ELECTROCHEMISTRY

Introduction

Electrochemistry is a branch of chemistry that deals with the study of the relationship between electrical energy and chemical energy. It explores the conversion of chemical energy into electrical energy and vice versa, involving the movement of electrons.

Applications of electrochemistry include various technologies such as batteries, fuel cells, corrosion prevention, electroplating, and sensors. It plays a vital role in both fundamental research and practical applications, contributing to advancements in energy storage, environmental protection, and materials science.

Cell Potential

Cell potential, also known as electromotive force (EMF) or cell voltage, is a measure of the electrical potential difference between the two half-cells of an electrochemical cell. It represents the driving force for the flow of electrons through an external circuit from the oxidation half-reaction to the reduction half-reaction. The cell potential is a key parameter in understanding the spontaneity and feasibility of electrochemical reactions.

Mathematically, cell potential (E_{cell}) is expressed as: $E_{cell} = E_{cathode} - E_{anode}$

Electrode Potential Measurement

It's important to note that the electrode potential is a measure of the tendency of a half-cell to undergo reduction. The more positive the electrode potential, the greater its tendency to be reduced. The standard hydrogen electrode is often used as a reference electrode, and its potential is defined as zero under standard conditions. Other reference electrodes are calibrated against the standard hydrogen electrode.

Nernst Equation

The Nernst equation is a mathematical expression that relates the concentration of ions in a solution to the electrode potential of an electrochemical cell under non-standard conditions. It is named after the German chemist Walther Nernst, who formulated this equation. The Nernst equation is particularly important in understanding and predicting how changing conditions, such as ion concentrations, affect the cell potential.

The general form of the Nernst equation for a half-cell reaction is as follows:

$E_{cell} = E^0 - [\frac{RT}{nF}] \ln Q$

Where,

- E_{cell} = cell potential of the cell
- E_0 = cell potential under standard conditions
- R = universal gas constant
- T = temperature
- n = number of electrons transferred in the redox reaction

- F = Faraday constant
- Q = reaction quotient

Oxidation

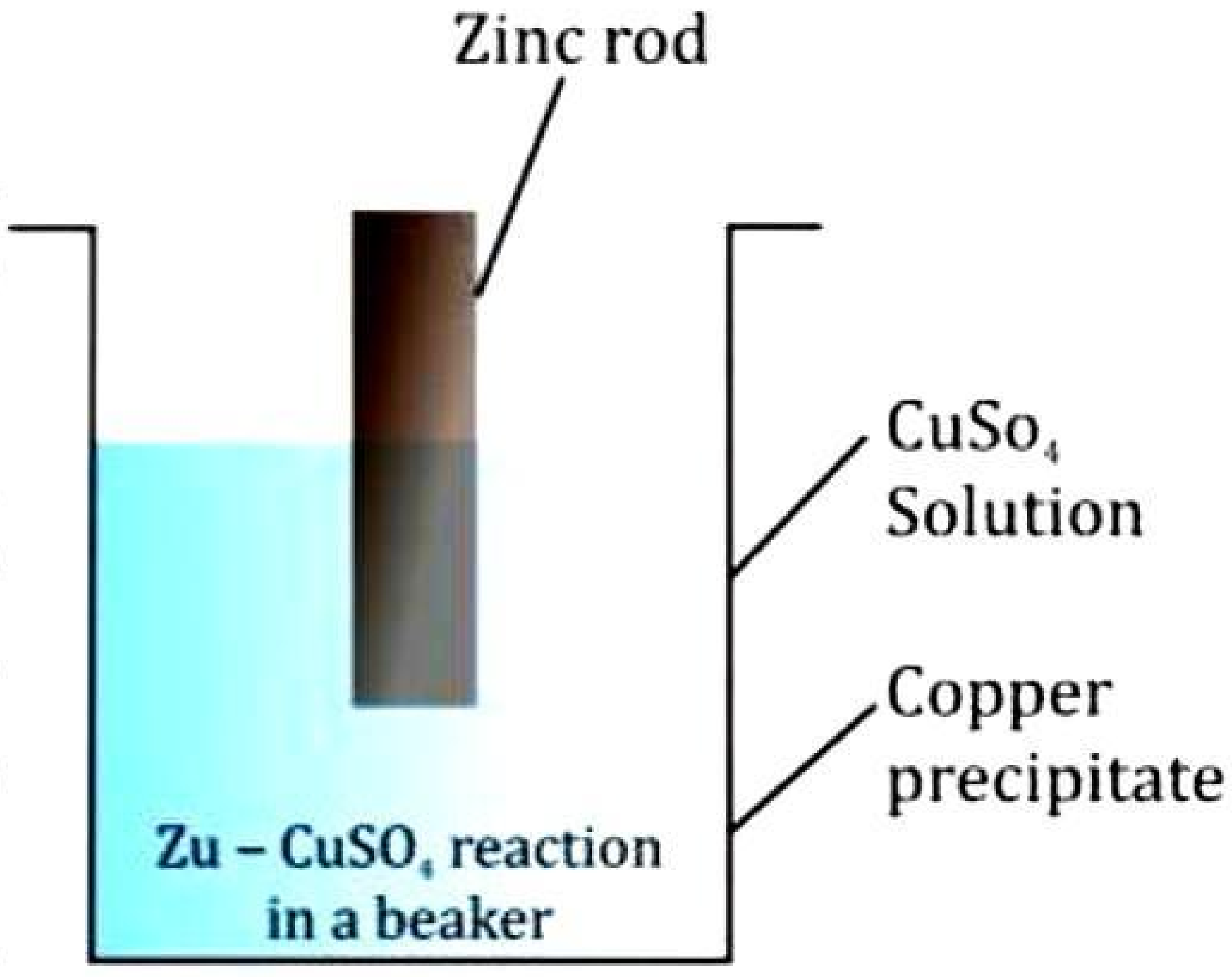
It is defined as a process which involves loss of electrons by a substance. The substance which loses electrons is said to be oxidized.

Reduction

It is defined as a process which involves gain of electrons by a substance. The substance which gains electrons is said to be reduced.

A substance cannot lose electrons unless another substance which can gain electrons is also present in its environment. In other words, oxidation can take place only if reduction can also take place at the same time. This can be illustrated by taking examples below.

$Zn - CuSO_4$ Redox Reaction in a Beaker (Oxidation of Zn metal by Cu^{2+} ions).



Redox reaction

Fig.1

When a zinc rod is placed in a solution of copper sulphate as shown in Fig.1. it is observed that:

(a) The zinc strip starts dissolving forming Zn^{2+} ions in solution. This indicates that the oxidation of zinc metal to zinc ions takes place, which is represented as:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-} \ldots (1)$$

(b) Simultaneously, copper starts precipitating out from the solution, indicating the reduction of Cu^{2+} ions which are present in solution to copper metal. This may be represented as:

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

The reactions (1) and (2) are known as half-reactions, i.e., oxidation half-reaction and reduction half-reaction.

The overall redox reaction is obtained by adding the two half-reactions (1) and (2) and is written as:

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

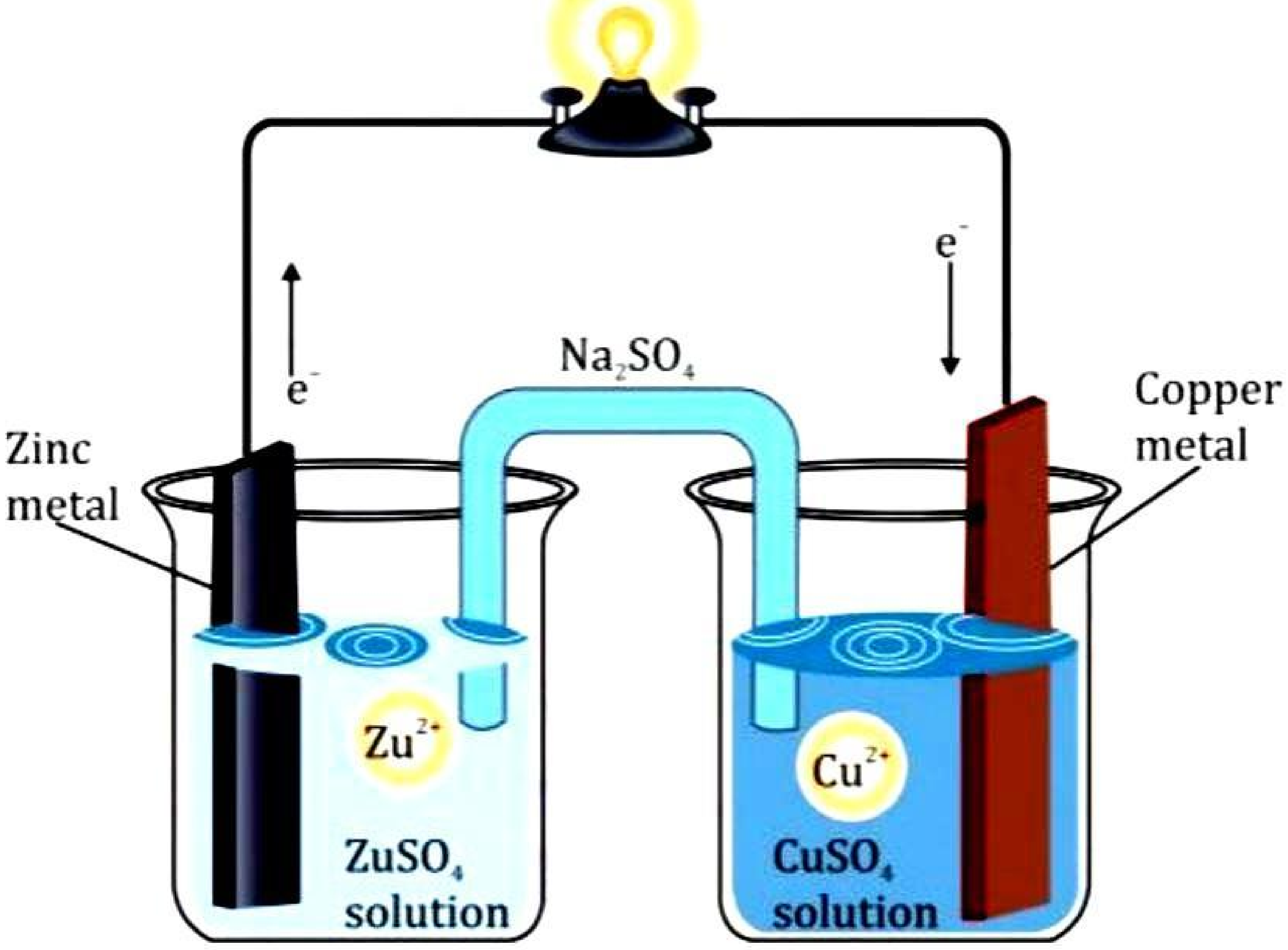
The reaction is accompanied by evolution of heat, i.e., reaction is exothermic and thus ΔH is negative.

But if we try to immerse copper rod in a solution of zinc sulphate we shall observe hardly any change, concluding thereby that the reverse reaction is not possible. So, zinc metal can be oxidized by Cu^{2+} ions but copper metal cannot be oxidized by Zn^{2+} ions.

Redox reaction in an electrochemical cell

In an electrochemical cell, the redox reaction takes place indirectly. Here, the oxidation and reduction take place in different vessels and the electrons are transferred from the reducing agent (the substance oxidized) to the oxidizing agent (the substance reduced) through connecting wires. Hence in such cells, chemical energy is converted into electrical energy. A simple laboratory form of electrochemical cell involving $Zn - CuSO_4$ reaction is shown in Fig.2.

Zinc rod is placed in a dilute $ZnSO_4$ solution in one beaker and copper rod is dipped in a $CuSO_4$ solution (dilute). The two solutions are connected with each other through an inverted U-tube containing a solution of potassium sulphate. This U-tube which helps to connect the two solutions with each other is called salt bridge.



$Zn - CuSO_4$ reaction in an electrochemical cell

Fig. 2

If the metal rods are not connected to each other or if the salt bridge is taken out, no current flows through the ammeter and no reaction takes place in the cell. But as soon as the connection is made as shown (Fig.2.), the current starts flowing as indicated by the ammeter reading and the chemical reaction takes place as:

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

The current continues to flow as long as the chemical reaction continues to take place. Electricity cannot flow from one point to another unless there is a potential difference between the two points. Hence, the flow of electricity from one electrode to another electrode in any cell indicates that the two electrodes have different potentials. The difference of potential which causes flow of current from one electrode (which is at a higher potential) to another electrode (which is at a lower potential) is called the electromotive force (EMF). The emf of a cell can be measured by connecting the two electrodes to the two terminals of a voltmeter. The potential difference is then read directly from the instrument. The emf is also known as cell potential and is measured in units of volts.