Ministry of Higher Education and Scientific Research

Al-Muthanna University

College of Science

وزارة الـتعليم الـعالـي والـبحث الـعلمي

جـــامعـــــة الــمثنـــــى

كليـــة الـعلــــــــوم

قـســــــــم الــكـــيمـياء

Electrochemistry

Lecture (10)

Stage 3

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Transport Numbers

The positive and negative ions transport the electric current through the solution during the electrolysis process. The number of load or transfer of that type of ion, which in turn depends on the concentration of the ion, its charge and the speed of its movement under the influence of the applied electric field $I = I_+ + I_-$ The load number of cations (t_+) is defined by the following equation:

$$t_+ = \frac{I_+}{I}$$
$$\Rightarrow t_+ = \frac{I_+}{I_+ + I_-}$$

As for the anion, its load number (-) is given by the following equation:

$$t_- = \frac{I_-}{I}$$
$$\Rightarrow t_- = \frac{I_-}{I_+ + I_-}$$

From the equation:

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$$I = I_+ + I_-$$
$$I = (\nu_+ \alpha\, C\, V_+\; A\, F) + (\nu_-\; \alpha\, C\, V_-\, A\, F)$$

Then :

$$t_+ = \frac{I_+}{I_+ + I_-}$$

$$t_+ = \frac{\nu_+ \alpha\, C\, V_+\, A\, F}{(\nu_+ \alpha\, C\, V_+\, A\, F) + (\nu_- \alpha\, C\, V_- A\, F)}$$

$$t_- = \frac{\nu_- \alpha\, C\, V_-\, A\, F}{(\nu_+ \alpha\, C\, V_+\, A\, F) + (\nu_- \alpha\, C\, V_- A\, F)}$$

And for the mono – mono valent electrolyte where ($z_+ = z_- = 1$) and ($\nu_+ = \nu_-$) where:

$$t_+ = \frac{\nu_+ \alpha\, C\, V_+\, A\, F}{(\nu_+ \alpha\, C\, V_+\, A\, F) + (\nu_- \alpha\, C\, V_- A\, F)} \quad \because (n_+ = n_-)$$

$$t_+ = \frac{\cancel{\nu_+} \cancel{\alpha} \cancel{C}\, V_+ \cancel{A} \cancel{F}}{\cancel{\nu_+} \cancel{\alpha} \cancel{C} \cancel{A} \cancel{F} (V_+ + V_-)}$$

$$\boxed{\Rightarrow t_+ = \frac{V_+}{V_+ + V_-}}$$

Also:

$$t_+ = \frac{\nu_+ \alpha\, C\, V_+\, A\, F}{(\nu_+ \alpha\, C\, V_+\, A\, F) + (\nu_- \alpha\, C\, V_- A\, F)} \quad \because (n_+ = n_-)$$

$$t_+ = \frac{\cancel{\nu_+} \cancel{\alpha} \cancel{C}\, V_+ \cancel{A} \cancel{F}}{\cancel{\nu_+} \cancel{\alpha} \cancel{C} \cancel{A} \cancel{F} (V_+ + V_-)}$$

$$\boxed{\Rightarrow t_+ = \frac{V_+}{V_+ + V_-}}$$

So that:

$$t_+ = \frac{\nu_+ \alpha\, C\, V_+\, A\, F}{(\nu_+ \alpha\, C\, V_+\, A\, F) + (\nu_- \alpha\, C\, V_- A\, F)} \quad \because (n_+ = n_-)$$

$$t_+ = \frac{\cancel{\nu_+} \cancel{\alpha} \cancel{C}\, V_+ \cancel{A} \cancel{F}}{\cancel{\nu_+} \cancel{\alpha} \cancel{C} \cancel{A} \cancel{F} (V_+ + V_-)}$$

$$\boxed{\Rightarrow t_+ = \frac{V_+}{V_+ + V_-}}$$

And since the relationship between the velocity of the ion (V) and its movement (μ) is given by the equation:

$$\boxed{V = \mu E}$$

The numbers of the porter can also be written in the following form:

$$t_+ = \frac{\mu_+ E}{\mu_+ E + \mu_- E}$$

$$t_+ = \frac{\mu_+ \cancel{E}}{\cancel{E}\,(\mu_+ + \mu_-)}$$

$$\boxed{\Rightarrow t_+ = \frac{\mu_+}{\mu_+ + \mu_-}}$$

$$t_- = \frac{\mu_- E}{\mu_+ E + \mu_- E}$$

$$t_- = \frac{\mu_- \cancel{E}}{\cancel{E}\,(\mu_+ + \mu_-)}$$

$$\boxed{\Rightarrow t_- = \frac{\mu_-}{\mu_+ + \mu_-}}$$

From the previous equations, it is clear that the load numbers depend on the nature and concentration of the ions present in the solution, because the ions move at different speeds in the presence of the same electric field, and accordingly, the total current passing through the solution Ions move parts of the body according to the speed of those ions. The ions with high velocity will contribute to the transfer of a large part of the current and vice versa. For example, the hydrogen ion (+ (H) in solution) is transported (0.1 mol L-1 HCl at a temperature) of (25 ºC) (about 83 percent) of the total current, and the rest is carried by the chlorine ion, i.e., % (17) of the total current. Perhaps from It is useful to mention that the greater the ratio between the concentration of a particular ion and the concentration of the rest of the ions in the solution, the lower the number of transfers of that ion, and this phenomenon is of great benefit in some methods of electrochemical analysis such as Polarography, whereby it intends to add an excessive amount of an appropriate electrolyte called the supporting electrolyte, Its concentration is much higher than that of the negative ion The number of its transmission will be very small, and therefore the ion will be transmitted through the store and by Diffusion, not ionic migration, is required essential to this type of analysis method.

The electrolyte is symmetrically strong and in the case of infinite dilution, using the equations:

$$\Lambda^{o} = \nu_{+}\lambda_{+}^{o} + \nu_{-}\lambda_{-}^{o}$$
$$\lambda_{+}^{o} = z_{+}\ F\ \mu_{+}^{o}$$
$$\lambda_{+}^{o} = z_{-}\ F\ \mu_{-}^{o}$$

The cation transfer number is given by the following relationship:

$$t_{+}^{o} = \frac{\nu_{+}\ \lambda_{+}^{o}}{\Lambda^{o}}$$

And the anion has the following relationship:

$$t_{-}^{o} = \frac{\nu_{-}\ \lambda_{-}^{o}}{\Lambda^{o}}$$

As for the carrying numbers of weak electrolyte ions at concentrations higher than in the dilute state, Infinite is given by the following two equations :

$$t_{+} = \frac{\nu_{+}\alpha\ \lambda_{+}}{\Lambda}$$
$$t_{-} = \frac{\nu_{-}\alpha\ \lambda_{-}}{\Lambda}$$

Which leads to the two equations $t_{+}^{\circ} = \frac{\nu_{+}\lambda_{+}^{\circ}}{\Lambda^{\circ}}$ and $t_{-}^{\circ} = \frac{\nu_{-}\lambda_{-}^{\circ}}{\Lambda^{\circ}}$ At the state of infinite dilution i.e ($\alpha = 1$).

that the two equations $t_+^\circ = \frac{\nu_+ \lambda_+^\circ}{\Lambda^\circ}$ and $t_-^\circ = \frac{\nu_- \lambda_-^\circ}{\Lambda^\circ}$ They show that to know the values of molar conductivity at infinite dilution of ions, a value that can neither be measured directly nor by extrapolation

It is necessary to know the value of the load number (t_o) for one of the electrolyte ions in addition to the value of (Λ_o). Therefore, it can be said that pregnancy numbers are a means of knowing the contribution of the ions. In the value of the molar conductance at infinite dilution, which is important for the calculation of those values for weak electrolytes

It should be noted that the values of (+) and (-) λ at concentrations other than the state of infinite dilution It is calculated by means of load numbers for ions that cannot be used to calculate (L) another electrolyte via K and Hallrauch law for independent ion conduction since that K The values are for the electrolyte rather than the independent ions, and this is evident from looking at the two equations $t_- = \frac{\mu_-}{\mu_+ + \mu_-}$ and $t_+ = \frac{\mu_+}{\mu_+ + \mu_-}$ Whereas, the transition number of an ion depends not only on its nature represented in its movement, but also on the nature of the other ion.

For example, the transfer number for a (Na^+) ion in 0.2 mol L^{-1} NaCl solution isequal to (0.382) while it is equal in (CH_3COONa) solution to at the same concentration value (0.561) due to the different nature of the ions in the two cases.

Example//

If the ratio between the velocities of silver and nitrate ions is equal to (0.916), then pregnancy for them

Solution//

$$\therefore t_+ = \frac{V_+}{V_+ + V_-}$$

$$t_- = \frac{V_-}{V_+ + V_-}$$

$$\therefore \frac{t_+}{t_-} = \frac{\left(\frac{V_+}{V_+ + V_-}\right)}{\left(\frac{V_-}{V_+ + V_-}\right)}$$

$$\frac{t_+}{t_-} = \frac{V_+ (V_+ + V_-)}{V_- (V_+ + V_-)}$$

$$\boxed{\Rightarrow \frac{t_+}{t_-} = \frac{V_+}{V_-}}$$

That is, the ratio between the numbers of loads is equal to the ratio between the velocity of the cation to the anion:

$$\frac{V_+}{V_-} = \frac{t_+}{t_-}$$

$$\frac{V_+}{V_-} = \frac{(1 - t_-)}{t_-}$$

$$\frac{V_{Ag^+}}{V_{NO_3^-}} = 0.916$$

$$\frac{1 - t_{NO_3^-}}{t_{NO_3^-}} = 0.916$$

$$0.916 \times t_{NO_3^-} = 1 - t_{NO_3^-}$$

$$\therefore t_{NO_3^-} = 0.512$$

$$t_{Ag^+} = 0.479$$