SUBJECT- CHEMISTRY
CLASS - B.Sc(Hons) PART-III
PAPER - V
TOPIC - Concentration cell with transference

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Q what do you understand by Concentration cell with transferenc
Determine the emf of such cell ?

Ans Concentration cell with transference :

A Concentration cell is the galvanic cell having the same half cells but at different Concentrations. The emf of such cell arises due to the free energy change of tranfer of electrolyte from high to low Concentrations. when two Solutions are in direct Contact, Then the transference of ions occurs from one to another Solution directly, then the cell is Called Concentratio cell with transference. Let us Consider the following Conceen - tration cell with transference —

$$Pt, H_2\,(1\,atm)\,HCl\,(a_1)\,|\,(a_2)\,HCl\,|\,H_2(1\,atm), Pt.$$

on passing one faraday of electricity through this cell, one g-atom of hydrogen gas is oxidised to one g-ion of H^+ ions at the left electrode and the same amount is reduced to produce one g-atom of hydrogen gas at the right electrode. If t_+ and t_- are the transport number of H^+ and Cl^- ions, Then during the passage of one faraday of electricity through the cell, t_+ faradays will be carried by t_+ g-ions of H^+ ions in one direction while t_- faradays will be carried by t_- g-ions of Cl^- ions in the opposite direction —

$$\frac{1}{2}H_2(g) \longrightarrow H^+(Soln) \xrightarrow{t_+} (Soln) \longleftarrow \frac{1}{2}H_2(g)$$

$$Cl^- \xleftarrow{t_-}$$

The net result is an increase in left electrode of $1-t_+ = t_-$ g-ion of H^+ ions and t- g-ion of Cl ions at the same time a decrease of $1-t_+ = t_-$ g-ion of H^+ ions and t- g-ion of H^+ ions and t- g-ion of Cl^- ions in the right electrode. This is equivalent to the transfer of t- g-ion of Cl^- ions from right to left. Hence free energy change accompanying the transfer,

$$\Delta F = t_- RT \ln \frac{(a_+)_1}{(a_+)_2} + t_- RT \ln \frac{(a_-)_1}{(a_-)_2} \quad -- (1)$$

Where (a_+) and (a_-) are the ionic activity of H^+ and Cl^- ions respectively

$$\therefore \Delta F = 2t_- RT \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

where $(a_\pm)_1$ and $(a_\pm)_2$ are the mean ionic activities of the ions in two HCl solutions And $\Delta F = -FE$ for $n=1$, hence the emf of the Concentration cell with transference,

$$E_t = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \quad -- (iii)$$

In other words, the emf. of such cells depends on the transport number of anion and the ratio of the mean activities.

Similarly, if electrodes are reversible with respect to the anion, then

$$E_t = 2t_+ \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

The emf includes the liquid junction potential between the two HCl solutions.