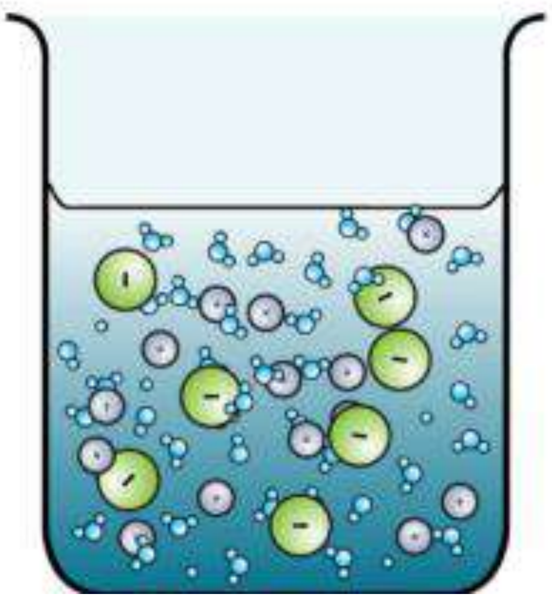
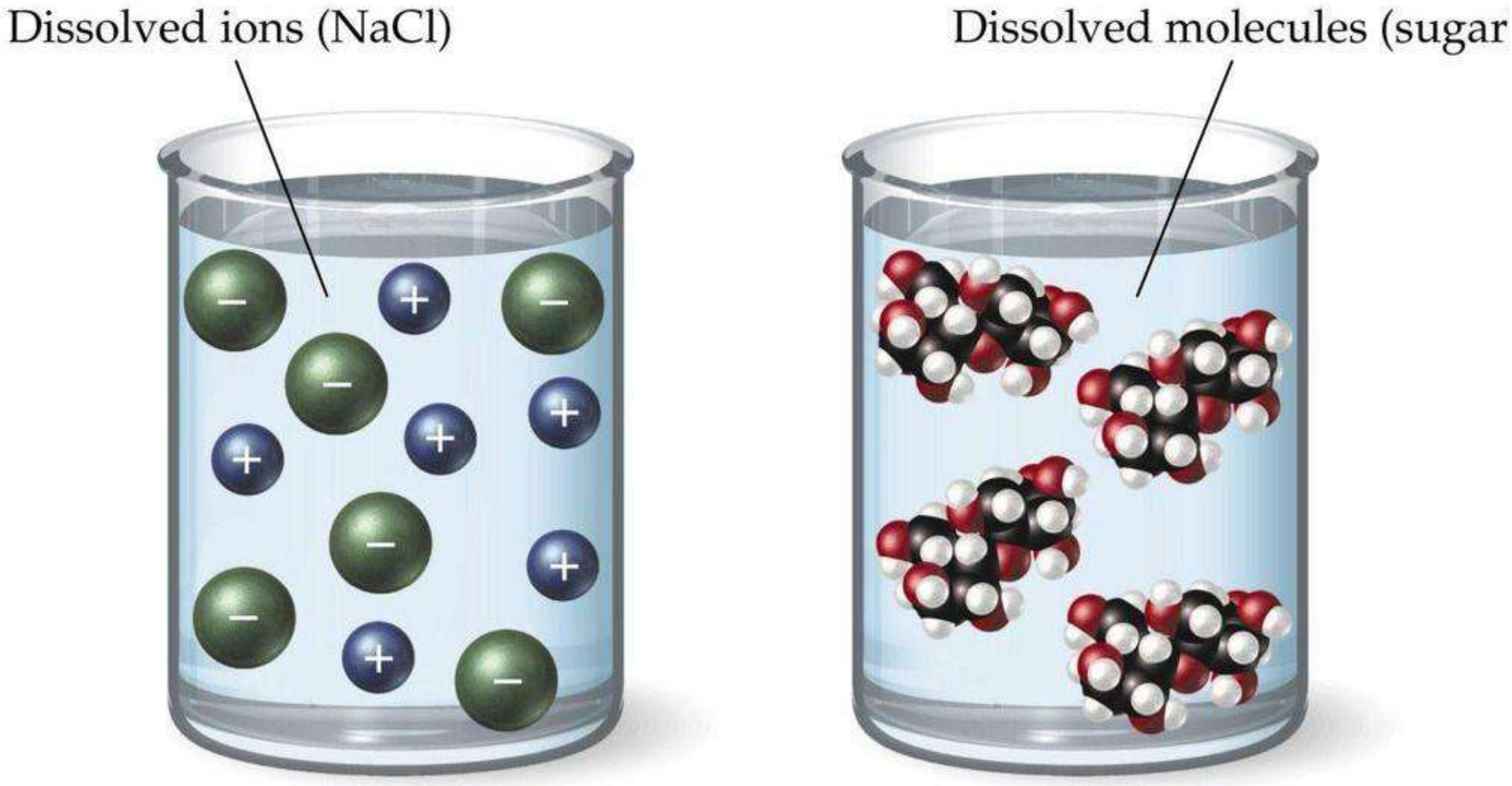
SOLUTIONS OF ELECTROLYTES

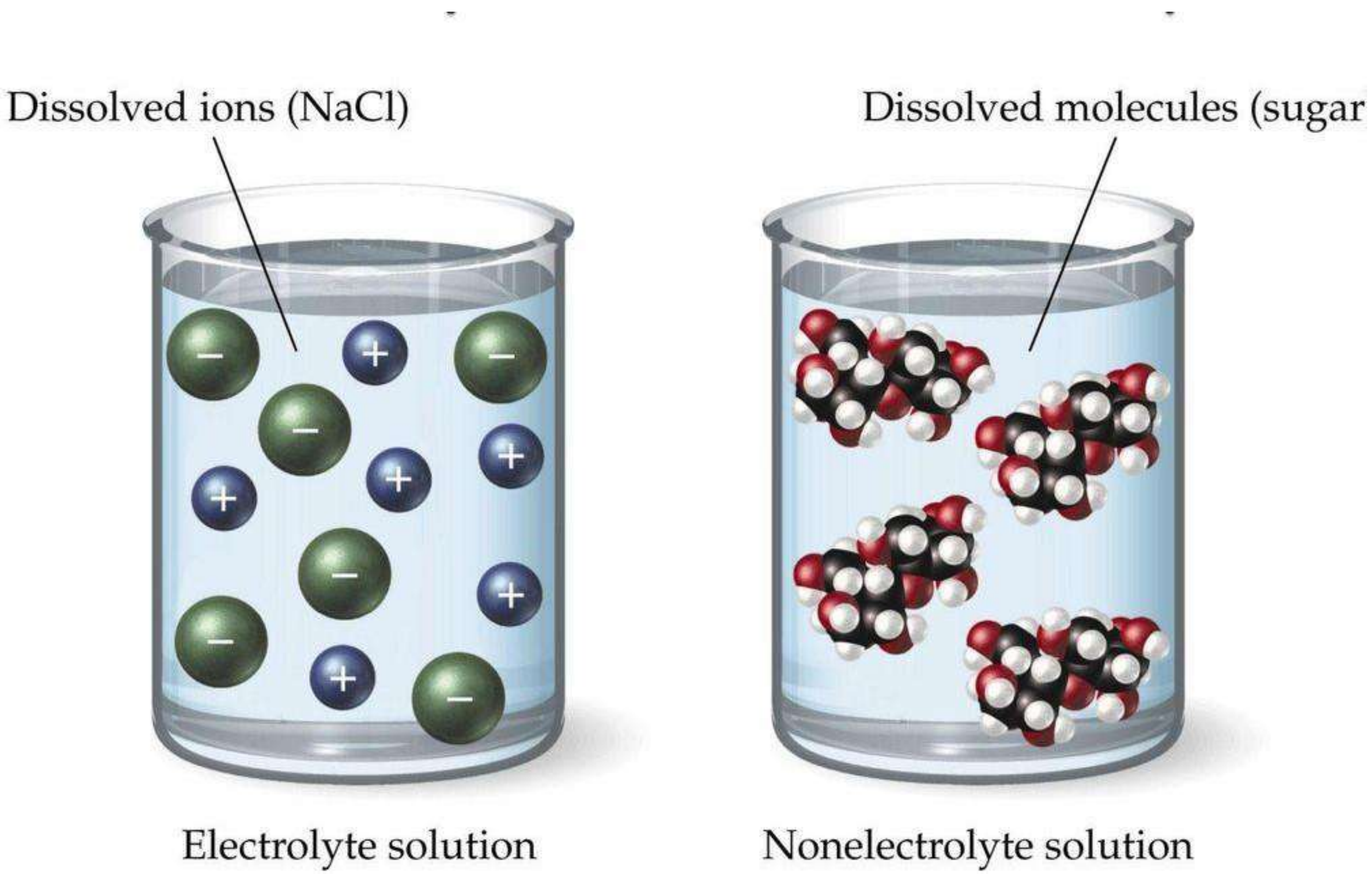




Electrolyte solution

Nonelectrolyte solution

$$CaCl_2\,(s) \rightarrow Ca^{2+}\,(aq) + 2Cl^{-}(aq)$$



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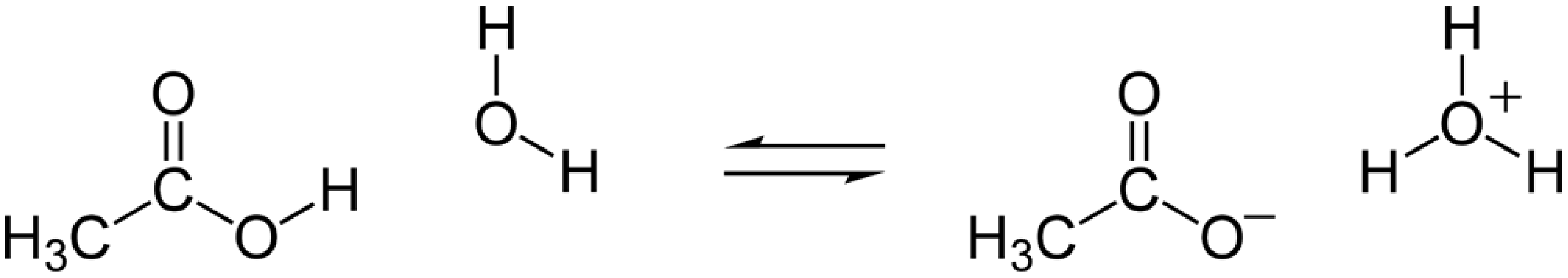
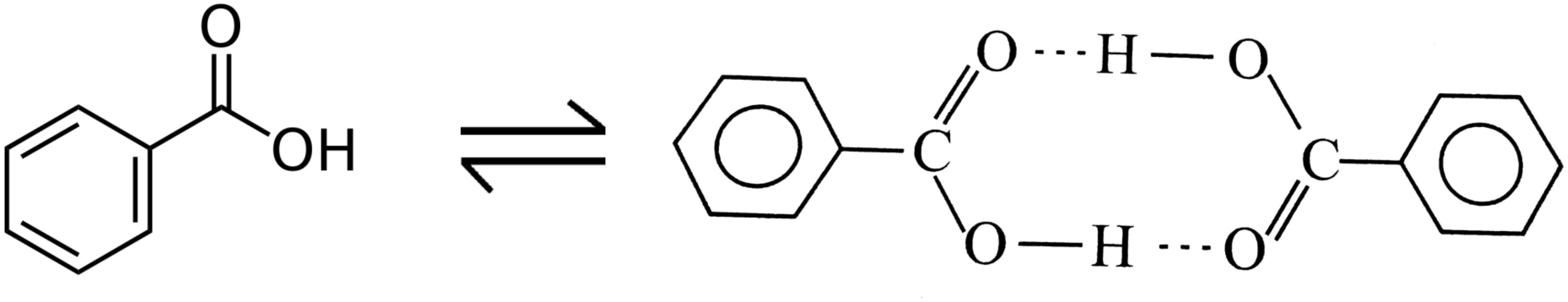




Interionic interaction

- Van’t Hoff factor (i)
- $i = \dfrac{\Delta T_f \ \ measured}{\Delta T_f \ \ calculated\ as\ a\ non\ electrolytes}$

van’t Hoff Factor (i)

i = 1

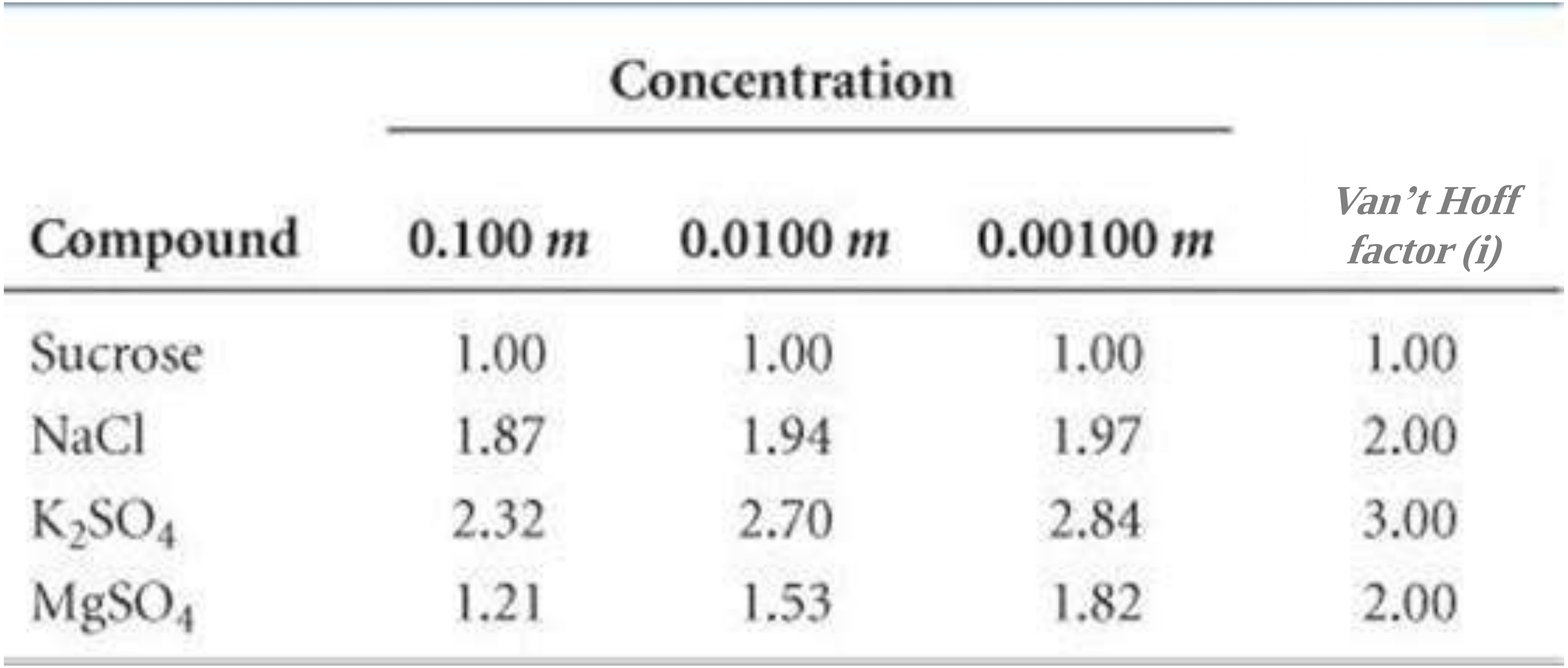
Sucrose dissolves but does not dissociate

i = 2

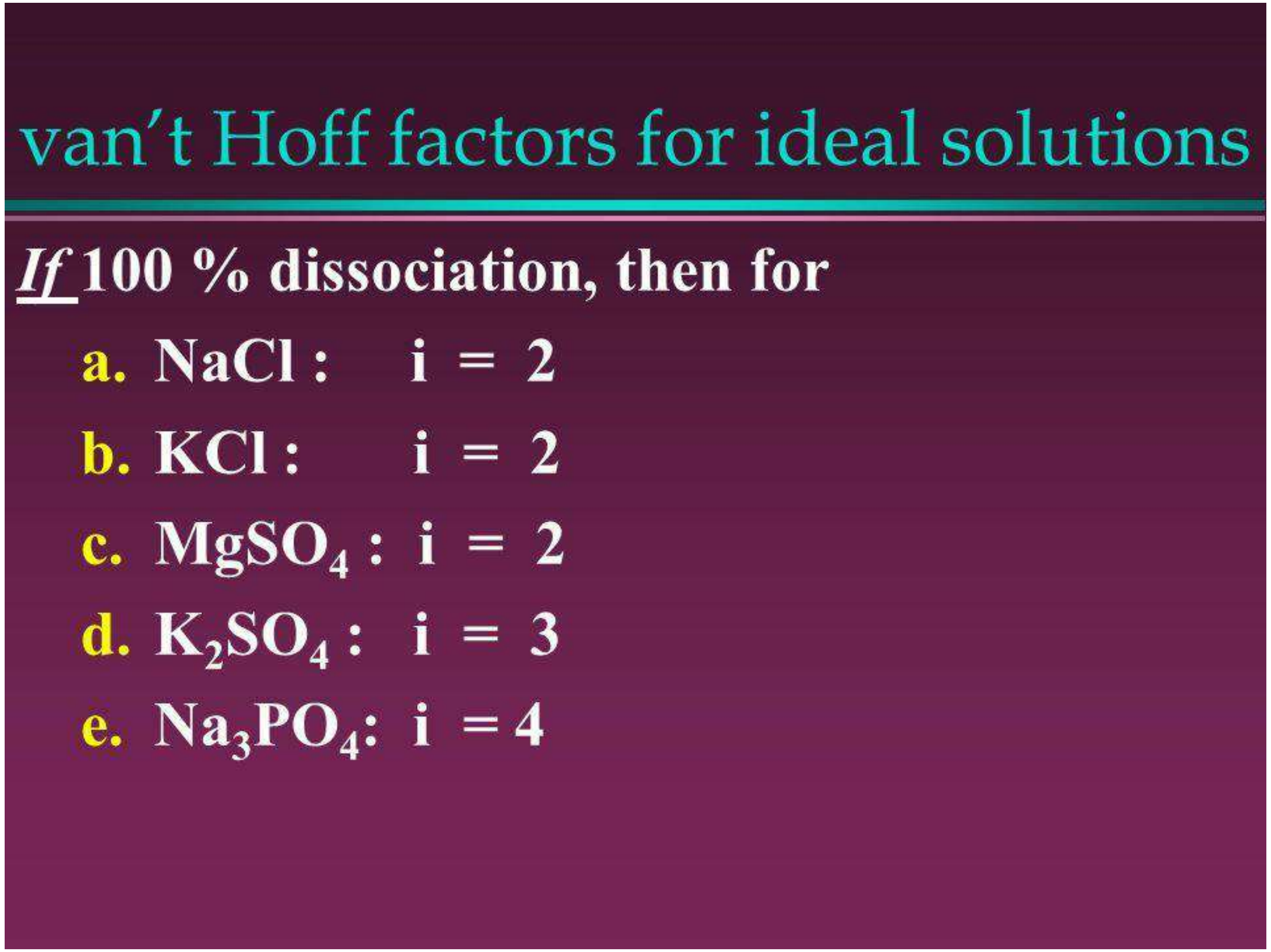
Sodium chloride dissociates to form two ions

i = 3

Calcium chloride dissociates to form three ions



	Concentration			
Compound	0.100 *m*	0.0100 *m*	0.00100 *m*	*Van't Hoff factor (i)*
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00



van't Hoff factors for ideal solutions

If **100 % dissociation, then for**

a. **NaCl : $i = 2$**

b. **KCl : $i = 2$**

c. **$MgSO_4$: $i = 2$**

d. **K_2SO_4 : $i = 3$**

e. **Na_3PO_4: $i = 4$**

Colligative properties of electrolytic solutions and concentrated solutions of non electrolytes

- van't Hoff found, however, that solutions of electrolytes gave osmotic pressures approximately two, three, and more times larger than expected from this equation, depending on the electrolyte investigated.
- Introducing a correction factor i to account for the irrational behavior of ionic solutions, he wrote

$$\pi = iRTc$$

- The colligative properties in dilute solutions of electrolytes are expressed on the molal scale by the equations

$$\Delta p = 0.018 i p_1{}^{\circ} m$$

$$\pi = iRTm$$

$$\Delta T_f = iK_f m$$

$$\Delta T_b = iK_b m$$

Example

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

The *i* factor for a solution of sodium chloride is about 1.9

Thus,

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

ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

$$H_2O + Na^+Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

[Ionic compound]

[Strong electrolyte]

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

[Covalent compound]

[Strong electrolyte]

$$H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

[Covalent compound]

[Weak electrolyte]

Degree of dissociation

- Arrhenius did not originally consider strong electrolytes to be ionized completely except in extremely dilute solutions.

- He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the degree of dissociation, α.

- A strong electrolyte was one that dissociated into ions to a high degree and a weak electrolyte was one that dissociated into ions to a low degree.

- Arrhenius determined the degree of dissociation directly from conductance measurements.
- He recognized that the equivalent conductance at infinite dilution $\Lambda 0$ was a measure of the complete dissociation of the solute into its ions and that Λc represented the number of solute particles present as ions at a concentration c.
- Hence, the fraction of solute molecules ionized, or the degree of dissociation, was expressed by the equation:

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

- the *conductance ratio*

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

Example

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

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

$$\boxed{\alpha = \frac{i-1}{\nu-1}}$$

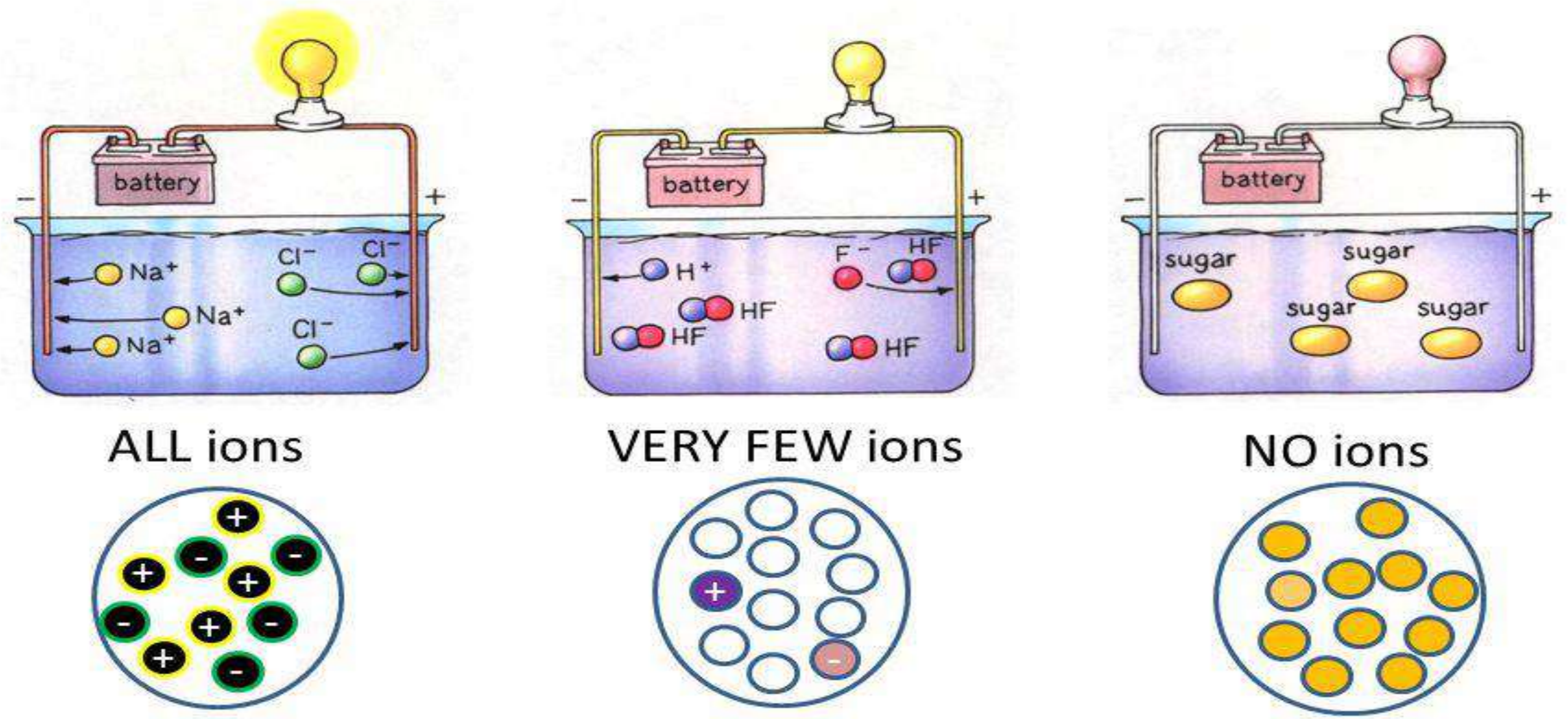
Example

The freezing point of a 0.10 *m* solution of acetic acid is –0.188°C. Calculate the degree of ionization of acetic acid at this concentration. Acetic acid dissociates into two ions, that is, $\nu = 2$. We write

$$i = \frac{0.188}{1.86 \times 0.10} = 1.011$$

$$\alpha = \frac{i-1}{\nu-1} = \frac{1.011-1}{2-1} = 0.011$$

THEORY OF STRONG ELECTROLYTES



strong electrolyte

ALL ions

Str Acids
Str Bases
Soluble Ionics

weak electrolyte

VERY FEW ions

Weak Acids
Weak Bases

non- electrolyte

NO ions

POLAR
molecular
compounds

- Arrhenius used α to express the degree of dissociation of both strong and weak electrolytes, and van’t Hoff introduced the factor i to account for the deviation of strong and weak electrolytes and nonelectrolytes from the ideal laws of the colligative properties, regardless of the nature of these discrepancies.
- 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 $\Lambda c/\Lambda o$ or obtained from the van’t Hoff i factor.
- consider a strong electrolyte as completely ionized and to introduce a factor that expresses the deviation of the solute from 100% ionization (Activity and Activity Coefficients)

Activity and Activity Coefficients

- a strong electrolyte may be completely ionized, yet incompletely dissociated into free ions.
- One may think of the solution as having an "effective concentration" or, as it is called, an activity.
- 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, expressed as molality or molarity. It is written on a molal basis at infinite dilution as

$$a = m \qquad \text{or} \qquad a/m = 1$$

- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of the ions becomes less than the molal concentration.
- This ratio is known as the practical activity coefficient, γ_m, on the molal scale, and the formula is written, for a particular ionic species, as

$$\frac{a}{m} = \gamma_m$$

$$a = \gamma_m m$$

- On the molarity scale, another practical activity coefficient, γ_c, is defined as

$$a = \gamma_c c$$

- and on the mole fraction scale, a rational activity coefficient is defined as

$$a = \gamma_x X$$

- A cation and an anion in an aqueous solution may each have a different ionic activity.
- This is recognized by using the symbol a+ when speaking of the activity of a cation and the symbol a− when speaking of the activity of an anion.
- An electrolyte in solution contains each of these ions, however, so it is convenient to define a relationship between the activity of the electrolyte a± and the activities of the individual ions.

- The activity of an electrolyte is defined by its mean ionic activity, which is given by the relation

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

- where the exponents m and n give the stoichiometric numbers of given ions that are in solution.
- Thus, an NaCl solution has a mean ionic activity of

$$a_{\pm} = (a_{\mathrm{Na}^{+}} a_{\mathrm{Cl}^{-}})^{1/2}$$

- whereas an FeCl3 solution has a mean ionic activity of

$$a_{\pm} = (a_{\mathrm{Fe}^{+3}} a_{\mathrm{Cl}^{-}}{}^{3})^{1/4}$$

- The ionic activities of previous equation can be expressed in terms of concentrations using any of equations

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

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

- The mean ionic activity coefficient for the electrolyte can be defined by

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

Example

What is the mean ionic activity of a 0.01 M solution of $FeCl_3$? We write

$$\begin{aligned} a_\pm &= \gamma_\pm(c_+c_-{}^3)^{1/4} = \gamma_\pm[(0.01)(3 \times 0.01)^3]^{1/4} \\ &= 2.3 \times 10^{-2}\gamma_\pm \end{aligned}$$

The Debye-H¨uckel Theory

- Debye and H¨uckel derived an equation based on the principles that strong electrolytes are completely ionized in dilute solution and that the deviations of electrolytic solutions from ideal behavior are due to the electrostatic effects of the oppositely charged ions.
- The equation relates the activity coefficient of a particular ion or the mean ionic activity coefficient of an electrolyte to the valence of the ions, the ionic strength of the solution, and the characteristics of the solvent.

$$\log \gamma_i = -A{z_i}^2\sqrt{\mu}$$