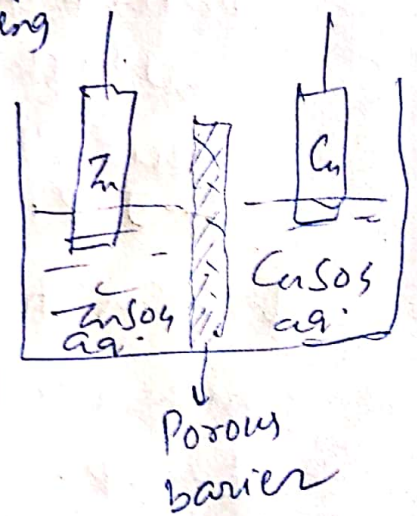


Electrochemistry

Liquid-Junction Potential (L.J.P)

When we consider a galvanic cell as Daniell Cell which consists of porous ceramic barrier separates a compartment containing a Zn rod in $ZnSO_4$ solution from compartment containing a Cu rod in $CuSO_4$ solution. Cu & Zn electrodes are attached to the wire terminals.



The porous membrane prevents extensive mixing of the solution by convection current but allows ions to pass from one solution to other.

If molarality of $CuSO_4$ and $ZnSO_4$ solutions are same and having equal concentration of SO_4^{2-} in both solutions. At junction point between the solutions ions from each solution diffuse into the other solution. As Cu^{+2} is more mobile than Zn^{+2} in aq. solution. So Cu^{+2} ion diffuse in $ZnSO_4$ solution faster.

This produces small excess positive charge on ZnSO₄ side of the boundary and a small excess of negative charge on CuSO₄ side. The negative charge builds up until a steady state is reached with the Zn²⁺ & Cu²⁺ ions migrating at equal rate across the boundary. The steady state charges on each side produces a potential difference $\phi(\text{aq. ZnSO}_4) - \phi(\text{aq. CuSO}_4)$ which contributes to measured cell emf. This potential difference is called L.J.P.

When two solutions are not in ^{direct} contact with each other, it does not include L.J.P.

The magnitude of L.J.P depends on the transference numbers of the anions and cations.

When transference numbers of the anion and cation of electrolyte are same then L.J.P. = 0 or negligible.

If transference no. of cation is greater than that of anion, L.J.P. = negative.

If reverse, then L.J.P. = positive.

Salt bridged containing galvanic cell, L.J.P. = 0 as no transference of ions or mobilities of ions K^+ & Cl^- in water are same.