Dr. L. K. Mishra
Deptt of chemistry

For Deg II chem Hons Paper – IV & Deg II sub Courses

Ionic Mobility & Transport Number

Strong Electrolyte	Equivalent Conductance at infinite dilution (Λ_o) $ohm^{-1} cm^2$
1) HCl	426.1 "
2) NaCl	126.45 "
3) LiCl	115.03 "
4) KBr	151.92 "
5) KCl	149.8 "

At infinite dilution all the strong electrolytes are completely ionised even then their equivalent conductance differ much from one another. This is due to the difference in the speed of the two ions.

The equivalent conductance of HCl is nearly three times than that of NaCl. Since Cl^- is common it is clear that speed of H^+ is more than three times, the speed of [illegible] Na^+ ion.

Since the speed of an ion varies with the applied potential it is better to use the term Ionic mobility. It is defined as the distance travelled by an ion per second under a Potential gradient of 1 volt/cm.

Potential gradient is the Potential difference applied at the electrodes divided by the distance between them.

$$\text{Mobility of an ion} = \frac{\text{speed}}{\text{potential gradient}}$$

Transport Number

The fraction of the total current carried by each ion is called its transport number.

U_c = Mobility of Cation

U_a = Mobility of anion

$\therefore$ Transport no of Cation (n_c)

$$= \frac{\text{Current Carried by the Cation}}{\text{Total current}}$$

$$= \frac{U_c}{U_c + U_a}$$

$$\text{Transport no of anion } (n_a) = \frac{U_a}{U_c + U_a}$$

$$n_c + n_a = 1$$

$\therefore n_c = 1 - n_a$

or $n_a = 1 - n_c$

Determination of Transport no

Hittorf's method:-

In this method the concentration change around the electrode is determined during the experiment.

$$\frac{U_c}{U_a} = \frac{\text{Fall of concentration around the anode}}{\text{Fall of concentration around the cathode}}$$

Transport no of cation (n_c)

$$= \frac{U_c}{U_c + U_a}$$

It follows therefore that

$$n_c = \frac{\text{Fall of concentration around the anode}}{\text{Fall of concentration around the anode} + \text{Fall of concentration around the cathode}}$$

or $$n_c = \frac{\text{Fall of concentration around the anode}}{\text{Total fall of concentration}}$$

If concentrations are measured in terms of gram-equivalents then

$$n_c = \frac{\text{Number of gram equivalent Lost from anodic Compartment}}{\text{Total number of gram-equivalent lost.}}$$

$$n_c = \frac{\text{Number of gram equivalent Lost from anodic compartment}}{\text{Number of gram-equivalent of Cu deposited in Coulometer.}}$$

$$n_c + n_a = 1$$

∴ Transport no of anion (n_a) $= 1 - n_c$

Cation	Solution used
Ag^+	$AgNO_3$ ($\frac{N}{15}$ or $\frac{N}{20}$)
Cu^{++}	$CuSO_4$
Zn^{++}	$ZnSO_4$