10.12. CONCENTRATION CELLS

The cells in which the electrical energy is produced due to physical transfer of material from one concentration to another, are called concentration cells.

or

The cells in which emf is produced due to decrease in free energy accompanying the physical transfer of material from one part of the cell to another part are called concentration cells. The difference in concentration may be in the electrode material or the electrolyte. On this basis, the concentration cells are of two types.

(i) Electrode concentration cells

(ii) Electrolyte concentration cells

(i) Electrode Concentration Cells: The concentration cells in which electrode of same material, having different concentrations, are dipped in the solution of the same electrolyte, are called electrode concentration cells. These may be of two types:-

Cells with Amalgam Electrodes:

In these cells, the concentration of electrode materials can be varied taking their amalgams, i.e., solution of metal electrode in mercury. For example,

$$\underset{a_1}{Zn - Hg} \,|\, ZnSO_4 \,|\, \underset{a_2}{Zn - Hg}$$

In order to get different concentrations of two electrodes,, zinc metal is dissolved in mercury with different activities. When the cell operates, zinc is converted into zinc ions at left hand electrode.

$$Zn(a_1) \longrightarrow Zn^{2+} + 2e^-$$

and emf is given by

$$E_1 = E^0_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} \qquad (10.19)$$

Similarly, zinc ions are converted into zinc metal at right hand electrode, i.e.,

$$Zn^{2+} + 2e^- \longrightarrow Zn(a_2)$$

and emf is given as

$$E_2 = E^0_{1\,Zn} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}} \qquad (10.20)$$

In this cell, the net process is

$$Zn(a_1) = Zn(a_2)$$

and the total emf is given by

$$E = E_1 + E_2 \qquad (10.21)$$

Substituting the values of E_1 and E_2 from Eqs. (10.19) and (10.20) in Eq(10.21), we get

$$E = E^0_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} + E^0_{1Zn} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}}$$

When $E^0_{Zn} = E^0_{1Zn}$

$$\therefore \quad E = -\frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}}$$

$$E = -\frac{RT}{2F} \ln \frac{a_2}{a_1}$$

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2} \qquad (10.22)$$

From equation (10.22), it follows that the emf of the cell is dependent upon the activity ratio of the two amalgams and not at all on the activity of Zn^{2+} ions in the solution.

with Gaseous Electrodes:

made up of gas material maintained at