Transport number or Transference number.

(1) **Definition : "**The fraction of the total current carried by an ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like t_+ and t_- or t_c and t_a or n_c and n_a."

From this definition,

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}\ ; \quad t_c = \frac{\text{Current carried by a cation}}{\text{Total current passed through the solution}}$$

Evidently, $t_a + t_c = 1$.

(2) **Determination of transport number:** Transport number can be determined by **Hittorf's method, moving boundary method, emf method and from ionic mobility**.

(3) **Factors affecting transport number**

(i) **Temperature:** A rise in temperature tends to bring the transport number of cation and anion more closely to 0.5. It means that the transport number of an ion, if less than 0.5 at the room temperature increases and if greater than 0.5 at room temperature decreases with rise in temperature.

(ii) **Concentration of the electrolyte:** Transport number generally varies with the concentration of the electrolyte. In case of partially dissociated CdI_2, the value decreases from 0.49 at low concentration to almost zero at higher concentration and becomes negative at still higher concentration. The transport numbers of Cd^{2+} ions in 0.01 N, 0.05 N, 0.02 N and 0.50 N CdI_2 at 25°C are 0.449, 0.402, 0.131 and 0.005 respectively. This abnormal behavior may be explained by assuming,

(a) That in very dilute solution: CdI_2 ionizes to Cd^{2+} ions and I^- ions. Thus Cd^{2+} shows the usual transport number.

(b) That with increase in concentration: CdI_2 takes on I^- ions and form complex, $CdI_2 + 2I^- \rightleftharpoons [CdI_4]^{2-}$. this explains the negative value for transport number of Cd^{2+} ions at higher concentration.

(iii) **Nature of the other ions present in solution:** The transport number of anion depends upon the speed of the anion and the cation and vice versa. For example, the transport number of Cl^- ion in NaCl is 0.0004 but in HCl it is 0.16. This is because H^+ moves faster than Na^+.

(iv) **Hydration of ion:**In general, a decrease in the degree of hydration of anion will increase its transport number. For example, the transport number of Li^{+}, Na^{+}, K^{+} ions in $LiCl, NaCl, KCl$ solutions are 0.328, 0.396, and 0.496 respectively. Thus the ionic mobility of the cations is in the order $Li^{+} \leq Na^{+} \leq K^{+}$ which is in the reverse order than that expected from the size of the ions. This

anomaly can be explained by saying that Li^{+} is hydrated to greater extent than Na^{+} which in turn is more than K^{+}. Thus the effective size of Li^{+} is more than that of Na^{+} which in turn is more than that of K^{+}.

(4) **Transport number and Ionic mobility: Ionic mobility or Ionic conductance** is the conductivity of a solution containing 1 g ion, at infinite dilution, when two sufficiently large electrodes are placed 1 cm apart.

$$\text{Ionic mobilities } (\lambda_a \text{ or } \lambda_c) \propto \text{speeds of ions } (u_a \text{ or } u_c)$$

Unit of ionic mobility is Ohm^{-1} cm^{2} or V^{-1}S^{-1}cm^{2} : Ionic mobility and transport number are related as:

$$\lambda_a \text{ or } \lambda_c = t_a \text{ or } t_c \times \lambda_\infty$$

Absolute ionic mobility is the mobility with which the ion moves under unit potential gradient. It's unit is $cm \sec^{-1}$.

$$\text{Absolute ionic mobility} = \frac{\text{Ionic mobility}}{96,500}$$