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وزارة التعليم العالي والبحث العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

Electrochemistry

Lecture (6)

Stage 3

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Mobility Ionic

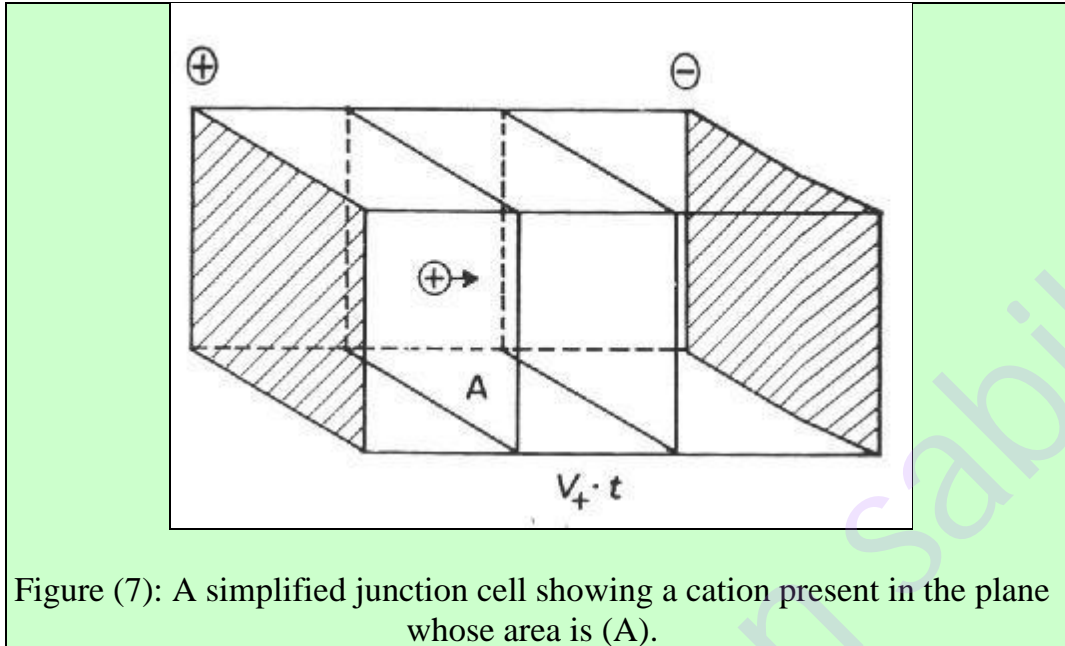
Electrolyte conductivity is a measure of its ability to conduct electrical current. On the rate of transfer of electrical charge by ions in the solution. So, if you can deliver it The electrolyte, in turn, depends on the rate at which these ions are transferred to the electric charge. κ and d The ability of the electrolyte to transmit electric current depends on three factors:

1. The number of charges carried by the ion, that is, the ion with higher equivalence has a greater capacity On the transfer of more charge than an ion of lower valence.
2. Ion concentration, the more ions there are, the greater the charge transfer rate.
3. The velocity of the ions, the higher the velocity of the ion, the higher it is able to transfer the electric charge. at a higher rate.

Among the factors that depend on the ion speed and the intensity of the electric field applied to it Which is equal to the product of the potential difference between the electrodes divided by the distance between them the electrodes. The ion will move at a speed that is directly proportional to the strength of the electric field.

And ionic motion is the speed with which the ion moves toward the electrode in any field. An electric force of unit intensity, i.e. (1 V) across a distance of (1 cm).

In order to know the type of relationship that links between molar conduction (Λ) and ion movement, we assume An electrolyte solution of a monovalent type has a concentration of ($C \text{ mol L}^{-1}$) where Totally like (v) (v_+) cation and (v_-) ion, and that the concentration of cations and anions equals (C) and ($z_+ = z_- = 1$), and that the velocities of the cation and ion are equal respectively (V_+) and (V_-) and that this electrolyte is present in a conductive cell represented in the figure (7):



A cation is present in the plane whose area (A) is located at a time of its value (t) distance value is (V_+ t) and the number of cations that crossed the level (A) at the same time. Equal:

$$(CV_+tA)$$

Thus, the amount of electric charge (Q) that is transferred across the level by The cations are:

$$(CV_+tAF)$$

The current (I) is the rate of change of the amount of electric charge with time, and therefore:

$$I_+ = \frac{Q}{t} = \frac{CV_+tAF}{t}$$

$$\Rightarrow I_+ = CV_+AF$$

$$I_- = \frac{Q}{t} = \frac{CV_-tAF}{t}$$

$$\Rightarrow I_- = CV_-AF$$

The total current is the sum of the currents carried by cations and anions. Therefore:

$$I = I_+ + I_-$$

$$I = (CV_+AF) + (CV_-AF)$$

And the two equations: $I_+ = CV_+AF$, $I_- = CV_-AF$ It can be circulated to all the electrolytes Assuming that the degree of ionization is (α), that is:

$$I = (n_+ \alpha CV_+AF) + (n_- \alpha CV_-AF)$$

$$\Rightarrow I = \alpha CAF (n_+ V_+ + n_- V_-)$$

The current density (J) is the ratio between the current to the area and therefore the the:

$$J = \frac{I}{A}$$

$$J = \frac{\alpha CAF (n_+ V_+ + n_- V_-)}{A}$$

$$\Rightarrow J = \alpha CF (n_+ V_+ + n_- V_-)$$

We have already known that the velocity of the ion (V) is proportional to the strength of the electric field, and therefore:

$$V = mE$$

Where (m) is the proportionality constant and is known as ionic motion, and by substitution in the equation:

$$J = \alpha CF (n_+ V_+ + n_- V_-)$$

$$J = \alpha CF (n_+ \mu_+ E + n_- \mu_- E)$$

$$\Rightarrow J = \alpha CFE (n_+ \mu_+ + n_- \mu_-)$$

Ohm's law is given by the following relationship:

$$I = \frac{V}{R}$$

$$\Rightarrow R = \frac{V}{I}$$

Where (V) is the potential difference.

The conductivity (k) is given by the following relationship:

$$k = \frac{1}{R} \left(\frac{L}{A} \right)$$

Substituting from the equation $R = \frac{V}{I}$ In the equation $k = \frac{L}{RA}$ then

$$k = \frac{1}{R} \left(\frac{L}{A} \right)$$

$$k = \frac{1}{\left(\frac{V}{I} \right)} \times \left(\frac{L}{A} \right)$$

$$k = \frac{IL}{VA}$$

$$k = \frac{I/A}{V/L}$$

$$\Rightarrow k = \frac{J}{E}$$

Substituting in the equation: $J = \alpha CFE (v_+ \mu_+ + v_- \mu_-)$ in the equation $k = \frac{J}{E}$ If:

$$k = \frac{J}{E}$$

$$k = \frac{\alpha CFE (v_+ \mu_+ + v_- \mu_-)}{E}$$

$$\Rightarrow k = \alpha CF (v_+ \mu_+ + v_- \mu_-)$$

Whereas:

$$\Lambda = \frac{k}{C}$$

$$\Lambda = \frac{\alpha CF (v_+ \mu_+ + v_- \mu_-)}{C}$$

$$\Rightarrow \Lambda = \alpha F (v_+ \mu_+ + v_- \mu_-)$$

And when the dimming is infinite, then ($\alpha = 1$) and according to H, the equation $\Lambda = \alpha F(v_+ \mu_+ + v_- \mu_-)$ devolve to:

$$\Lambda^\circ = F(v_+ \mu_+^\circ + v_- \mu_-^\circ)$$

When comparing the equation:

$$\Lambda^\circ = F(v_+ \mu_+^\circ + v_- \mu_-^\circ)$$

$$\Lambda^\circ = F v_+ \mu_+^\circ + F v_- \mu_-^\circ$$

Kohlrausch's law of independent ionic conduction as:

$$\Lambda^\circ = n_+ \lambda_+^\circ + n_- \lambda_-^\circ$$

The two equations are equivalent, i.e.:

$$\Lambda^\circ = F v_+ \mu_+^\circ + F v_- \mu_-^\circ = n_+ \lambda_+^\circ + n_- \lambda_-^\circ$$

From this we conclude that:

$$\lambda_+^\circ = F \mu_+^\circ$$

$$\lambda_-^\circ = F \mu_-^\circ$$

In the case of non-monoelectrolytes, the previous two equations are written in the form:

$$\lambda_+^\circ = z_+ F \mu_+^\circ$$

$$\lambda_-^\circ = z_- F \mu_-^\circ$$

where (μ_-°, μ_+°) are the cation and instantaneous velocities released alone (cm s^{-1}) below The effect of an electric field of intensity (1 V cm^{-1}) in the case of infinite dilution of the solution.

And (z_+, z_-) are the cation and ion charges, respectively.

The following table shows some ionic movements of some ions when infinite dilution And at (25°C).

Table (8): The ionic movements of some ions calculated by the two equations
 at 25 °C $\lambda_o = z F \mu_o$, $\lambda_o = z F \mu_o$

Cation	$\mu^o / 10^{-4} \text{ (cm}^2\text{V}^{-1}\text{s}^{-1} \text{)}$	Anion	$\mu^o / 10^{-4} \text{ (cm}^2\text{V}^{-1}\text{s}^{-1} \text{)}$
H ⁺	36.23	OH ⁻	20.64
Na ⁺	5.19	Cl ⁻	7.91
K ⁺	7.62	Br ⁻	8.09
Zn ²⁺	5.47	SO ₄ ²⁻	8.29
Ba ²⁺	6.60	NO ₃ ⁻	7.40

Almost all ions except hydrogen and hydroxide ions have an ionic movement of approximately $(6 \times 10^{-4} \text{ cm s}^{-1})$ in the presence of an electric field of intensity equal to (1 V cm^{-1}) and a distance of 1 V. The velocity of the ions is very slow, but on the molecular scale, the ion is moving at a velocity. An average of $(6 \times 10^{-4} \text{ cm s}^{-1})$ cuts in one second a distance of ten lengths. Thousands of solvent molecules are stacked next to each other.

Example

If the ionic movement of two ions in an electrolyte is of the type mono-monad is equal to $(6.85 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ at 25 °C calculate the molar conductivity of the vessels at the same temperature, given that: $(1F = 96500 \text{ C})$

solution

By applying the relationship:

$$\lambda_o = z F \mu_o$$

$$\lambda_o = 1 \times 96500 \times 6.85 \times 10^{-4}$$

$$\lambda_o = 66.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example

Calculate the ionic motion of d infinite dilution of the sulfur ion if you know that (λ°) Equal ($160 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) at (25°C), ($1F = 96500 \text{ C}$).

solution

$$\lambda^\circ = z F \mu^\circ$$

$$\mu^\circ = \frac{\lambda^\circ}{z F}$$

$$\mu^\circ = \frac{160 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}{2 \times 96500}$$

$$\mu^\circ = 8.29 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$