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Topic :- Electrochemistry (Continued)

Liquid-Liquid junction Potential :-

When two salt solution of different concentration are placed in contact with one another, the ions from the concentrated solution will tend to diffuse into the dilute solution. The rate of diffusion of each ion is approximately proportional to the speed of the ions in the electric field.

Suppose that positive ion moves with a greater speed than the negative ion. It means that the positive ion from the concentrated solution will diffuse ahead of the negative ion in the dilute solution. Then the dilute solution becomes positively charged with respect to concentrated solution.

Suppose that the negative ion moves faster. It means that negative ion will diffuse rapidly in dilute solution than the positive ion and the dilute solution get's a negative charge.

In both the above cases an electrical double layer is set up at the junction of two solutions and thus a potential difference is set up at this junction. This potential difference developed at the junction of two solutions of different concentration is termed as Liquid – Liquid junction Potential which is designated as E_L.

It means that if two ions are moving with the same speed, there will not be any Liquid – Liquid junction Potential.

Let us consider a cell where two hydrogen electrodes are dipped in two solutions of HCl at different concentration.

$$H_2(Pt) \,\Big|\, \frac{N}{10}\ HCl \,\Big\|\, \frac{N}{100}\ HCl \,\Big|\, H_2(Pt)$$

As the two solutions are of different concentrations, there will be the diffusion of concentrated solution into dilute solution. The diffusion of the solution occurs due to H^+ and Cl^- ions. As the speed of H^+ ion is greater than that of Cl^- ion, the H^+ ion will move more rapidly than Cl^- ion. Then the dilute solution will possess excess of H^+ ion whereas the concentrated solution has an excess of Cl^- ions. Hence the dilute solution will be +vely charged whereas the concentrated solution will be −vely charged. Thus there will be difference of potential at the junction of two solutions. This is known as Liquid-Liquid junction potential. This will persist until both the solution attain the same concentration.

Determination of formula for Liquid-Liquid junction Potential

Let us consider the solution of some uni-univalent electrolyte i.e. KCl

$$KCl(a_1) = KCl(a_2)$$

The left hand electrode is the source of electron. If one faraday of electricity is passed through the cell, t_c gram ion of cation (K^+) migrate from left to right and t_a gram ion of anion (Cl^-) from

If it is assumed that the transport number is independent of concentration then the free energy change for the passage of one Faraday of electricity can be calculated.

The free energy change for positive ion in the left compartment

$$\Delta F_1 = t_c RT \log_e \frac{(a+)_2}{(a+)_1}$$

Free energy change for negative ion in the right compartment

$$\Delta F_2 = t_a RT \log_e \frac{(a-)_1}{(a-)_2}$$

The net change in free energy is given by

$$\Delta F = \Delta F_1 + \Delta F_2 = t_c RT \log_e \frac{(a+)_2}{(a+)_1} + t_a RT \log_e \frac{(a-)_1}{(a-)_2} \quad \text{—— (1)}$$

If E_L is the liquid-liquid junction potential it means that electrical work done is $n E_L F$

where n = number of faraday [F = 96500 Coulomb

$$\therefore \Delta F = - E_L \cdot F \quad [\text{As } n = 1] \quad \text{—(II)}$$

By combining equation (I) and (II) we get

$$E_L = -t_c \frac{RT}{F} \log_e \frac{(a+)_2}{(a+)_1} - t_a \frac{RT}{F} \log_e \frac{(a-)_1}{(a-)_2}$$

$$= -t_c \frac{RT}{F} \log_e \frac{a_2}{a_1} - t_a \frac{RT}{F} \log_e \frac{a_1}{a_2}$$

[a is the mean activity of both ion

$$a = a_+ = a_-$$

$$E_L = -t_c \frac{RT}{F} \log_e \frac{a_2}{a_1} + t_a \frac{RT}{F} \log_e \frac{a_2}{a_1} \quad \text{(III)}$$

$t_a = 1 - t_c$

Putting the value of t_a in equation (III) we get

$$E_L = -t_c \frac{RT}{F} \log_e \frac{a_2}{a_1} + (1 - t_c) \frac{RT}{F} \log_e \frac{a_2}{a_1}$$

$$= -2t_c \frac{RT}{F} \log_e \frac{a_2}{a_1} + \frac{RT}{F} \log_e \frac{a_2}{a_1}$$

$$E_L = (1 - 2t_c) \frac{RT}{F} \log_e \frac{a_2}{a_1} \quad \text{—(IV)}$$

Equation (IV) represents the expression for the Liquid-Liquid junction Potential of the Cell. $t_a + t_c = 1$, $1 - 2t_c = t_a - t_c$

Putting the value of $(1 - 2t_c)$ in equation (IV)

$$\boxed{E_L = (t_a - t_c) \frac{RT}{F} \log_e \frac{a_2}{a_1} \quad \text{—(V)}}$$