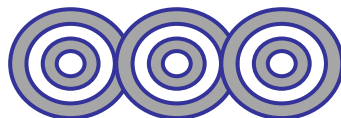




Chemistry, Raymond Chang
10th edition, 2010
McGraw-Hill



Chapter 12

Physical Properties of Solutions

Ahmad Aqel Ifseisi

Assistant Professor of Analytical Chemistry
College of Science, Department of Chemistry
King Saud University

P.O. Box 2455 Riyadh 11451 Saudi Arabia

Building: 05, Office: 1A7 & AA53

Tel. 014674198, Fax: 014675992

Web site: <http://fac.ksu.edu.sa/aifseisi>

E-mail: ahmad3qel@yahoo.com

aifseisi@ksu.edu.sa



كرسي أبحاث
المواد المتقدمة
Advanced Materials
Research Chair



جامعة
الملك سعود
King Saud University



12.6

Colligative properties of nonelectrolyte solutions

Colligative properties (or collective properties) are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.

The colligative properties are:

- Vapor pressure lowering.
- Boiling point elevation.
- Melting point depression.
- Osmotic pressure.

Vapor-Pressure Lowering

If a solute is nonvolatile (that is, it does not have a measurable vapor pressure), the vapor pressure of its solution is always less than that of the pure solvent.

The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration. This relationship is expressed by **Raoult's law**.

$$P_1 = X_1 P_1^\circ$$

where:

X_1 : is the mole fraction of a solvent in a solution.

P_1° : is the vapor pressure of pure solvent at that temperature.

P_1 : is the vapor pressure of a solvent over a solution (above the solution).

In a solution containing only one solute, $X_1 = 1 - X_2$, where X_2 is the mole fraction of the solute.

$$P_1 = (1 - X_2)P_1^\circ$$

$$P_1 = P_1^\circ - X_2 P_1^\circ$$

$$P_1^\circ - P_1 = \Delta P = X_2 P_1^\circ$$

the decrease in vapor pressure, ΔP , is directly proportional to the solute concentration (measured in mole fraction).

EXAMPLE

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30°C = 31.82 mmHg. Assume the density of the solution is 1.00 g/mL.

First we calculate the number of moles of glucose and water in the solution:

$$n_1(\text{water}) = 460 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 25.5 \text{ mol}$$

$$n_2(\text{glucose}) = 218 \text{ g} \times \frac{1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol}$$

The mole fraction of water, X_1 ,

$$\begin{aligned} X_1 &= \frac{n_1}{n_1 + n_2} \\ &= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955 \end{aligned}$$

Therefore, the vapor pressure of the glucose solution is

$$\begin{aligned} P_1 &= X_1 P_1^\circ \\ P_1 &= 0.955 \times 31.82 \text{ mmHg} \\ &= 30.4 \text{ mmHg} \end{aligned}$$

Finally, the vapor-pressure lowering is $(31.82 - 30.4) = 1.4 \text{ mmHg}$.

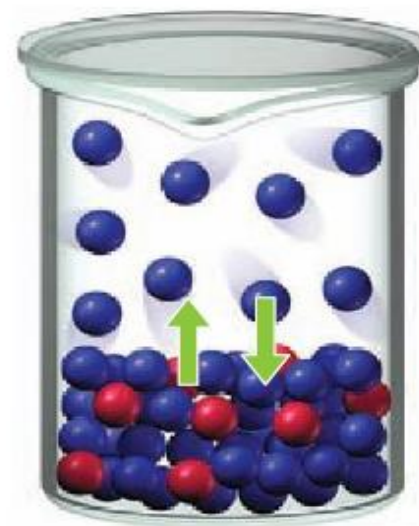
Why is the vapor pressure of a solution less than that of the pure solvent?

As solute molecules are added to a solution, the solvent becomes less volatile (decreased vapor pressure).

Solute-solvent interactions contribute to this effect, because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.



Solvent alone



Solvent + solute

The greater the disorder, the more favorable the process; a solution is more disordered than a pure solvent.

If both components of a solution are **volatile** (that is, have measurable vapor pressure), the vapor pressure of the solution is the sum of the individual partial pressures.

Raoult's law holds equally well in this case:

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

where:

- P_A and P_B are the partial pressures over the solution for components **A** and **B**;
- P_A° and P_B° are the vapor pressures of the pure substances;
- X_A and X_B are their mole fractions.

The total pressure is given by Dalton's law of partial pressure

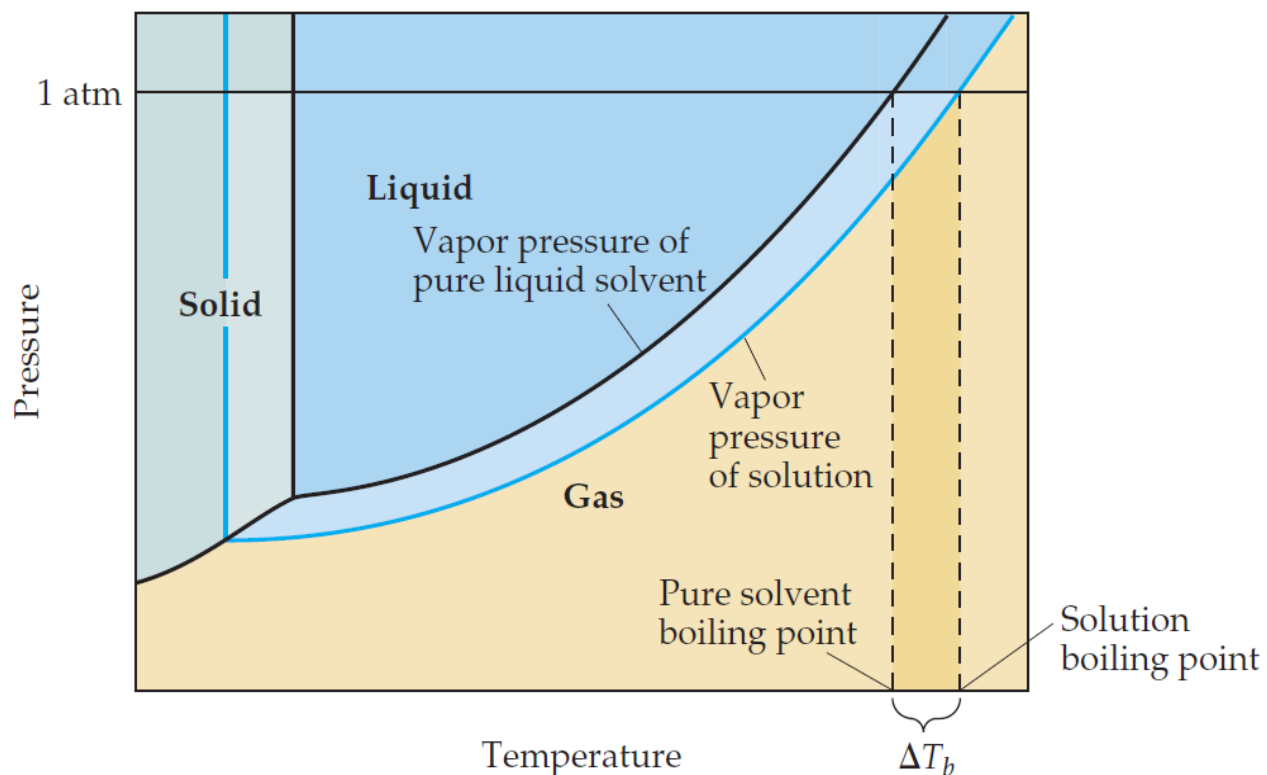
$$P_T = P_A + P_B$$

$$P_T = X_A P_A^\circ + X_B P_B^\circ$$

Boiling-Point Elevation

The **boiling point** of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points than the pure solvent.



Phase diagram for a pure solvent and for a solution of a nonvolatile solute.

At the normal boiling point of the pure liquid, the vapor pressure of the solution will be less than 1 atm. Therefore, a higher temperature is required to attain a vapor pressure of 1 atm. Thus, the boiling point of the solution is higher than that of the pure liquid.

The change in boiling point is proportional to the **molality** (m) of the solution:

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

where:

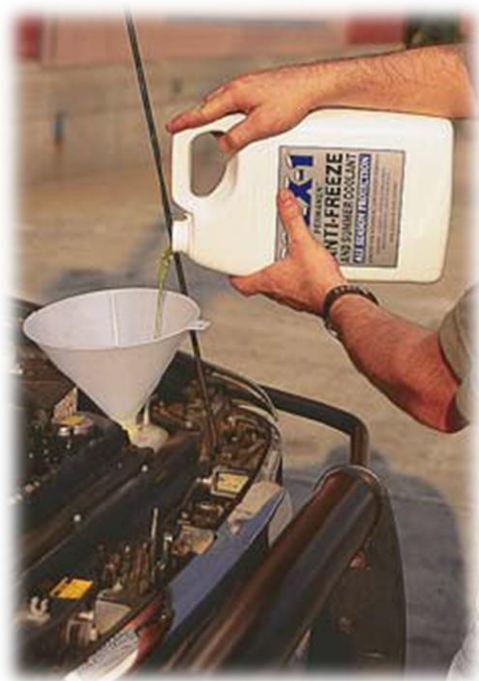
K_b is the molal boiling point elevation constant, a property of the solvent.
 ΔT_b is added to the normal boiling point of the solvent.

The increase in boiling point relative to that of the pure solvent, ΔT_b is a +ve quantity obtained by subtracting the boiling point of the pure solvent from the boiling point of the solution.

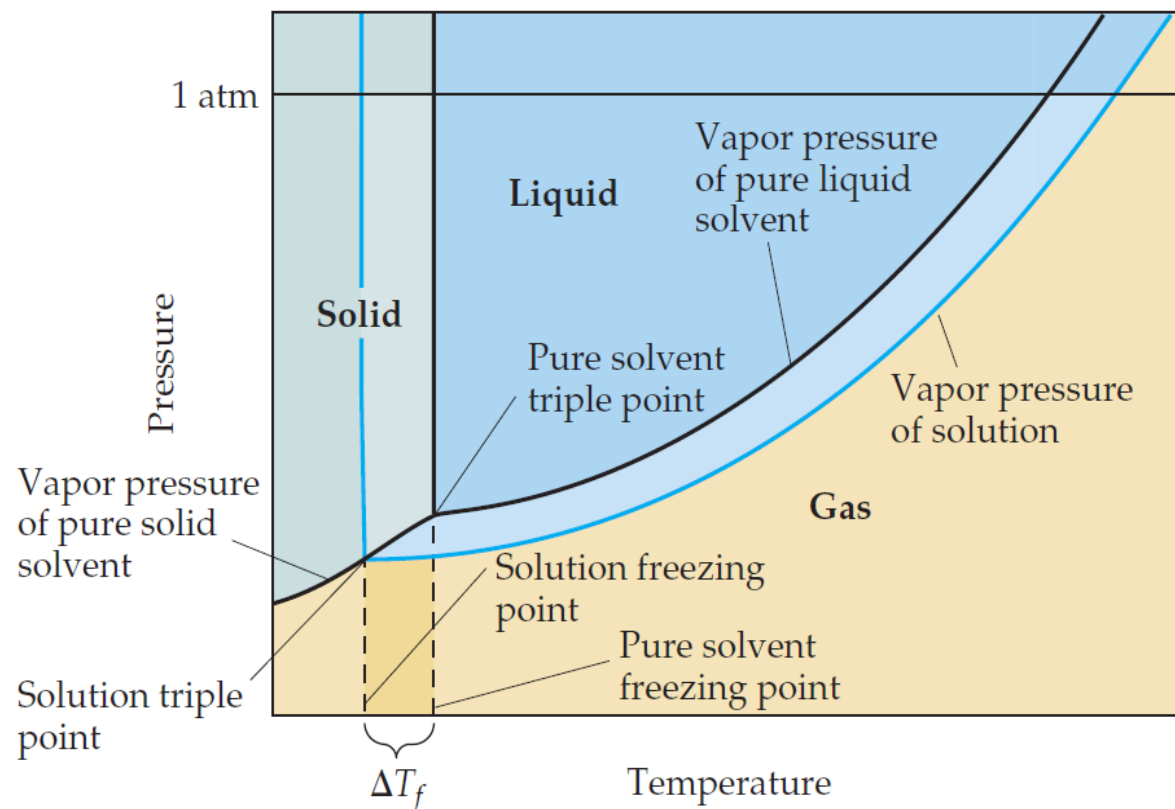
$$\Delta T_b = T_{soln} - T_{pure\ solvent} \quad (T_{soln} > T_{pure\ solvent})$$

Freezing-Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have lower freezing points than the pure solvent.



e.g., Antifreeze being added to an automobile radiator. Antifreeze consists of an aqueous solution of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$.



Phase diagram for a pure solvent and for a solution of a nonvolatile solute

The change in freezing point can be found similarly:

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where:

K_f is the molal freezing point depression constant of the solvent.

ΔT_f is subtracted from the normal freezing point of the solvent.

The decrease in freezing point, ΔT_f is a +ve quantity obtained by subtracting the freezing point of the solution from the freezing point of the pure solvent.

$$\Delta T_f = T_{\text{pure solvent}} - T_{\text{soln}} \quad (T_{\text{pure solvent}} > T_{\text{soln}})$$

Boiling Point Elevation
and
Freezing Point Depression

$$\Delta T_b = K_b m$$

$$\Delta T_f = K_f m$$

Molal boiling-point elevation and freezing-point depression constants of several common liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/m)	Normal Boiling Point (°C)*	K_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	-117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

For water,

K_b is 0.52 °C/m; therefore, a 1 *m* aqueous solution of sucrose or any other aqueous solution that is 1 *m* in nonvolatile solute particles will boil 0.52 °C higher than pure water.

K_f is 1.86 °C/m; therefore, a 1 *m* aqueous solution of sucrose or any other aqueous solution that is 1 *m* in nonvolatile solute particles will freeze 1.86 °C lower than pure water.

EXAMPLE

Ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C). Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water. Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g.

$$651 \text{ g EG} \times \frac{1 \text{ mol EG}}{62.07 \text{ g EG}} = 10.5 \text{ mol EG}$$
$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$
$$= \frac{10.5 \text{ mol EG}}{2.505 \text{ kg H}_2\text{O}} = 4.19 \text{ mol EG/kg H}_2\text{O}$$
$$= 4.19 m$$

$$\Delta T_f = K_f m$$
$$= (1.86^\circ\text{C}/m)(4.19 m)$$
$$= 7.79^\circ\text{C}$$

Because pure water freezes at 0°C , the solution will freeze at $(0 - 7.79) = -7.79^\circ\text{C}$.

We can calculate boiling-point elevation in the same way as follows:

$$\Delta T_b = K_b m$$
$$= (0.52^\circ\text{C}/m)(4.19 m)$$
$$= 2.2^\circ\text{C}$$

Because the solution will boil at $(100 + 2.2) = 102.2^\circ\text{C}$, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

Example

Automotive antifreeze consists of ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass % solution of ethylene glycol in water.

Solution

The molality of the solution is calculated as follows:

$$\begin{aligned}\text{Molality} &= \frac{\text{moles C}_2\text{H}_6\text{O}_2}{\text{kilograms H}_2\text{O}} = \left(\frac{250 \text{ g C}_2\text{H}_6\text{O}_2}{750 \text{ g H}_2\text{O}} \right) \left(\frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.1 \text{ g C}_2\text{H}_6\text{O}_2} \right) \left(\frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} \right) \\ &= 5.37 m\end{aligned}$$

We can now use Equations to calculate the changes in the boiling and freezing points:

$$\begin{aligned}\Delta T_b &= K_b m = (0.51 \text{ }^\circ\text{C}/m)(5.37 m) = 2.7 \text{ }^\circ\text{C} \\ \Delta T_f &= K_f m = (1.86 \text{ }^\circ\text{C}/m)(5.37 m) = 10.0 \text{ }^\circ\text{C}\end{aligned}$$

Hence, the boiling and freezing points of the solution are

$$\begin{aligned}\text{Boiling point} &= (\text{normal bp of solvent}) + \Delta T_b \\ &= 100.0 \text{ }^\circ\text{C} + 2.7 \text{ }^\circ\text{C} = 102.7 \text{ }^\circ\text{C} \\ \text{Freezing point} &= (\text{normal fp of solvent}) - \Delta T_f \\ &= 0.0 \text{ }^\circ\text{C} - 10.0 \text{ }^\circ\text{C} = -10.0 \text{ }^\circ\text{C}\end{aligned}$$

Comment: Notice that the solution is a liquid over a larger temperature range than the pure solvent.

Practice Exercise

Calculate the boiling point and freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.

Answer:

$$T_b: 101.3^{\circ}\text{C}.$$

$$T_f: -4.48^{\circ}\text{C}.$$

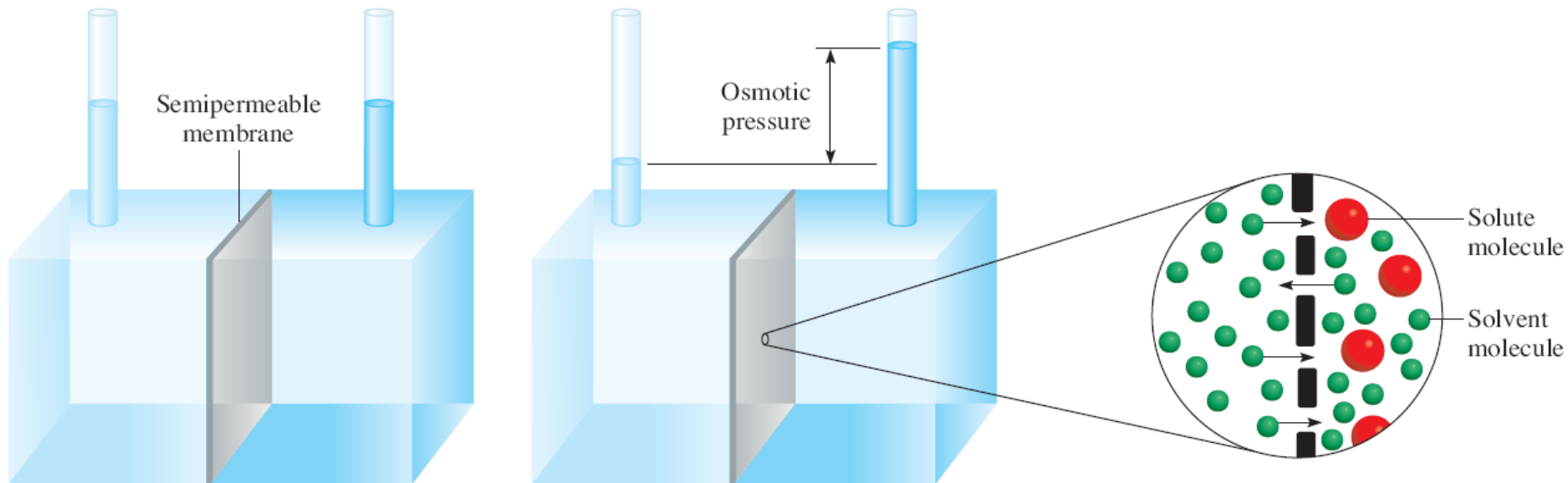
Osmotic Pressure

The pressure required to stop or to prevent osmosis by pure solvent, known as **osmotic pressure**, π , of the solution.

The osmotic pressure obeys a law similar in form to the ideal gas law:

$$\pi = MRT$$

where: M is the molarity of solution, R is the gas constant (0.0821 L atm/K mol), and T is the absolute temperature. The osmotic pressure, π , is expressed in atm.



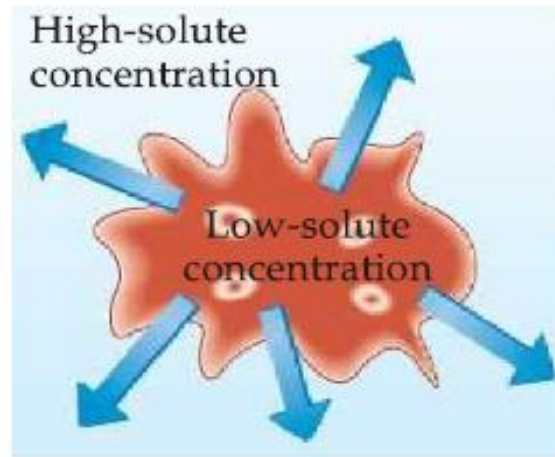
The levels of the pure solvent (left) and of the solution (right) are equal at the start.

During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium.

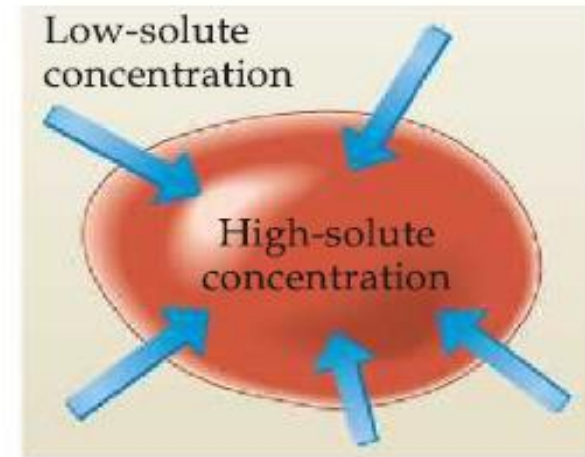
If two solutions are of equal concentration and, hence, have the same osmotic pressure, they are said to be **isotonic**. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be **hypertonic** and the more dilute solution is described as **hypotonic**.

Osmosis plays a very important role in living systems.

The membranes of red blood cells, for example, are semipermeable.



(a) Crenation



(b) Hemolysis

The blue arrows represent the net movement of water molecules.

Water will flow out of the cell, and **crenation** results (causes the cell to **shrink**).

Water will flow into the cell, and **hemolysis** results (causes the cell to **rupture**).

EXAMPLE

The average osmotic pressure of seawater, measured in the kind of osmotic pressure apparatus, is about 30.0 atm at 25°C. Calculate the molar concentration of an aqueous solution of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) that is isotonic with seawater.

$$\begin{aligned}\pi &= MRT \\ M &= \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} \\ &= 1.23 \text{ mol/L} \\ &= 1.23 M\end{aligned}$$

Practice Exercise

What is the osmotic pressure (in atm) of a 0.884 *M* urea solution at 16°C?

Using Colligative Properties to Determine Molar Mass

The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute. Theoretically, any of the four colligative properties is suitable for this purpose. In practice, however, only freezing-point depression and osmotic pressure are used because they show the most pronounced changes.

freezing-point depression → molality → number of moles → molar mass

osmotic pressure → molarity → number of moles → molar mass

EXAMPLE

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene. The freezing point of the solution is 1.05°C below that of pure benzene. What are the molar mass and molecular formula of this compound?

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05^\circ\text{C}}{5.12^\circ\text{C}/m} = 0.205\ m$$

$$0.301\ \text{kg} \times \frac{0.205\ \text{mol}}{1\ \text{kg}} = 0.0617\ \text{mol}$$

$$\begin{aligned}\text{molar mass} &= \frac{\text{grams of compound}}{\text{moles of compound}} \\ &= \frac{7.85\ \text{g}}{0.0617\ \text{mol}} = 127\ \text{g/mol}\end{aligned}$$

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127\ \text{g/mol}}{64\ \text{g/mol}} \approx 2$$

Therefore, the molecular formula is $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

EXAMPLE

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

$$\begin{aligned}\pi &= MRT \\ M &= \frac{\pi}{RT} \\ &= \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} \\ &= 5.38 \times 10^{-4} M\end{aligned}$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb.

$$\begin{aligned}\text{moles of Hb} &= \frac{\text{mass of Hb}}{\text{molar mass of Hb}} \\ \text{molar mass of Hb} &= \frac{\text{mass of Hb}}{\text{moles of Hb}} \\ &= \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}} \\ &= 6.51 \times 10^4 \text{ g/mol}\end{aligned}$$

