MIST | Technology for Advancement
Military Institute of Science and Technology

Fundamentals of Chemistry

CHEM 101

Electrochemistry

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Lesson: Electrochemistry

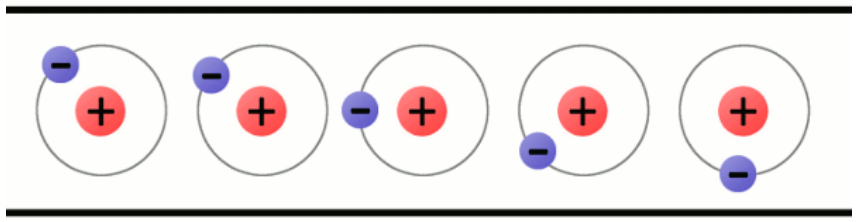
1. Basics of Electrochemistry
2. Electrolysis and related laws
3. Different Types of Electrochemical Cell
4. Conductance: Definitions and Classifications
5. Factor Influencing Conductivity
6. Conductometric Titrations

Electrochemistry

Electrochemistry is the branch of chemistry that deals with the relationship between electrical energy and chemical reactions.

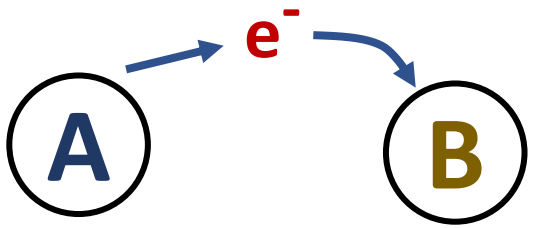
- **Electricity**

Movement of electrons



- **Chemical Reactions**

Electrons move between atoms



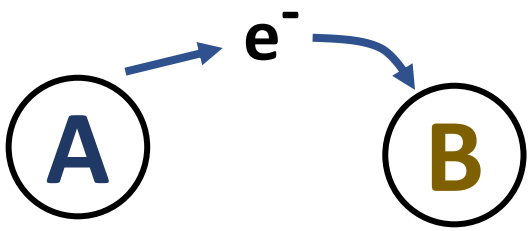
Can create electricity

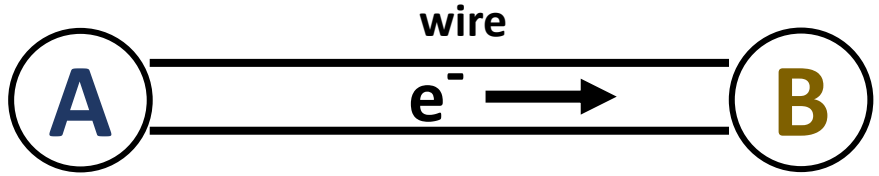
✓ **This branch deals with the study of chemical changes caused by the passage of electric current and the production of electrical energy by chemical reactions**

Electrochemistry

- **Certain chemical reactions can create electricity**

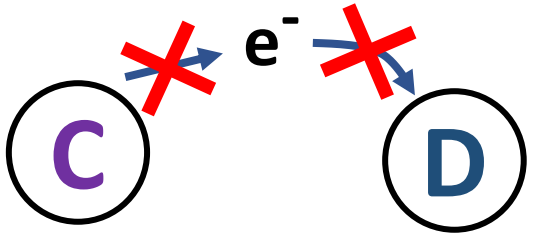
  ✓ Conversion of chemical energy into electrical energy. i.e., the generation of electricity by spontaneous redox reactions.



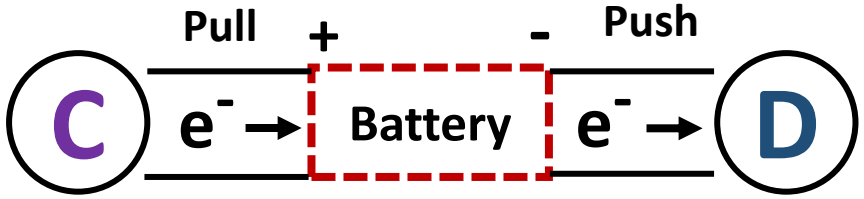


- **Electricity can make certain chemical reactions happen that wouldn't happen otherwise**

  ✓ Production of chemical change by electrical energy with the need of an external source. i.e. the phenomenon of electrolysis



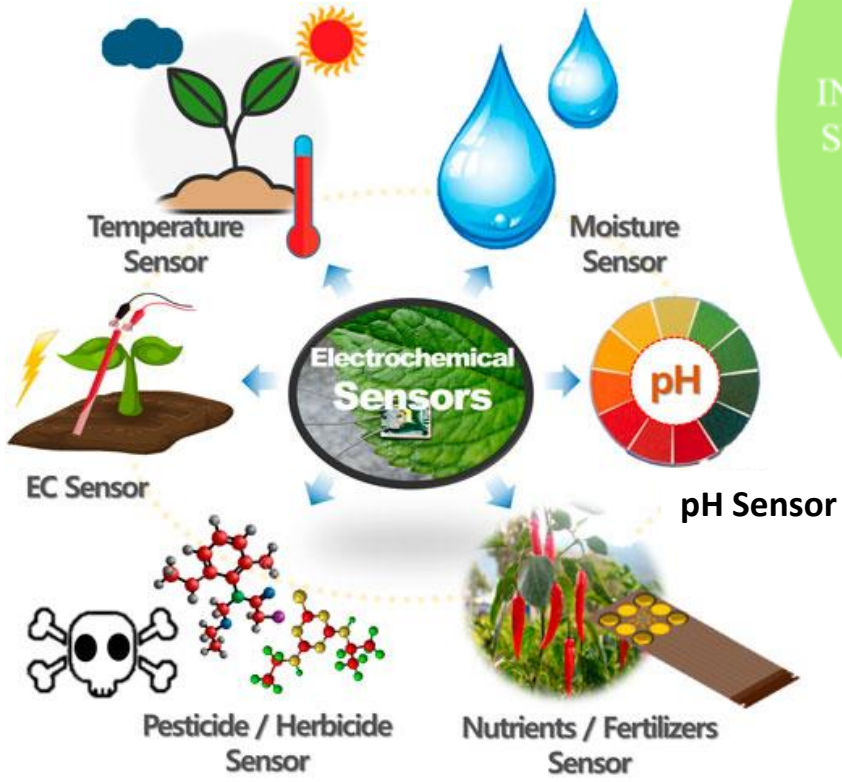
Won't normally happen

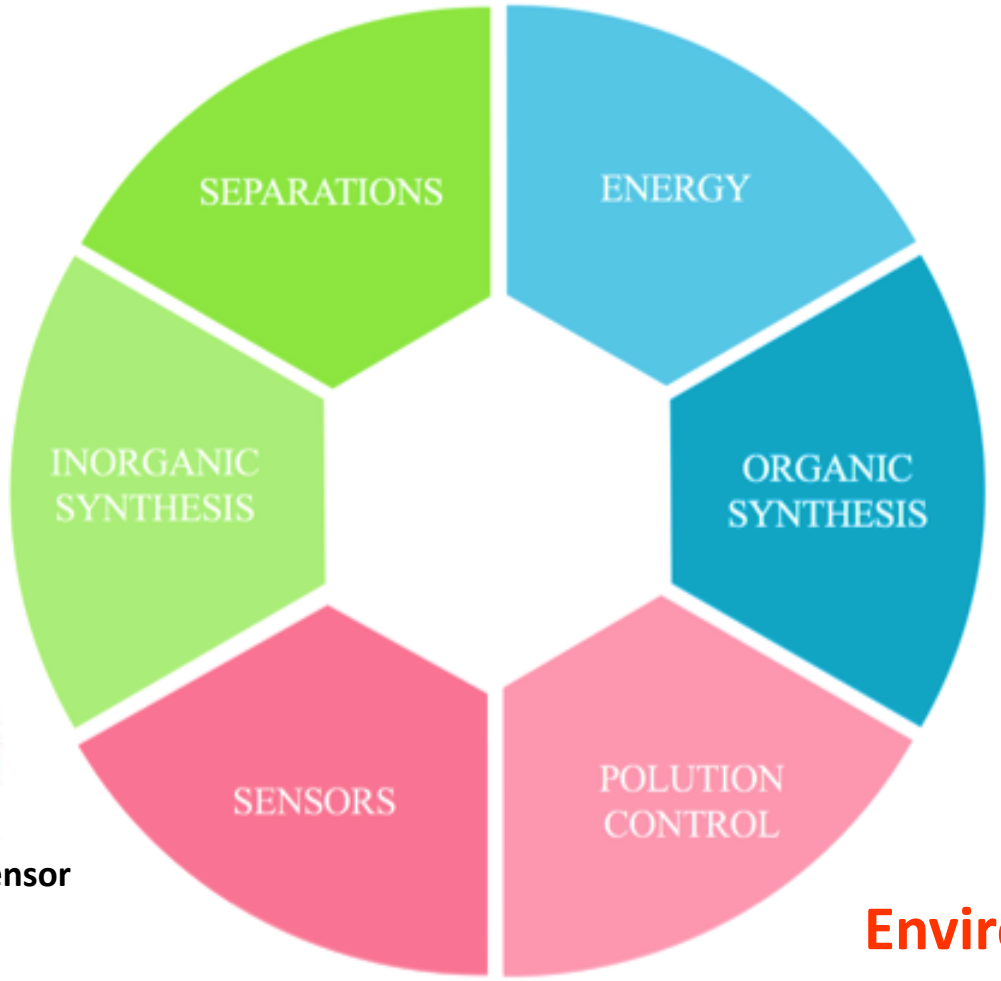


Applications of Electrochemistry

Separations

- Electrodialysis
- Salt Splitting





Energy

- Redox Flow cells
- Fuel Cells
- Batteries

Synthesis

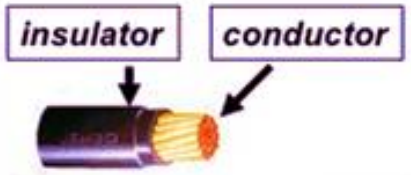
- Inorganic
- Organic
- Pharmaceuticals

Environmental Electro-technology

- Metal recovery
- Water treatment

Conductor –

Any material that allows electric current to pass through it



- copper
- aluminum
- steel



- any metal

Metallic

Insulator –/ Non-Conductor

Any material that does not allow electric current to pass through it

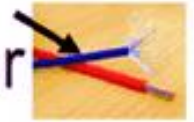
- like the protective coating on wires



- plastic



- cloth



- rubber



- glass



- wood

Electrolytic

- **Aqueous solutions of acid, base and salts**
- **Impure water**

DIFFERENCE BETWEEN METALLIC AND ELECTROLYTIC CONDUCTION :

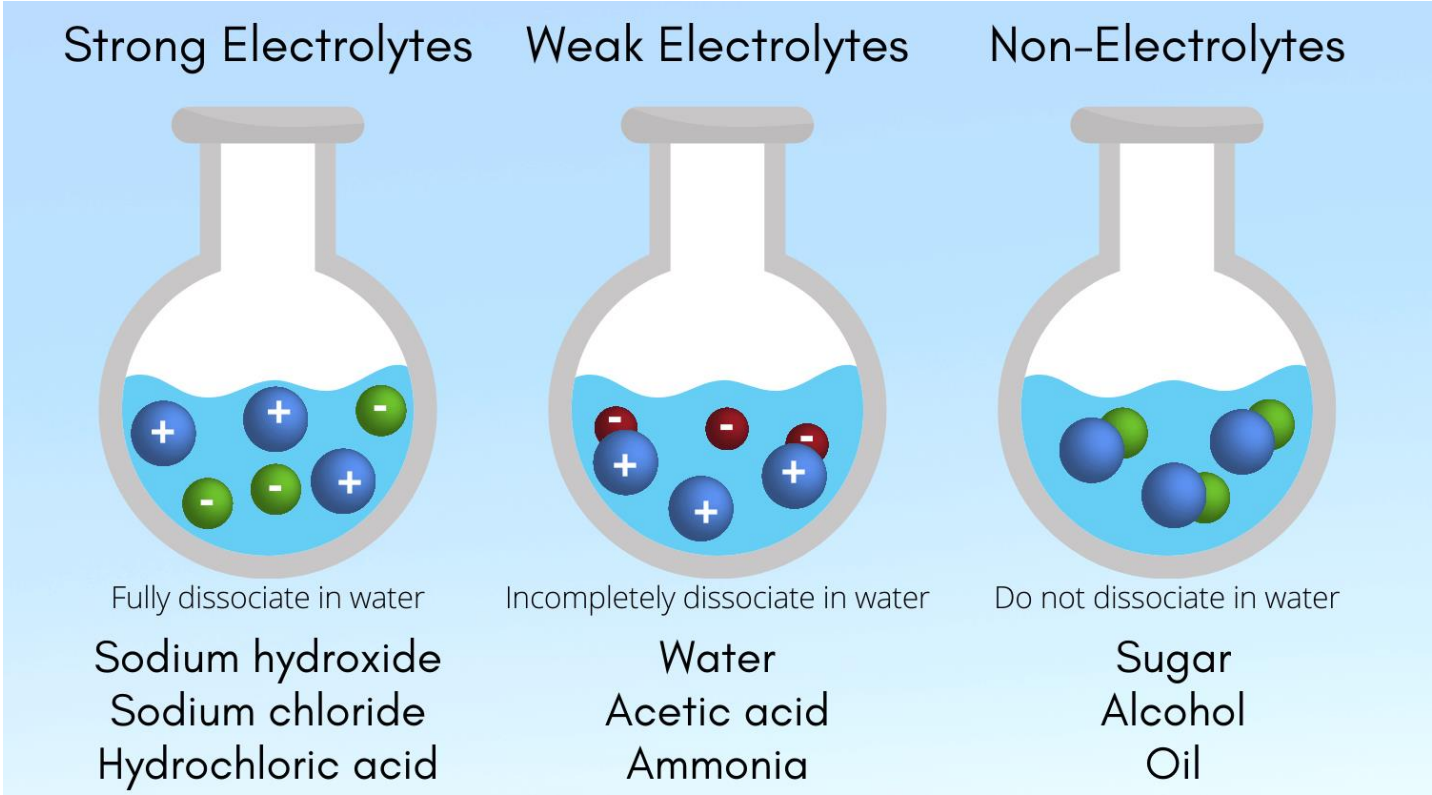
	Metallic conduction	Electrolytic conduction
(i)	Flow of electricity takes place without the decomposition of the substance	Flow of electricity takes place by chemical changes at electrodes.
(ii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions
(iii)	The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

Electrochemistry

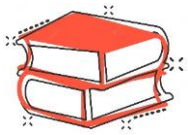
Electrolyte: An electrolyte is a substance that conducts an electric current when dissolved in a solvent, such as water.

- Electrolytes are typically ionic compounds that dissociate into positive and negative ions in solution, allowing the flow of electrical current through the solution.

- Some common examples of electrolytes include sodium, potassium, calcium, magnesium, chloride, and bicarbonate. These electrolytes are found in many fluids in the body, including blood, urine, and sweat.

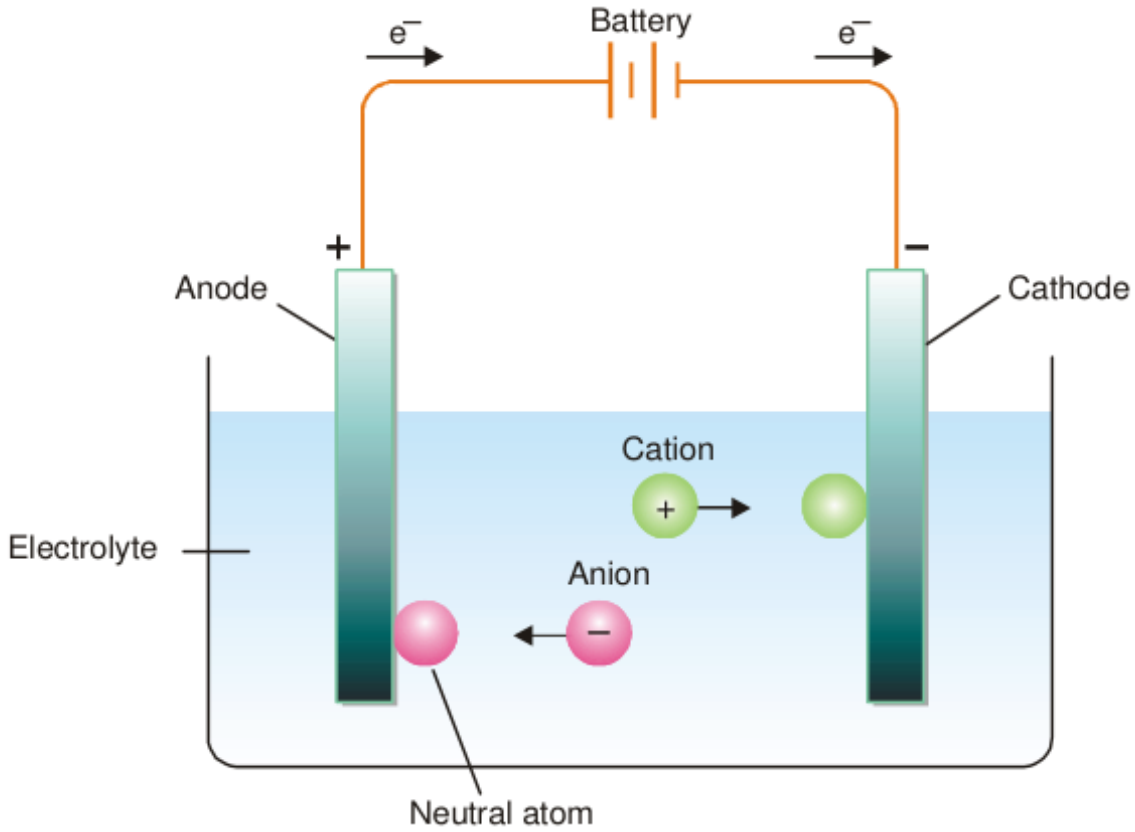


Electrolysis



The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed Electrolysis.

The process of electrolysis is carried in an apparatus called the Electrolytic cell



APPLICATIONS

- Production of metals
- Electroplating
- Electrolytic refining
- Production of chemicals
- Battery technology
- Water treatment

Mechanism of Electrolysis

- **Direct current is passed through the compound**
- **Electrical energy (From direct current) is changed into chemical energy (the decomposition of the compound).**

In solution, HCl is ionised, $HCl \longrightarrow H^+ + Cl^-$

In the electrolytic cell, Cl^- ions will move toward the anode and H^+ ions will move toward the cathode.

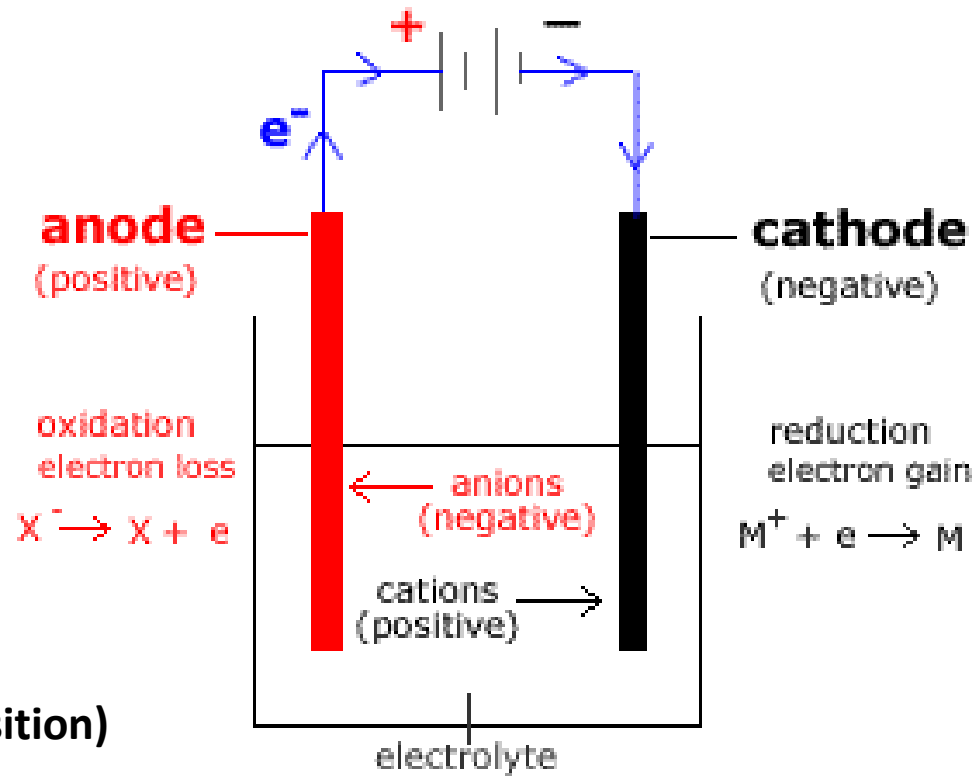
At anode : $Cl^- \longrightarrow Cl + e^-$

Pair of Cl atoms unite to form Cl gas, Cl_2.

At cathode : $H^+ + e^- \longrightarrow H$

Pairs of H atoms then unite to form molecules of H gas, H_2.

The overall reaction is : $2HCl \longrightarrow H_2 + Cl_2$ **(Decomposition)**



Faraday's laws of Electrolysis

- **Faradays First Law (the Law of Electrochemical Equivalence)**

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passing through the electrolyte.

The more electricity passes through the system, the greater the amount of substance will be produced.

If w is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity,

$$W \propto Q$$

We know, Q = It

The quantity of electricity passed in 1 second by a current of 1 ampere

$$\boxed{W = Z\,I\,t}$$

Here, **Z** is a constant and known as **electrochemical equivalent**.

It is the amount of substance liberated when 1 A current is passed through the electrolyte for 1 sec or when 1 C electricity is passed.

Faraday's laws of Electrolysis

It has been found experimentally that the quantity of electricity required to liberate one gram-equivalent/chemical equivalent of a substance is 96,500 coulombs.
This quantity of electricity is known as Faraday and is denoted by the symbol F.

One mole of substance contains Avogadro's No. of particles.

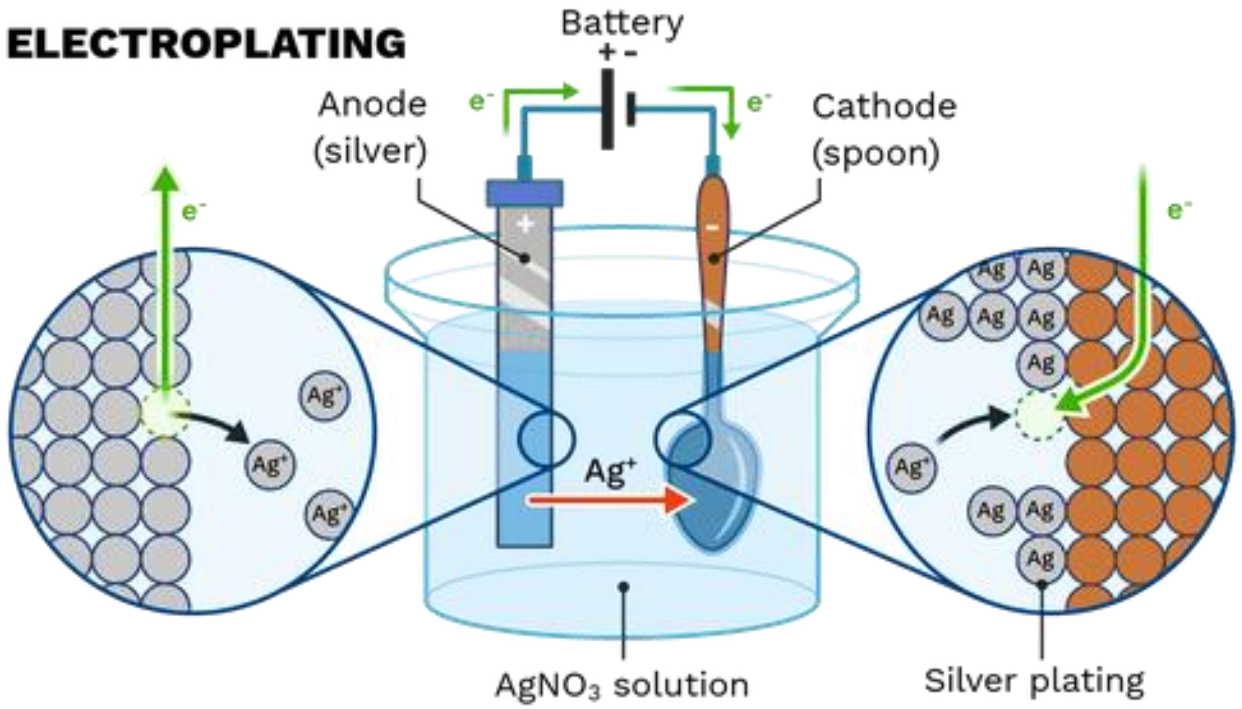
Since one mole of electrons carries a charge of $6.02 \times 10^{23} \times 1.6 \times 10^{-19}$ coulombs (the charge of one electron), one mole of electrons carries a total charge of approximately 96,500 coulombs.

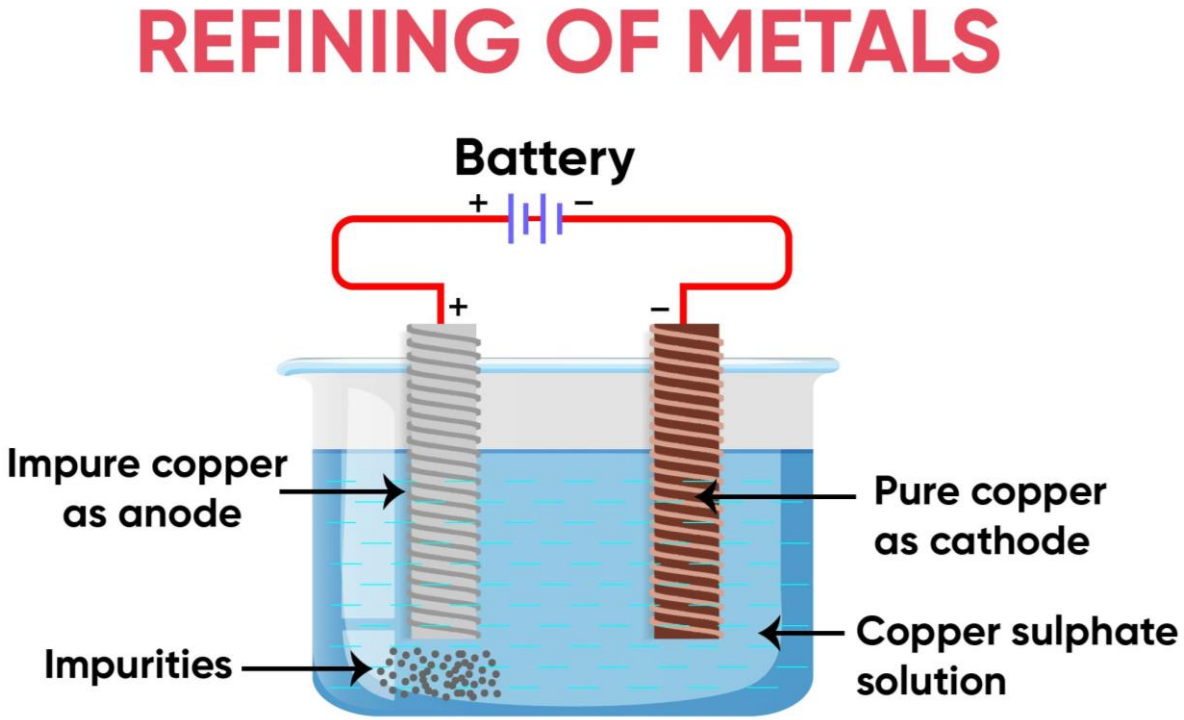
1 Faraday = 96,500 coulombs = 1 Mole electrons

DO Numericals from Bahl and Tuli

Faraday's laws of Electrolysis

Applications of Faradays First Law





At the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

At the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Faraday's laws of Electrolysis

- **Faradays Second Law**

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of substances liberated at the electrodes are directly proportional to their chemical equivalents or equivalent weight(E).

For acids $E = \dfrac{\text{Molecular weight}}{\text{protocity or basicity of acid}}$

For example, for H_3PO_4, $E = \dfrac{M}{3}$

For H_2SO_4, $E = \dfrac{M}{2}$ (Also for $H_2C_2O_4 \cdot 2H_2O$)

For bases $E = \dfrac{\text{Molecular weight}}{\text{Acidity or number of } OH^- \text{ ions}}$

For example, for $Ca(OH)_2$, $E = \dfrac{M}{2}$

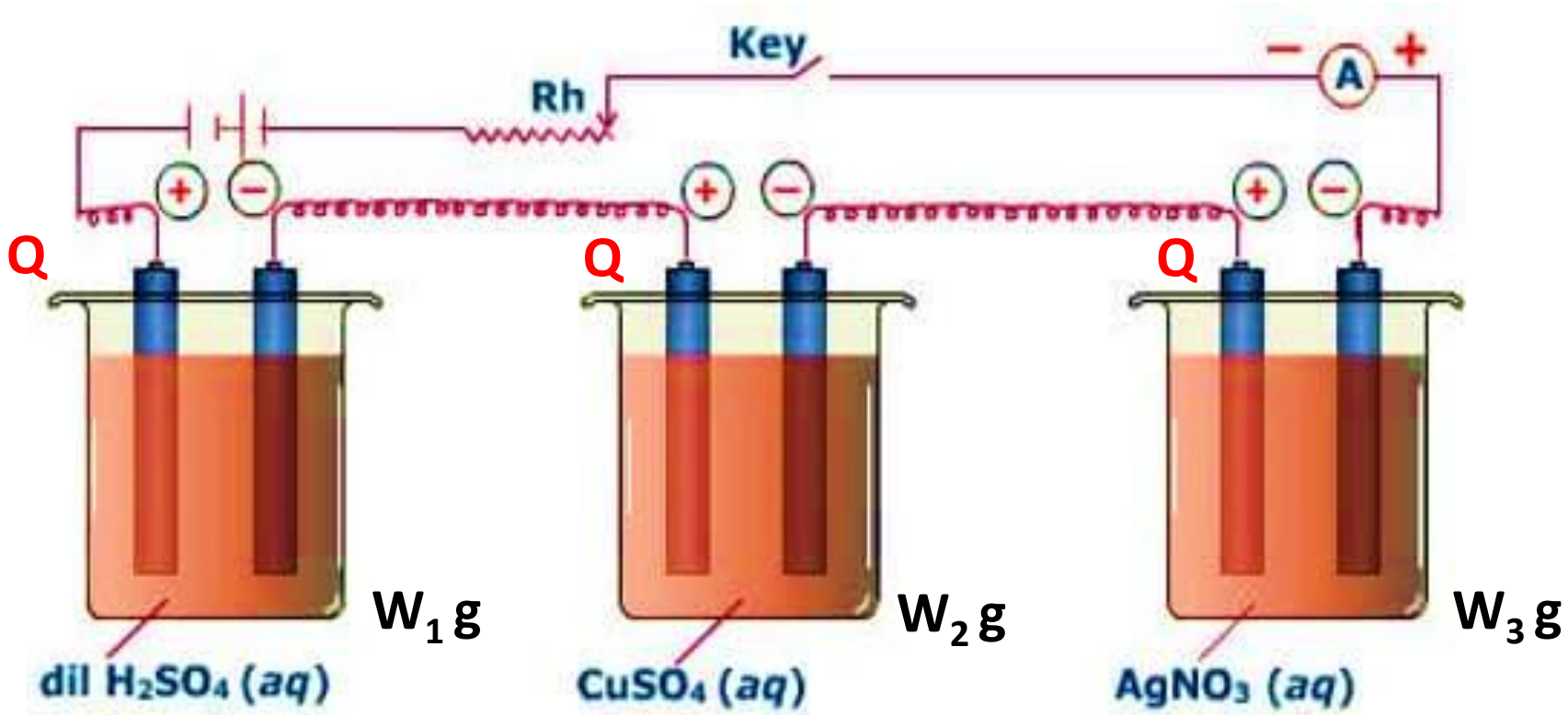
For $Al(OH)_3$, $E = \dfrac{M}{3}$

For ions $E = \dfrac{\text{Molecular weight}}{\text{Charge on ion}}$

For example, for SO_4^{2-}, $E = \dfrac{M}{2}$

For PO_4^{3-}, $E = \dfrac{M}{3}$

Faraday's laws of Electrolysis



$W_1 \propto E_1$

$W_2 \propto E_2$

$W_3 \propto E_3$

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

Combination of Faraday's laws of Electrolysis

Faraday's First Law of electrolysis,

$W \propto Q$, when Z is constant

Faraday's Second Law of electrolysis,

$W \propto E$, when Q is constant

By combining, $W \propto Q \times E$

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

Here, $\frac{1}{F}$ is constant and $F = 96500C$

Faraday's laws of Electrolysis

Relation between Chemical Equivalence and Electrochemical Equivalence

From First Law,

$$W = Z \times Q \text{ , when Z is constant}$$

From Combination law,

$$W = \frac{Q \times E}{F} \quad \text{Here, } \frac{1}{F} \text{ is constant and } F = 96500C$$

Now,

$$Z \times Q = \frac{Q \times E}{F}$$

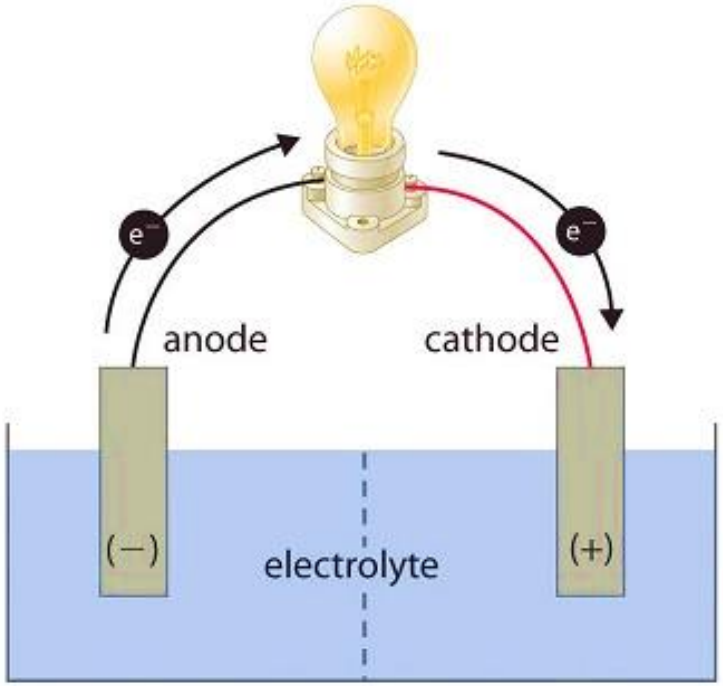
$$Z = \frac{E}{F} \qquad \boxed{E = Z \times F}$$

Chemical Equivalence = Electro-chemical Equivalence × 96500C

Electrochemical Cell

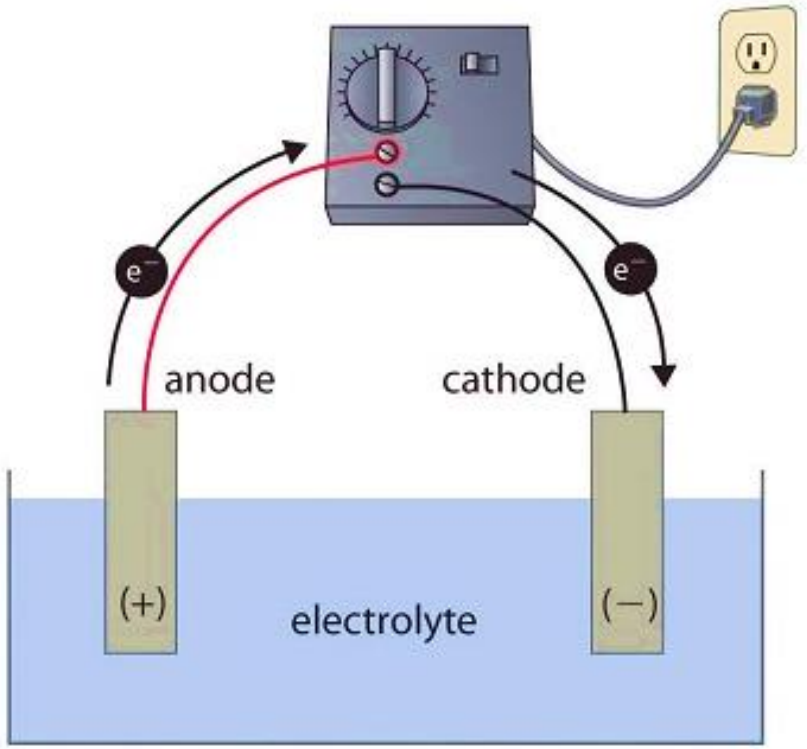
A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

Types: Galvanic (Voltaic) Cell



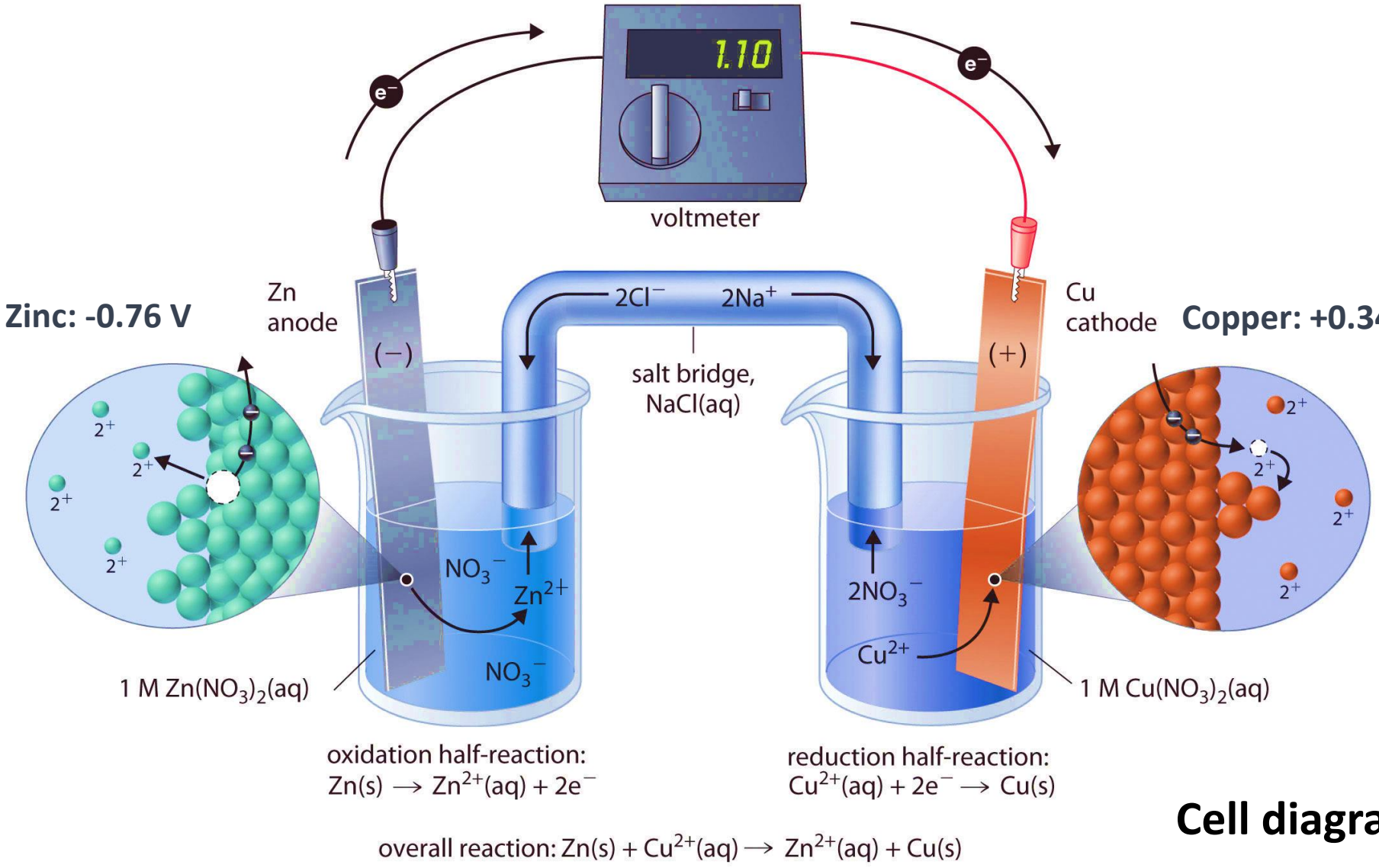
Spontaneous redox reaction produces electricity. Composed of two half-cells.

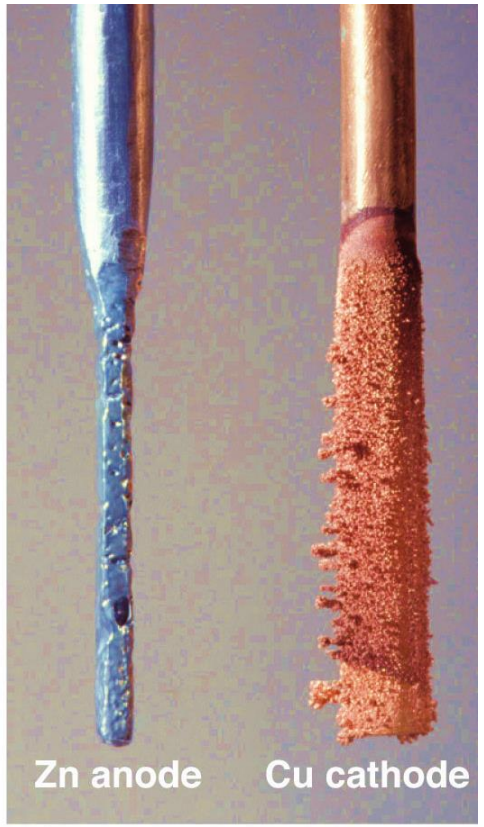
Electrolytic Cell



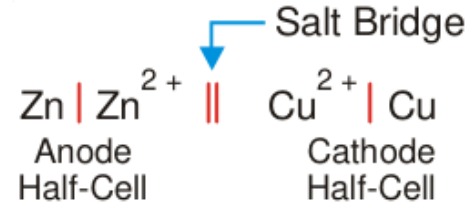
Non-spontaneous redox reaction forced to occur with external power source.

Galvanic(Voltaic) Cell



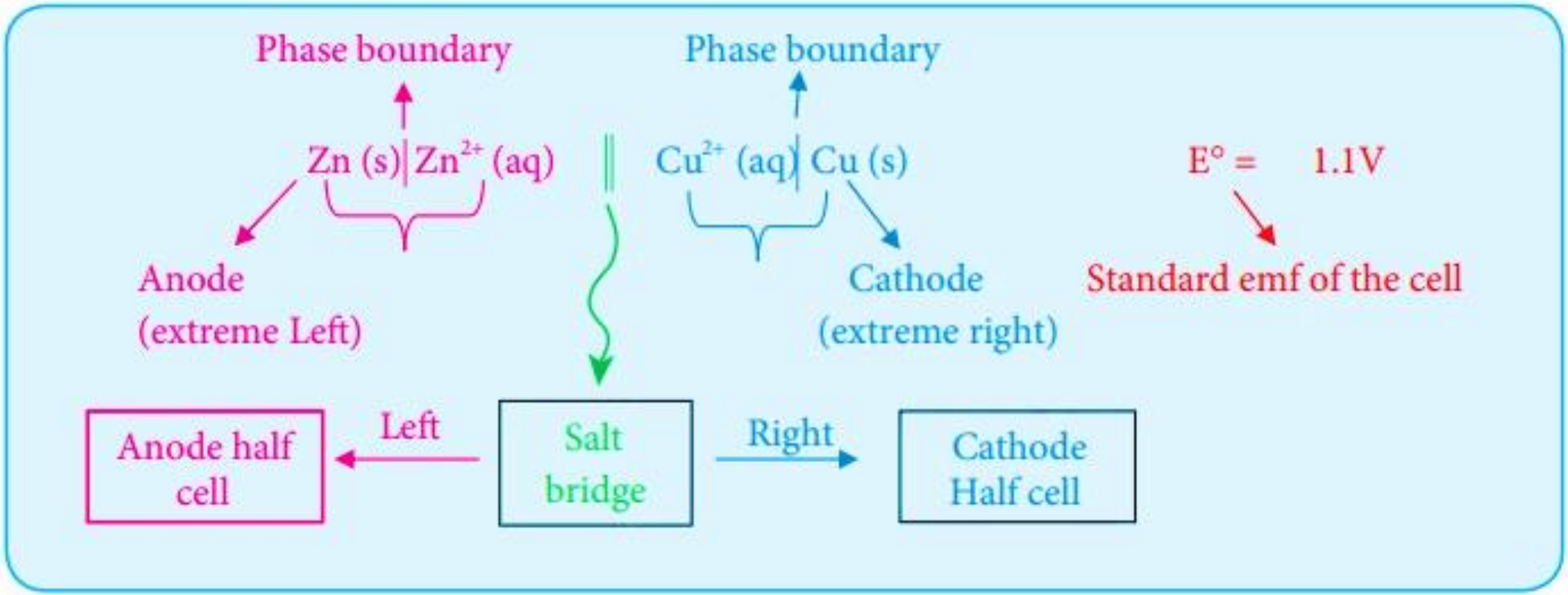


Cell diagram:



Cell diagram or Notation

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell.
In 1953, IUPAC recommended the following conventions for writing cell diagrams.



Role of Salt Bridge

Charge balance is important because it is essential for the proper functioning of any electrochemical cell

The electrons flow from the anode to the cathode. The oxidation reaction that occurs at the anode generates electrons and positively charged ions.

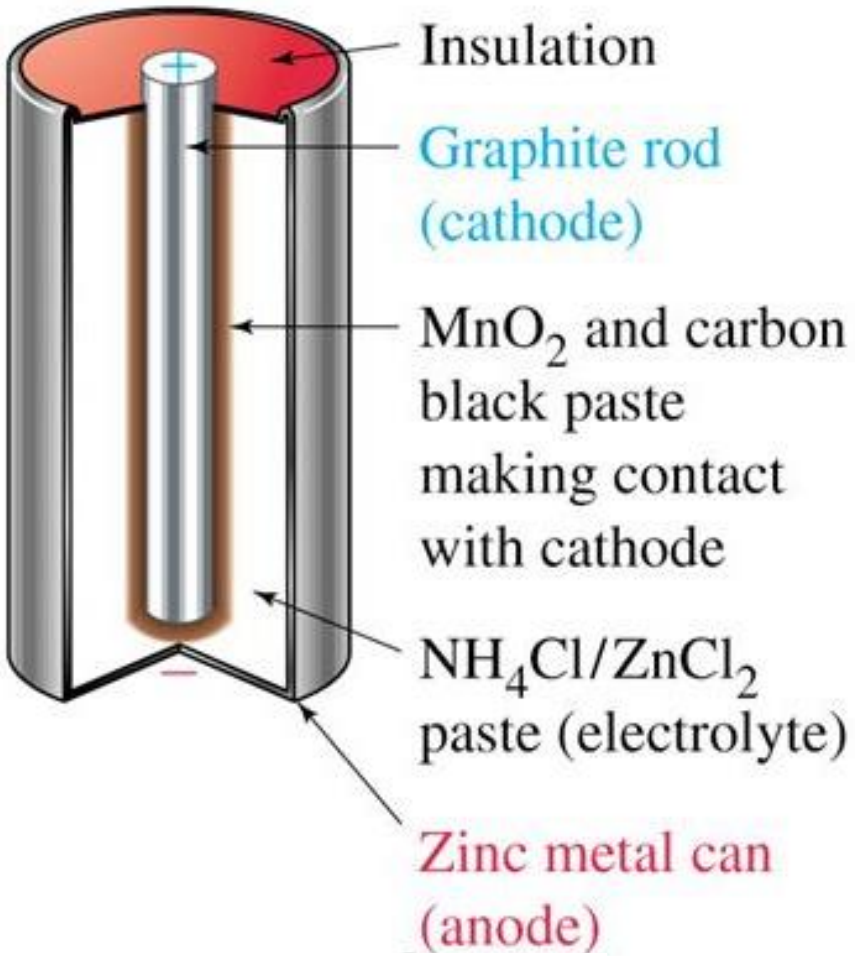
The electrons move through the wire leaving the unbalanced positive charge in this vessel. In order to maintain neutrality, the negatively charged ions in the salt bridge will migrate into the anodic half cell.

A similar (but reversed) situation is found in the cathodic cell, where Cu^{2+} ions are being consumed, and therefore electroneutrality is maintained by the migration of K^{+} ions from the salt bridge into this half cell.

1 M: **KCl solution** **Agar gel** **Sodium sulfate solution** **Potassium nitrate solution** **Gelatin**

Types of Cell

Primary Cell/ Dry Cell/ Leclanché cell



Anode:

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

Cathode:

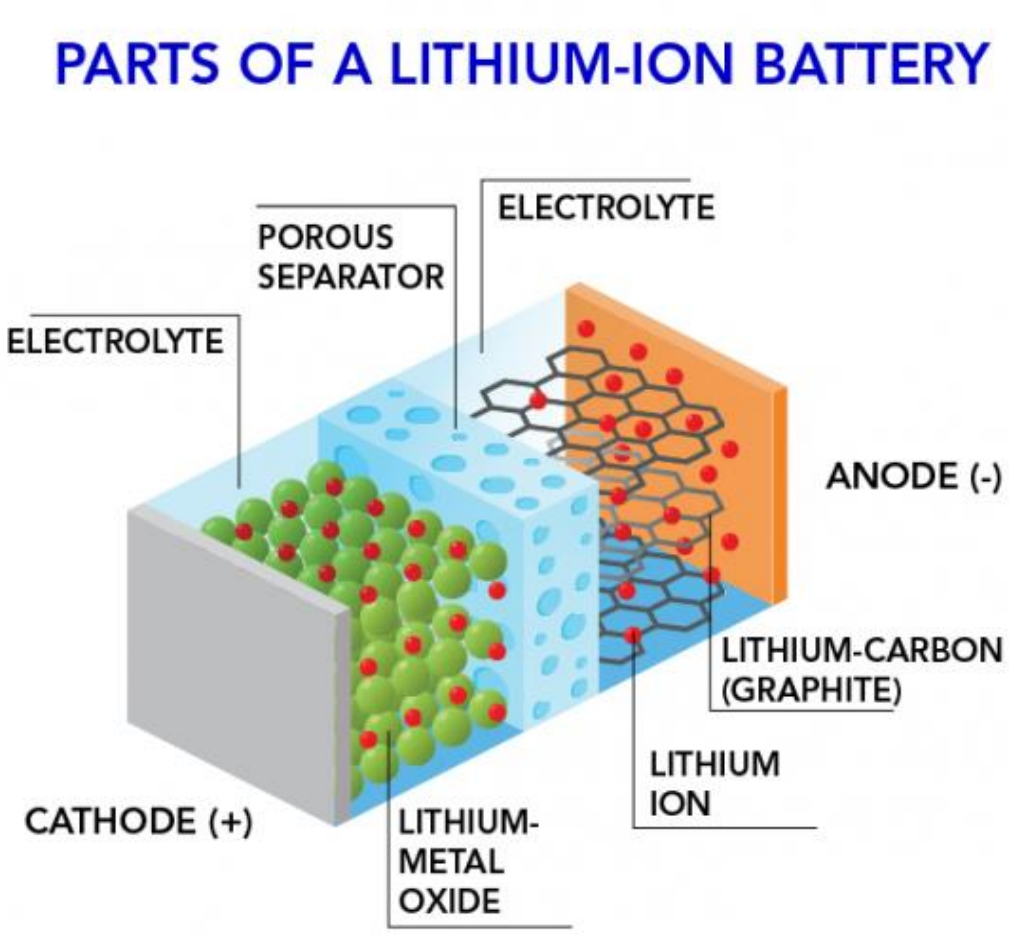
$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + OH^-$$

Overall Reaction:

$$Zn + 2MnO_2 \rightarrow Zn^{2+} + Mn_2O_3 + OH^-$$

Types of Cell

Secondary Cell



Industrial Machinery

Electric carts

Electric forklifts

Elevators

Power tools

Uninterruptible Power Supply

Relay base stations for communication

Data centers

Mobile Device Field

IoT sensors

Wearable devices

Advanced Technology Field

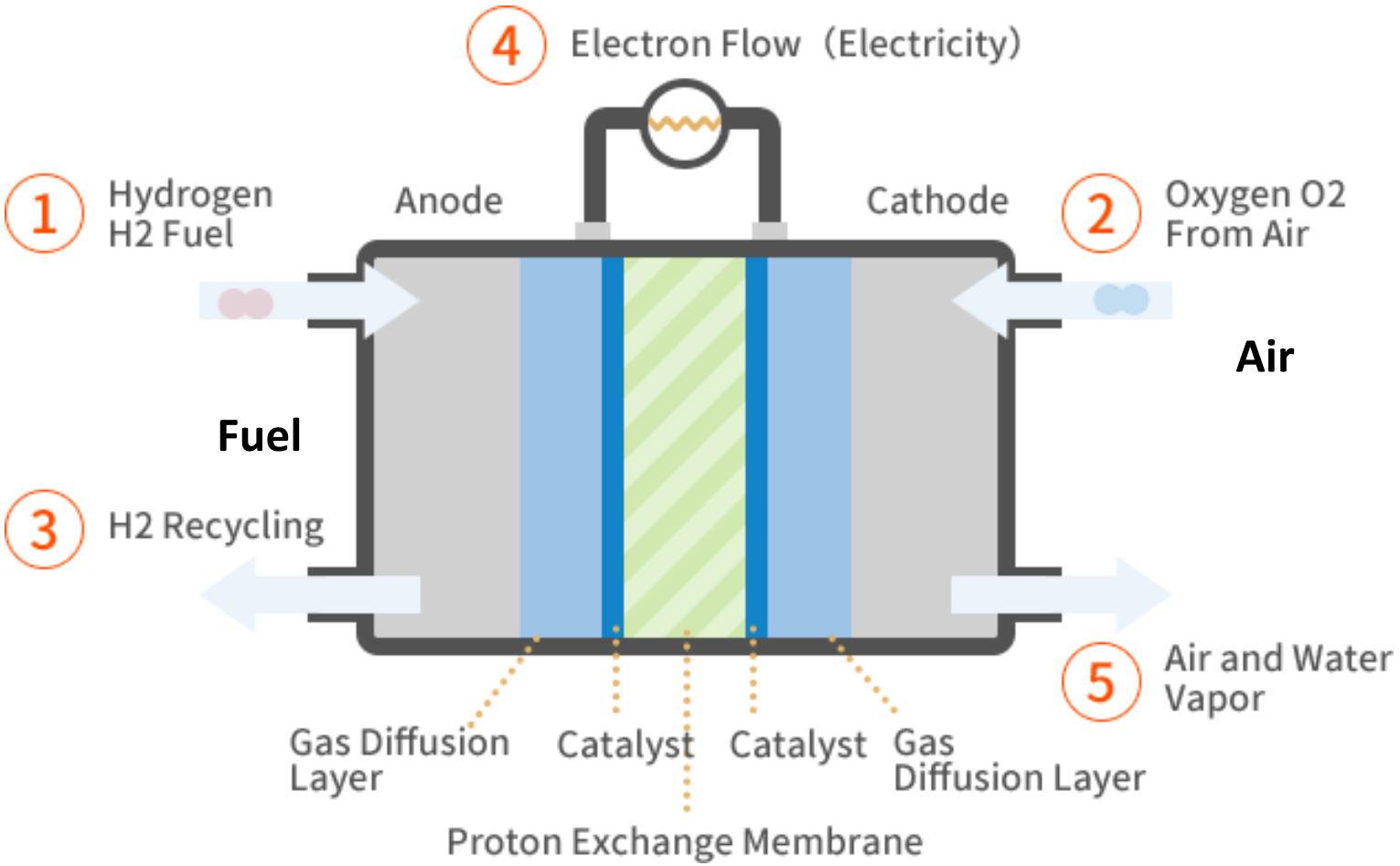
Satellites

Robots

Submarines

Fuel Cell

An electrochemical cell that converts chemical energy into electrical energy through redox reactions.



Anode side reaction:

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Cathode side reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Net reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$