

SUBJECT - CHEMISTRY

CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC - Liquid Junction Potential ( $E_L$ )

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Liquid Junction Potential ( $E_L$ ): If  $H^+$  and  $Cl^-$  ions have the same activity in a given solution, then  $a_+ = a_-$  and the emf of the cell in which  $E_L$  is eliminated would become,

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

$$\therefore E_L = E_t - E = (2t_- - 1) \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} \quad \text{--- (2)}$$

This equation holds good for uni-univalent electrolytes.

Again -

$$t_+ + t_- = 1$$

$$\therefore t_- - 1 = -t_+$$

on adding  $t_-$  both sides, we get -

$$t_- + (t_- - 1) = t_- - t_+$$

$$\text{or } 2t_- - 1 = t_- - t_+$$

putting this value of  $(2t_- - 1)$ , we get -

$$E_L = (t_- - t_+) \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} \quad \text{--- (3)}$$

Thus the sign and magnitude of  $E_L$  depends upon the transport number of cation and anion. If the transport number of ions are not very different,  $E_L$  will be small. This explains the use of concentrated solution of KCl to minimise  $E_L$  as the transport numbers of  $K^+$  and  $Cl^-$  ions are almost equal.