

AL-Mustaqbal university
Pharmacy college



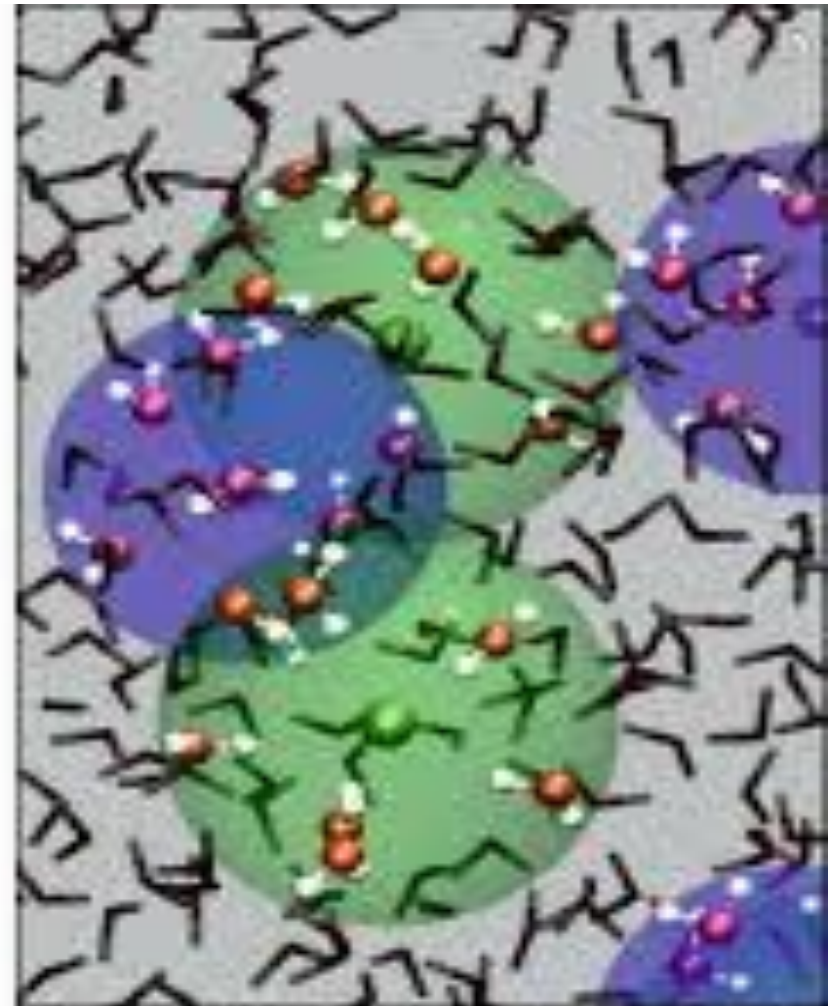
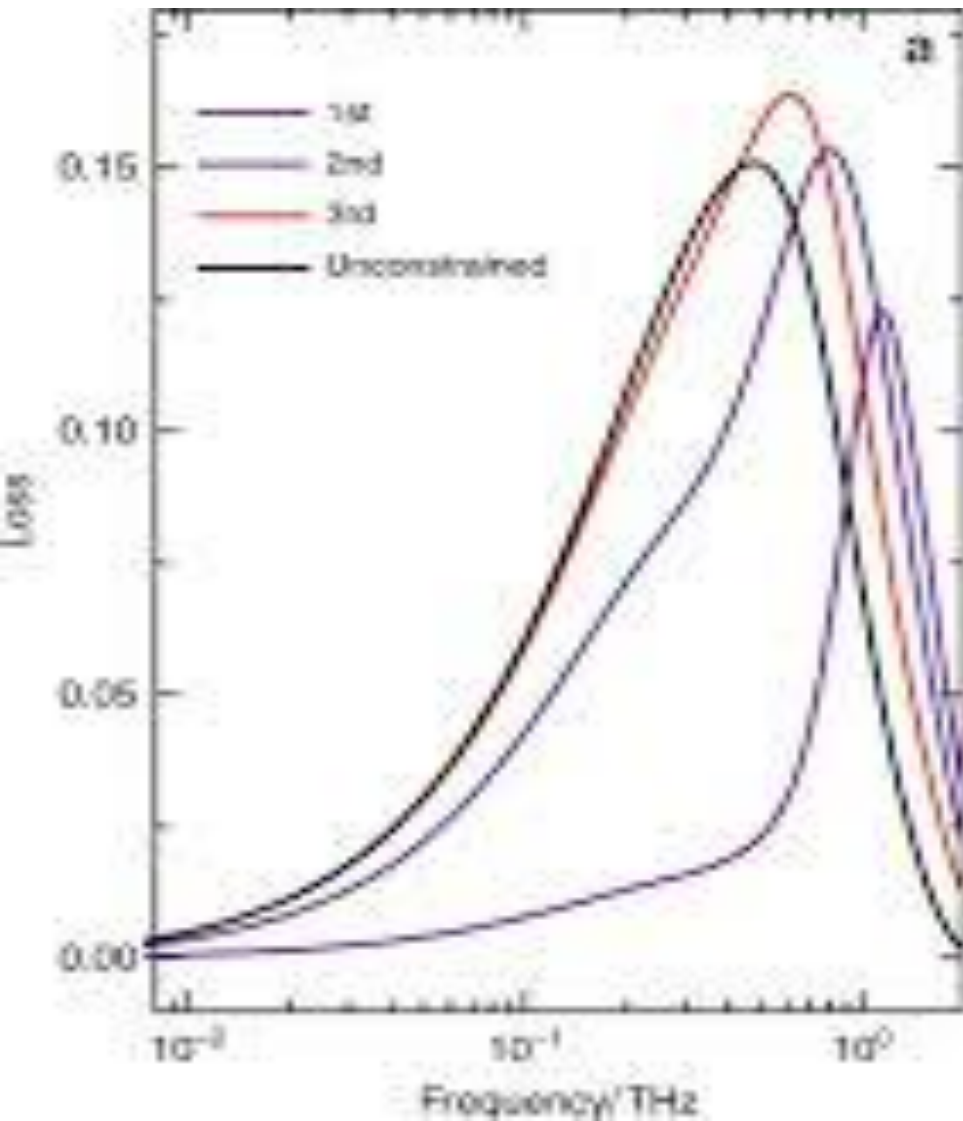
Physical pharmacy I

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Solutions of Electrolytes



Overview

Electrolytes Properties

Definition

Colligative Properties

Electrolyte Conductance

Electrolytic Dissociation

Strong Electrolytes

Theory of Strong Electrolytes

Ionic strength

Activity and Activity Coefficients

Learning Objectives

- Understand the important properties of solutions of electrolytes.
- Compare and contrast the colligative properties of electrolytic solutions and concentrated solutions of nonelectrolytes.
- Apply the Arrhenius theory of electrolytic dissociation.
- Apply the theory of strong electrolytes; for example , calculate degree of dissociation, activity coefficients, and so on.
- Calculate ionic strength.
- Calculate osmotic coefficients, osmolality, and osmolarity .
- Understand the differences between osmolality and osmolarity

Electrolytes Properties

Definition

Colligative Properties

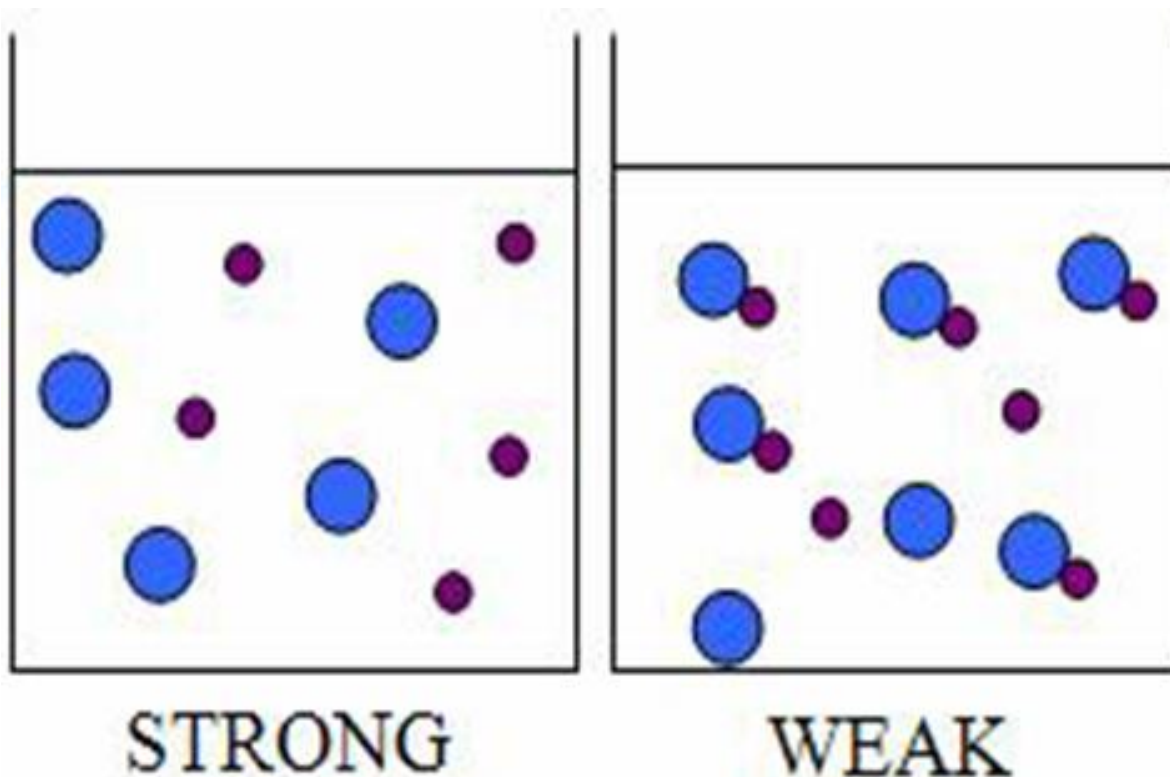
Electrolyte Conductance

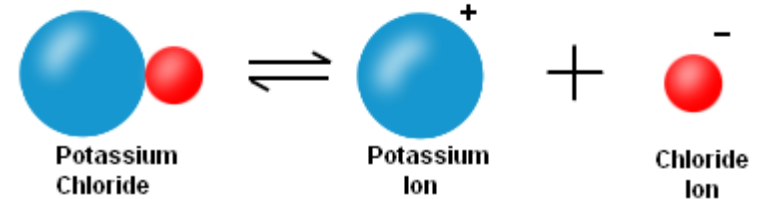
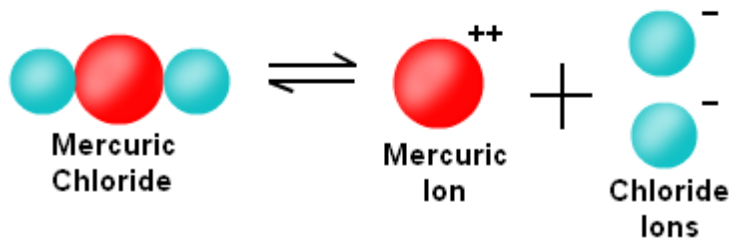
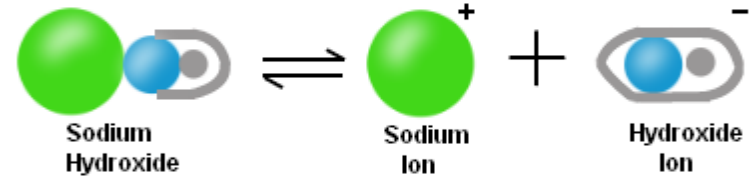
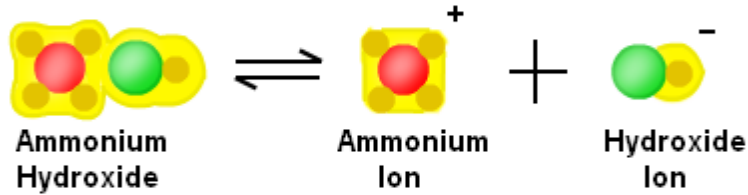
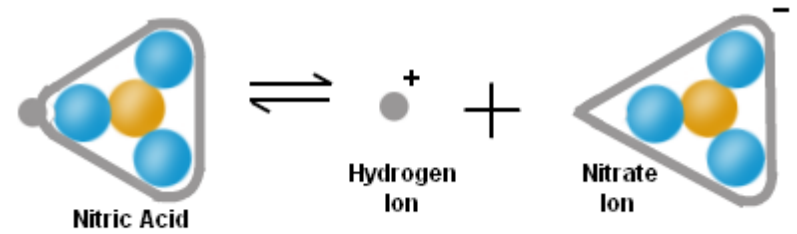
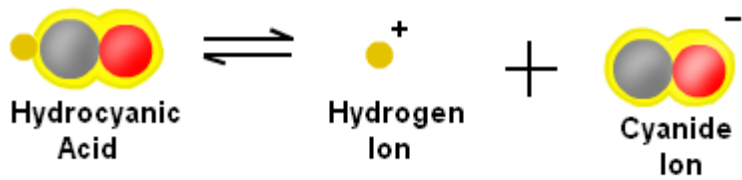
Electrolytic Dissociation

Definition

- Electrolytes are substances that form ions in solutions, conduct the electric current.
- Electrolytes may be subdivided further into strong electrolytes (hydrochloric acid, sodium sulphate) and weak electrolytes (ephedrine, phenobarbital).
- Strong electrolytes are substances that are completely ionized when they are dissolved in water. They conduct electrical currents very efficiently. The classes of strong electrolytes include:
 - (a) soluble salts e.g. BaCl_2 ,
 - (b) strong acids e.g. HCl , HNO_3 , H_2SO_4 ,
 - (c) strong bases e.g. NaOH , KOH

- Weak electrolytes are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water. Their solutions produce a small current. The most common weak electrolytes are weak acids (e.g. acetic acid) and weak bases (ammonium hydroxide – NH_4OH).



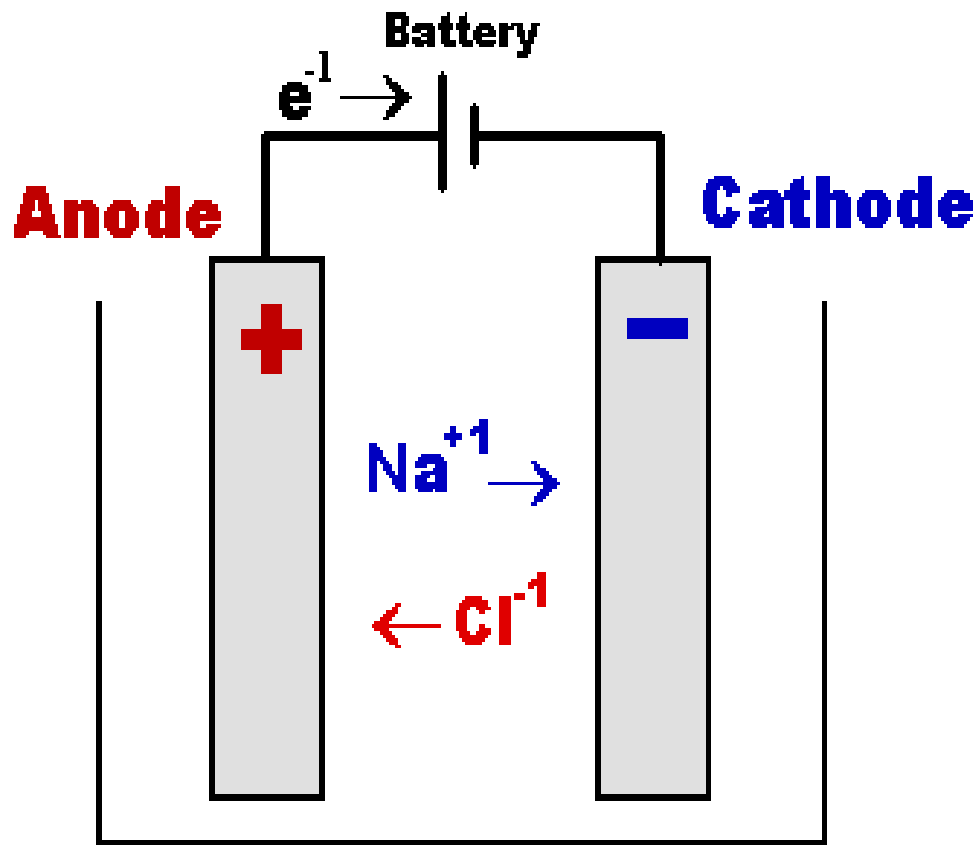


Weak acids (e.g. CH_3COOH), weak bases (e.g. NH_3), and slightly soluble salts (e.g. AgCl).

Strong electrolytes includes strong acids (e.g. HCl), strong bases (e.g. NaOH), and most salts (e.g. NaCl).

Properties of electrolyte solutions

- **Electrolysis:** When a direct electric current flows through an electrolytic cell, a chemical reaction occurs. This process is known as electrolysis.
- Electrons enter the cell from the battery or generator at the cathode, they combine with positive ions or cations, in the solution, and the cations are accordingly reduced.
- The negative ions, or anions, carry electrons through the solution and discharge them at the anode, and the anions are accordingly oxidized.
- **Reduction** is the addition of electrons to a chemical species, and **oxidation** is removal of electrons from a species.



Electrolysis

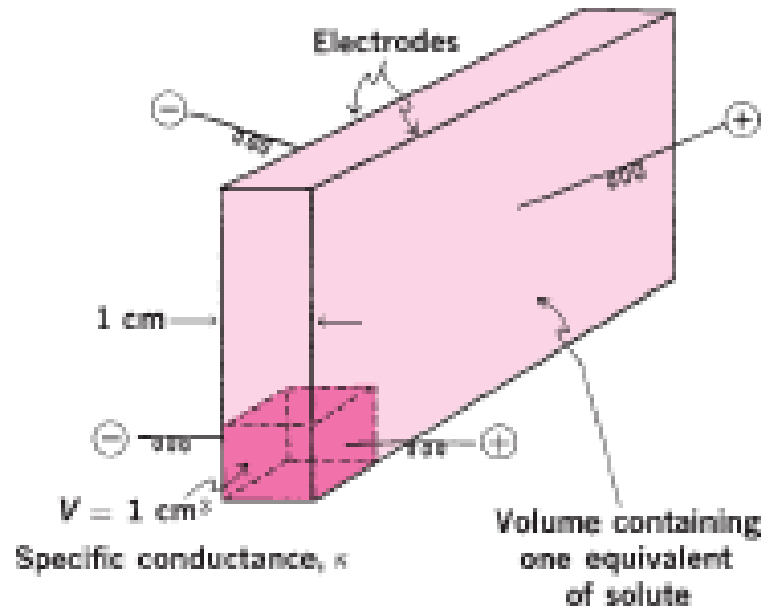
Electrolytic conductance

- The conductance, C , is the reciprocal of the resistance, therefore it is a measure of the ease with which current can pass through the conductor (or a solution). Expressed as ohms^{-1} or mhos.

$$C=1/R$$

R:resistance

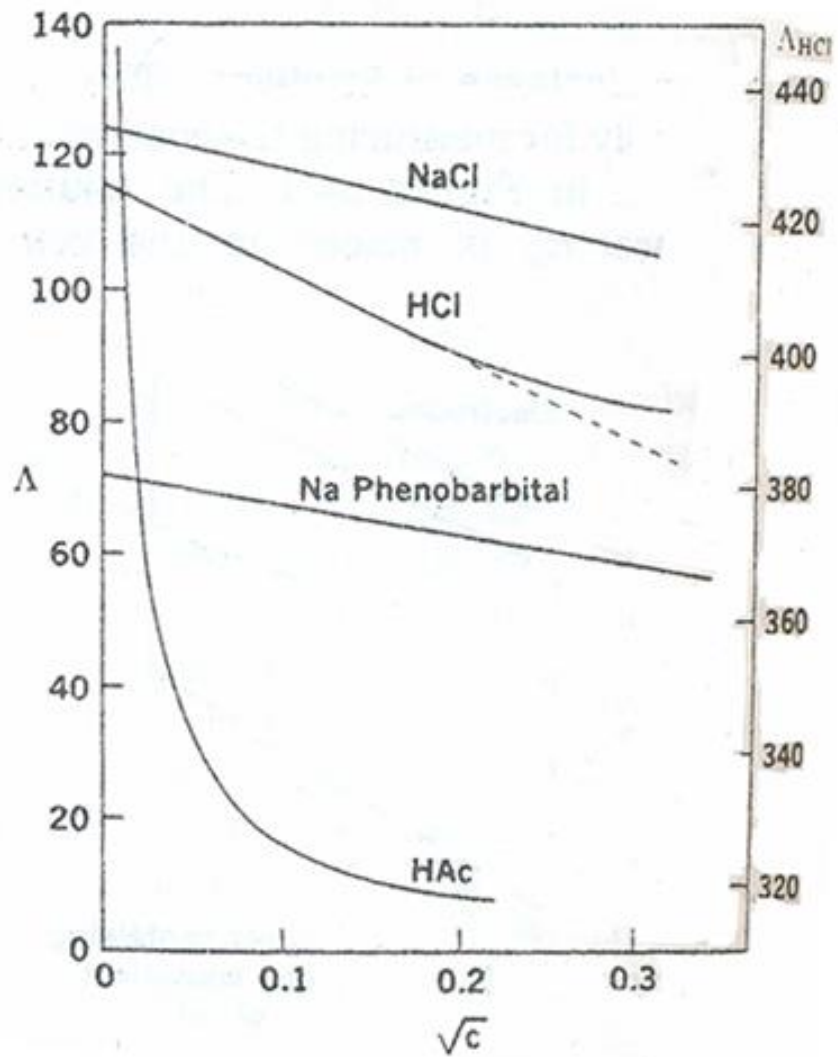
- The specific conductance (κ) is the conductance of a solution confined in a cube 1 cm(cm^3) on an edge as seen below



- ❑ To study the dissociation of molecules into ions, independent of the concentration of the electrolyte, it is convenient to use the **equivalent conductance** rather than the **specific conductance**. All solutes of equal normality produce the same number of ions when completely dissociated, and
- ❑ **equivalent conductance** measures the current-carrying capacity of these given number of ions.
- ❑ **Specific conductance**, on the other hand, measures the current-carrying capacity of all ions in a unit volume of solution and accordingly varies with concentration

- ❑ **Equivalent conductance Λ** is defined as the conductance of a solution of sufficient volume to contain 1 gram equivalent of solute when measured in a cell in which the electrodes are spaced 1cm apart. Expressed as $\text{mho}\cdot\text{cm}^2/\text{Eq}$.
- ❑ If the solution is 0.1 N in concentration, then the volume containing 1 gram equivalent of the solute will be 10 liters (10,000 cm^3) and the equivalent conductance will be 10,000 times more than the specific conductance.
- ❑ The specific conductance of a strong electrolytic solution (κ) steadily decreases on dilution, while the equivalent conductance Λ of a strong electrolyte solution steadily increases on dilution .

- ❑ Kohlrausch studied the effect of dilution on Λ of both strong and weak electrolytes and found a discrepancy in their behavior as follows:
 - ❑ In strong electrolytes such as NaCl, Λ increases linearly with decreasing square root of concentration. Extrapolation of a plot of Λ versus \sqrt{c} to $\sqrt{c}=0$ yields a value of Λ_0 , the equivalent conductance at infinite dilution; Λ_0 is the intercept on the vertical axis of Λ versus \sqrt{c} plot.
 - ❑ A quite different behavior is observed with weak electrolytes such as acetic acid. A considerable increase in Λ is noted at low concentrations, which prevents an accurate estimate of Λ_0 . The steeply rising curve for acetic acid results from the fact that the dissociation of weak electrolytes increases on dilution, with a large increase in the number of ions capable of carrying the current.



- Kohlrausch concluded that ions of all electrolytes begin to migrate independently as the solution is diluted; the ions in dilute solutions are so far apart that they do not interact in any way. Under these circumstances, Λ_0 is the sum of the equivalent conductance of the cations l_c^0 and the anions l_a^0 at infinite dilution.

$$\Lambda_0 = l_c^0 + l_a^0$$

e.g. $\Lambda_{0 \text{ CH}_3\text{COOH}} = l_{c^0 \text{ H}^+} + l_{a^0 \text{ CH}_3\text{COO}^-}$

- Based on this law, the known Λ_0 values for certain electrolytes can be added and subtracted to yield Λ_0 for the desired weak electrolyte.

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

- Van't Hoff observed that the osmotic pressure of dilute solutions of nonelectrolytes could be expressed satisfactorily by the equation

$$\pi = RTC$$

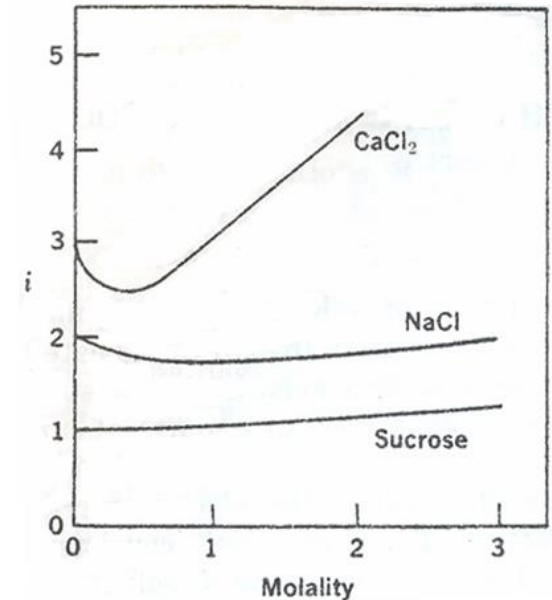
in which R is the gas constant and T is the absolute temperature, and C is the concentration in moles per liter.

- Van't Hoff found, however, that solutions of electrolytes gave osmotic pressure approximately two, three, and more times larger than expected from this equation, depending on the **electrolyte** investigated.

- ❑ Van'tHoff introduced a correction factor i to account for the irrational behavior of ionic solutions.

$$\pi = iRTC$$

- ❑ i approached the number of ions into which the molecule dissociated as the solution was made increasingly dilute.
- ❑ The van't Hoff factor i accounts for the deviations of real solutions of nonelectrolytes and electrolytes regardless of the reason for the discrepancies
- ❑ The i factor is plotted against the molal concentration of both electrolytes and nonelectrolytes in the following figure.



- For nonelectrolytes, i is seen to approach unity, and for strong electrolytes, it tends towards a value equal to the number of ions formed upon dissociation e.g. i approaches the value of 2 for solutes such as NaCl and CaSO₄, 3 for K₂SO₄ and CaCl₂, and 4 for FeCl₃.
- The van't Hoff factor can also be expressed as the ratio of any colligative property of a real solution to that of an ideal solution, since i represents the number of times greater that the colligative effect is for a real solution (electrolyte or nonelectrolyte) than for an ideal solution.

$$\Delta p = 0.018 i p_1^0 m$$

$$\Delta T_f = i K_f m$$

$$\pi = i R T m$$

$$\Delta T_b = i K_b m$$

Example:

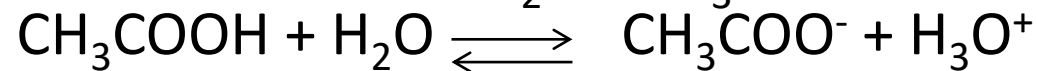
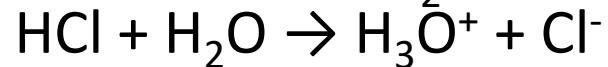
What's the osmotic pressure of a 2.0 m solution of sodium chloride at 20°C?

Answer: the i factor for a 2 m solution of sodium chloride as observed in the figure is about 1.9

$$\begin{aligned}\pi &= iRTm \\ &= 1.9 \times 0.082 \times 293 \times 2 = 91.3 \text{ atm}\end{aligned}$$

Arrhenius Theory of Electrolytic Dissociation

- Arrhenius proposed the now classic theory of dissociation: when electrolytes are dissolved in solution, the solute exists in the form of ions in the solution.



- In fact, Arrhenius did not consider strong electrolytes to be ionized completely except in extremely **diluted solutions**. He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the degree of dissociation α .
- A strong electrolyte is one that dissociated into ions to a high degree and a weak electrolyte is one that dissociated into ions to a low degree.

- Two methods can be used to determine the degree of dissociation:
- First method: the degree of dissociation can be determined from conductance measurements. Equivalent conductance at infinite dilution Λ_0 was a measure of the complete dissociation of the solute into its ions and that Λ_c represented the number of solute particles present as ions at concentration c .
- Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

in which Λ_c/Λ_0 is known as the conductance ratio

Example:

The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 mho cm²/Eq.

The equivalent conductance of a 5.9x10⁻³ M solution of acetic acid is 14.4 mho cm²/Eq. What's the degree of dissociation of acetic acid at this concentration?

Answer:

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

$$= 14.4/390.7$$

$$= 0.037 \text{ or } 3.7\%$$

Second method to find α : The van't Hoff factor i can be connected with the degree of dissociation α in the following way

$$\alpha = \frac{i - 1}{v - 1}$$

where v is the number of ions produced from the electrolyte ionization e.g. for NaCl $v=2$, for CaCl_2 $v=3$

- The cryoscopic method is used to determine i from the expression

$$i = \frac{\Delta T_f}{k_f m}$$

Example:

Calculate the degree of ionization of 0.1 m acetic acid providing that its freezing point is -0.188°C .

Answer: Acetic acid dissociates into two ions, so $v = 2$.

To calculate i :

$$i = \frac{\Delta T_f}{k_f m}$$
$$= 0.188 / (1.86 * 0.1) = 1.011$$

It is possible now to calculate the degree of ionization:

$$\alpha = \frac{i - 1}{v - 1}$$
$$= (1.011 - 1) / (2 - 1) = 0.011 \text{ or } 1.1\%$$

- ❑ The Arrhenius theory is now accepted for describing the behavior only of weak electrolytes. The degree of dissociation of a weak electrolyte can be calculated satisfactorily from the conductance ratio or obtained from the van't Hoff factor i .
- ❑ As for strong electrolytes, they dissociate completely in dilute and moderately concentrated solution.
- ❑ Moreover, a discrepancy exists between α calculated from i ratio and α calculated from the conductivity ratio for strong electrolyte solutions at concentrations greater than about 0.5 M.
- ❑ Thus degree of dissociation according to Arrhenius theory does not account for behavior of strong electrolyte. Instead, it is more convenient to consider a strong electrolyte as completely ionized and to introduce a factor that expresses the deviation of the solute from 100% ionization. The activity and activity coefficient are used for this purpose

Activity and Activity Coefficient

The large number of oppositely charged ions in solutions of strong electrolytes influence one another through interionic attractive forces.

For solution of nonelectrolytes, regardless of concentration, the number of ions is small and the interionic attractive forces are insignificant.

As for strong electrolytes, ions can associate at high concentrations into groups known as ion pairs. Thus the values of the freezing point depression and the other colligative properties are less than expected for solutions of unhindered ions. **Consequently, a strong electrolyte may be completely ionized, yet incompletely dissociated into free ions.**

You may think of the solution as having an “**effective concentration**” or, as it is called, an **activity**. This concept was first introduced by Lewis and Randall.

- The activity (a), in general, is less than the actual or stoichiometric concentration of the solute (m), not because the strong electrolytes are partly ionized, but rather because some of the ions are effectively “taken out of play” by the electrostatic forces of interaction.
- At infinite dilution in which the ions are so widely separated that they do not interact with one another, the activity a of an ion is equal to its concentration

$$a = m.$$

- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of ions becomes less than the molal concentration. This ratio is known as the practical activity coefficient (γ), thus

$$a = \gamma m$$

- A cation and an anion in an aqueous solution may each have a different ionic activity.

- The activity of an electrolyte is defined by its mean ionic activity a_{\pm}

$$a_{\pm} = (a_+^m a_-^n)^{1/(m+n)}$$

- where a_+ is the activity of the cation, and a_- is the activity of the anion, the exponents m and n give the stoichiometric number of given ions that are in solution.

- Thus an NaCl solution has a mean ionic activity of $a_{\pm} = (a_{\text{Na}^+} a_{\text{Cl}^-})^{1/2}$

- Whereas an FeCl₃ solution has a mean ionic activity of $a_{\pm} = (a_{\text{Fe}^{3+}} a_{\text{Cl}^-}^3)^{1/4}$

Kohlrausch found that the equivalent conductance was a linear function of the square root of the concentration for strong electrolytes.

The expression for ΛC , the equivalent conductance at a concentration c (Eq/L):

$$\Lambda C = \Lambda_0 - b\sqrt{c}$$

Λ_0 : intercept on the vertical axis known as the equivalent conductance at infinite dilution.

b : slope of the line for the strong electrolytes

The steeply rising curve for acetic acid results from an increase in the dissociation of weak electrolytes on dilution (increase in the number of ions capable of carrying the current).

Example 1

The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 mho. The equivalent conductance of a 5.9×10^{-3} M solution of acetic acid is 14.4 mho. What is the degree of dissociation of acetic acid at this concentration?

$$\alpha = \Lambda_c / \Lambda_0 = 14.4 / 390.7 = 0.037 = 3.7\%$$

Example 2

The freezing point depression of 0.1m solution of acetic acid is 0.188°C. Calculate the degree of ionization if acetic acid at this $K_f = 1.86$. Acetic acid dissociates into 2 ions, i.e. $v=2$.

$$i = (\Delta T_f) / (K_f m) = 0.188 / (1.86 \times 0.1) = 1.011$$

$$\alpha = (i - 1) / (v - 1) = (1.011 - 1) / (2 - 1) = 0.011$$

The fraction of acetic acid present as free ions in a 0.1m solution is 0.011 (approximately=1%)

a note to say,

thank you

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