

CLASS - B.Sc (Hons) PART-III

PAPER - V

TOPIC - The Concentration cell without transference

Dr. Hari Mohan Prasad Singh

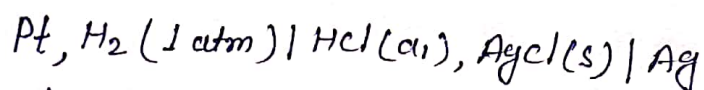
Department of Chemistry

Dr. L. K. V. D. College Tajpur Samastipur

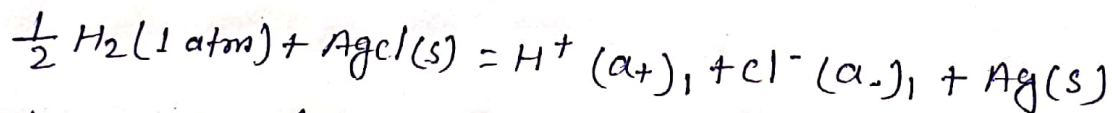
Q Discuss the Concentration cell without transference and compare it with the Concentration cell with transference.

Ans Concentration cell without transference:

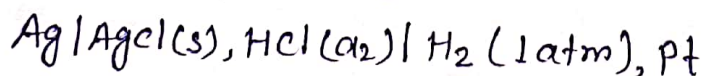
The Concentration cell in which there is neither direct contact nor direct transference of ions between two electrolytic solutions is called the Concentration cell without transference. Let us consider the following Concentration cell without transference -



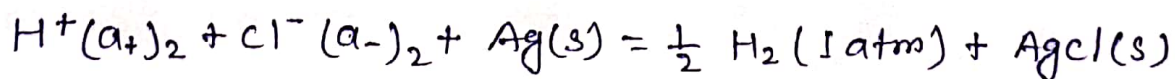
The cell reaction is given as -



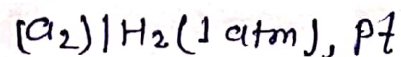
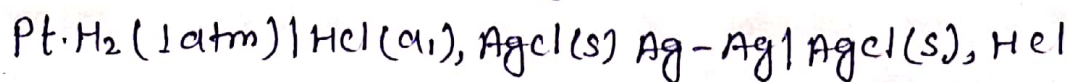
where  $(a_+)_1$  and  $(a_-)_1$  are the activities of  $\text{H}^+$  and  $\text{Cl}^-$  ions in HCl solution of activity  $a_1$ . If the same cell is reversed when activity changes to  $a_2$  -



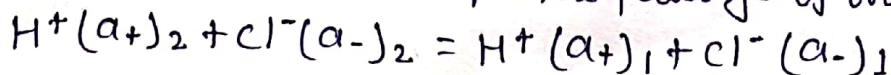
Then the cell reaction becomes -



When these cells are connected so as to oppose each other, then the overall cell is given as



The overall reaction for the passage of one faraday is given by -



The cell reaction for the passage of one faraday is thus a decrease of one g-ion of  $H^+$  ions and one g-ion of  $Cl^-$  ions in Solution (2) and an equal increase in Solution (1) of  $H^+$  and  $Cl^-$  ions. Hence transfer takes place from Solution (2) to (1). Hence

The free energy change accompanying the transfer is given as -

$$\Delta F = RT \ln \frac{(a_+)1}{(a_+)2} + RT \ln \frac{(a_-)1}{(a_-)2}$$

and  $\Delta F = -EF$  for  $n=1$  then -

$$E = \frac{2RT}{F} \ln \frac{(a_{\pm})2}{(a_{\pm})1}$$

Where  $(a_{\pm})_1$  and  $(a_{\pm})_2$  are the mean ionic activities in two solutions. A cell of this type is called Concentration cell without transference in which the emf depends on the relative activities of the two solutions. The operation of such cell is not followed by direct transfer of electrolyte from one solution to another. The transfer occurs indirectly due to chemical reaction.

Comparison :

A Concentration cell with transference having electrodes reversible with respect to cation can be converted into one without transference by introducing an electrode which is reversible with respect to anion of the electrolyte between two electrode solutions. The emf of the cells with and without transference are given by the expressions -

$$E_t = 2t - \frac{RT}{F} \ln \frac{(a_{\pm})2}{(a_{\pm})1} \quad \text{and} \quad E = \frac{2RT}{F} \ln \frac{(a_{\pm})2}{(a_{\pm})1}$$

Therefore the emf of the cells with and without transference is equal to the transport number of anion  $\frac{E_t}{E} = t_-$

If the end electrodes are reversible with respect to the anion then

$$\frac{E_t}{E} = t_+$$

Thus transport number of ions can also be calculated from  $E_t$  and  $E$  values.