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Deg III Chem. Hons, Paper- V

Topic :- Electrochemistry (continued)

Concentration Cell with transference

In this type of cell, Liquid junction Potential between the junction of two solution is taken into account. Let us consider the cell of the type

$$H_2\,(1\text{ atm}) \,|\, HCl\,(a_1) \,\vdots\, HCl\,(a_2) \,|\, H_2\,(1\text{ atm})$$

E_1 E E_2

In the above cell the two solutions of HCl are in contact with each other and thus there is a direct transfer of HCl from the more concentrated solution (a_2) to the less concentrated solution (a_1).

Whenever two solution of electrolyte of two concentrations are placed together and the same electrode reversible with respect to one of the ions of the electrolyte is kept in each solution then a concentration cell with transport will be obtained. In the above cell dotted line represent

Liquid junction Potential.

When $a_2 > a_1$ then left hand electrode will become negative whereas the right hand electrode will get Positive charge.

If one faraday of electricity is Passed through the cell then 1 gm-atom of hydrogen dissolves at negative electrode ie at left electrode

$$\frac{1}{2} H_2 \rightarrow H^+ + e \quad \text{——— (I)}$$

and the reduction will take place at right electrode

$$H^+ (a_2) + e \rightarrow \frac{1}{2} H_2 \quad \text{— (II)}$$

The overall reaction is obtained by adding (I) and (II)

$$H^+(a_2) = H^+(a_1) \quad \text{—— (III)}$$

The electron will flow from left to right. As the electric current is Constituted by H^+ and Cl^- it means that H^+ ions are moving from left to right while Cl^- ions are moving from right to left.

suppose t_c and t_a are the transport number of H^+ and Cl^- respectively It can be said that t_c equivalent of current is carried by H^+ ions whereas t_a equivalent of the current by Cl^- ion.

For the Passage of 1 faraday of electricity through the cell then t_c faraday is carried by t_c gram ion of hydrogen from left to right ie from a solution of activity a_1 to a_2.

$$t_c\ H^+(a_1) = t_c\ H^+(a_2) \quad \text{---(IV)}$$

$[t_c + t_a = 1 \text{ or } t_c = 1 - t_a]$

$$\text{or } (1-t_a)\ H^+(a_1) = (1-t_a)\ H^+(a_2) \quad \text{---(V)}$$

Also t_a faraday of electricity will be carried by t_a gm of chloride ion from right to left ie from the solution of activity a_2 to a_1

$$t_a\ Cl^-(a_2) = t_a\ Cl^-(a_1) \quad \text{---(VI)}$$

The net transfer of material from the two solution will be obtained by adding III, (V) & (VI)

$H^+(a_2) + (1-t_a)H^+(a_1) + t_a Cl^-(a_2)$
$= H^+(a_1) + (1-t_a)H^+(a_2) + t_a Cl^-(a_1)$

or $t_a H^+(a_2) + t_a Cl^-(a_2)$
$= t_a H^+(a_1) + t_a Cl^-(a_1)$

$t_a HCl(a_2) = t_a HCl(a_1)$ —(VII)

From equation (VII) it is clear that ta equivalent of HCl is transferred from a solution of activity a_2 to a_1 by the passage of one faraday.

EMF of the complete cell will be given by $E = E_1 - E_2$

But $E_1 = E^\circ - \frac{RT}{F} \log_e a_1^{t_a}$

$E_2 = E^\circ - \frac{RT}{F} \log_e a_2^{t_a}$

$\therefore E = \left(E^\circ - \frac{RT}{F} \log a_1^{t_a}\right) -$

$\left(E^\circ - \frac{RT}{F} \log a_2^{t_a}\right)$

or $E = -\frac{RT}{F} \log a_1^{t_a} + \frac{RT}{F} \log a_2^{t_a}$

$= -\frac{RT}{F} \log \frac{a_1^{t_a}}{a_2^{t_a}}$

$$\text{or } E = -t_a \frac{RT}{F} \log \frac{a_1}{a_2}$$

$$\text{or } E = t_a \frac{RT}{F} \log \frac{a_2}{a_1}$$

The E.M.F in terms of valency

$$E = t_a \frac{V}{V_+ Z_+} \frac{RT}{F} \log \frac{a_2}{a_1}$$

V = Total number of ions in solution

Z = Valency of ions

Here $V = 2 \quad V_+ = 1$

$$\therefore E = 2 t_a \frac{RT}{F} \log \frac{a_2}{a_1}$$