



# CHAPTER 14

## Solutions

### **The Dissolution Process**

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# Effect of Temperature on Solubility

- **LeChatelier's Principle**

When stress is applied to a system at equilibrium, the system responds in a way that best relieves the stress.

# Molality and Mole Fraction

- Molality is a concentration unit based on the number of moles of solute per kilogram of solvent.

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

in dilute aqueous solutions molarity and molality are nearly equal

# Molality and Mole Fraction

- Mole fraction is the number of moles of one component divided by the moles of all the components of the solution

$$X_A = \frac{\text{number of moles of A}}{\text{number of moles of A} + \text{number of moles of B}}$$

$$X_B = \frac{\text{number of moles of B}}{\text{number of moles of A} + \text{number of moles of B}}$$

Note that  $X_A + X_B = 1$

The sum of all the mole fractions must equal 1.00.

# Colligative Properties of Solutions

- Colligative properties are properties of solutions that depend solely on the **number of particles** dissolved in the solution.
  - Colligative properties do not depend on the kinds of particles dissolved.
- Colligative properties are a physical property of solutions.

# Colligative Properties of Solutions

- There are four common types of colligative properties:
  1. Vapor pressure lowering
  2. Freezing point depression
  3. Boiling point elevation
  4. Osmotic pressure

# Lowering of Vapor Pressure and Raoult's Law

- Addition of a nonvolatile solute to a solution lowers the vapor pressure of the solution.
  - The effect is simply due to fewer solvent molecules at the solution's surface.
  - The solute molecules occupy some of the spaces that would normally be occupied by solvent.
- Raoult's Law models this effect in ideal solutions.

# Lowering of Vapor Pressure and Raoult's Law

- Derivation of Raoult's Law.

$$P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^0$$

where  $P_{\text{solvent}}$  = vapor pressure of solvent *in solution*

$P_{\text{solvent}}^0$  = vapor pressure of pure solvent

$X_{\text{solvent}}$  = mole fraction of solvent *in solution*



# Lowering of Vapor Pressure and Raoult's Law

- Lowering of vapor pressure,  $\Delta P_{\text{solvent}}$ , is defined as:

$$\begin{aligned}\Delta P_{\text{solvent}} &= P_{\text{solvent}}^0 - P_{\text{solvent}} \\ &= P_{\text{solvent}}^0 - (X_{\text{solvent}})(P_{\text{solvent}}^0) \\ &= (1 - X_{\text{solvent}})P_{\text{solvent}}^0\end{aligned}$$

# Lowering of Vapor Pressure and Raoult's Law

- Remember that the sum of the mole fractions must equal 1.
- Thus  $X_{\text{solvent}} + X_{\text{solute}} = 1$ , which we can substitute into our expression.

$$X_{\text{solute}} = 1 - X_{\text{solvent}}$$

$$\Delta P_{\text{solvent}} = X_{\text{solute}} P_{\text{solvent}}^0$$

which is Raoult's Law



# Fractional Distillation

- Distillation is a technique used to separate solutions that have two or more volatile components with differing boiling points.
- A simple distillation has a single distilling column.
  - Simple distillations give reasonable separations.
- A fractional distillation gives increased separations because of the increased surface area.
  - Commonly, glass beads or steel wool are inserted into the distilling column.

# Boiling Point Elevation

- Addition of a **nonvolatile** solute to a solution raises the boiling point of the solution above that of the pure solvent.
  - This effect is because the solution's vapor pressure is lowered as described by Raoult's law.

# Boiling Point Elevation

- Boiling point elevation relationship is:

$$\Delta T_b = K_b m$$

where :  $\Delta T_b$  = boiling point elevation

$m$  = molal concentration of solution

$K_b$  = molal boiling point elevation constant  
for the solvent

# Boiling Point Elevation

- What is the normal boiling point of a 2.50 *m* glucose,  $C_6H_{12}O_6$ , solution?

$$\Delta T_b = K_b m$$

$$\Delta T_b = (0.512 \text{ } ^\circ\text{C}/m)(2.50m)$$

$$\Delta T_b = 1.28^\circ\text{C}$$

$$\text{Boiling Point of the solution} = 100.0^\circ\text{C} + 1.28^\circ\text{C} = 101.28^\circ\text{C}$$

# Freezing Point Depression

- Addition of a **nonvolatile** solute to a solution lowers the freezing point of the solution relative to the pure solvent.

# Freezing Point Depression

- Relationship for freezing point depression is:

$$\Delta T_f = K_f m$$

where:  $\Delta T_f$  = freezing point depression of solvent

$m$  = molal concentration of solution

$K_f$  = freezing point depression constant for solvent



# Freezing Point Depression

- Notice the similarity of the two relationships for freezing point depression and boiling point elevation.

$$\Delta T_f = K_f m \text{ vs. } \Delta T_b = K_b m$$

- Fundamentally, freezing point depression and boiling point elevation are the same phenomenon.
  - The only differences are the size of the effect which is reflected in the sizes of the constants,  $K_f$  &  $K_b$ .

# Freezing Point Depression

- Calculate the freezing point of a 2.50 m aqueous glucose solution.

$$\Delta T_f = K_f m$$

$$\Delta T_f = (1.86^\circ \text{C}/m)(2.50m)$$

$$\Delta T_f = 4.65^\circ \text{C}$$

$$\text{Freezing Point of solution} = 0.00^\circ \text{C} - 4.65^\circ \text{C} = -4.65^\circ \text{C}$$

# Determination of Molecular Weight by Freezing Point Depression

- The size of the freezing point depression depends on two things:
  1. The size of the  $K_f$  for a given solvent, which are well known.
  2. And the molal concentration of the solution which depends on the number of moles of solute and the kg of solvent.

- A 37.0 g sample of a new covalent compound, a nonelectrolyte, was dissolved in  $2.00 \times 10^2$  g of water. The resulting solution froze at  $-5.58^\circ\text{C}$ . What is the molecular weight of the compound?

$$\Delta T_f = K_f m \text{ thus the}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{5.58^\circ\text{C}}{1.86^\circ\text{C}} = 3.00m$$

In this problem there are  
200 mL = 0.200 kg of water.

$$\begin{aligned} ? \text{ mol compound in } 0.200 \text{ kg H}_2\text{O} &= 3.00 m \times 0.200 \text{ kg} \\ &= 0.600 \text{ mol compound} \end{aligned}$$

$$\text{Thus the molar mass is } \frac{37 \text{ g}}{0.600 \text{ mol}} = 61.7 \text{ g/mol}$$

# Colligative Properties and Dissociation of Electrolytes

- Electrolytes have larger effects on boiling point elevation and freezing point depression than nonelectrolytes.
  - This is because the number of particles released in solution is greater for electrolytes
- One mole of NaCl dissolves in water to produce two moles of aqueous ions:
  - 1 mole of  $\text{Na}^+$  and 1 mole of  $\text{Cl}^-$  ions

# Colligative Properties and Dissociation of Electrolytes

- The **van't Hoff factor**, symbol  $i$ , is used to introduce this effect into the calculations.
- $i$  is a measure of the extent of ionization or dissociation of the electrolyte in the solution.

$$i = \frac{\Delta T_{f(\text{actual})}}{\Delta T_{f(\text{if nonelectrolyte})}}$$

# Colligative Properties and Dissociation of Electrolytes

- $i$  has an ideal value of **2** for 1:1 electrolytes like NaCl, KI, LiBr, etc.



- $i$  has an ideal value of **3** for 2:1 electrolytes like  $\text{K}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{SrI}_2$ , etc.



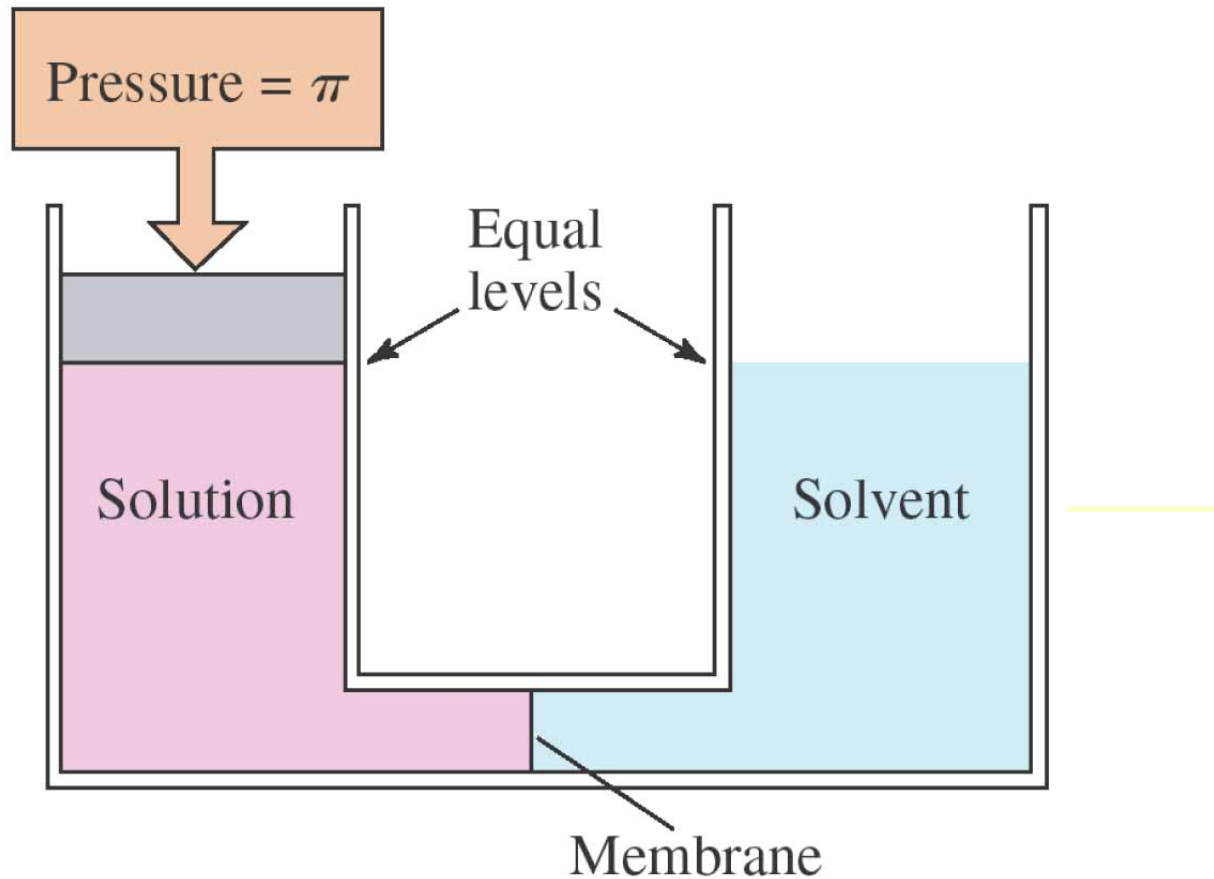


# Osmotic Pressure

- **Osmosis** is the net flow of a solvent between two solutions separated by a semipermeable membrane.
  - The solvent passes from the lower concentration solution into the higher concentration solution.
- Examples of semipermeable membranes include:
  1. cellophane and saran wrap
  2. skin
  3. cell membranes



# Osmotic Pressure





# Osmotic Pressure

$$\pi = MRT$$

where:  $\pi$  = osmotic pressure in atm

$M$  = molar concentration of solution

$$R = 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

$T$  = absolute temperature

- For very dilute aqueous solutions, molarity and molality are nearly equal.

- $M \approx m$

$$\pi = mRT$$

*for dilute aqueous solutions only*

Osmotic pressure measurements can be used to determine the molar masses of very large molecules such as:

Polymers, proteins and ribonucleotides

**Chemistry is fun!**