An Introduction to Electro-analytical Chemistry

Subject: Chemistry
Subject Code: EAS-206

Dr. Raj Kumar
Assistant Professor
Department of Chemistry
School of Basic & Applied Sciences
Maharaja Agrasen University
Email: rajkumar@mau.edu.in

Objectives

- To Understand the fundamental concepts of electrochemistry.
- Differentiate between galvanic and electrolytic cells.
- Explore the role of oxidation and reduction in electrochemical reactions.
- Analyze electron flow, electrode reactions, and cell potentials.
- Examine electrolysis and its applications in industrial processes.
- Interpret standard cell notation and conventions.

Electrochemistry

The study of the interchange of chemical and electrical energy

Oxidation **i**s the **l**oss of electrons (Increase in charge).

Reduction **i**s the **g**ain of electrons (Decrease in charge)

Electrochemical Cells:

1. Galvanic Cells:

Produces electrical current

spontaneous chemical reactions

→ **Battery**

$Cu^{2+} + 2e^- \leftrightarrows Cu \quad E^0 = +0.34\ V$

$Zn^{2+} + 2e^- \leftrightarrows Zn \quad E^0 = -0.76V$

$Cu^{2+} + Zn \leftrightarrows Cu + Zn^{2+} \quad E^0 = 0.34 - (-0.76) = 1.10\ V$

2. Electrolytic Cells

Consumes electrical current

$Zn^{2+} + Cu \leftrightarrows Zn + Cu^{2+} \quad E^0 = -1.10\ V$

non-spontaneous and require external e-source (DC power source)

Parts of the voltaic or galvanic cell…

Anode → the electrode where oxidation occurs

After a period of time, the anode may appear to become smaller as it falls into solution.

Cathode → the anode where reduction occurs

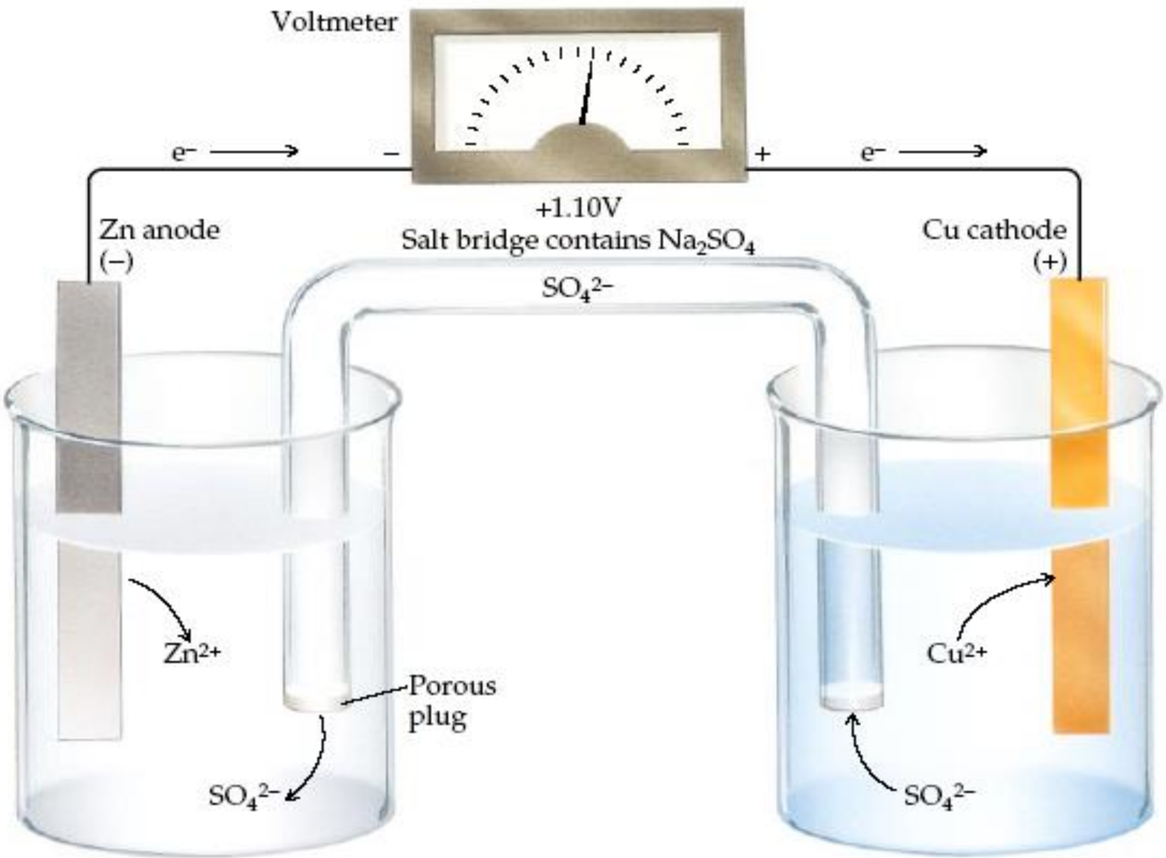
After a period of time it may appear larger, due to ions from solution plating onto it.

Salt Bridge → a device used to maintain electrical neutrality in a galvanic cell

This may be filled with agar which contains a neutral salt or it may be replaced with a porous cup.

Electron Flow → always from anode to cathode (through the wire)

Parts of the voltaic or galvanic cell…



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

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

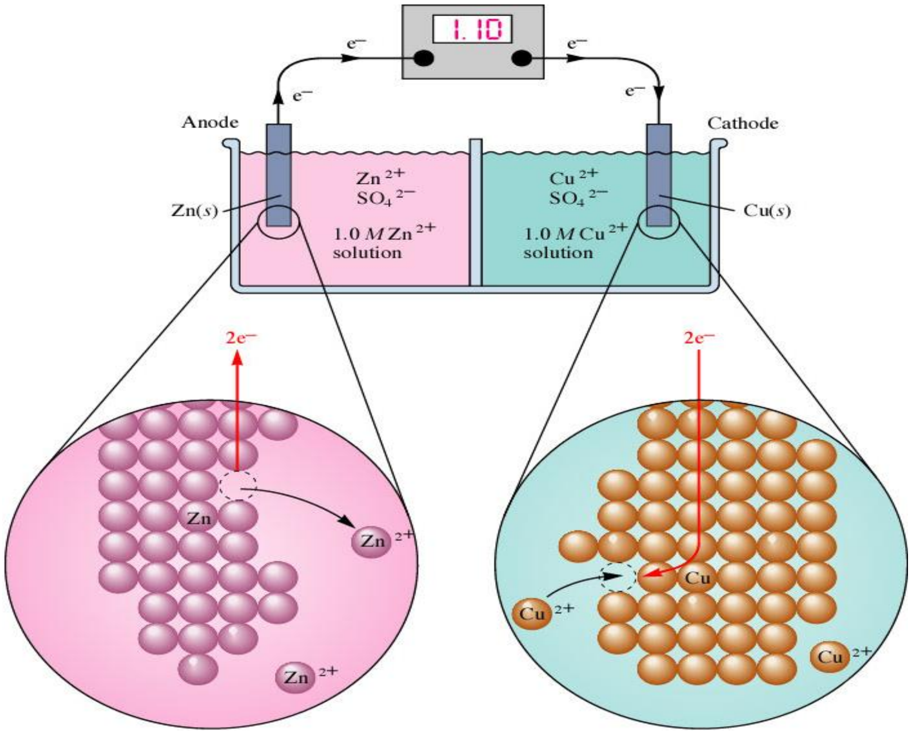
Net reaction: $Zn (s) + Cu^{2+} (aq) \longrightarrow Zn^{2+} (aq) + Cu (s)$

Anode

Cathode

Example of a Galvanic cell

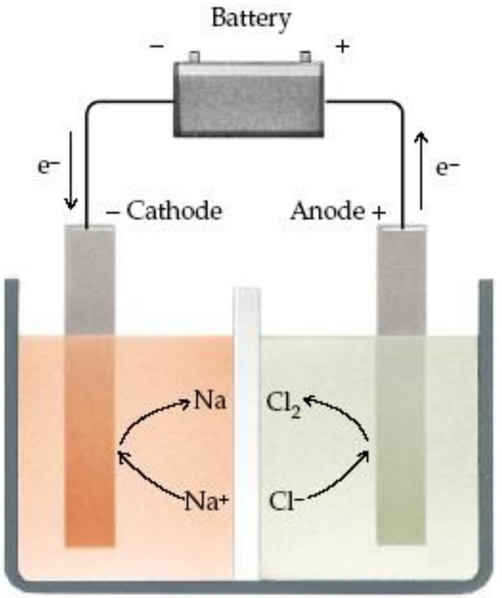
The diagram to the right illustrates what really happens when a Galvanic cell is constructed from zinc sulfate and copper (II) sulfate using the respective metals as electrodes.



Electrolytic cells

Electrolysis of molten sodium chloride

- None spontaneous reaction converted to spontaneous reaction
- Electrical energy converted into chemical energy



Conduction in Electrochemical cells:

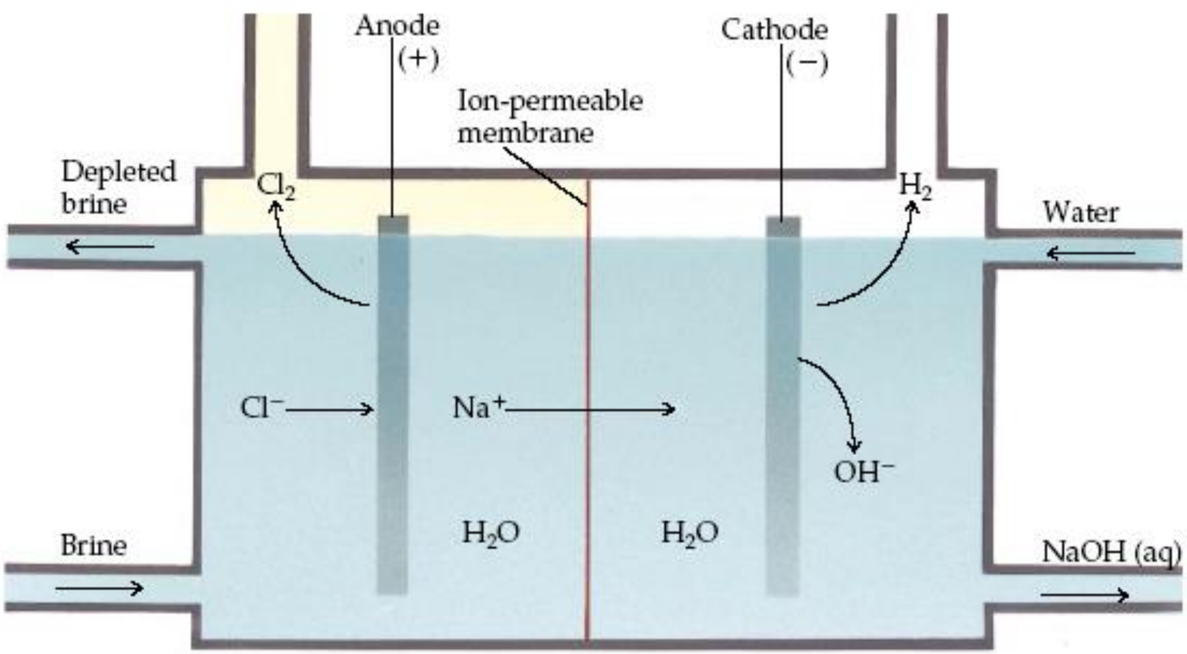
a. External connection → Movement of electrons through the external wire.

b. Within the solution → migration of cations and anions

c. At the electrode surface → Oxidation/Reduction reaction

Membrane cell

A simplified drawing of a membrane cell for the production of NaOH and Cl2 gas from a saturated, **aqueous solution of NaCl** (brine).



Electrolysis from aqueous solution

Consider electrolysis of aqueous NaCl. The process become complex in the presence of water as the water itself can be oxidized or reduced.

Cathode – H_2 is released

Anode – O_2 is released for dilute NaCl

Cl_2 is released for conc. NaCl

Experimental results

Cathode : 2 competing reactions

$$2H_2O + 2e \rightarrow H2 + 2OH^- \qquad E^o = -0.83\ V$$

$$Na^+ + e \rightarrow Na + OH^- \qquad E^o = -2.71\ V$$

H2O with higher red. potential is reduced.

Anode : 2 competing reactions

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad E^o = -1.23\ V$$

$$2Cl^- \rightarrow Cl_2 + 2e \qquad E^o = -1.36\ V$$

The oxidation pot for H2O is a little higher and since the conc of Cl^- is low H_2O is oxidized. However, if high conc. Of is used NaCl, due to the concentration effect Cl^- is oxidized.

Cathodes and Anodes

→ **Cathode** of an electrochemical cell is the electrode at which reduction occurs

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

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

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

→ **Anode** of an electrochemical cell is the electrode at which oxidation

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

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

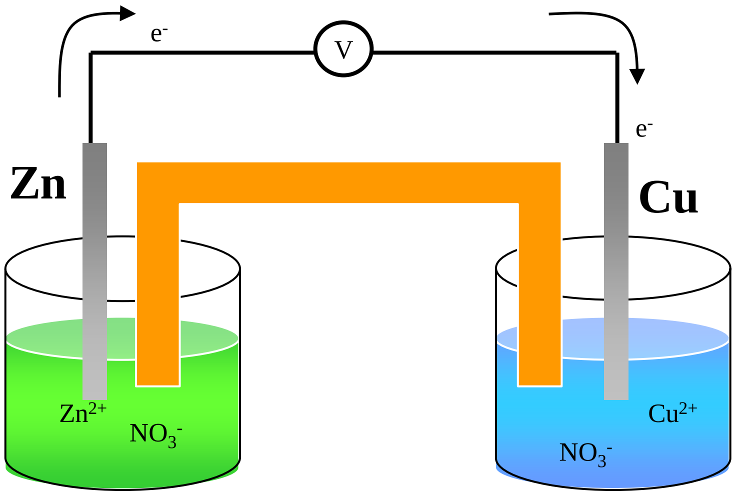
Standard Cell Notation (line notation)

- **Conventions:**

→ **Anode on Left**

→ Single line : represent phase boundaries

→ Two line : represent liquid junction



Anode / anode solution // cathode solution / Cathode

Example: Zn / Zn^{2+} (1.0 M) // Cu^{2+} (1.0M) / Cu

Summary

- Electrochemistry deals with the conversion between chemical and electrical energy.
- Galvanic cells generate electrical energy from spontaneous chemical reactions, while electrolytic cells require an external power source for non-spontaneous reactions.
- Key components include anode (oxidation site), cathode (reduction site), salt bridge, and electron flow direction.
- Electrolysis allows the breakdown of compounds, such as in sodium chloride electrolysis for NaOH and Cl_2 production.
- Standard cell notation helps in representing and understanding electrochemical reactions systematically.

Suggested Readings

- “Chemistry: The Central Science" – Brown, LeMay, Bursten, Murphy, Woodward
- "Physical Chemistry" – Peter Atkins, Julio de Paula
  - (Comprehensive and widely used)
- “Electrochemical Methods: Fundamentals and Applications" – Allen J. Bard, Larry R. Faulkner