Ministry of Higher Education and

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College of Science

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كليـــــة الـعلـــــــــوم

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Electrochemistry

Lecture (7)

Stage 3

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Theories of Electrolytic Conduction

In the previous part, we explained the relationship of molar connectivity with concentration and showed that connectivity The molar decreases with the increase in the electrolyte concentration, whether it is strong or weak, and that was just description, and in what we will touch on two theories to explain the decrease in conductivity with increased concentration.

The Electrolytic Dissociation Theory of Arrhenius

The conduction of electrolyte solutions to the electric current is a clear indication of the presence of Free ions in the solution, and a number of theories and attempts have appeared to explain the existence of These ions were in solution during the nineteenth century, the most important of which was the Arrhenius theory. (1887 AD) in which he tried to explain the different results of the properties of electrolyte solutions. Among them is its ability to conduct electrolyte.

Arrhenius' theorem determines that when electrolytes dissolve in water, a part of It spontaneously ionizes into charged bodies, which are positive and negative ions, which form in A state of chemical equilibrium with non-ionized molecules such that the number of charges they carry The positive ions are equal to the number of charges that the negative ions carry, so The electrolyte solutions are electrically neutral despite the fact that they contain ions. The theory also assumes that these ions move freely in the solution, both in the presence and in the body or the absence of an electric field.

If we symbolize the electrolyte with the symbol (BA), then its ionization is as follows:

$$BA \rightleftharpoons B^+ + A^-$$
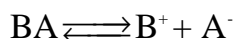
For example, the electrolyte KCl and the electrolyte $BaCl_2$ are ionized as follows:

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$
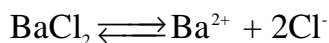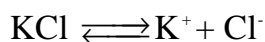
Arrhenius suggested that the amount of ionization of the electrolyte T changes with the concentration of the electrolyte T. and d Introduced the Arrhenian concept of the degree of ionization, which is the ratio between The number of ionized molecules to the total number of molecules in the solution. According to the law of mass action, The previous equilibrium will shift to the right with further dilution until we reach a state Complete ionization is when infinite dilution, and accordingly, the degree of ionization will increase by increasing dilution.

Concerning the electrolytic conduction, Arrhenius considered the ratio between molar conduction At a concentration with yen (Λ) to molar conductivity at infinite dilution (Λ_o) of the electrolyte equal to the degree of ionization (α) that is:

$$\alpha = \frac{\Lambda}{\Lambda^o}$$

This is because (L) at a certain concentration is a measure of the number of ions at that concentration, while That (Λo) is considered a measure of the total number of ions in a solution that can be formed. According to Arrheny's theory, the concentration of KCl is 0.001 mol L-1. It will be ionized by (98 percent), and if the concentration is increased to (0.1 mol L-1), the ionization rate will be equals (86 percent). From the above, it can be concluded that the number of ions in the solution does not depend on The number of molecules that can be ionized (i.e. the concentration) plus the degree of ionization.

Q) What are the assumptions of Arrhenius' theory? What are the defects of this theory?

Evidence has emerged after Arhin and his theory of electrolytic dissociation supports the idea of Electrolytes dissociate into charged particles in solution. Among these indications are:

a) Heat of Neutralization

The temperature of the equivalent of a dilute solution of a strong acid with another of a strong base can be taken as a guide. On the validity of Arhini's theory. It was found experimentally that the heat released is a result of Hydrochloric acid solution, hydrogen acetate, hydrochloric acid solution, sodium hydroxide (57 kJ at (25 °C). These two substances are fully ionized strong electrolytes. The same is true of the salt formed from them, except that the water resulting from the reaction is not ionized at all Therefore, the neutralization reaction can be summarized as follows:

$$H^+ + OH^- \longrightarrow H_2O$$
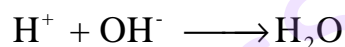
This is a reaction that does not depend on the type of acid and base, and therefore it is certain that the temperature of The reaction of the equation of any acid with a strong base will be equal to the same amount. But the matter is different if the acid is weak, the heat released in this case will be Less than (57 kJ), since part of the heat is consumed in the process of completing the acid ionization Weak or weak base so that they can be equalized.

## B) Collegative Properties of Electrolytic Solutions

Solutions consisting of a solute and a non-volatile solute are distinguished from pure liquids by a number of properties. It was found that these properties depend on the number of solute particles in the solution. These properties include both the decrease in vapor pressure, and the rise in temperature. Boiling, freezing point, and osmotic pressure.

Quantitative relationships that relate these four properties to the number of solute particles in a mass or A specific volume of solvent takes the following formulas:

1. Decrease in vapor pressure	$\Delta P = X_2 P^{o}$ ΔP **: Decrease in Steam Pressure** X_2 **: Molar fraction of the dissolved** P^o **: The vapor pressure of the pure solvent.**
2- The rise in the **degree of boiling**	$\Delta T_b = k_b m$ ΔT_B**: Height in** the **degree of boiling** K_B **: Constant height in boiling point** m **: Molali concentration**
3. Decrease in freezing point	$\Delta T_f = k_f m$ ΔT_F**: Decrease in freezing point** K_F **: Constant drop in freezing point** m **: Molali concentration**
4. Osmotic pressure	$\pi = M R T$ π**: osmotic pressure** M**: Molar concentration** R **: Thap-T G-Azat $^{K-1}$ atm L. 0.082 = (R** mol^{-1}) T**: Absolute Temperature**

The previous four properties depend on the concentration only and are not affected by the nature of the dissolved substance. For example, one mole of any indivisible (i.e. non-electrolytic) substance in a given volume of the solution will have the same osmotic cover regardless of what the substance is. that Because one mole will also give one mole of the molecules of this solute. However, the situation is It differs when the dissolved substance is divisible, that is, the electrolyte. The collective property of a solution of an electrolyte is always greater than that of a solution of a substance Non-electrolyte and at the same conditions of concentration and temperature.

The electrolyte in the solution will have more particles than this which dissolved in the beginning. The example that illustrates the division of matter (AB) is:

$$\underset{(1\ mol)}{AB} \longrightarrow \underset{(1\ mol)}{A^+} + \underset{(1\ mol)}{B^-}$$
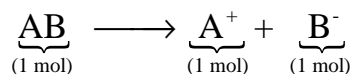
Any one mole of (AB) being a mole of ions, so it is expected that this The number of particles in the solution is twice as much as if it (AB) was indivisible

Illustrative example:

Dissolving (0.1 mol NaCl) in (1000 g) of water will lower the freezing point. By (0.186 ºC), this is if we assume that (NaCl) is not ionized. But if we assume that (NaCl) is ionized. Totally to (Na^+) and (Cl^-), the decrease in the degree of ionization will be by .(0.372 ºC).

Note

The previous four laws of group properties are true only in dilute solutions For indivisible materials which can be considered as an ideal solution, so solutions of Electrolytes deviate from this ideal behavior.

Van Hoff has amended the four laws in order to be able to describe Aggregate properties of electrolyte solutions by entering a custom parameter. by Vant Hoff coefficient and denoted by the symbol (i .). And (i) expresses the ratio between the amount of actual and experimentally measured change in the aggregate characteristic. Or empirical to those calculated theoretically, that is:

$$i = \frac{\Delta}{\Delta_o}$$

Where (Δ) represents the experimental change in one of the aggregative properties while (Δ) represents (Δ_o). The theoretically calculated change, given that the solution behaves in an ideal way.

Therefore, the four laws can be written after entering the Vant Hoff coefficient on them as follows:

$$\Delta P = i \, X \, P^o$$
$$\Delta T_b = i \, k_b \, m$$
$$\Delta T_f = i \, k_f \, m$$
$$\pi = i \, M \, R \, T$$

The following table shows the values of the Van Thove coefficient for some electrolytes at different concentrations. Different.

Table: (9) Vant Hoff coefficient (i) for some electrolytes at different concentrations in water.

Molality	Vant Hof Coefficient (i)			
	NaCl	CuSO$_4$	Pb(NO$_3$)$_2$	K$_3$Fe(CN)$_6$
0.001	1.97	-	2.89	3.82
0.01	1.94	1.45	2.63	3.36
0.1	1.87	1.12	2.13	2.85
1.0	1.81	0.93	1.31	-

The values of (i) shown in the table mean that the change in one of the aggregative properties of the materials mentioned as electrolyte equals 2, 3 or 4 times the change in value and considered The substance is non-electrolyte, which also means that the solutions will have the same complications. Of the particles resulting from the division of the substance in the solution. However, check the previous table It is shown, for example, that (i) in the solution state (NaCl) has met a number of moles of ions. The resultant of the dissociation of one mole of it is (2) the more the concentration decreases, but it is less than That is, the higher the concentration, and the more obvious the diffraction. The ion is larger.

Does the above indicate that the ionization of the electrolyte in the solution is incomplete?

It is possible to link between Arrhenius theorem and the Van Thoef coefficient to calculate the degree of Tin The electrolyte is as follows:

Let's assume an electrolyte on the general picture (A$_a$B$_b$ concentration) (m) and disintegrate it to a degree is equal to (α) according to the following equation:

$$A_aB_b \rightleftharpoons aA^{b+} + bB^{a-}$$
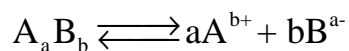
If a mole of (A_aB_b) forms a number of ions of (ν), the electrolyte concentration is not The ionic ion is $m(1 - \alpha)$ and the concentration of the ions is $(\nu m \alpha)$, meaning that the concentration of the particles in The solution is $(m(1- \alpha)+ \nu \alpha m)$.

The Van Thof coefficient represents the ratio between the concentration of ions produced by the partial ionization The expected concentration in the case of non-ionization, i.e:

$$i = \frac{m(1 - \alpha) + \nu m \alpha}{m}$$

$$i = \frac{\cancel{m}\left[(1- \alpha)+ \nu\alpha\right]}{\cancel{m}}$$

$$i = 1 - \alpha + \nu \alpha$$

$$i - 1 = - \alpha + \nu \alpha$$

$$i - 1 = \alpha(-1 + \nu)$$

$$i-1=\alpha(\nu - 1)$$

$$\Rightarrow \alpha = \frac{i-1}{(\nu - 1)}$$

And using the equation $\alpha = \frac{i-1}{(\nu-1)}$ and from knowing the value of (i) the degree of ionization can be calculated of the electrolyte by studying one of its aggregative properties. It was found that this method gives results Identical with the (α) values calculated from the conductivity measurements as previously known, and this is considered In support of the aforementioned Arrhenius theory.

Q) When does the Vant Hove coefficient approach its final value of the electrolyte and why?

Example//

The freezing point of a solution (0.1 mol/Kg NaCl) is 0.347 ºC if known. That (Kf = 1.86 ºC mol/kg Fah due to van thof coefficient (i) and ion degree Electrolyte (α) and then compare it with the degree of ionization from electrical conductivity measurements. Note that:
(Λ_{NaCl} = 106.7 Ω^{-1} cm2 mol^{-1}, $\Lambda o NaCl$ = 126.45 Ω^{-1} cm^2 mol^{-1})

Solution//

In the question, we gave the value of the decrease in freezing point, which is the observed value from Experience. In order to obtain Vanthof coefficient, we find the value of the decrease theoretically from the relationship math:

$$\left(\Delta T_f\right)_o = k_f \cdot m$$
$$\left(\Delta T_f\right)_o = \left(1.86 \,^{o}C \, mol^{-1} \, kg\right) \times \left(0.1 \, mol \, kg^{-1}\right)$$
$$\left(\Delta T_f\right)_o = 0.186 \,^{o}C$$

So the Vanthofe coefficient is(i):

$$i = \frac{\Delta T_f}{\left(\Delta T_f\right)_o} = \frac{0.347}{0.186} = 1.865$$

To calculate the degree of ionization of the electrolyte according to the Vant Hof coefficient:

$$\alpha = \frac{i - 1}{v - 1}$$
$$\alpha = \frac{1.865 - 1}{2 - 1} = 0.865$$

That is, (NaCl) is a percentage of (86.5%) and calculates the degree of ionization from the measurements. electrical conduction

$$\alpha = \frac{\Lambda}{\Lambda^o} = \frac{106.7}{126.45} = 0.844$$

That is, the degree of ionization (NaCl) is approximately (86.5%) as a result of the conduction results. Close to that calculated by Vant Hof coefficient.

The Ostwald's Dilution Law

The mouse was able to harness the laws of chemical equilibrium on the theory of ionization electrolyte Electrolyte by conduction measurements.

Let us assume that the electrolyte concentration (AB) is equal to (C mol L^{-1}) and the degree of ionization is (α), (α). And that it self-ionizes to form ions (A^+), (B^-) as follows:
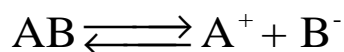
$$AB \rightleftharpoons A^+ + B^-$$

And when in equilibrium, the concentration of (A^+, B^-) is equal to (α c) and the non-ionized concentration of AB will be equal to (($1- \alpha$)C) and the equilibrium constant is given by the following relationship:

$$K = \frac{\left[A^+ \right]\left[B^- \right]}{\left[AB \right]}$$

$$K = \frac{(\alpha c)(\alpha c)}{(1 - \alpha)c}$$

$$K = \frac{\alpha^2 c^{\cancel{2}}}{(1 - \alpha)\cancel{c}}$$

$$\Rightarrow K = \frac{\alpha^2 c}{1 - \alpha}$$

And know the relationship $K = \frac{\alpha^2 c}{1 - \alpha}$ Law of Os Wald to mitigate and compensate for the value of (α). The equation $\left(\alpha = \frac{\Lambda}{\Lambda^\circ} \right)$ in the equation $\left(K = \frac{\alpha^2 c}{1 - \alpha} \right)$