

conductance), is multiplied by  $V$ , the volume in  $\text{cm}^3$  that contains 1 g equivalent weight of solute. Hence, the equivalent conductance,  $\Lambda_c$ , expressed in units of  $\text{mho cm}^2/\text{Eq}$ , is given by the expression

$$\begin{aligned}\Lambda_c &= \kappa \times V \\ &= \frac{1000 \kappa}{c} \text{ mho cm}^2/\text{Eq} \quad (6-21)\end{aligned}$$

If the solution is 0.1 N in concentration, then the volume containing 1 g equivalent of the solute will be  $10,000 \text{ cm}^3$ , and, according to equation (6-21), the equivalent conductance will be 10,000 times as great as the specific conductance. This is seen in the following example.

### Example 6-3

#### Specific and Equivalent Conductance

The measured conductance of a 0.1 N solution of a drug is 0.0563 ohm<sup>-1</sup> at  $25^\circ\text{C}$ . The cell constant at  $25^\circ\text{C}$  is  $0.520 \text{ cm}^{-1}$ . What is the specific conductance and what is the equivalent conductance of the solution at this concentration? We write

$$\kappa = 0.0563 \times 0.520 = 0.0293 \text{ mho/cm}$$

$$\Lambda_c = 0.0293 \times 1000/0.1$$

$$= 293 \text{ mho cm}^2/\text{Eq}$$

### ***Equivalent Conductance of Strong and Weak Electrolytes***

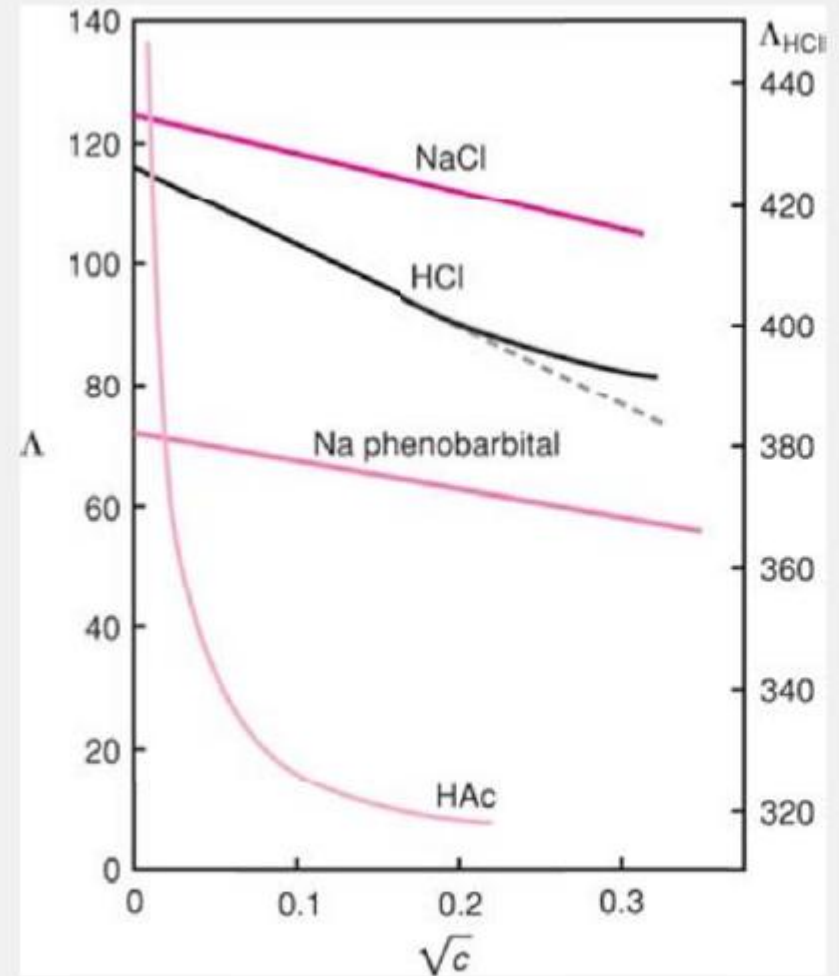
As the solution of a strong electrolyte is diluted, the *specific conductance*  $\kappa$  decreases because the number of ions per unit volume of solution is reduced. It sometimes goes through a maximum before

# Equivalent conductance ( $\Lambda$ ) of *strong and weak electrolyte*

- $\Lambda$  of **strong** electrolyte  $\uparrow$  on dilution, because the ions are **hindered less** by their neighbors and move faster.
- The relationship between the  $\Lambda$  and the concentration of solution follow ***Kohlarush equation:-***
- $\Lambda_c = \Lambda_0 - b\sqrt{c}$
- $\Lambda_0$ :- ***equivalent conductance at infinite dilution***

- For **weak** electrolyte  $\Lambda_c$  steeply rising ( $\uparrow$ ) on dilution because the **dissociation** of weak electrolyte  $\uparrow$  on dilution

$b$  is the slope of the line for the strong electrolytes shown in Figure 6-4.



**Fig. 6-4.** Equivalent conductance of strong and weak electro

# Calculation of $\Lambda_0$

- The ions in infinite dilution are so far apart, they don't interact and  $\Lambda^0$  is the sum of equivalent of anions  $\iota_a^0$  and cations  $\iota_c^0$
- $\Lambda^0 = \iota_c^0 + \iota_a^0$

example: calculation  $\Lambda^0$  HP from  $\Lambda^0$ NaCl,  $\Lambda^0$  HCl,  $\Lambda^0$  NaP

$$\Lambda^0 \text{NaP} = \cancel{\iota_{\text{Na}^+}^0} + \iota_{\text{P}^-}^0$$

$$\Lambda^0 \text{HCl} = \iota_{\text{H}^+}^0 + \cancel{\iota_{\text{Cl}^-}^0}$$

$$(\Lambda^0 \text{NaCl} = \cancel{\iota_{\text{Na}^+}^0} + \cancel{\iota_{\text{Cl}^-}^0}) * -$$

$$\Lambda^0 \text{HP} = \Lambda^0 \text{NaP} + \Lambda^0 \text{HCl} - \Lambda^0 \text{NaCl} = \iota_c^0 + \iota_a^0$$

$\Lambda_0$  for the desired weak electrolyte. The method is illustrated in the following example.

### Example 6-4

#### Equivalent Conductance of Phenobarbital

What is the equivalent conductance at infinite dilution of the weak acid phenobarbital? The  $\Lambda_0$  of the strong electrolytes HCl, sodium phenobarbital (NaP), and NaCl are obtained from the experimental results shown in Figure 6-4. The values are  $\Lambda_{0,\text{HCl}} = 426.2$ ,  $\Lambda_{0,\text{NaP}} = 73.5$ , and  $\Lambda_{0,\text{NaCl}} = 126.5$  mho cm<sup>2</sup>/Eq.

Now, by Kohlrausch's law of the independent migration of ions,

$$\Lambda_{0,\text{HP}} = l_{\text{H}^+}^{\circ} + l_{\text{P}}^{\circ}$$

and

$$\Lambda_{0,\text{HCl}} + \Lambda_{0,\text{NaP}} - \Lambda_{0,\text{NaCl}} = l_{\text{H}^+}^{\circ} + l_{\text{Cl}^-}^{\circ} + l_{\text{Na}^+}^{\circ} + l_{\text{P}}^{\circ} - l_{\text{Na}^+}^{\circ} - l_{\text{Cl}^-}^{\circ}$$

which, on simplifying the right-hand side of the equation, becomes

$$\Lambda_{0,\text{HCl}} + \Lambda_{0,\text{NaP}} - \Lambda_{0,\text{NaCl}} = l_{\text{H}^+}^{\circ} + l_{\text{P}}^{\circ}$$

Therefore,

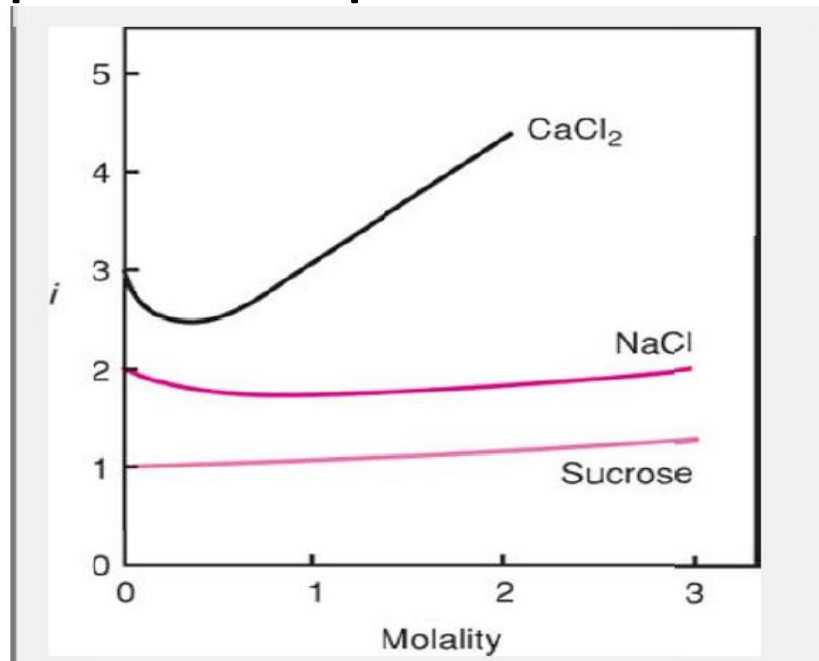
$$\Lambda_{0,\text{HP}} = \Lambda_{0,\text{HCl}} + \Lambda_{0,\text{NaP}} - \Lambda_{0,\text{NaCl}}$$

and

$$\begin{aligned}\Lambda_{0,\text{HP}} &= 426.2 + 73.5 - 126.5 \\ &= 373.2 \text{ mho cm}^2/\text{Eq}\end{aligned}$$

# Colligative properties

- For electrolyte and concentrated non electrolyte solution colligative properties expressed as:
- $\Delta p = 0.018 \cdot i \cdot P^0 \cdot m$
- $\pi = i \cdot R T m$
- $\Delta T_f = i K_f m$
- $\Delta T_b = i K_b m$



***i***: ***i*** van't Hoff factor deviation for **concentrated** non electrolyte solution

***i***: ***i*** is number of ions formed upon **dissociation** of electrolyte solution in infinite dilution

equations

$$\Delta p = 0.018ip_1^\circ m \quad (6-25)$$

$$\pi = iRTm \quad (6-26)$$

$$\Delta T_f = iK_f m \quad (6-27)$$

$$\Delta T_b = iK_b m \quad (6-28)$$

Equation (6-25) applies only to aqueous solutions, whereas (6-26) through (6-28) are independent of the solvent used.

### Example 6-5

#### Osmotic Pressure of Sodium Chloride

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

The *i* factor for a 2.0 *m* solution of sodium chloride as observed in Figure 6-5 is about 1.9.

Thus,

$$\pi = 1.9 \times 0.082 \times 293 \times 2.0 = 91.3 \text{ atm}$$

# Drug and ionization

- 1- Anionic and cationic Antibacterial and Antiprotozoal agents, are more active when in **ionic** state.
- 2- Hydroxybenzoate ester (parabens) and many general anesthetics, bring about their biological effects as **nonelectrolytes**.
- 3- Sulfonamides are thought to exert their drug action, both as **ions** and **neutral** molecules

# Degree of dissociation ( $\alpha$ )

- The fraction of weak electrolyte solute molecules ionized is called degree of dissociation and is expressed by:-
  - $\alpha = \Lambda_c / \Lambda_0$
  - $\text{HOAC} \xrightleftharpoons{\text{H}_2\text{O}} \text{H}_3\text{O}^+ + \text{OAC}^-$
  - $(1 - \alpha)C \qquad \alpha C \qquad \alpha C$
  - $\alpha = 0 \xleftrightarrow{\hspace{2cm}} 1$   
          weak           strong

$\Lambda_c$ : represented the **number** of solute particle present as ions at **C** concentration

$\Lambda_0$ : was measured for **complete** dissociation at **infinite** dilution.

ions at a concentration  $c$ . Hence, the fraction of solute molecules ionized, or the degree of dissociation, was expressed by the equation<sup>4</sup>

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \quad (6-32)$$

where  $\Lambda_c/\Lambda_0$  is known as the *conductance ratio*.

## Example 6-6

### Degree of Dissociation of Acetic Acid

The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 ohm cm<sup>2</sup>/Eq. The equivalent conductance of a  $5.9 \times 10^{-3}$  M solution of acetic acid is 14.4 ohm cm<sup>2</sup>/Eq. What is the degree of dissociation of acetic acid at this concentration? We write

$$\alpha = \frac{14.4}{390.7} = 0.037 \text{ or } 3.7\%$$

The van't Hoff factor,  $i$ , can be connected with the degree of dissociation,  $\alpha$ , in the following way.

The  $i$  factor equals unity for an ideal solution of a nonelectrolyte; however, a term must be added to

# Determination of ( $\alpha$ ) degree of dissociation

- For 1M CaCl<sub>2</sub> 3 ions per molecule.
- $i = 1 + \alpha (3-1)$
- For general electrolyte yielding  $v$  ions
- $i = 1 + \alpha (v-1)$
- $\alpha = (i-1)/(v-1)$
- $i$  determine from cryoscopic method
- $\Delta T_f = i K_f m$
- $i = \Delta T_f / K_f m$

electrolytes and nonelectrolytes from the ideal laws of the colligative properties, regardless of the nature of these discrepancies. According to the early ionic theory, the degree of dissociation of ammonium chloride, a strong electrolyte, was calculated in the same manner as that of a weak electrolyte.

### **Example 6-8**

#### **Degree of Dissociation**

The freezing point depression for a 0.01 *m* solution of ammonium chloride is 0.0367°C.

Calculate the “degree of dissociation” of this electrolyte. We write

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.0367^\circ\text{C}}{1.86 \times 0.010} = 1.97$$

$$\alpha = \frac{1.97 - 1}{2 - 1} = 0.97$$

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  $\Lambda_c/\Lambda_0$  or