<h1 style="text-align:center">CHAPTER 8</h1>
<h2 style="text-align:center">ELECTROCHEMISTRY</h2>

Electrochemistry

Electrochemistry is best defined as *the study of the interchange of chemical and electrical energy.* It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

Terms Associated with Electrochemistry

Cell Notation

An electrochemical cell consists of two half-cells, which can be represented by cell notation. An example of electrochemical cell is the Daniel Cell. The Daniel cell is composed of two half cells. It is represented by the cell notation:

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

The anodic half is written first on the left hand side.
The single line denotes the boundary between a metal and its ions in solution.
The double line represents the porous partition or salt bridge.

Standard Electrode Potentials (Reduction Potentials)

The standard electrode potential of a cell is the potential difference or voltage of the cell at equilibrium under standard conditions. Under such standard condition, the anode is a standard hydrogen electrode, where hydrogen is oxidized:

$$\tfrac{1}{2}\,H_{2(g)} \rightarrow H^{+}_{(aq)} + e^{-}$$
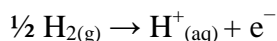
The cathode reaction is the half reaction that is been considered.

The electrode potential is also known as the reduction potential E^0_{red}. The reduction potential expresses the tendency of the oxidizing agent to be reduced (i.e the ease with which an oxidizing agent gains electron and become reduced).

Hydrogen is assigned a value of zero. Oxidizing agents stronger than H^+ (i.e lower than hydrogen in the electrochemical series) have positive values e.g (F_2 = +2.866 V) and negative foroxidizing agents that are weaker than H^+ (e.g., −0.763 V for Zn^{2+}).

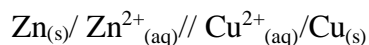Mathematically, the potential difference of a cell in a redox reaction is given as

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

$E°$ cell = E ° reduced - E ° oxidised

= E ° right - E ° left

Question 1

What is the EMF of the Daniel Cell represented by the notation:

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

Given that:

$$Zn^{2+} + 2e- \rightarrow Zn_{(s)}; \qquad E° = -0.76V$$

$$Cu^{2+} + 2e- \rightarrow Cu_{(s)}; \qquad E° = +0.34V$$
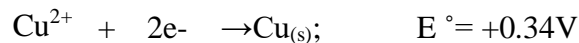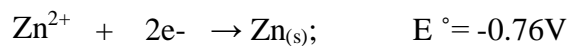
Solution: $\qquad\qquad E° = E° \text{ cathode} - E° \text{ anode}$

$$= 0.34 - (-0.76)$$

$$= 0.34 + 0.76 = 1.10V$$

Electrochemical Cells

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

Voltaic Cells

A Voltaic cell, also known as a galvanic cell is one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown below. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$
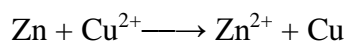
A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.
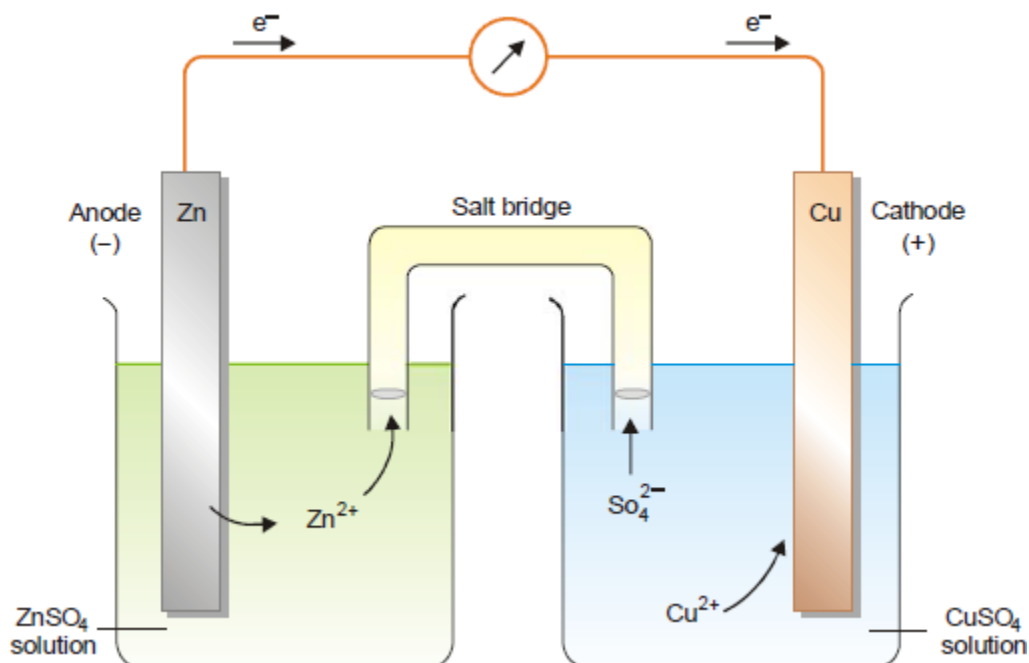
The oxidation half-reaction occurs in the anode compartment.

$$Zn \longrightarrow Zn^{2+} + 2e-$$
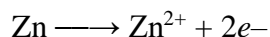
The reduction half-reaction takes place in the cathode compartment.

$$Cu^{2+} + 2e- \longrightarrow Cu$$
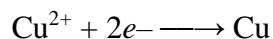
Anode

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time,

SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up.

Daniel Cell

It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc copper cell like the one described above.
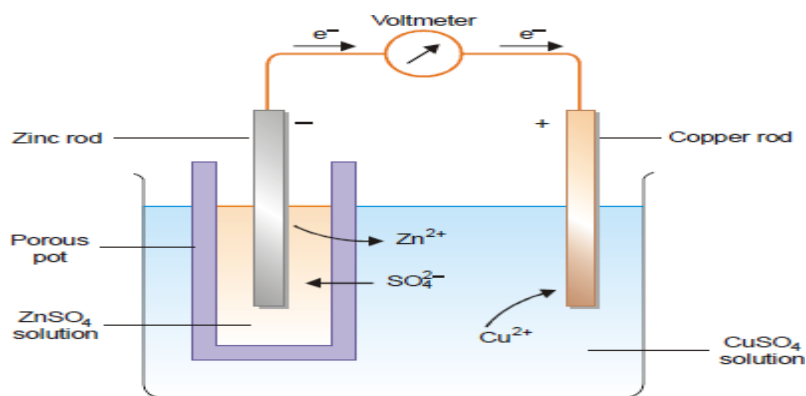
In this cell the salt-bridge has been replaced by a porous pot. Daniel cell resembles the above voltaic cell in all details except that Zn^{2+} ions and SO_4^{2-} ions flow to the cathode and the anode respectively through the porous pot instead of through the salt-bridge. Inspite of this difference, the cell diagram remains the same.
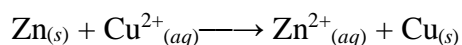
Cell reaction

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(a) Half-reactions:

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

$Cu^{2+}_{(aq)} + 2e- \longrightarrow Cu_{(s)}$
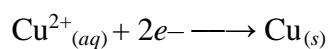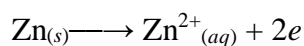
(b) Cell reaction by adding up the half-reactions:

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

Cell potential or EMF

The flow of current through the circuit is determined by the „push", of electrons at the anode and „attraction" of electrons at the cathode. These two forces constitute the „driving force" or „electrical pressure" that sends electrons through the circuit.

This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.**

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell. It may be noted that the metal electrode **in anode** half-cell is on the left, while **in cathode** half-cell

(1)   a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). It is on the right of the metal ion.

(2) A **double vertical line** (||) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

 (3) Anode half-cell is written on the left and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as

Salt Bridge

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

Anode Half-Cell   Cathode Half-Cell
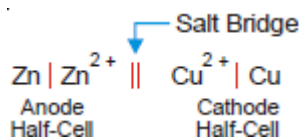
(5) The symbol for an **inert electrode,** like the platinum electrode is often enclosed in a bracket.
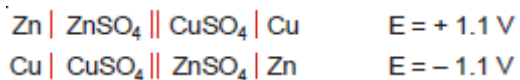
For example,

$Mg / Mg^{2+} / H^+ / H_2 (Pt)$
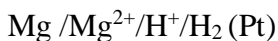
 (6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1V and is represented as

$Zn / ZnSO4 // CuSO4 / Cu \ E = + 1.1 \ V$

Convention regarding sign of emf value

Thus the emf of the cell is given the +**ve sign.** If the emf acts in the opposite direction through the cell circuit, it is quoted as –**ve value.** For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \mid \text{Cu} \qquad E = +1.1 \text{ V}$$
$$\text{Cu} \mid \text{CuSO}_4 \parallel \text{ZnSO}_4 \mid \text{Zn} \qquad E = -1.1 \text{ V}$$

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.

Calculating the emf of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

Ecell = Ecathode – Eanode

$$= E_R - E_L$$

where ER and EL are the reduction potentials of the right-hand and left-hand electrodes respectively.

It may be noted that absolute values of these reduction potentials cannot be determined. These are found by connecting the half-cell with a standard hydrogen electrode whose reductionpotential has been arbitrarily fixed as zero.

Some important points concerning the Table of Standard Reduction Potentials

(1) The more positive the value of E°, the better the oxidising ability (the greater the tendency to be reduced) of the ion or compound, on moving upward in the Table.

(2) The more negative the value of E° the better the reducing ability of the ions, elements or

compounds on moving downward in the Table.

(2)   Under standard conditions, any substance in this Table will spontaneously oxidise any other substance lower than it in the Table.

USES OF ELECTRODE POTENTIAL

1. Predicting Feasibility of Reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series.

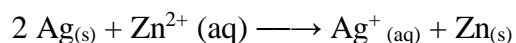The net emf of the reaction, Ecell, can be calculated from the expression

$E°cell = E°cathode – E°anode$

In general, if $E°cell = +$ ve, the reaction is feasible

$E°cell = –$ ve, the reaction is not feasible

Practice:

1. Predict whether the reaction

$2 Ag_{(s)} + Zn^{2+} (aq) \longrightarrow Ag^+_{(aq)} + Zn_{(s)}$

is feasible or not. Consult the table for the E° values.

Given :

Ag/Ag+ E° = 0.80V

Zn^{2+}/Zn E° = -0.763

solution

The cell half reactions are

Anode : $2Ag_{(s)} \longrightarrow 2Ag^+(aq) + 2e– E° = 0.80$ V

Cathode : $Zn^{2+}_{(aq)} + 2e– \longrightarrow Zn_{(s)} E° = – 0.763$ V
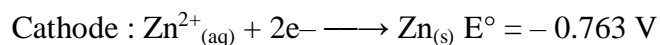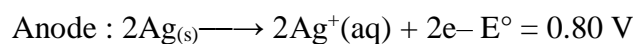
$E°cell = E°cathode – E°anode$

$\therefore E°cell = – 0.763$ V $– 0.80$

= – 1.563

Since E°cell is negative, the given reaction is not feasible

2. Determine the feasibility of the reaction

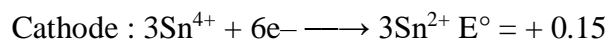$2Al_{(s)} + 2Sn^{4+}_{(aq)} \longrightarrow 2Al^{3+} + 3Sn^{2+}_{(aq)}$
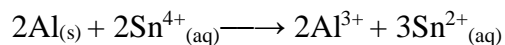
Given

Al/Al^{3+} $E° = -1.66V$

Sn^{4+}/Sn^{2+} $E° = +0.15V$

Solution

The given reaction consists of the following half reactions

Anode : $2Al(s) \longrightarrow 2Al^{3+} + 6e^- \quad E° = – 1.66$ V

Cathode : $3Sn^{4+} + 6e– \longrightarrow 3Sn^{2+} \quad E° = + 0.15$

E°cell = 0.15 – (– 1.66)

= 1.81 V

Since E°cell is positive, the reaction is feasible.

2. Uses of electrode potential in predicting displacement reactions of aqueous salt solutions

Metals near the bottom of the electrochemical series are strong reducing agents and are themselves oxidised to metal ions. For example,

zinc lying down below the series is oxidised to Zn^{2+} ion, while copper which is higher up in the series is produced by reduction of Cu^{2+} ion.

$Zn \longrightarrow Zn^{2+} + 2e–$

$Cu^{2+} + 2e- \longrightarrow Cu\downarrow$
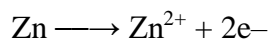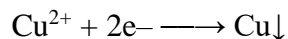
Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated. In general we can say that a metal lower down the electrochemical series can precipitate the one higher up in the series.

3. **Use of EP in predicting whether a metal will displace hydrogen from a dilute acid solution**

Any metal above hydrogen in the electrochemical series is a weaker reducing agent than hydrogen itself and cannot reduce H^+ to H_2. Any metal lying below hydrogen is a stronger reducing agent than hydrogen and will convert H^+ to H_2. This explains why Zn lying below hydrogen reacts with dil H_2SO_4 to liberate H2, while Cu lying above hydrogen does not react.

$Zn + H^+ (dil\ H_2SO_4) \longrightarrow Zn^{2+} + H_2 \uparrow$

$Cu + H^+ (dil\ H_2SO_4) \longrightarrow Cu^{2+} + H_2$
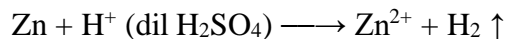
CONCEPT OF ELECTROLYSIS

Electrolysis is the passage of a current (direct current) through an ionic substance that is either molten or dissolved in a suitable solvent, producing chemical reactions at the electrodes and decomposition of the substance.

Terms associated with electrolysis

Electrolyte: this is a substance that contains free ions, which carry electric current in the electrolyte. The ions in a substance must be in a mobile state for electrolysis to occur.

Direct current (DC): this provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by electrons in the external circuit.

Electrodes: they are electrical conductors (e.g metals, graphite) that provide the physical interface between the electrolyte and the electrical circuit that provides the energy.

Faraday's First Law of Electrolysis

The mass of a substance formed at an electrode during electrolysis is directly proportional to the quantity of electricity that passes through the electrolyte.

Mathematically:

m α Q

where Q is quantity of electricity in coulomb

since Q = It

then m α It

m= EIt

E is a constant known as the electrochemical equivalent of the substance.

Faraday's Second Law

Faraday"s second law states that when the same amount of current is passed through different electrolytes/elements connected in series, the mass of substance deposited at the electrodes is directly proportional to their equivalent weight.

Differences	Electrolytic cell	Electrochemical cell
i. Electrical Structure	There is supply of electricity (direct current).	No electrical supply.
i. Electrodes	Metals can be the same or different	Both metals must be different
iii.Direction of electron flow	From anode to cathode through external circuit	From the more electropositive metal to the

		less electropositive metal
iv.Energy transformation	Electrical energy to chemical	Chemical energy to electrical energy
v.Reactions at the terminals	Oxidation occurs at the positive terminal while reduction occurs at the negative terminal	Reduction occurs at the positive terminal while oxidation occurs at the negative terminal