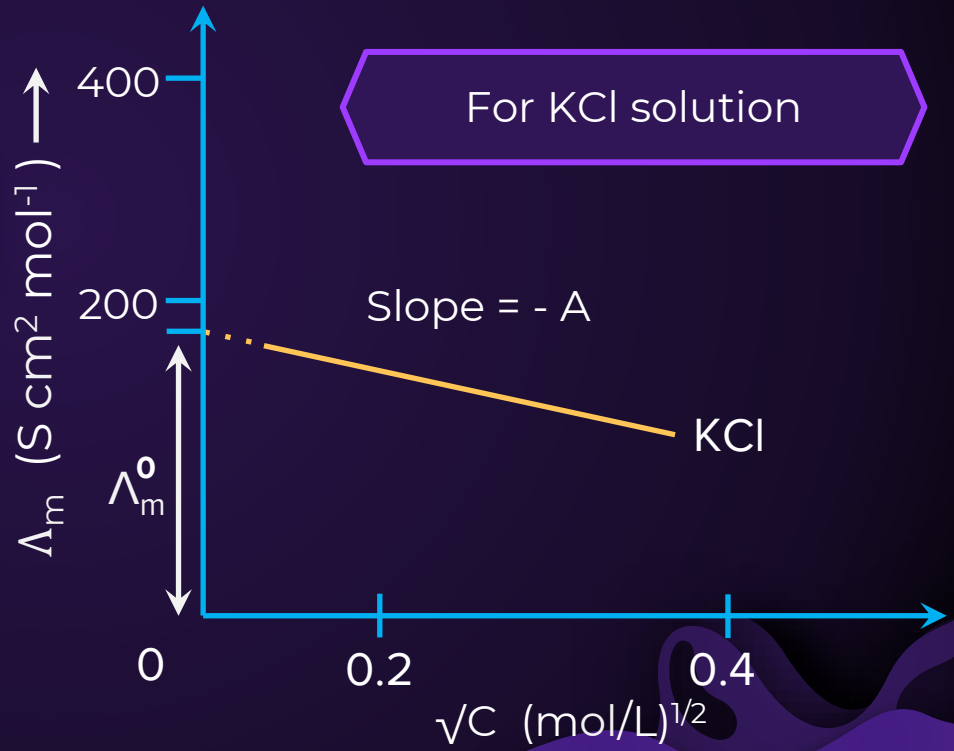
The variation in Λ_m for **strong electrolyte** is given by

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

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

Λ_m : Molar conductivity
Λ_m^0 : Limiting molar conductivity
C : Concentration of electrolyte
A : Constant

For KCl solution



Plot of Λ_m vs. $\sqrt{C}$

Value of the constant 'A' for a given solvent and temperature depends on the **type of electrolyte** i.e., the **charges** on the cations and anion produced on the dissociation of the electrolyte in the solution.

Types of Electrolytes

All electrolytes of a particular type have the **same value** of 'A'.

Examples

Electrolyte	Type
NaCl	1 - 1
$CaCl_2$	2 - 1
$MgSO_4$	2 - 2

Dielectric constant of solvent ↑, A ↓

Temperature ↑, Viscosity ↓, A ↓

Λ_m^0 for **strong electrolyte** can be determined by **extrapolation** (as variation is **linear**).

↓

But not for **weak electrolyte** (as variation is **non-linear**).

Ionic Mobility (μ)

Speed of an ion per unit electric field (potential gradient).

Denoted by symbol **'μ'**

$$\mu = \frac{\text{Speed}}{\text{Electric field}}$$

$$= \frac{\text{Speed}}{\text{Potential gradient}}$$

Unit of μ : $V^{-1} cm^2 sec^{-1}$

Kohlrausch's Law

Kohlrausch examined Λ_m^0 **values** for a number of strong electrolytes and observed **certain regularities**.

He noted that the **difference in** Λ_m^0 of the electrolytes NaX and KX for any 'X' is **nearly constant**.

At 298 K,

$$\Lambda_m^0(KCl) - \Lambda_m^0(NaCl) = \Lambda_m^0(KBr) - \Lambda_m^0(NaBr)$$

$$= \Lambda_{m\,(KI)}^0 - \Lambda_{m\,(NaI)}^0 \simeq 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

Similarly, it was found that

$$\Lambda_{m\,(NaBr)}^0 - \Lambda_{m\,(NaCl)}^0 = \Lambda_{m\,(KBr)}^0 - \Lambda_{m\,(KCl)}^0$$

$$\simeq 1.8 \text{ S cm}^2 \text{ mol}^{-1}$$

Kohlrausch's Law of Independent Migration of Ions

At **infinite dilution** or near zero concentration when dissociation is 100%, each ion makes a **definite contribution** towards molar conductivity of electrolyte **irrespective** of the nature of the other ion.

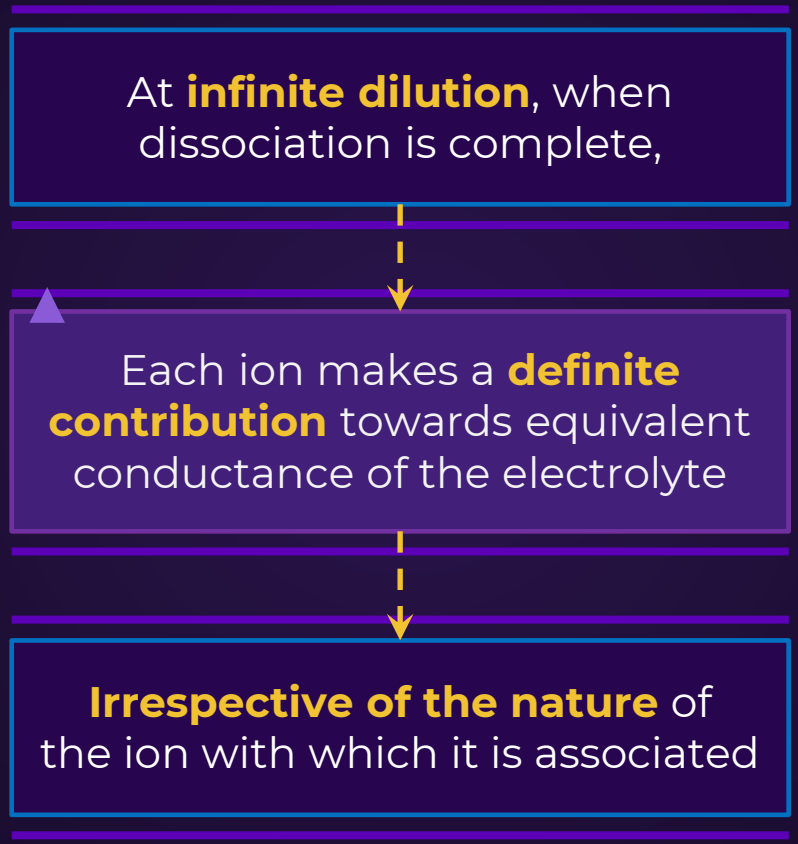
A_xB_y solution

$$A_xB_y\,(aq) \longrightarrow xA^{y+}\,(aq) + yB^{x-}\,(aq)$$

$$\Lambda^0_m = x\,\lambda^0_{A^{y+}} + y\,\lambda^0_{B^{x-}}$$

x and y are the number of cations and anions, respectively, after dissociation of the electrolyte

Kohlrausch's Law of Independent Migration of Ions



General Case:

$$A_xB_y\,(aq) \uparrow xA^{y+}\,(aq) + yB^{x-}\,(aq)$$

$$\Lambda^0_m = x\,\lambda^0_{m\,(A^{y+})} + y\,\lambda^0_{m\,(B^{x-})}$$

$$\Lambda^0_{eq} = \frac{\Lambda^0_m}{\text{n-factor}}$$

$$\Lambda_{eq} = \frac{1}{y}\,\lambda^0_{m\,(A^{y+})} + \frac{1}{x}\,\lambda^0_{m\,(B^{x-})}$$

$$\Lambda^0_{eq} = \frac{y}{y}\lambda^0_{eq(A^{y+})} + \frac{x}{x}\lambda^0_{eq(B^{x-})}$$

$$\Lambda^0_{eq(A_xB_y)} = \lambda^0_{eq(A^{y+})} + \lambda^0_{eq(B^{x-})}$$

$Al_2(SO_4)_3$ solution

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

Applications of Kohlrausch's Law

1

To calculate limiting molar conductivity (Λ_m^0) for weak electrolytes.

CH_3COOH, NH_4OH etc.

Kohlrausch law is used to evaluate Λ_m^0 for weak electrolytes.

From the individual values of Λ_m^0 of the ions.

Limiting Molar Conductivity of Weak Electrolytes

CH_3COOH solution

At infinite dilution,

$$CH_3COOH\ (aq) \rightarrow CH_3COO^-\ (aq) + H^+\ (aq)$$

Limiting molar conductivity of CH_3COOH,

$$\Lambda^0_{m\,[CH_3COOH]} = \Lambda^0_{m\,[CH_3COO^-]} + \Lambda^0_{m\,[H^+]} \quad ...(1)$$

Limiting Molar Conductivity of Weak Electrolytes

The Λ_m^0 values of strong electrolytes can be graphically obtained.

For different electrolytes having **common ion**, limiting molar conductivity of the common ion remains **same** for all such electrolytes.

The Λ_m^0 values of weak electrolytes are calculated indirectly by evaluating Λ_m^0 values of selected strong electrolytes.

E.g:- $\lambda_{m\ (H^+)}^0$ is same for both the electrolytes, CH_3COOH and HCl.

Applications of Kohlrausch's Law

2

To determine the degree of dissociation **(α)** and dissociation constant 'K_a' of a weak electrolyte.

Degree of Dissociation

Dissociation of weak electrolyte 'HA'

$$HA \rightleftharpoons H^+ + A^-$$

	HA	H^+	A^-
t = 0	C	0	0
$t = t_{eq}$	$C - C\alpha$	$C\alpha$	$C\alpha$

where, C: Initial concentration of HA

$\Lambda_m \propto$ Degree of ionisation

$$\frac{\Lambda_m^{c_1}}{\Lambda_m^{c_2}} = \frac{\alpha_1}{\alpha_2}$$

If $C_2 \rightarrow 0$, $\alpha_2 \rightarrow 1$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} \quad ...(1)$$

Dissociation Constant (K_a)

Dissociation of weak electrolyte 'HA'

	HA	⇌	H^+	+	A^-
t = 0	C		0		0
$t = t_{eq}$	C − Cα		Cα		Cα

So, $K_a = \frac{[H^+][A^-]}{[HA]}$

$K_a = \frac{(C\alpha)(C\alpha)}{(C - C\alpha)}$

$K_a = \frac{C\alpha^2}{1 - \alpha}$ ...(2)

where,
C: Initial concentration of undissociated electrolyte
α: Degree of dissociation

Dissociation Constant of Weak Electrolyte

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} \quad ...(1)$$

$$K_a = \frac{C\alpha^2}{1-\alpha} \quad ...(2)$$

Put eq. (1) in eq. (2)

$$K_a = \frac{C\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2}{1-\left(\frac{\Lambda_m}{\Lambda_m^0}\right)} \simeq C\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2$$

Application of Kohlrausch's Law

3

To determine **solubility** and solubility product constant **(K_{sp})** of a sparingly soluble salt.

Sparingly soluble salt

Very small solubility

Solubility = Molarity ≃ 0

Solution can be considered to be of zero concentration or **infinite dilution**.

Hence,

$$\Lambda_m \simeq \Lambda_m^0$$

Solubility and K_{sp}

If the conductivity (κ) and Λ_m^0 of a sparingly soluble salt is known, then **solubility & K_{sp}** of the salt can be calculated.

In C.G.S unit

$$\Lambda_m = \Lambda_m^0 = \frac{\kappa \times 1000}{\text{Solubility (S)}}$$

$$S = \frac{\kappa \times 1000}{\Lambda_m^0}$$

S: Molarity of dissolved electrolyte

Example

$$AB_2\,(s) \rightleftharpoons A^{2+}\,(aq) + 2B^{-}\,(aq)$$

$$S = \frac{K_{AB_2} \times 1000}{\Lambda^{0}_{m,\,(AB_2)}}$$

$$K_{sp} = S \times (2S)^2$$

$$= 4S^3$$

Ionic Mobility

Speed of an ion per unit electric field(potential gradient).

Denoted by symbol **'μ'**

$$\mu = \frac{\text{Speed}}{\text{Electric field}}$$

$$= \frac{\text{Speed}}{\text{Potential gradient}}$$

Unit of **μ** $V^{-1}\ cm^2\ sec^{-1}$

Conductometric Titrations

The **principle** of conductometric titrations is based on the fact that during the titration, one of the **ions is replaced** by the other.

These two ions **differ** in the **ionic conductivity** with the result that the conductivity of the solution **varies** during the course of the titration.

H^+ (aq) and OH^- (aq) ions have exceptionally **high ionic conductivity**.

Smaller is the ionic size → Greater is the hydrated size → Lesser should be ionic mobility

Then why ionic mobility of H^+ is **very high**?

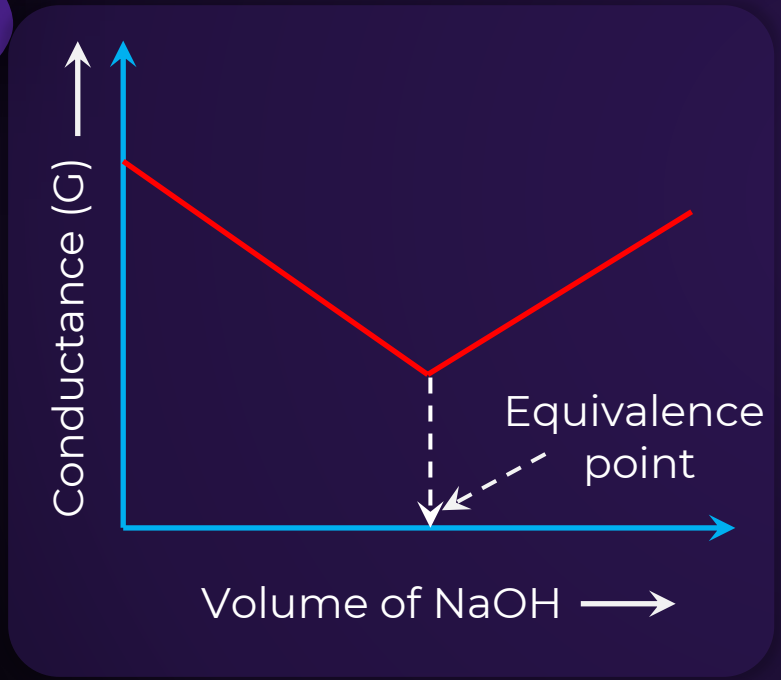
According to the **Grotthuss mechanism**, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules.

Conductometric Titrations

Plot of Conductance vs. Volume of NaOH

Example

HCl (strong acid) with NaOH (strong base)



The conductance of pure HCl is **very high,** due to the highly conducting **H^+ ions**

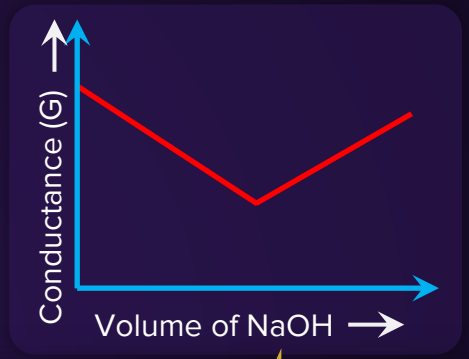
Strong Acid vs. Strong Base

Once we start adding **NaOH**,

H^+ (faster moving) are replaced with **Na^+ (slow moving)**

Decreasing the overall conductance till the **equivalence point**.

This explains first part of the graph.



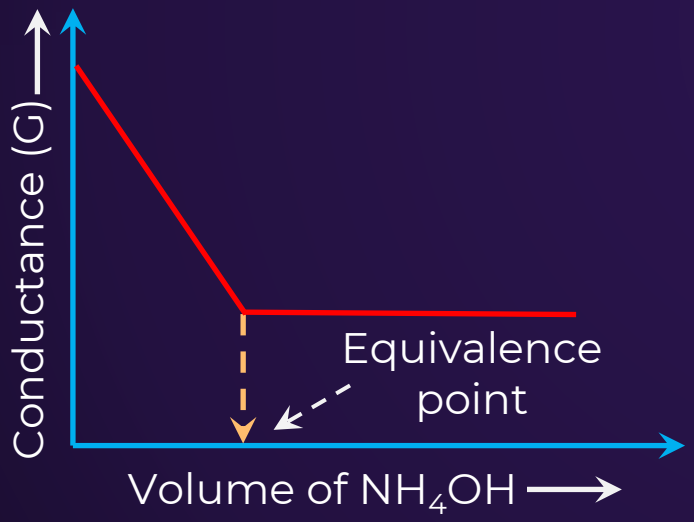
By further addition of **NaOH**, the **OH^-** conc. in the solution increases gradually, which **increases** the conductivity

This explains second part of the graph.

Strong Acid vs. Weak Base

Example

NH_4OH (weak base) with HCl (strong acid)



Once the addition of weak base (NH_4OH) started, a replacement of highly conducting **H^+ ions by NH_4^+** causes fall in conductance observed up to the equivalence point.

Strong Acid vs. Weak Base

After the equivalence point

The conductance remains almost **constant,** because in the solution only NH_4OH is added now

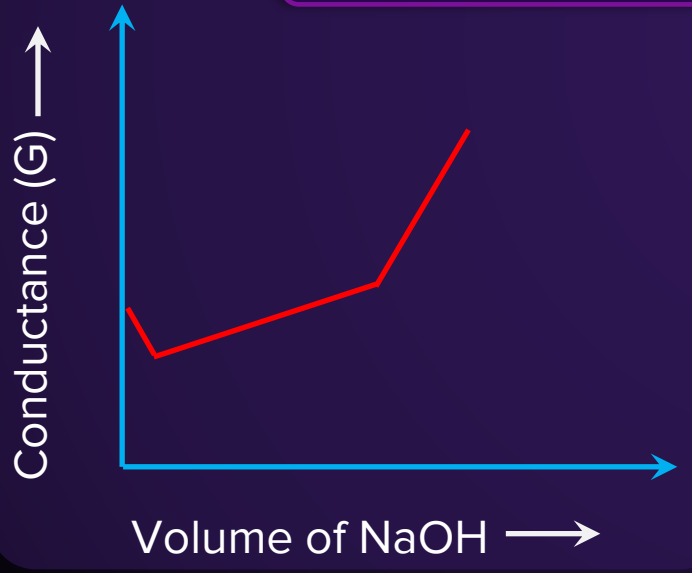
It's a **weak electrolyte**, so further addition **does not increase** conductance significantly.

Weak Acid vs. Strong Base

Example

Acetic acid being titrated against NaOH

CH_3COOH (weak acid) with NaOH (strong base)



Before the addition of alkali, the solution shows **poor conductance** due to feeble ionization of acetic acid.

Weak Acid vs. Strong Base

After the addition of alkali, conductance of the solution **decreases in the beginning** because:

1. Replacement of **H^+ ions by Na^+ ions**.
2. **Suppression of dissociation** of acetic acid due to the common ion CH_3COO^-.

After some time, conductance starts **increasing**

Addition of NaOH neutralizes the undissociated **CH_3COOH to $CH_3COO^-Na^+$**

↓

Replacing the non-conducting CH_3COOH with **strong-conducting electrolyte, $CH_3COO^-Na^+$**

Weak Acid vs. Strong Base

The **increase** in conductance continues right up to the **equivalence point**.

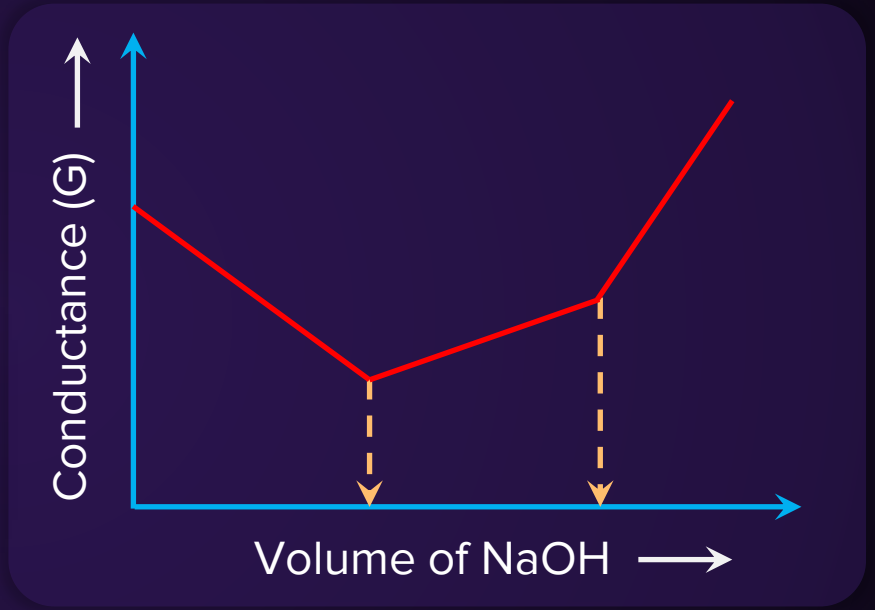
Beyond this point conductance **increases more rapidly** with the addition of NaOH due to the highly conducting OH^- ions.

Mixture of Acids vs. Strong Base

Example

HCl (Strong acid) and CH_3COOH (weak acid) with NaOH (strong base)

As, HCl is stronger acid → It first reacts with NaOH

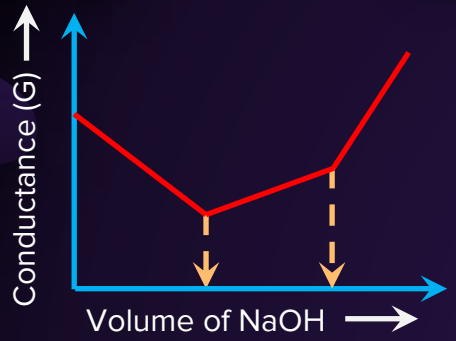


The graph has **three** parts.

Neutralisation reaction

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Mixture of Acids vs. Strong Base



When HCl is consumed → CH_3COOH starts reacting with NaOH

Neutralisation reaction

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

The conductance of the solution gradually **decreases** due to the replacement of H^+ ions by Na^+ ions.

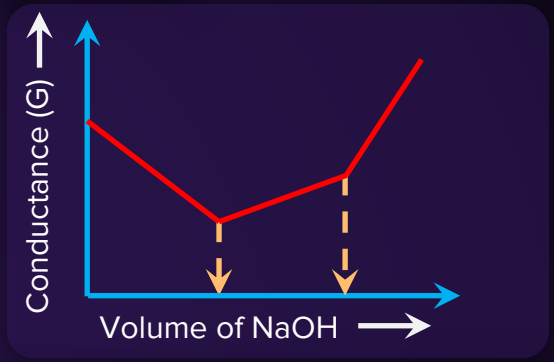
This explains the **first part** of the graph.

Mixtures of Acids vs. Strong Base

The feebly ionised weak acid (CH_3COOH) is neutralised.

The conductance **increases** marginally due to the salts (CH_3COONa) produced.

Which explains the **second part** of the graph.

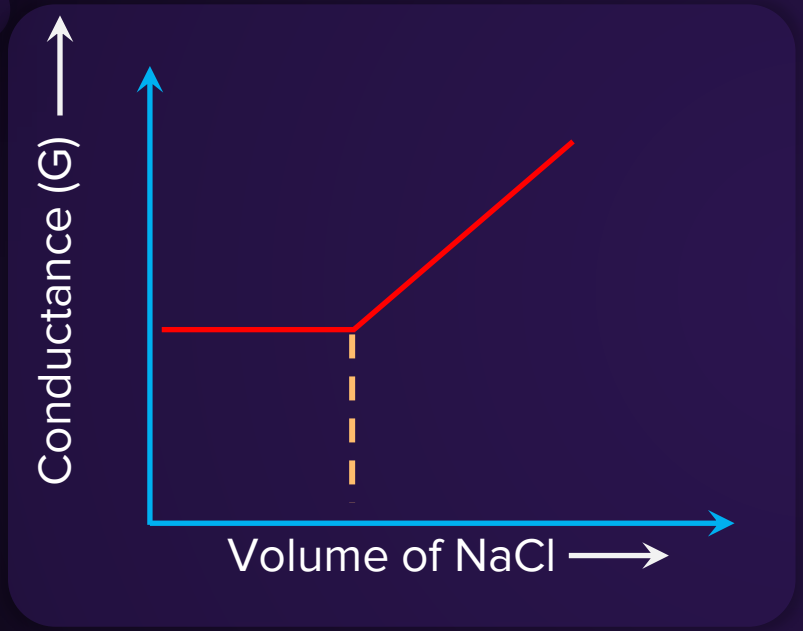


After the equivalence point

The increase in conductance is appreciable due to the added OH^- ions

Which explains the **third part** of the graph.

$AgNO_3$ vs. NaCl



NaCl is added to a solution of $AgNO_3$,

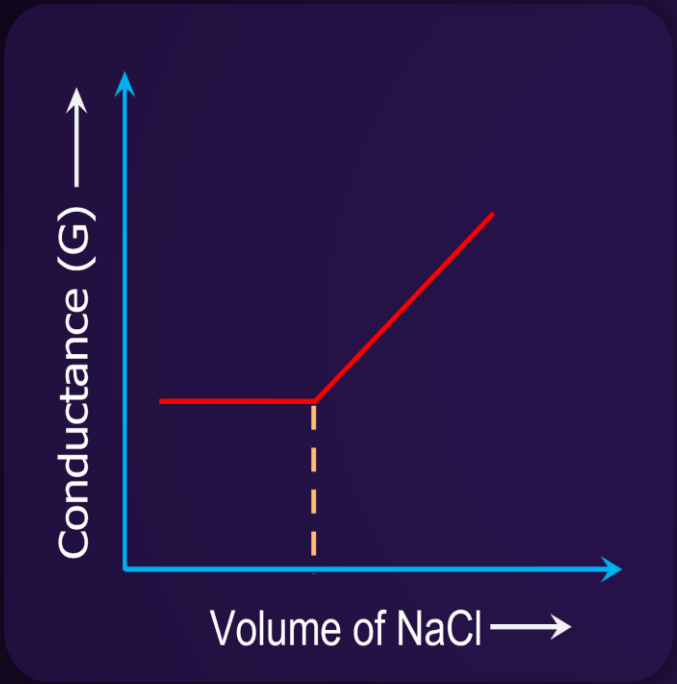
↓

Conductance **remains constant** till all $AgNO_3$ is used up as AgCl is weak electrolyte.

↓

NO_3^- are replaced by Cl^- ions

$AgNO_3$ vs. NaCl



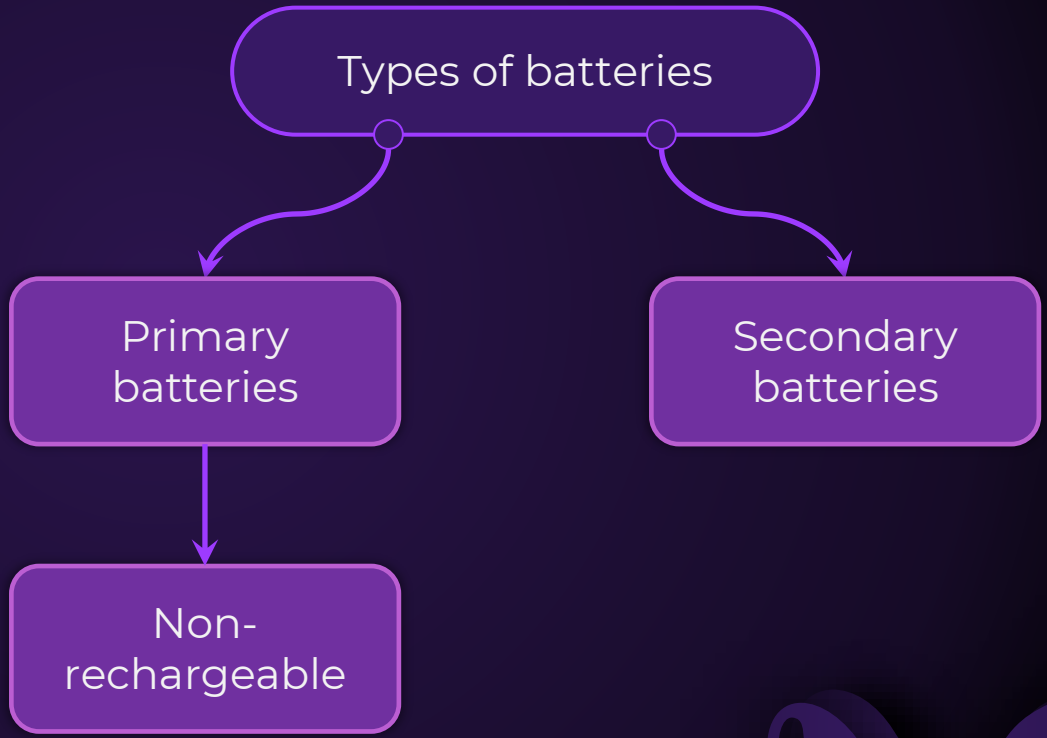
After $AgNO_3$ is used completely

There is an **increase in conductance** as the amount of NaCl increases.

Strong electrolyte

Batteries

Cell refers to a **single** galvanic cell, Whereas **battery** is formed when **two or more** cells are connected in series or in series-parallel.



Primary Batteries

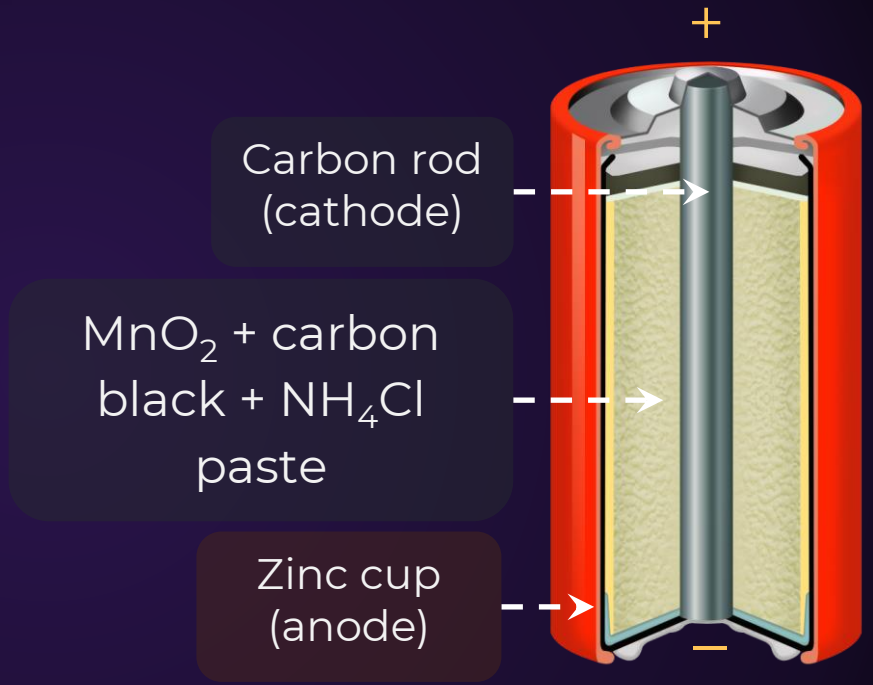
Primary cells can be used only so long the active materials are present.

Once these are consumed, the cell **cannot be recharged** by passage of current through it

Hence, it has to be **discarded**.

Examples

- Dry cell or Leclanche cell
- Mercury Cell



Dry Cell

Anode	Cathode
Zinc container	Carbon (graphite) rod surrounded by powdered manganese dioxide and carbon.

The space between the electrodes is filled by a moist paste of **ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$).**

Cathode:

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

Anode:

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

Dry Cell

Ammonia produced in the reaction **forms a complex** with Zn^{2+}

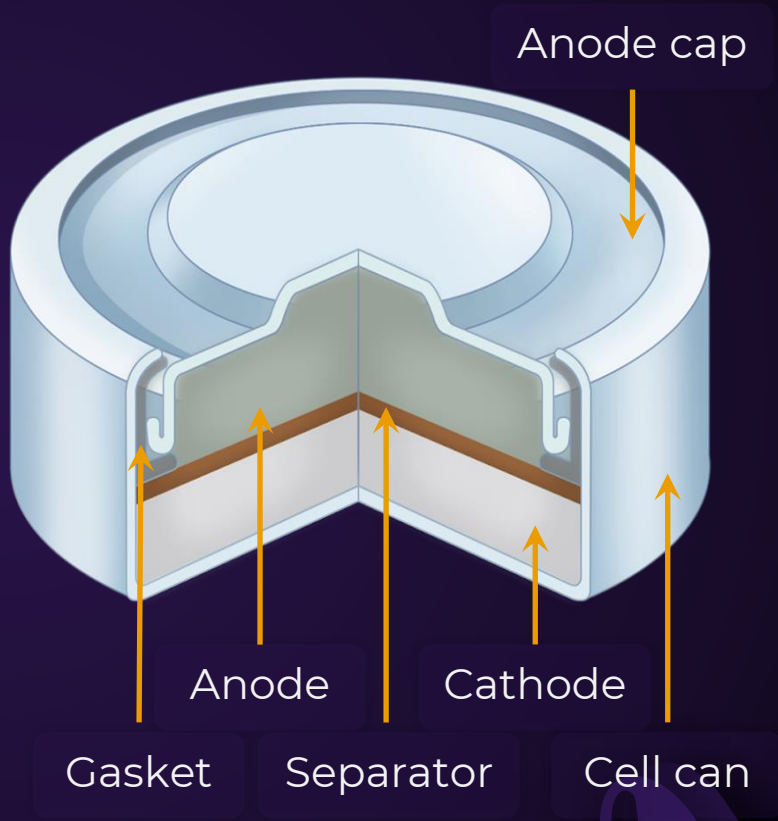
$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

Cell potential - - → 1.5 V - - → It **decreases** over use

Used in flashlights, portable radios, etc.

Mercury Cell

Zinc - mercury amalgam	**Anode**
Paste of HgO and carbon	**Cathode**
Paste of KOH and ZnO	**Electrolyte**



Mercury Cell

At the **anode**:

$$Zn(Hg) + 2OH^- \longrightarrow ZnO\ (s) + H_2O + 2e^-$$

At the **cathode**:

$$HgO + H_2O + 2e^- \longrightarrow Hg\ (l) + 2OH^-$$

Overall cell reaction

$$Zn(Hg) + HgO\ (s) \longrightarrow ZnO\ (s) + Hg\ (l)$$

$E_{Cell} = 1.35\ V$

Overall reaction **does not involve** any ion in the solution whose concentration can change during its life time.

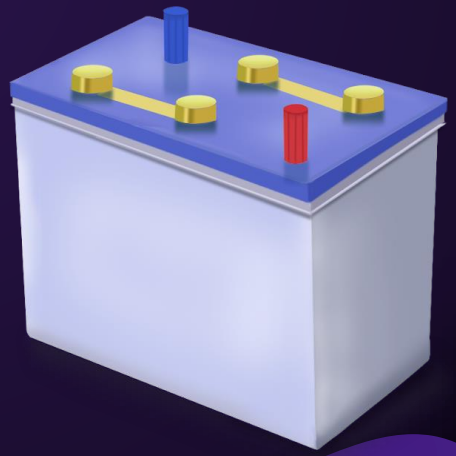
Used in watches, hearing aids, calculators, etc.

Secondary Batteries

A secondary cell after use **can be recharged** by passing current through it in the opposite direction so that it can be used again.

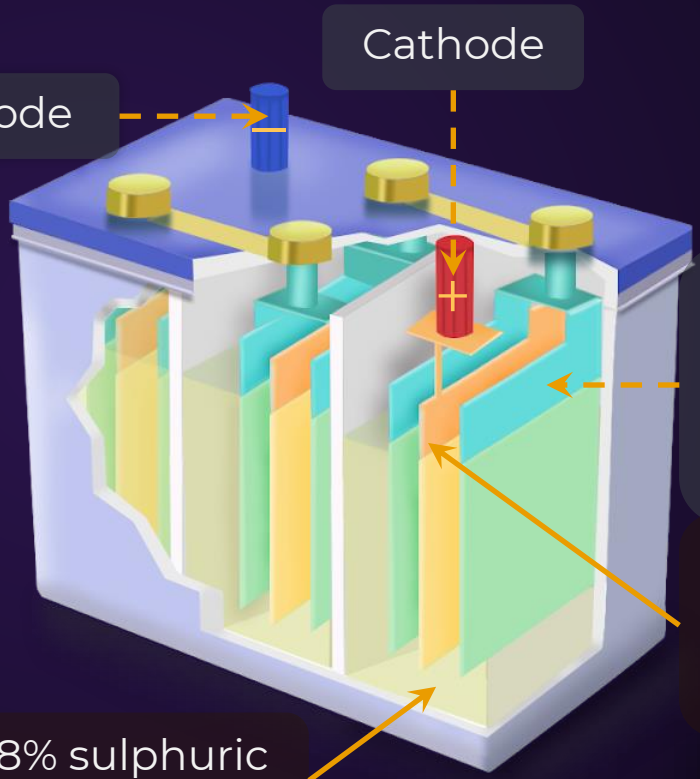
Examples

- Lead storage cell
- Nickel-cadmium cell



Lead Storage Cell

Lead	**Anode**
Grid of lead packed with lead dioxide (PbO_2)	**Cathode**
38% solution of sulphuric acid	**Electrolyte**



Lead Storage Cell

When battery is in use

At the **anode**:

$$Pb\,(s) + SO_4^{2-}\,(aq) \longrightarrow PbSO_4\,(s) + 2e^-$$

At the **cathode**:

$$PbO_2\,(s) + SO_4^{2-}\,(aq) + 4H^+\,(aq) + 2e^- \longrightarrow PbSO_4\,(s) + 2H_2O\,(l)$$

Lead Storage Cell

Overall reaction (when in use)

$$Pb\,(s) + PbO_2\,(s) + 2H_2SO_4\,(aq) \longrightarrow 2PbSO_4\,(s) + 2H_2O\,(l)$$

On charging the battery the **reaction is reversed**.

$PbSO_4\,(s)$ on anode and cathode is converted into **Pb** and **PbO_2**, respectively.

While discharging lead storage battery

If **1 F** of electricity is withdrawn from battery, **1 mol** of H_2SO_4 is consumed

During **working** of cell

H_2SO_4 will be **consumed** → $[H_2SO_4]$ in solution ↓ → Density of solution ↓

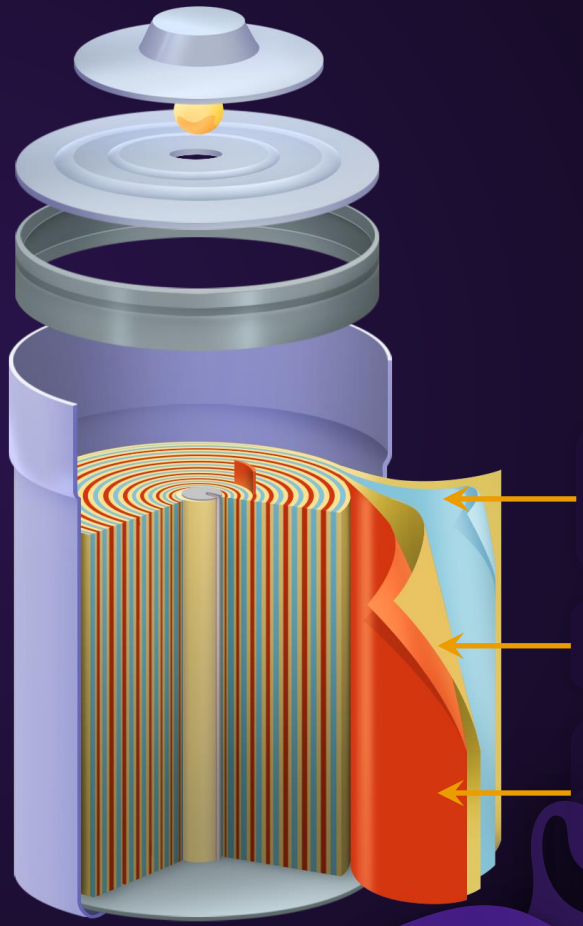
Used in **automobiles** (cars/bikes) and **inverters.**

During **charging** of cell

$PbSO_4$ will get converted into Pb (s) and PbO_2 (s) and H_2SO_4 will be **produced**.

Nickel–Cadmium Cell

Cadmium	Anode
Nickel dioxide (NiO_2)	Cathode
KOH	Electrolyte



Nickel–Cadmium Cell

Anode:

$$Cd\ (s) + 2OH^-\ (aq) \longrightarrow Cd(OH)_2\ (s) + 2e^-$$

Cathode:

$$NiO_2\ (s) + 2H_2O\ (l) + 2e^- \longrightarrow Ni(OH)_2\ (s) + 2OH^-\ (aq)$$

Nickel–Cadmium Cell

Overall reaction:

$$Cd\,(s) + NiO_2\,(s) + 2H_2O\,(l) \longrightarrow Cd(OH)_2\,(s) + Ni(OH)_2\,(s)$$

$E_{Cell} = 1.4\ V$

Used in **cordless razors, portable electronics,** etc.

This cell has comparatively **longer life** than a lead storage cell.

Fuel Cell

Galvanic cell that are designed to convert the **energy of combustion** of fuels like H_2, CH_4, CH_3OH, etc, directly into **electrical energy**.

Here, the cathode and anode constituents are **continually supplied.**

Thus, energy can be **withdrawn indefinitely** from a fuel cell as long as the outside supply of **fuel is maintained**.

H_2–O_2 Fuel Cell

Electrodes

Made of a conducting material, such as **graphite**, with a sprinkling of **platinum**

Acts as catalyst

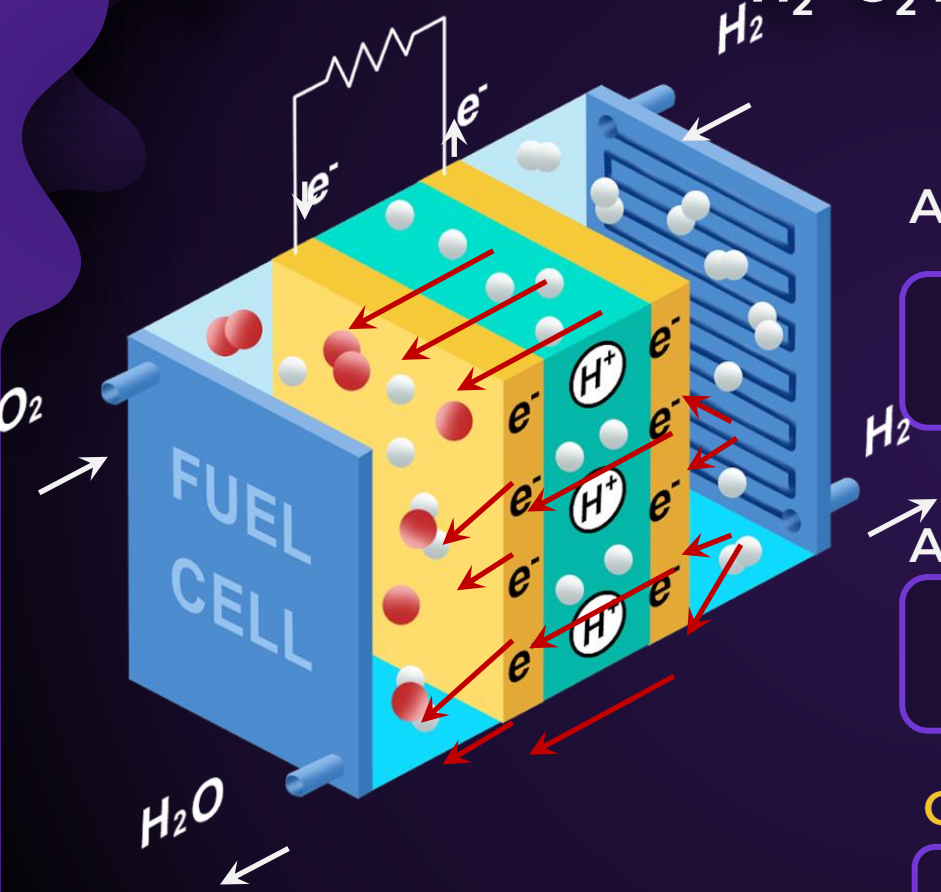
Electrolyte

Aqueous solution of a **base**

H_2 gas is fed into one compartment and the **O_2 gas** is fed into another compartment.

These gases **diffuse slowly** through the electrodes and react with an electrolyte that is in the **central** compartment.

H_2–O_2 Fuel Cell



At the **cathode**:

$$O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-\,(aq)$$

At the **anode**:

$$2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4e^-$$

Overall reaction:

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

H_2–O_2 Fuel Cell

Cell used for providing electrical power in the **Apollo space program**

The water vapour produced during the reaction were **condensed** and added to the **drinking water supply** for the astronauts.

Advantages of Fuel Cells

1. They offer **high energy conversions** (almost **70%**). Compared to thermal plants whose efficiency is about **40%**.

2. These cells are **pollution-free**.

Corrosion

Slowly coating of the surfaces of metallic objects with **oxides** or other **salts** of the metal.

1. Rusting of **iron**
2. Tarnishing of **silver**
3. Development of green coating on **copper** and **bronze**

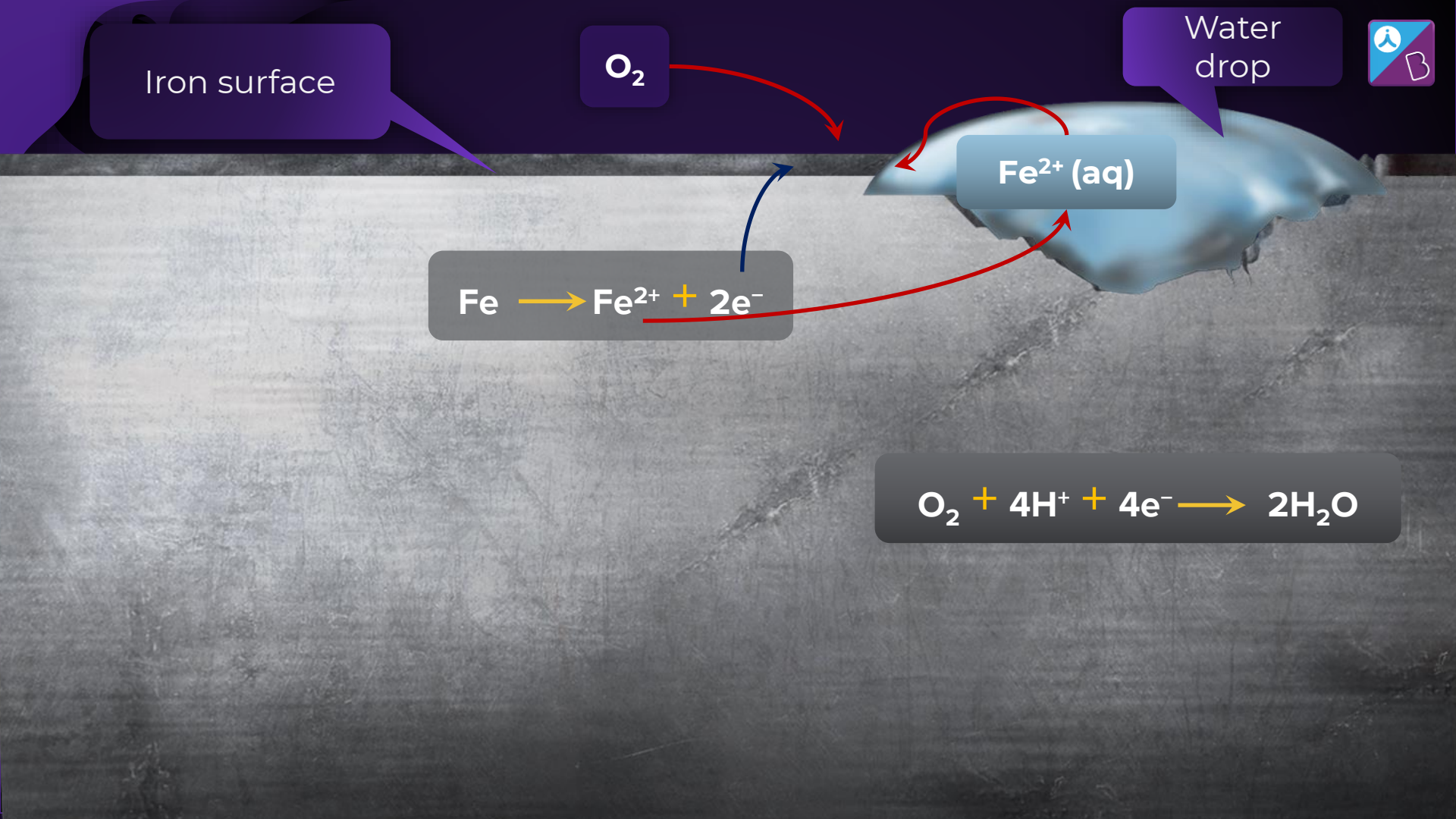
Tarnishing of Silver

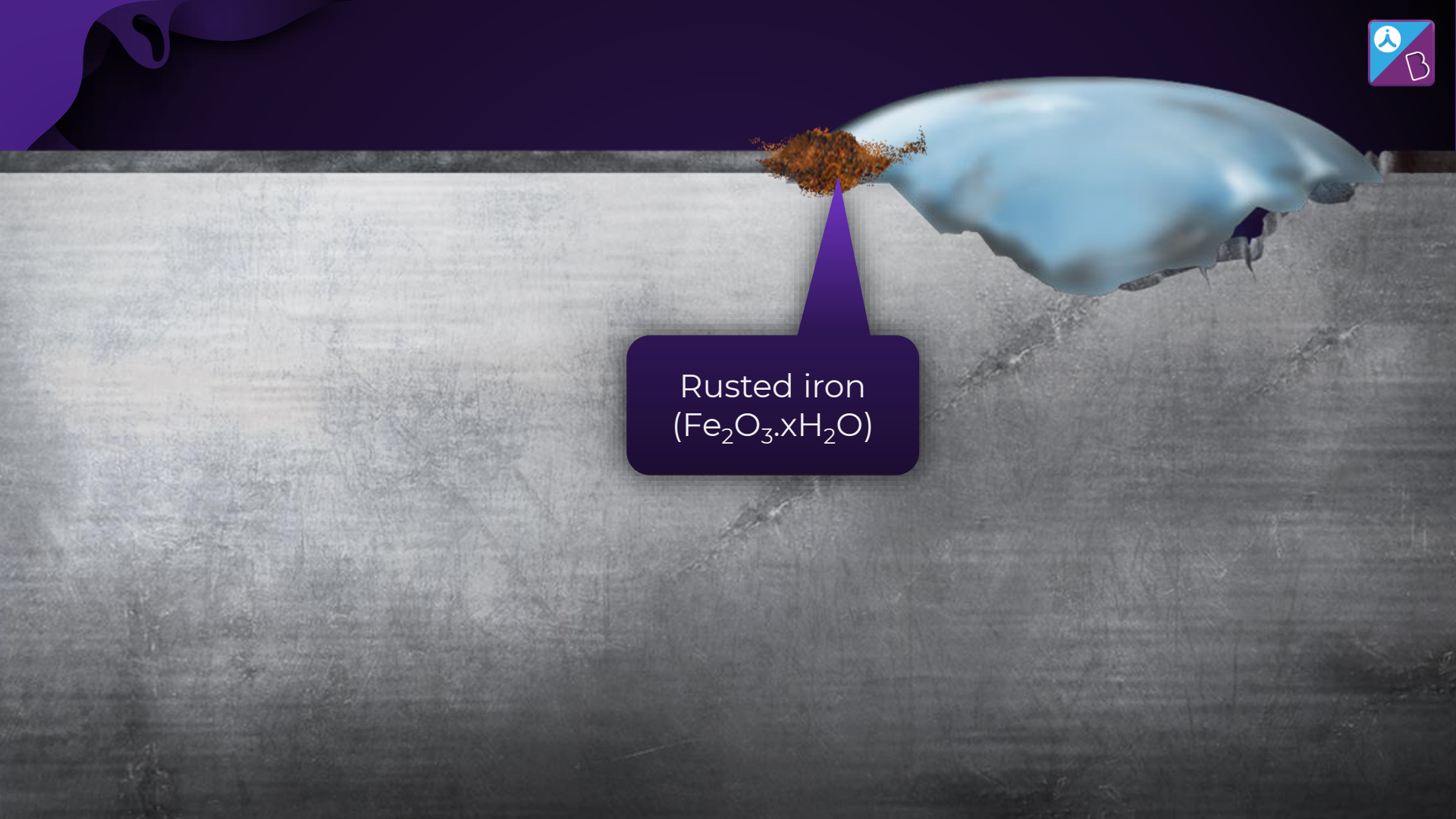
Green Coating on Copper

Rusting of Iron

Formation of porous coating of iron oxide **($Fe_2O_3.xH_2O$)** on iron surface in moist air

May be considered as an **electrochemical** phenomenon


Iron surface
O_2
Water drop
Fe^{2+} (aq)
$Fe \longrightarrow Fe^{2+} + 2e^-$
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$


Rusted iron
($Fe_2O_3.xH_2O$)

Anode reaction

$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^{-}$ ... (1)

$E^{0}_{ox} = 0.44\ V$

Behaves as **cathodic region**

Cathode reaction

Electrons released at **anodic spot** move through the metal

↓

Go to another **spot** on the metal

↓

Reduce oxygen (of air) in the presence of H^{+}

Cathode reaction

O_2 (g) + $4H^+$ (aq) + $4e^-$ → $2H_2O$ (l) .... (2)

E^0 = 1.23 V

H^+ available can be from

- **H_2CO_3** formed due to dissolution of CO_2 from air into water
- Dissolution of other **acidic oxides** from the atmosphere

Overall Reaction

$Fe\ (s) \longrightarrow Fe^{2+}\ (aq) + 2e^-$ ...1

$O_2\ (g) + 4H^+\ (aq) + 4e^- \longrightarrow 2H_2O\ (l)$ ...2

Overall reaction

$$2Fe\ (s) + O_2\ (g) + 4H^+\ (aq) \longrightarrow 2Fe^{2+}\ (aq) + 2H_2O\ (l)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = 1.23 - (-0.44)$$

$$E^0_{cell} = 1.67\ V$$

Rusting of Iron

Fe^{2+} is further **oxidised** by atmospheric oxygen to Fe^{3+}.

This comes out as rust in the form of **hydrated ferric oxide** with further production of H^+ ions.

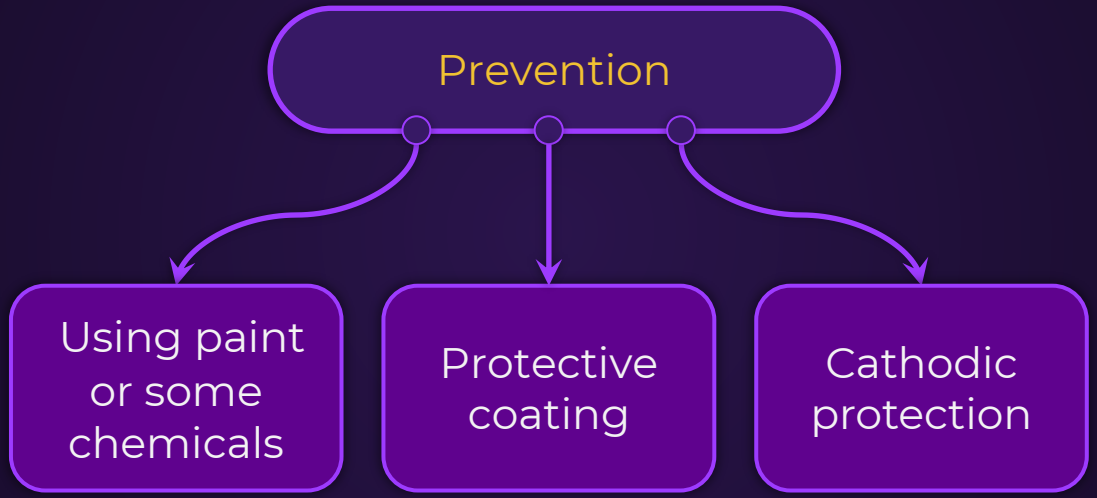
$Fe_2O_3.xH_2O$

Due to porous **coating of rust**

Further attack of **moist air** occur on iron metal

Strength of metal ↓

Prevention of Corrosion



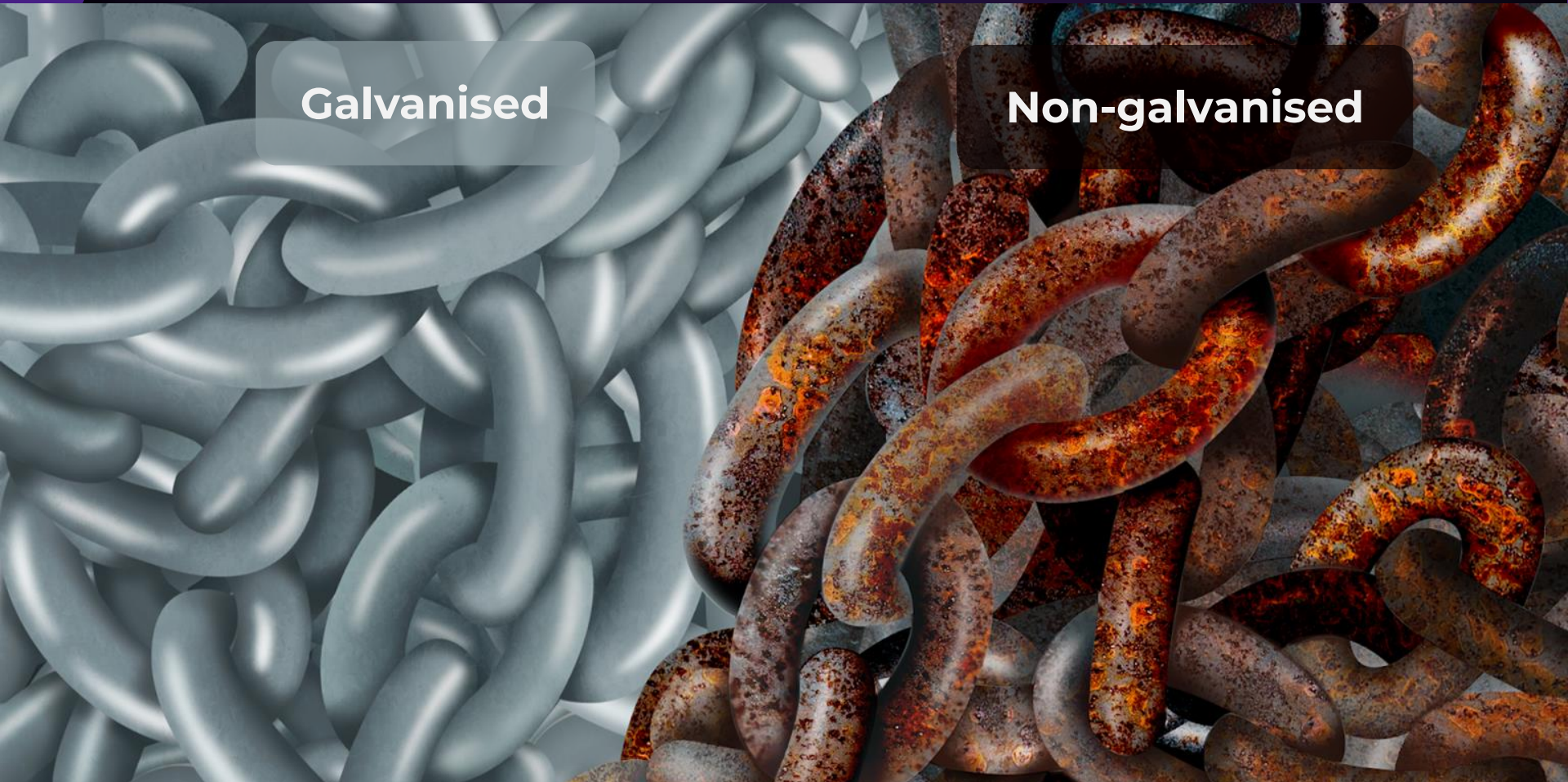
Prevention of Corrosion

1. Using Paint or Some Chemicals

Covering the surface with **paint** or by some chemicals (e.g. **bisphenol**) prevent the surface of the metallic object to come in contact with the atmosphere.

2. Protective Coating

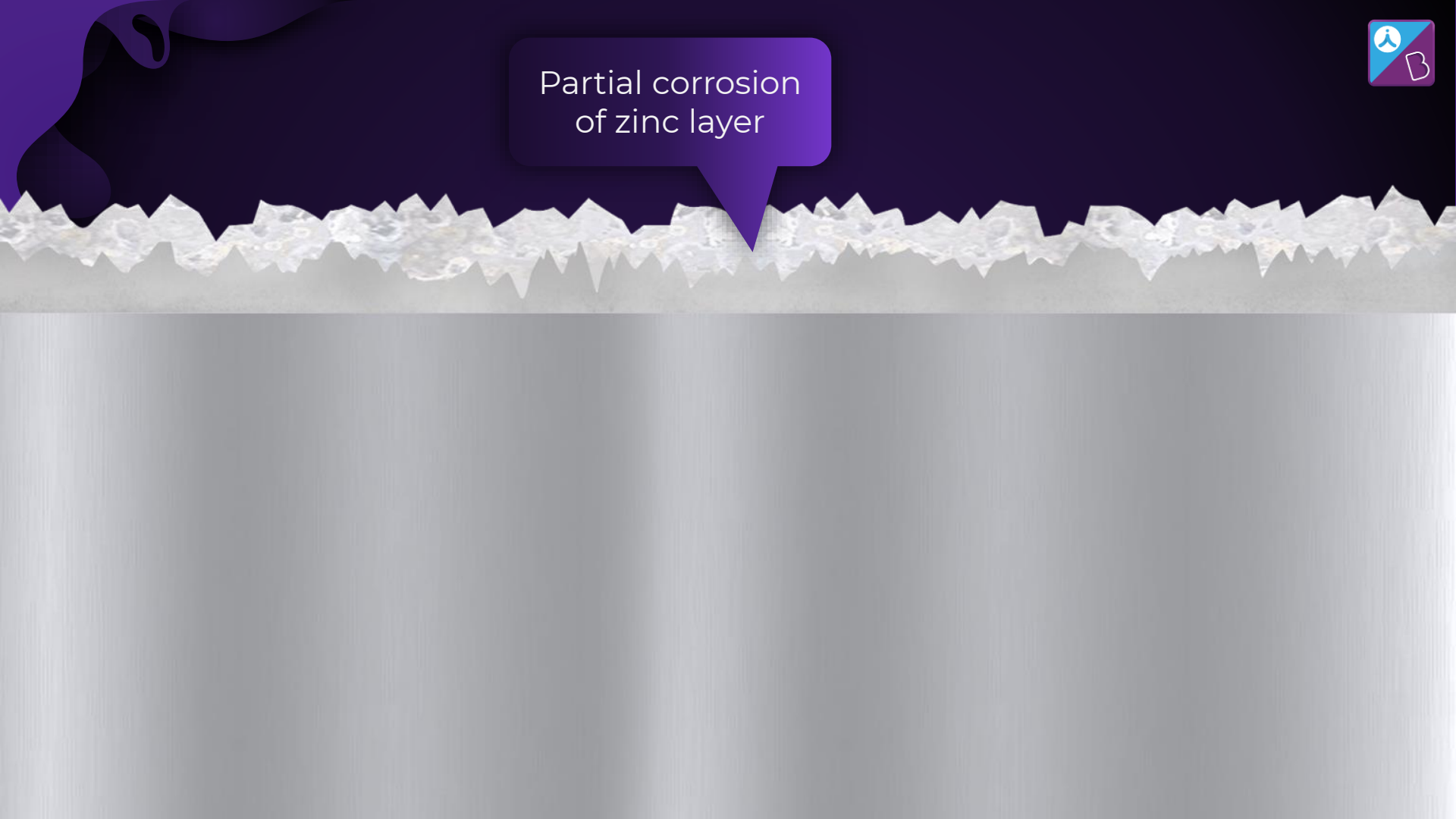
Cover the surface by other metals that are inert or react to save the object.
Galvanisation: Coating of Zn metal


Galvanised
Non-galvanised

Atmosphere

Zinc layer

Iron slab (to be protected)


Partial corrosion
of zinc layer


Complete corrosion of
zinc layer and appearance
of rust on Fe surface

Prevention of Corrosion

3. Cathodic Protection

In cathodic protection, the object is connected to a metal with a **more negative** standard reduction potential (E.g.: Mg, $E^0 = -2.36$ V).

Mg acts as a **sacrificial anode**, supplying its own electrons to the iron and becoming **oxidised to Mg^{2+}** in the process.

A block of magnesium replaced occasionally is **much cheaper** than the ship, building, or pipeline for which it is being sacrificed.

Cathodic Protection