Cardamom Planters' Association College
(Re-accredited with 'B' Grade by NAAC)
Pankajam Nagar, Bodinayakanur - 625 582.

Electrochemistry

Electrochemical cells and Nernst equation

Dr. B. Kavitha
Assistant Professor
PG and Research Department of Chemistry
C.P.A. College, Bodinayakanur

Elector chemical cells

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

When a bar of Zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar. The net reaction is

Figure (a) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

This is a redox reaction and the two half reactions are :

$Zn \longrightarrow Zn^{2+} + 2e^-$

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

In this change, Zn is oxidized to give Zn^{2+} ions, and Cu^{2+} ions are reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction. Both the half reactions occur on the zinc bar itself and there is no net charge

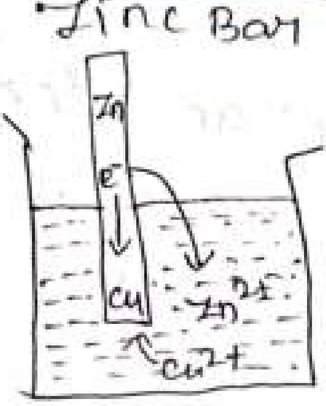
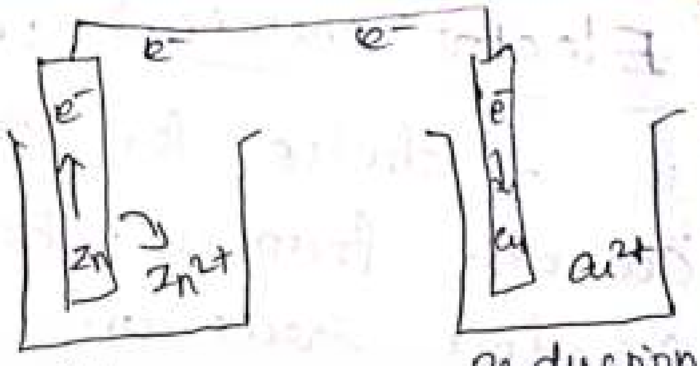


Figure a



Oxidation Half-reaction (Figure b) Reduction Half-reaction

Now, let the two half-reactions occur in separate compartments which are connected by a wire (Figure. b). The electrons produced in the left compartment flow through the wire to the other compartment. However, the current will flow for an instant and then stop. The current stops flowing because of the charge build up in the two compartments. The electrons leave the left compartment and it would become positively charged. The right compartment receives electrons and becomes negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops.

This problem can be solved very simply. The solutions in the two compartments may be connected say, by a salt bridge. The salt bridge is a U-tube filled with an electrolyte such as NaCl, KCl or K_2SO_4. It provides a passage to ions from one compartment to the other compartment without extensive mixing of the two solutions. with this ion flow, the circuit is complete and electrons pass freely through the wire to keep the net charge zero in two compartments.

The Nernst equation

We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889, walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard electrode potential, E° and the temperature of the cell. this relation known as the Nernst equation can be stated as,

$$E = E^{o} - \frac{2.303\,RT}{nF} \log K \quad —①$$

where, E^0 = Standard electrode potential

R = gas constant

T = Kelvin Temperature

n = number of electrons transferred in the half-reaction

F = Faraday of electricity

K = equilibrium constant for the half-cell reaction as in equilibrium law.

Calculation of Half-cell potential

For an oxidation half-cell reaction when the metal electrode M gives M^{n+} ion,

$$M \longrightarrow M^{n+} + e^-$$

the Nernst equation takes the form

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]} \quad (2)$$

the concentration of solid metal [M] is equal to zero. Therefore, the Nernst equation can be written as:

$$E = E^0 - \frac{2.303RT}{nF} \log [M^{n+}] \quad (3)$$

Substituting the values of R, F and T at $25^\circ c$, the quantity $\frac{2.303RT}{F}$ comes to be

0.0591. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E^0 - \frac{0.0591}{n} \log [M^{n+}]$$

Calculation of cell potential

The Nernst equation is applicable to cell potentials as well. Thus,

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log K$$

K is the equilibrium constant of the redox cell reaction.

Calculation of Equilibrium constant for the cell reaction:

The Nernst equation for a cell is

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log K$$

At equilibrium, the cell reaction is balanced and the potential is zero. The Nernst equation may now be written as

$$0 = E^0_{cell} - \frac{0.0591}{n} \log K$$

$$\frac{0.0591}{n} \log K = E^0_{cell}$$

$$\log K = \frac{n E^0_{cell}}{0.0591}$$