

# **Electrochemistry**

## **(Concentration Cells)**

**Dr.S.SURESH**

**Assistant Professor**

**Email:[avitsureshindia@gmail.com](mailto:avitsureshindia@gmail.com)**

## CONCENTRATION CELLS

In concentration cells, the EMF arises because of a difference in the concentration of the species involved. Concentration cells are of two types.

*(a) Electrode concentration cell.*

*(b) Electrolyte concentration cell.*

## Electrode concentration cell

*In these cells, two like electrodes at different concentration are dipping in the same solution. Two hydrogen electrodes at unequal gas pressure immersed in the same solution of hydrogen ions constitute an electrode-concentration cell. This may be represented by*



## Electrolyte concentration cells

In these cells, both the electrodes are of the same metal (Zn) and these are in contact with solutions of the same ions ( $\text{Zn}^{2+}$ ). The concentrations and hence activities of the ions are, however different. Let ( $a_1$ ) and ( $a_2$ ) be the activities of zinc ions in the two electrolytes surrounding the electrodes. One such cell is represented as



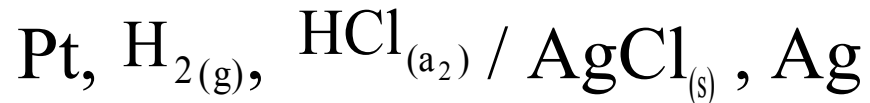
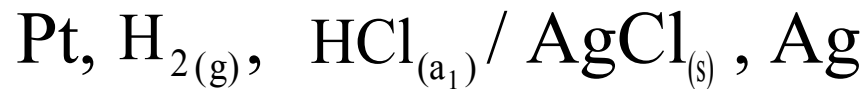
**Electrolyte concentration cells are of two types**

**(a) Concentration cells without transference**

**(b) Concentration cells with transference**

# Concentration cells without transference

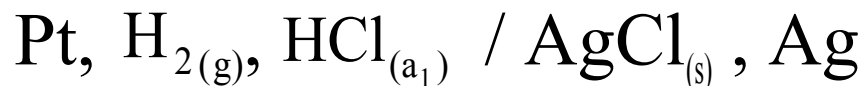
To understand the setting up of such a cell, let us consider two simple cells. Such as



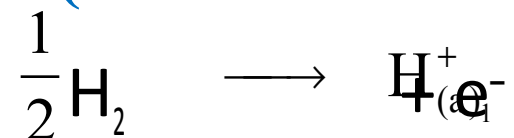
The two electrolytes are thus not in direct contact with one another. Let the activity of  $\text{H}^+$  ions in the two solutions be  $(\text{a}_1)$   $(\text{a}_2)$ . The cells are combined together in such a way that they oppose each other

# Concentration cells without transference

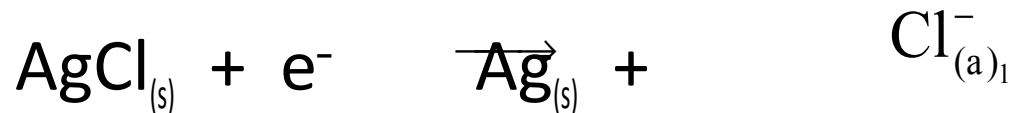
Let us consider the cell



**Anode (oxidation half cell reaction)**

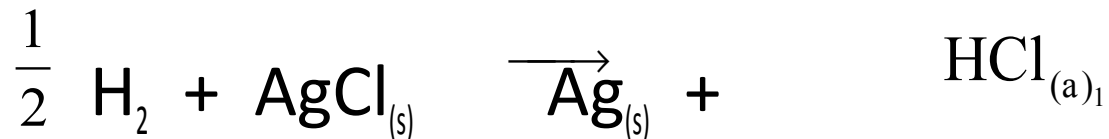


**Cathode (Reduction half cell reaction)**



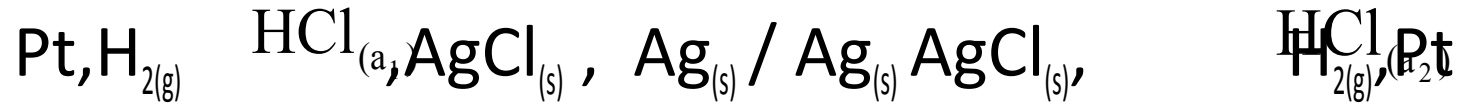
**The net cell reaction is**

---



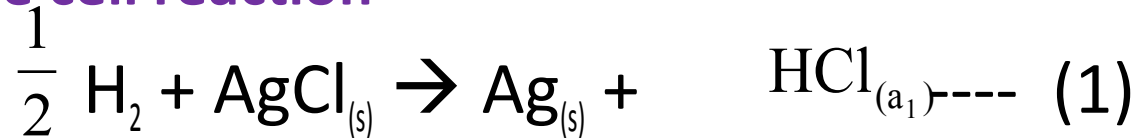
# Concentration cells without transference

The cells are connected together and it is represented as

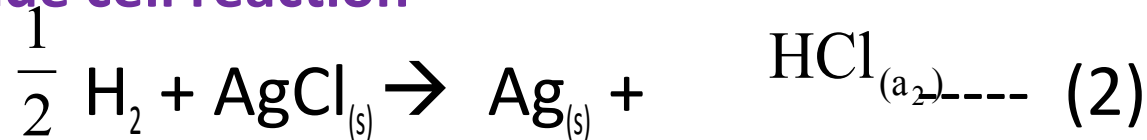


## Cell reactions

### Left side cell reaction



### Right side cell reaction



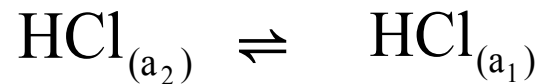
### Subtract eq (2) minus eq (1)





# Concentration cells without transference

The overall reaction of the combined cell for the passage of one faraday of electricity, will be obtained as

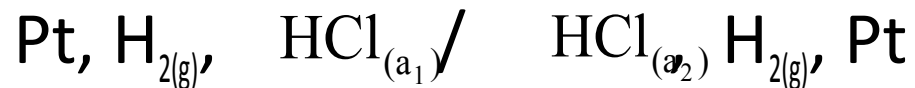


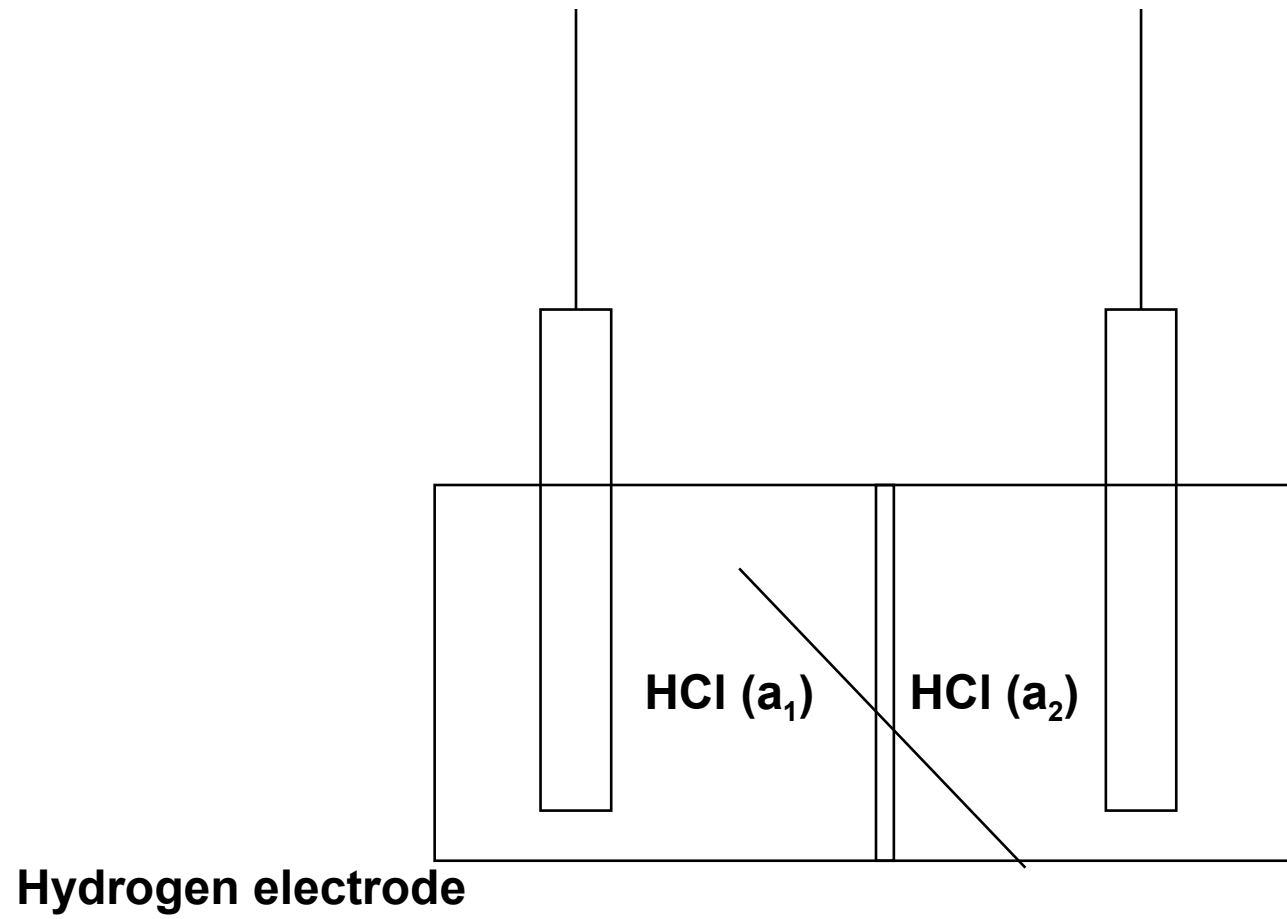
Hence EMF of such a cell is given by

$$E_{\text{w.o.t}} = \frac{RT}{F} \ln \frac{a_2}{a_1}$$

## Concentration cells with transference

Consider a concentration cell formed by combining two hydrogen gas electrodes in contact with HCl solutions of different concentrations. The two solutions are in direct contact with each other.





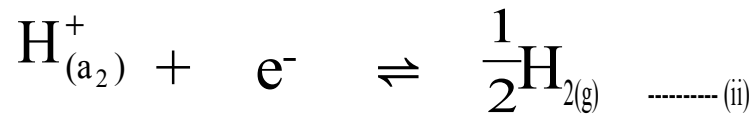
## Concentration cells with transference

The following changes are involved for the flow of one faraday of electricity

Left hand side electrode



Right hand side electrode

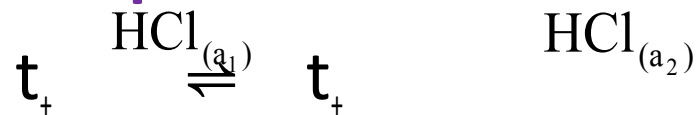


Thus  $\text{H}^+$  ions are generated at the left hand electrode and consumed at the right hand electrode, The solutions are in direct contact with each other and the ions are free to move from one solution to the other, when current flows through the cell.

## Concentration cells with transference

Let  $t_-$  be the transport number of  $\text{Cl}^-$  ion and  $t_+$  that of  $\text{H}^+$  ion in  $\text{HCl}$ . The cell reaction involves the transport of  $t_+$  moles of  $\text{HCl}$  from the LHS to the RHS of the cell.

Hence,  $t_+$  equivalent of  $\text{H}^+$  ions will be transferred from the solution of activity  $a_1$  to that of activity  $a_2$ , which may be represented as

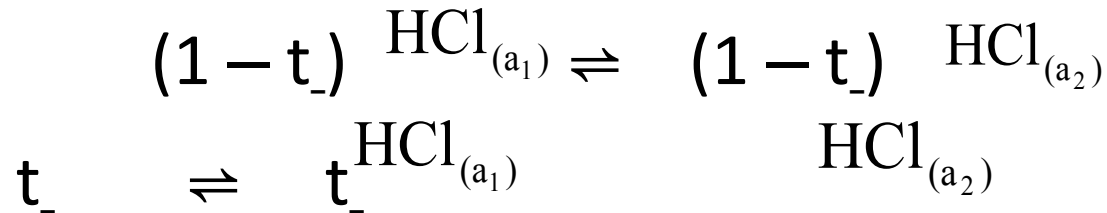


# Concentration cells with transference

Since,

$$t_+ = 1 - t_-$$

Hence the changes are represented as



The mean ionic activity of ions is defined as  $(a_{\text{H}^+} a_{\text{Cl}^-}) = a_{(\pm)}^2$ ), Hence

The EMF of concentration cell is given by

$$E_{\text{w.t}} = 2 t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

# Liquid Junction potential

# Liquid Junction Potential

$$E_{w.t} = 2t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{a_2}{a_1}$$

Hence liquid junction potential ( $E_l$ ) is given by

$$\begin{aligned} E_l &= E_{w.t} - E_{w.o.t} \\ &= (2t_- - 1) \frac{RT}{F} \ln \frac{a_2}{a_1} \end{aligned}$$

We know that ( $t_+ + t_- = 1$  ; Then  $t_- = 1 - t_+$ )

$$\begin{aligned} &= (t_- + (1 - t_+) - 1) \frac{RT}{F} \ln \frac{a_2}{a_1} \\ &= (t_- - t_+) \frac{RT}{F} \ln \frac{a_2}{a_1} \end{aligned}$$