Types of Electrolyte concentration cells

1. Concentration cell without transference.
2. Concentration cell with transference.

(I) Concentration cell without Transference.

When two electrolytic solutions are not in direct contact with each other and transference of ions from one solution to the other solution does not take place directly. These are called concentration cells without transference.

We consider a simple electrochemical cell

$$Pt, H_2(g), HCl(a_1) \mid AgCl(s), Ag$$

Let the activity of H^+ ions in the solution is $(a_+)_1$ and that of Cl^- ion is $(a_-)_1$

Reduction half cell reaction is

$$AgCl(s) + e \longrightarrow Ag(s) + Cl^-(a_-)_1 \quad \text{—(1)}$$

Oxidation half cell reaction is

$$\tfrac{1}{2}H_2(g) - e \longrightarrow H^+(a_+)_1 \quad \text{—(2)}$$

Net cell rxn is

$$AgCl(s) + e \longrightarrow Ag(s) + Cl^-(a_-)_1$$

$$\tfrac{1}{2}H_2(g) - e \longrightarrow H^+(a_+)_1$$

$$\tfrac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(a_+)_1 + Cl^-(a_-)_1 + Ag(s) \quad \text{—(3)}$$

Now we consider same cell with difference that activity of HCl solution is now a_2

$$Pt, H_2(g), HCl(a_2) \mid AgCl(s), Ag$$

The net cell reaction for one faraday of electricity will be

$\frac{1}{2} H_2(g) + AgCl(s) \longrightarrow H^+(a_+)_2 + Cl^-(a_-)_2 + Ag(s)$ —— (4)

connecting above cells we have.

Pt, $H_2(g)$ 1 atm, $HCl(a_1)$, $AgCl(s)$, Ag | Ag, $AgCl(s)$, $HCl(a_2)$, $H_2(g)$ 1 atm, Pt

The overall cell reaction of combined cell for passage of one faraday of electricity will be obtained by substracting eqn (4) from eqn (3)

$$\frac{1}{2} H_2(g) + AgCl(s) \longrightarrow H^+(a_+)_1 + Cl^-(a_-)_1 + Ag(s)$$
$$\frac{1}{2} H_2(g) + AgCl(s) \longrightarrow H^+(a_+)_2 + Cl^-(a_-)_2 + Ag(s)$$

$$H^+(a_+)_2 + Cl^-(a_-)_2 \longrightarrow H^+(a_+)_1 + Cl^-(a_-)_1$$ —— (5)

Thus for flow of one faraday of electricity, the overall reaction is the transfer of one gram-equiv of each H^+ and Cl^- ions or one gram equivalent of HCl from a solution of activity a_2 to that of activity a_1.

Hence Emf of the cell $= \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1}$

$$= \frac{RT}{F} \left\{ \ln \frac{(a_+)_2}{(a_+)_1} + \ln \frac{(a_-)_2}{(a_-)_1} \right\}$$

$$= \frac{RT}{F} \left\{ \ln \frac{(a_+)_2 \cdot (a_-)_2}{(a_+)_1 \cdot (a_-)_1} \right\}$$

$$= \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad \left\{ \begin{array}{l} a = a_+ a_- \\ a = (a_\pm)^2 \end{array} \right\}$$

Concentration cell with transference

When two electrolyte solutions are in direct contact with each other and transference of ions from one solution to other takes place directly then such cells are called concentration cell with transference.

We consider a concentration cell formed by combining two hydrogen electrodes in contact with HCl solutions of different concentrations:

$$Pt, H_2(g), HCl(a_1) \mid HCl(a_2), H_2(g), Pt$$

$$H^+ \longrightarrow$$
$$\longleftarrow Cl^-$$

Following changes take place for flow of one faraday of electricity.

At L.H.E

$$\frac{1}{2} H_2(g) - e \longrightarrow H^+ (a_+)_1 \quad \text{——— (1)}$$

At R.H.E

$$H^+ (a_+)_2 + e \longrightarrow \frac{1}{2} H_2(g) \quad \text{——— (2)}$$

Since solutions are in direct contact with each other, the ions are free to move from one solution to other when current flow through the cell.

Evidently H^+ ions generated at LHE move from the solution towards right hand side. Since, anions move in direction opposite to which cation move. So Cl^- ion migrate from right to left in above cell.

Let t_- be the transport number of Cl^- and t_+ be the transport number of H^+ ion in HCl.

Then, for one faraday of electricity passing through t_- faraday will be carried by Cl^- ions and t_+ faraday by H^+ ions

So, $$t_- Cl^- (a_-)_2 \longrightarrow t_- Cl^- (a_-)_1 \quad \text{——— (3)}$$

and $$t_+ H^+ (a_+)_1 \longrightarrow t_+ H^+ (a_+)_2 \quad \text{——— (4)}$$

The net result for flow of one faraday of electricity

At Left-hand electrode LHE

gain of 1 gram-equiv. of H^+ ions by process (1)

Loss of t_+ gram-equiv of H^+ ions by process (4)

∴ Net gain of H^+ ions = $(1-t_+)$ equiv. = t_- gram equiv.

At the same time

net gain of Cl^- ions = t_- gram equiv by process (3)

At right hand electrode (R.H.E)

Loss of 1 gram equiv of H^+ ions by process (2)

gain of t_+ gram-equiv of H^+ ions by process (4)

∴ Net loss of H^+ ions = $(1-t_+)$ gram equivalent

= t_- gram equiv.

At the same time

Net loss in Cl^- ions = t_- gram equiv. by process (3)

Thus for every one faraday of electricity, there is net transfer of t_- gram-equiv. of H^+ ions and t_- gram equiv of Cl^- ions from right to left. i.e from solution in which activity of HCl is a_2 to that in which activity of HCl is a_1

$$t_- H^+ (a_+)_2 \longrightarrow t_- H^+ (a_+)_1$$

$$t_- Cl^- (a_-)_2 \longrightarrow t_- Cl^- (a_-)_1$$

$$t_- H^+ (a_+)_2 + t_- Cl^- (a_-)_2 \longrightarrow t_- H^+ (a_+)_1 + t_- Cl^- (a_-)_1$$

$$E_{w.t} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_- \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} \quad \text{— (5)}$$

$$= t_- \frac{RT}{F} \left\{ \ln \frac{(a_+)_2}{(a_+)_1} + \ln \frac{(a_-)_2}{(a_-)_1} \right\}$$

$$= t_- \frac{RT}{F} \ln \frac{(a_+)_2 \cdot (a_-)_2}{(a_+)_1 \cdot (a_-)_1} \qquad \left\{ \begin{array}{l} a = a_+ a_- \\ a = (a_+)^2 \end{array} \right.$$

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