conductance, and (iii) equivalent conductance and molar conductance of K_2SO_4 solution.

[Ans: (i)$2281cm^{-1}$, (ii) $0.006997 ohm^{-1}cm^{-1}$,

(iii) $139.9 \, ohm^{-1}cm^2 eqv^{-1}$, $279.8 \, ohm^{-1}cm^2 mol^{-1}$]

3.2. Electrochemical cell

3.2.1 Introduction

An electrochemical cell is a device for the conversion of chemical energy to electrical energy or vice versa. Electrochemical cells are two types:

• Galvanic cell or voltaic cell
• Electrolytic cell

Galvanic Cell : A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it or in other words galvanic cell transduces chemical energy to electrical energy when it is a part of a complete electrical circuit.

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

Chemical energy $\underset{\text{Electrolytic cell}}{\overset{\text{Galvanic cell}}{\rightleftharpoons}}$ Electrical energy

### 3.2.2 Direct & indirect electron transfer

When a piece of metallic zinc is dipped in a solution of copper sulfate, the zinc is coated with metallic copper, and zinc ions pass into the solution due to the following reaction.

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

This is a redox reaction which is the sum of the two half-reactions shown below:

Reduction : $Cu^{+2}(aq) + 2e \rightarrow Cu(s)$
Oxidation : $Zn(s) \longrightarrow Zn^{+2}(aq) + 2e$
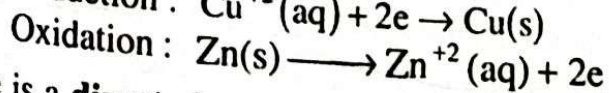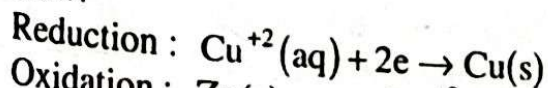
There is a **direct electron transfer** occur from zinc to copper ions, since the two half-reactions take place at the same site. It is possible to build an apparatus where the two half-reactions take place at separate sites, with electrons being transferred indirectly. Such an apparatus is known as a **voltaic cell or galvanic cell**. A wide variety of such cells may be constructed. To explain the general principle involved in a galvanic cell, are illustrated the Cu-Zn or Daniel cell.
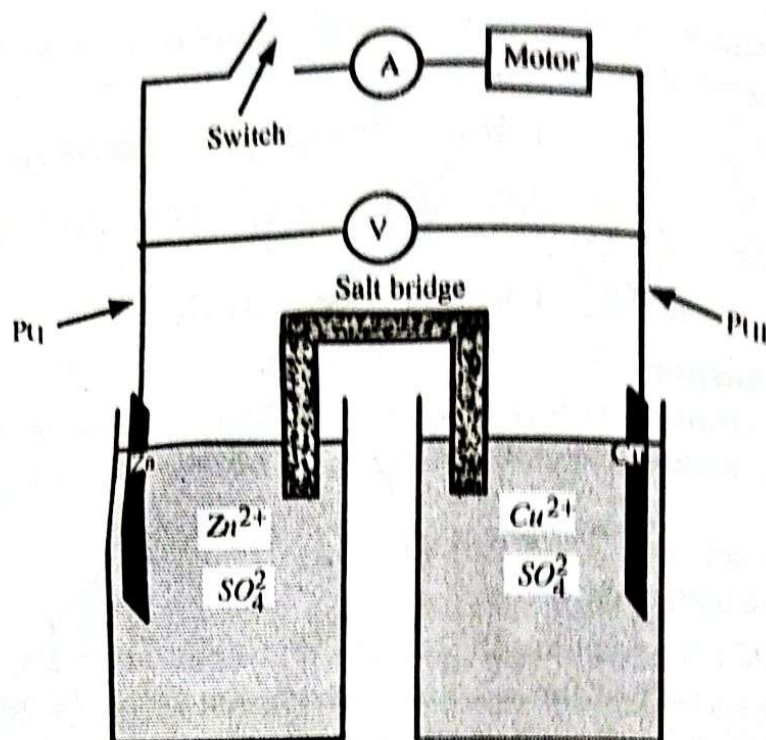
Fig. 3. 7 *Schematic diagram of Daniel Cell*

In this cell, (shown in Fig. 3.7) the left hand compartment consists of a copper plate partly immersed in a solution of copper (II) sulfate. The right hand compartment consists of a zinc plate dipping into a solution of zinc sulfate. Each compartment is called half cell and each metallic plate is called electrode.

The half-cell called the **anode** is the site at which the oxidation of zinc occurs as shown below.

$$Zn(s) \longrightarrow Zn^{+2}(aq) + 2e$$
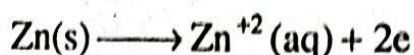
The half-cell, called the **cathode** is the site at which the reduction of copper (II) ions occurs as shown below.

$$Cu^{+2}(aq) + 2e \longrightarrow Cu(s)$$
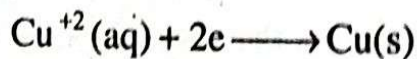
The individual reactions which are taking place in the anode and cathode compartments result in zinc cations (Zn^{+2}) being produced in the anode compartment, and surplus sulfate anions (SO_4^{-2}) being left in the cathode compartment.

The reaction in each half-cell does not occur unless the two half-cells are electrically connected to each other. Contact between the two compartments is made by a "**salt bridge**"[1].

The two half-cells are also connected externally by a conducting

wire, which complete the circuit. Once these half cells are electrically connected, the reaction occurs spontaneously at the two compartments, and electron produced by the oxidation reaction at anode are forced to travel via the external circuit to the site of the reduction reaction at cathode, due to difference in potential energy of this two electrodes. This difference in potential energy of the two electrodes is called **the electromotive force (EMF)** of the cell. Alternatively, *EMF* or **cell potential** is defined as the amount of electrical energy available per unit charge from the Galvanic cell and denoted by E. Energy per unit charge is expressed in **volts**.

The magnitude of *EMF* of a cell depends on concentration, pressure and temperature of the reactants in two half cells. When all the reactants are in one molar concentration, one atmosphere pressure and at 25°C temperature the *EMF* so obtained in this condition is known as the standard *EMF* of the cell. Standard cell potential is denoted by E^0.

2.3 Cell description conventions

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the Daniel cell would be

$$Zn(s) \mid Zn^{+2}(aq) \parallel Cu^{+2}(aq) \mid Cu(s)$$
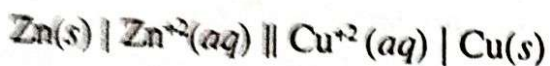
In this notation, the vertical bars indicate phase boundaries; the double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the electrode corresponding to the reduction reaction, i.e., cathode should be written on the right side and the electrode corresponding to oxidation reaction, i.e.,

anode should be written on the left side.

Problem : Design a cell in which the following reaction occurs

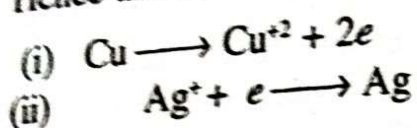$$Cu + 2AgNO_3 \rightleftharpoons Cu(NO_3)_2 + 2Ag$$
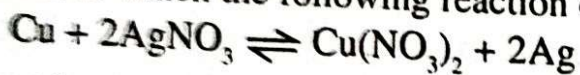
Ans: The reaction may be written in ionic form as given below

A "**salt bridge**" is a special type of barrier that prevents the spontaneous mixing of the aqueous solutions in each compartment, but allows the migration of ions in both directions to maintain the electrical neutrality. It is prepared in U shape glass tube filled with a jelly containing a suitable electrolyte such as potassium sulfate or potassium nitrate or ammonium nitrate. As the redox reaction occurs, surplus cations (Zn^{+2}) from the anode compartment migrate via the salt bridge to the cathode compartment, while anions (SO_4^{2-}) migrate in the opposite direction to maintain the electrical neutrality.

$$Cu + 2Ag^+ + 2NO_3^- \rightleftharpoons Cu^{+2} + 2NO_3^- + 2Ag$$
$$\text{or} \quad Cu + 2Ag^+ \rightleftharpoons Cu^{+2} + 2Ag$$
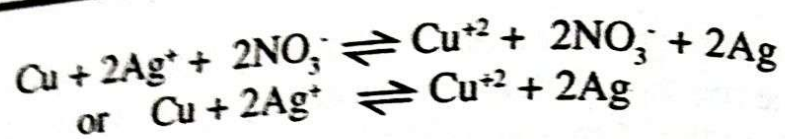
Hence the two half-reactions are

(i) $Cu \longrightarrow Cu^{+2} + 2e$

(ii) $\quad Ag^+ + e \longrightarrow Ag$

Process (i) is oxidation and represented as a redox couple $Cu \,|$ Cu^{+2}, hence it acts as anode.

Process (ii) is reduction and represented as a redox couple $Ag^+ |\, Ag$, hence it acts as the cathode.

Hence the cell is $\quad Cu \,|\, Cu^{+2} \,\|\, Ag^+ \,|\, Ag$

NOTE

- The *anode* is where oxidation occurs, and the *cathode* is the site of reduction. In an actual cell either electrode can have either identity, depending on the direction in which the net cell reaction is occurring.

- When the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the *cell potential* will be *positive*.

  "Conventional current flow" is from positive to negative electrode, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

3.2.4 Reversible and irreversible cells

Galvanic cells may be divided into two broad categories based on the chemical reaction occurring on application of reverse potential on it by an external source. These are reversible cell and irreversible cell.

When the chemical reaction in a cell occurrs in exactly reverse direction on application of little higher external electrical potential [$E_{ext} = E_{cell} + \Delta E$] on it in reverse direction, the cell is called reversible cell and if the reaction is not exactly reverse the cell is called irreversible cell. Consider Daniel cell,

$$Zn \,|\, ZnSO_4 \, soln \,\|\, CuSO_4 \,|\, Cu,$$
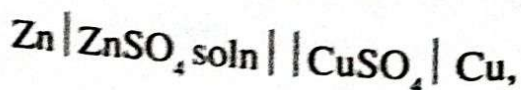
$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times \left(-1.2 \times 10^{-3}\right) JK^{-1}$$

$$= -231.6 \ JK^{-1}$$

Enthalpy change,

$$\Delta H = nF\left\{T\left(\frac{\partial E}{\partial T}\right)_P - E\right\}$$

$$= 2 \times 96500\left\{298 \times \left(1.2 \times 10^{-3}\right) - 1.42\right\}$$

$$= -205043.2 \ J$$

32.6 Nernst equation

The cell potential for a voltaic cell under standard conditions can be calculated from the standard electrode potential. But real voltaic cells will typically differ from the standard conditions. The Nernst equation relates the cell potential E_{cell} to its standard cell potential E^0_{cell} by the following reaction.
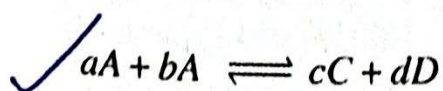
$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q$$

R = gas constant

T = temperature in Kelvin's

Q = thermodynamic reaction quotient

F = Faraday's constant

The quantity Q, the thermodynamic reaction constant, is like a dynamic version of the equilibrium constant in which the concentrations and gas pressures are the instantaneous values in the reaction mixture. For a reaction
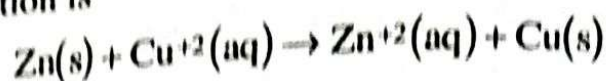
$$aA + bA \rightleftharpoons cC + dD$$

the quantity, $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

where [C] is understood to be the molar concentration of product C or the partial pressure in atmospheres if it is a gas.

Applied to the Daniel cell where zinc and copper form the electrodes,

the reaction is

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

the form of Q is

$$Q = \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]} = \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

since the concentrations of the pure metal solids are assigned the value 1. This implies that the departure of the cell potential from its standard value of 1.10 volts will be influenced by the temperature and the ion concentrations.

Problem: Calculate the value of $\dfrac{2.303RT}{F}$ at 298 K.

Ans: Here $T = 298$ K , and we know $F = 96500$ coulombs mol^{-1}, $R = 8.314$ joule K^{-1} mol^{-1}.

Hence the value of the quantity,

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 \ Joule \ K^{-1} mol^{-1} \times 298 \ K}{96500 \ coulombs \ mol^{-1}}$$

$$= 0.059 \ \text{volt.} \quad [\text{Since, volt X coulomb} = \text{joule}]$$

Problem: Calculate the EMF of the cell,

$$Zn(s) \,|\, ZnSO_4\,(0.1M)\,|\,|\,CuSO_4(0.001M)\,|\,Cu(s)$$

when E^0 of this cell is 1.103 volt at 25°C.

Ans: For the given cell, the cell reaction is

$$Zn + CuSO_4 \rightleftharpoons ZnSO_4 + Cu$$

Hence reaction quotient $\quad Q = \dfrac{[ZnSO_4][Cu]}{[Zn][CuSO_4]}$

and the two moles of electron transfered corresponding to the above cell reaction, i.e., $n = 2$

The EMF (E_{cell}) of the cell is given by the Nernst equation

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[ZnSO_4][Cu]}{[Zn][CuSO_4]}$$

Since zinc and copper are in solid pure state, it is assumed that active mass of Zn and Cu are unit, i.e., $[Zn] = [Cu] = 1$ and given; $[ZnSO_4] = 0.1M$, $[CuSO_4] = 0.001M$

$$Hence\ E_{cell} = 1.103 - \frac{0.059}{2} \log_{10} \left\{ \frac{(0.1) \times (1)}{(1) \times (0.001)} \right\}$$

$$= 1.103 - 0.059 = 1.044\ volt.$$
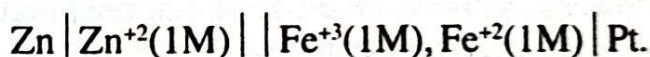
3.27 Single Electrode Potential

Since the reaction involved in a galvanic cell is the combination of two half cell reactions at two electrodes, the cell potential is the resultant of the electrode potentials. If E_r and E_l be the reduction potentials of the two electrodes, the cell potential E_{cell} according to the international convention would be

$$E_{cell} = E_r - E_l$$

The reduction potential of a redox couple is a measure of its tendency to gain electron in a redox reaction. Since oxidation is the reverse process of reduction, the values of reduction potential with opposite sign give the oxidation potential of a redox couple.

Thus it may be stated that the electrode potential is the tendency of an electrode in a half cell to lose or gain electrons, whereas *EMF* of a cell is a measure of relative oxidizing and reducing power of the electrodes of the cell.

Problem: Calculate standard *EMF* of the cell

$$Zn \,|\, Zn^{+2}(1M) \,|\,|\, Fe^{+3}(1M), Fe^{+2}(1M) \,|\, Pt.$$

Given that, $E^0_{Zn^{+2}/Zn} = -0.761\ volt$ and $E^0_{Fe^{+3}/Fe^2} = 0.771\ volt$ at 298K.

Ans: $E^0_{cell} = E^0_r - E^0_l = E^0_{Fe^{+3}/Fe^{+2}} - E^0_{Zn^{+2}/Zn}$

$$= 0.771 - (-0.761) = 1.532\ volt$$

3.28 Standard Hydrogen electrode

Although the cell potential is determined experimentally, the determination of individual electrode potential or half cell potential is not possible. Hence the potential values of individual electrodes are determined with respect to an arbitrary standard electrode, whose potential is arbitrarily chosen. For this purpose, the standard hydrogen electrode is used as the reference electrode, and its half cell potential is taken as zero.

Hydrogen half-cell is constructed by immersing a platinum plate coated with platinum black in a 1M H$^+$ ion solution through which the pure H$_2$