

Ministry of Higher Education and
Scientific Research
Al-Muthanna University
College of Science



وزارة التعليم العالي والبحث العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

Electrochemistry

Lecture (5)

Stage 3

Prof. Hassan Sabih

Variation of Molar Conductivity with Concentration

An electrolyte solution gives a substance at a concentration with a specific molar conductivity under conditions. fixed. The molar conductivity of a solution depends on many factors including the nature of the electrolyte, The type of solvent in addition to the temperature and pressure. But most of the factors have an impact on the Molar conductivity is the change in the concentration of a solution, increasing or decreasing, when other factors are held constant. Table (5) shows the effect of concentration on the molar conduction of some electrolytes.

Table (5) Effect of concentration on the molar conduction of some electrolytes at (25 °C)

Molarity	$\Lambda (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$				
	HCl	NaCl	AgNO ₃	ZnSO ₄	HAC
0.000	426.1	126.4	133.3	265.6	390.7
0.0005	422.7	124.5	131.4	242.8	-
0.001	421.4	123.7	130.5	229.0	48.63
0.005	415.8	120.7	127.2	191.0	22.80
0.01	412.0	118.5	124.8	169.8	16.20
0.02	407.2	115.8	121.4	148.4	11.57
0.05	399.1	111.1	115.2	122.4	7.36
0.10	391.3	106.7	109.1	105.2	5.20

It is expected that increasing the concentration will lead to an increase in the number of charge carriers, which are ions. And then increase the molar conduction, but the experimental results shown in the table (5) Emphasizes the opposite, as a decrease in concentration (i.e., an increase in dilution) leads to an increase in delivery. The figure (5) shows the relationship between (Λ) and the volume of the solution (V). As well as the relationship between (Λ) and the logarithm of concentration ($\log C$).

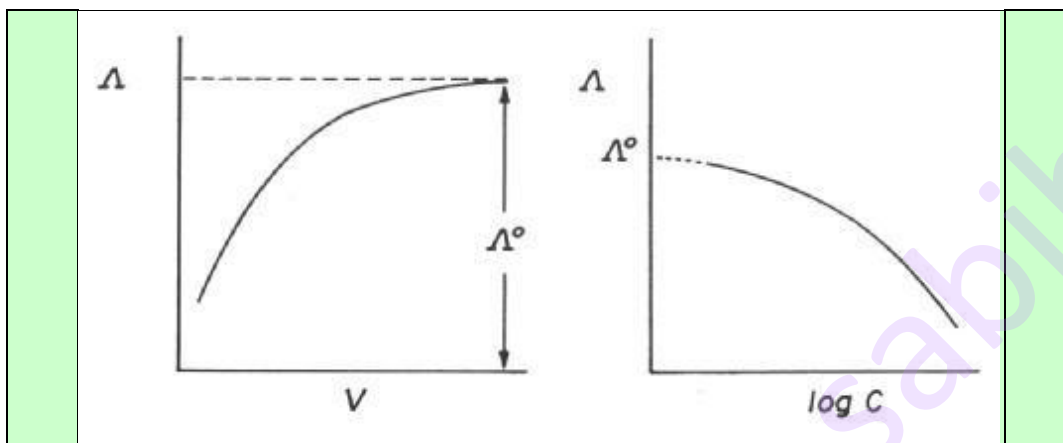


Figure (5): The molar conductivity changes with concentration or dilution, as the concentration decreases or the dilution increases. (Λ) went towards a specific value of (Λ°)

Increasing the dilution (decreasing the concentration) causes (Λ) to increase and bring its value close to its final value. or specific, called molar conduction at infinite dilution It may come to mind that the molecular conductivity at infinite dilution (Λ_o) When infinite dilution gives a value (Λ_o) conduct a solute to the absence and presence of ions in shop and for. However, the state of infinite dilution describes a place that does not contain mol or mol. The electrolyte in the volume of the solution is so diluted that further dilution will not change from The value of (L) which then equals y (Λ°). The reason for this is that when diluting The solution is infinite, so the ions are far apart from each other by large distances. compared to their sizes, and therefore there are no mutual effects between positive and negative ions, That is, every ion moves absolutely freely in the solution. The value of (Λ°) represents the largest value for the ability of the electrolyte to conduct electrolyte, and it can also be considered as a reference Suitable for comparing the conductivity of electrolytes.

After extensive experimentation, Kohlrausch was able to connect some Dilute electrolyte solutions to establish an empirical relationship between molar conduction (Λ) And focus (C) write on the following:

$$\Lambda = \Lambda^\circ - A\sqrt{C}$$

It is the equation of a straight line ($y = ax + b$), whose slope is $(-A)$ and its transversal is equal to (Λ°) .

The Kohlrausch equation is an empirical equation that has no theoretical basis, and despite that It has been very useful in developing the chemistry of ionic solutions.

And the equation: $\Lambda = \Lambda^\circ - A\sqrt{C}$ in this form is correct to describe a change (Λ) The square root of the molar concentration in dilute solutions only.

The Kohlrausch equation is graphically represented in the figure (6).

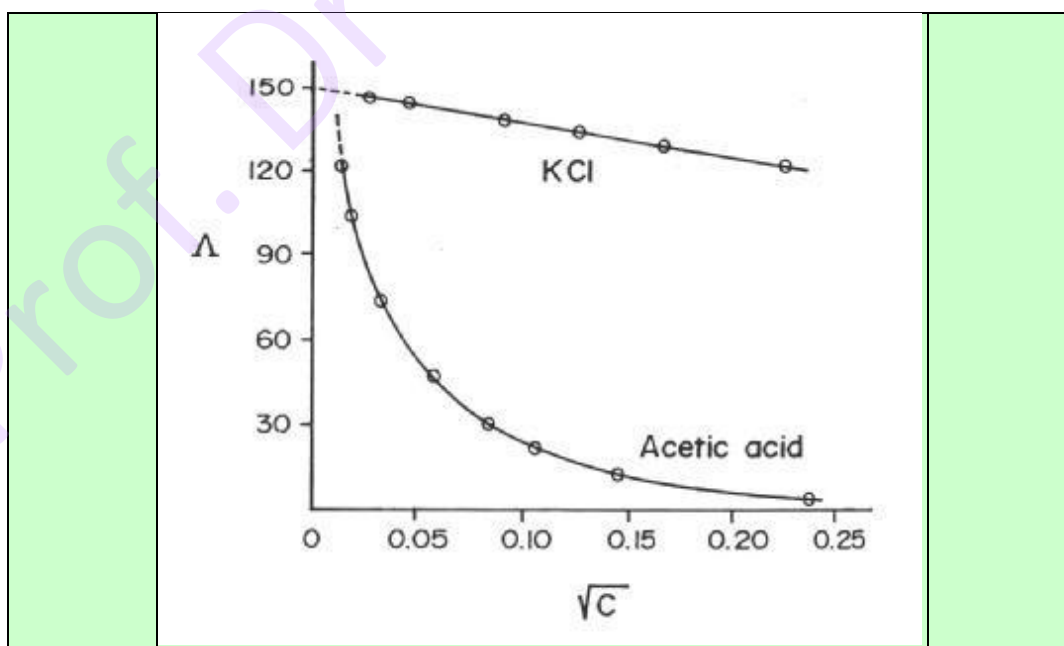


Figure (6): The relationship between (Λ) and \sqrt{C} of potassium chloride and acetic acid.

Which explains the change in the concentration of electrolyte (KCl) and acetic acid.

It is clear from Figure (6) two different behaviors of the change of molar conductivity with the concentration of a solution of water Potash chloride and acetic acid, where it is noted that (Λ) of a solution (KCl) is taken all The linear relationship represented by the Kohlrausch equation while (Λ) for a solution of acetic acid It does not change linearly with (\sqrt{C}) , but rather takes a curve that increases in value (Λ) significantly. At very low concentrations.

It is also noticed from Figure (6) that the values of (Λ) vary greatly. Electrolytes are like (KCl), which has a high molar conductivity, is called strong electrolyte. () Strong electrolytes have a behavior similar to that shown (KCl) Figure (6).

In contrast, there are classes of electrolytes that have a low molar conductivity. It increases significantly if their solutions are very dilute, and they are called weak electrolytes. (Weak electrolytes) This represents the behavior of vinegar acid, also shown in Fig. (6).

It is also not easy to put a separating and distinguishing line between these two categories, as it is There are a number of electrolytes that have an average behavior between strong electrolytes. And the weak. Some salts of transition metals such as sulfur are included under this category. Zinc ($ZnSO_4$) and copper sulfate ($CuSO_4$).

The Kohlraush Law of Independent Ionic Conductivity

When the solution reaches the infinite dilution state, the molar conduction of the electrolyte is It reaches its highest value, which is (Λ°), and this quantity can be found for the strong electrolyte Extrapolation of the linear relationship between molar conductivity and the square root of molar concentration According to the equation, $\Lambda = \Lambda^\circ - A\sqrt{C}$ knowing that there are equations that describe this relationship More precisely, we will not really deal with it.

When reviewing the values of (Λ°) a number of strong electrolytes that have a cation or anion. common, the difference between them is always constant, regardless of the nature of these electrolytes. This is evident from a review of the values (Λ°) in the table:

Table (6): The difference between Λ° electrolytes have a common ion

Electrolyte pairs	Λ°	difference		Electrolyte pairs	Λ°	difference
KCl	149.86	23.41		KCl	144.86	4.90
NaCl	126.45			KNO ₃	144.96	
KNO ₃	144.96	NaCl		126.45	4.90	
NaNO ₃	121.55	NaNO ₃		121.55		
KI	150.32	23.41		HCl	426.14	4.90
NaI	126.91			HNO ₃	421.24	

The difference between the (Λ°) values of electrolytes that always share the same instantaneous value is equal to (23.41), This is attributed to the difference between the conductivities of cations in the three pairs of Electrolytes. The above can be generalized to the other group of electrolytes. Which has the same cation and differs in time, as it is noticed that the difference is always (4.90). This is due to a difference in the conductivity of the anions.

The interpretation of the previous observation is possible if we consider that the value of (Λ°) for electrolytes is made up of two parts, one for the cation and the other for the ion, which is known as the law. **Kohlrausch for independent ionic conduction** which states that: (when attenuated in infinite then each ion will share a portion of the value of (Λ°) regardless of the nature of the other ion).

This law can be expressed in the following relationship:

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

Where (λ_-°) , (λ_+°) are the molar conduction by infinite dilution of the cation and the instantaneous, respectively, while (n_-) , (n_+) are the number of moles of cations Anions resulting from the ionization of one mole of the electrolyte.

substance	dissociation-equation	(n_+)	(n_-)
NaCl	$\text{NaCl} \longrightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	1	1
MgCl ₂	$\text{MgCl}_2 \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	1	2
Na ₂ SO ₄	$\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	2	1

Illustrative example:

The (Λ°) of an electrolyte such as sodium chloride is written as follows:

$$\Lambda_{\text{NaCl}}^\circ = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

While it is an electrolyte such as magnesium chloride, it is on the picture:

$$\Lambda_{\text{MgCl}_2}^\circ = \lambda_{\text{Mg}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ$$

But the separation of the cation and ionic contributions to molar conduction is not done arbitrarily. Rather, it is determined by the ability of each of them to carry a part of the total electrolyte current. Transfusion is what is known as the number of pregnancies or transfusions, and it is an amount that is determined empirically. Table (7) It shows the values of (λ°) for some ions at (25 °).

Table (7): Molar conduction at infinite dilution of some ions at (25 °C)

Cation	λ_+°	Anion	λ_-°
H ⁺	349.8	OH ⁻	199.1
Na ⁺	30.10	F ⁻	55.40
K ⁺	73.30	Cl ⁻	76.35
Cs ⁺	77.26	NO ₃ ⁻	71.46
Ba ²⁺	127.26	Acetate, CH ₃ COO ⁻	40.90
Mg ²⁺	106.10	SO ₄ ²⁻	160.0

As mentioned earlier, it is possible to determine the value of (Λ) for a strong electrolyte by extrapolating the relationship B (Λ) and the concentration as in the figure (6), but this is not possible for the electrolyte The weak because of the accompanying line A in the value of (Λ°). Therefore, he resorts to using the law of K Wellrauch for independent ionic conductivity to create a value (Λ°) electrolyte cannot She knows it from induction, or has not assigned a value to it (Λ°) yet.

Illustrative example:

The molar conduction of vinegar acid at infinite dilution is the conduction The molarity of the hydrogen and acetate ions upon infinite dilution is:

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = \lambda_{\text{H}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ$$

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = 349.8 + 40.9$$

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = 390.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

The same result can be obtained by using (Λ°) values as well. Thus, the connection The molar upon infinite dilution of the electrolyte (MA) is equal to the following sum:

$$\Lambda_{(MA)}^\circ = (\lambda_{M^+}^\circ + \lambda_{A^-}^\circ)$$

We can write this equation as:

$$\Lambda_{(MA)}^\circ = \Lambda_{(MCl)}^\circ + \Lambda_{(NaA)}^\circ - \Lambda_{(NaCl)}^\circ$$

Where:

$$\Lambda_{(MA)}^\circ = \Lambda_{(MCl)}^\circ + \Lambda_{(NaA)}^\circ - \Lambda_{(NaCl)}^\circ$$

$$\Lambda_{(MA)}^\circ = \lambda_{M^+}^\circ + \lambda_{Cl^-}^\circ + \lambda_{Na^+}^\circ + \lambda_{A^-}^\circ - (\lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ)$$

$$\Lambda_{(MA)}^\circ = \lambda_{M^+}^\circ + \lambda_{Cl^-}^\circ + \lambda_{Na^+}^\circ + \lambda_{A^-}^\circ - \lambda_{Na^+}^\circ - \lambda_{Cl^-}^\circ$$

$$\Lambda_{(MA)}^\circ = \lambda_{M^+}^\circ + \lambda_{A^-}^\circ$$

Example//

If you know that the values of Λ° in units of $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at (25 °C) each of:

$$(\Lambda_{\text{HCl}}^\circ = 426.15, \Lambda_{(\text{CH}_3\text{COONa})}^\circ = 91.0, \Lambda_{(\text{NaCl})}^\circ = 126.45)$$

Calculate ($\Lambda^\circ_{(\text{CH}_3\text{COOH})}$) for acetic acid

Solution

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = \Lambda_{\text{HCl}}^\circ + \Lambda_{\text{CH}_3\text{COONa}}^\circ - \Lambda_{\text{NaCl}}^\circ$$

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = 426.15 + 91.0 - 126.45$$

$$\Lambda_{(\text{CH}_3\text{COOH})}^\circ = 390.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$