

Chapter 12

Physical Properties of Solutions

A **solution** is a homogenous mixture of 2 or more substances.



The **solute** is(are) the substance(s) present in the smaller amount(s).

The **solvent** is the substance present in the larger amount.

TABLE 12.1 Types of Solutions

Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO ₂ in water)
Gas	Solid	Solid	H ₂ gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

A ***saturated solution*** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An ***unsaturated solution*** contains less solute than the solvent has the capacity to dissolve at a specific temperature.



“like dissolves like”

Two substances with similar *intermolecular* forces are likely to be soluble in each other.

- non-polar molecules are soluble in non-polar solvents



- polar molecules are soluble in polar solvents

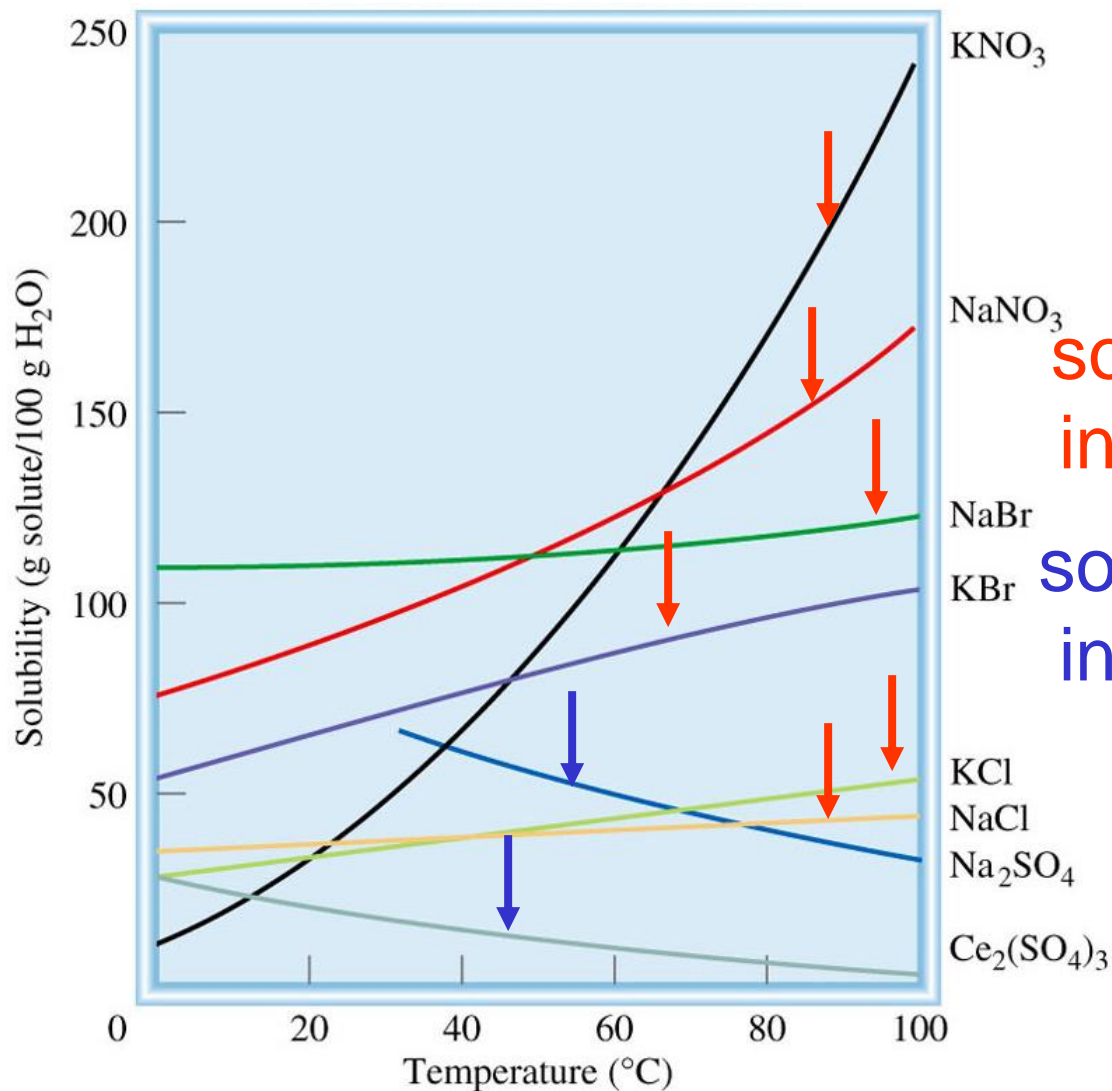


- ionic compounds are more soluble in polar solvents



Temperature and Solubility

Solid solubility and temperature

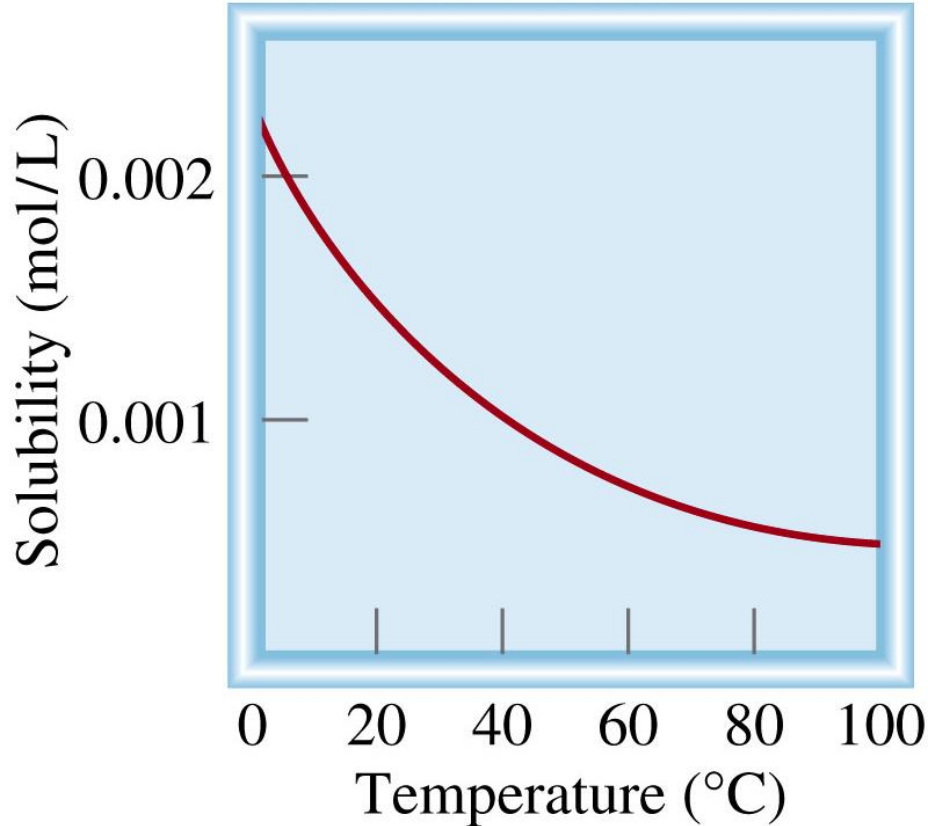


solubility increases with increasing temperature

solubility decreases with increasing temperature

Temperature and Solubility

O₂ gas solubility and temperature



solubility usually
decreases with
increasing temperature

Concentration Units

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Molarity (M) or ***molar concentration***, which is *the number of moles of solute per liter of solution*.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$



Molality (m) is *the number of moles of solute dissolved in 1 kg (1000 g) of solvent*

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

Comparison of Concentration Units

- The advantage of **molarity** is that it is generally easier to measure the volume of a solution.

For this reason, molarity is often preferred over molality.

- **Molality** is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent.

The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 M at 25°C may become 0.97 M at 45°C because of the increase in volume on warming.

- This concentration dependence on temperature can significantly affect the accuracy of an experiment.

Therefore, it is sometimes preferable to use molality instead of molarity.

What mass of KI is required to make 500. mL of a 2.80 M KI solution?

volume of KI solution $\xrightarrow{M\text{ KI}}$ moles KI $\xrightarrow{M\text{ KI}}$ grams KI

$$500. \cancel{\text{ mL}} \times \frac{\cancel{1\text{ L}}}{\cancel{1000\text{ mL}}} \times \frac{2.80 \cancel{\text{ mol KI}}}{\cancel{1\text{ L soln}}} \times \frac{166 \text{ g KI}}{\cancel{1\text{ mol KI}}} = 232 \text{ g KI}$$

EXAMPLE 4.6

How many grams of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are required to prepare a 250-mL solution whose concentration is 2.16 M ?

Solution The first step is to determine the number of moles of $\text{K}_2\text{Cr}_2\text{O}_7$ in 250 mL or 0.250 L of a 2.16 M solution. Rearranging Equation (4.1) gives

$$\text{moles of solute} = \text{molarity} \times \text{L soln}$$

$$\begin{aligned}\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{2.16 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \times 0.250 \text{ L soln} \\ &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

The molar mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is 294.2 g, so we write

$$\begin{aligned}\text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 159 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

EXAMPLE 4.7

In a biochemical assay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

Solution From the molar mass of glucose, we write

$$3.81 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

Next, we calculate the volume of the solution that contains 2.114×10^{-2} mole of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned} V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{2.53 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6/\text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 8.36 \text{ mL soln} \end{aligned}$$

EXAMPLE 12.3

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.09 g.

Solution The definition of molality (m) is

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

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor.

$$\begin{aligned}\text{moles of H}_2\text{SO}_4 &= 24.4 \text{ g } \cancel{\text{H}_2\text{SO}_4} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g } \cancel{\text{H}_2\text{SO}_4}} \\ &= 0.249 \text{ mol H}_2\text{SO}_4\end{aligned}$$

The mass of water is 198 g, or 0.198 kg. Therefore,

$$\begin{aligned}m &= \frac{0.249 \text{ mol H}_2\text{SO}_4}{0.198 \text{ kg H}_2\text{O}} \\ &= 1.26 m\end{aligned}$$

Percent by Mass The **percent by mass** (also called percent by weight or weight percent) is the ratio of the mass of a solute to the mass of the solution, multiplied by 100 percent:

$$\begin{aligned}\% \text{ by mass} &= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\% \\ &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%\end{aligned}$$

Mole Fraction (X) The ***mole fraction*** of a component of a solution, say, component A, is written X_A and is defined as

$$X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

EXAMPLE 12.2

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in the solution?

Solution We write

$$\begin{aligned}\text{percent by mass of KCl} &= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \\ &= \frac{0.892 \text{ g}}{0.892 \text{ g} + 54.6 \text{ g}} \times 100\% \\ &= 1.61\%\end{aligned}$$

EXAMPLE 12.5

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H_3PO_4). The molar mass of phosphoric acid is 97.99 g.

Solution From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

$$\begin{aligned}\text{moles of H}_3\text{PO}_4 &= 35.4 \text{ g } \cancel{\text{H}_3\text{PO}_4} \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g } \cancel{\text{H}_3\text{PO}_4}} \\ &= 0.361 \text{ mol H}_3\text{PO}_4\end{aligned}$$

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

$$\begin{aligned}\text{molality} &= \frac{0.361 \text{ mol H}_3\text{PO}_4}{0.0646 \text{ kg H}_2\text{O}} \\ &= 5.59 \text{ m}\end{aligned}$$

To convert one concentration unit of a solution to another

Example;

Express the concentration of a 0.396 *m* glucose ($C_6H_{12}O_6$) solution in molarity? (density of solution=1.16 g/mL)

0.396 *m* glucose ($C_6H_{12}O_6$) i.e. there is 0.396 mole of glucose in 1000 g of the solvent.

To calculate molarity; we need to determine the volume of this solution.

First, we calculate the mass of the solution from the molar mass of glucose:

$$\left(0.396 \text{ mol } \cancel{C_6H_{12}O_6} \times \frac{180.2 \text{ g}}{1 \text{ mol } \cancel{C_6H_{12}O_6}} \right) + 1000 \text{ g H}_2\text{O} = 1071 \text{ g}$$

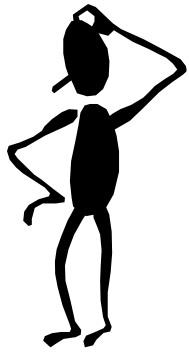
The density of the solution is 1.16 g/mL.

We can now calculate the volume of the solution in liters

$$\begin{aligned}\text{volume} &= \frac{\text{mass}}{\text{density}} \\ &= \frac{1071 \text{ g}}{1.16 \text{ g/mL}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \\ &= 0.923 \text{ L}\end{aligned}$$

The molarity of the solution is given by

$$\begin{aligned}\text{molarity} &= \frac{\text{moles of solute}}{\text{liters of soln}} \\ &= \frac{0.396 \text{ mol}}{0.923 \text{ L}} \\ &= 0.429 \text{ mol/L} = 0.429 \text{ M}\end{aligned}$$



What is the molality of a 5.86 *M* ethanol (C₂H₅OH) solution whose density is 0.927 g/mL?

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

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol

927 g of solution (1000 mL x 0.927 g/mL)

$$\begin{aligned} \text{mass of solvent} &= \text{mass of solution} - \text{mass of solute} \\ &= 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg} \end{aligned}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles C}_2\text{H}_5\text{OH}}{0.657 \text{ kg solvent}} = 8.92 \text{ } m$$

EXAMPLE 12.4

The density of a 2.45 *M* aqueous solution of methanol (CH₃OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

Solution Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 *M* solution of methanol is

$$1 \text{ L soln} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{0.976 \text{ g}}{1 \text{ mL soln}} = 976 \text{ g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

$$\begin{aligned} \text{mass of H}_2\text{O} &= \text{mass of soln} - \text{mass of solute} \\ &= 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \end{aligned}$$

The molality of the solution can be calculated by converting 898 g to 0.898 kg:

$$\begin{aligned} \text{molality} &= \frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}} \\ &= 2.73 \text{ m} \end{aligned}$$

Pressure and Solubility of Gases

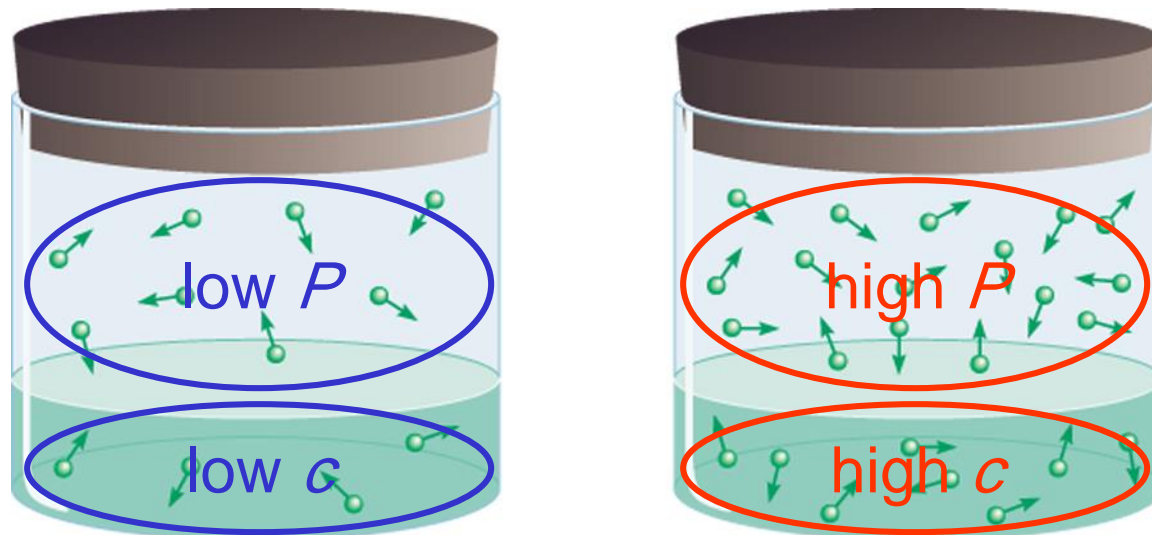
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = k_H P$$

c is the concentration (M) of the dissolved gas

P is the pressure of the gas over the solution

k_H is a constant for each gas ($\text{mol/L}\cdot\text{atm}$) that depends only on temperature

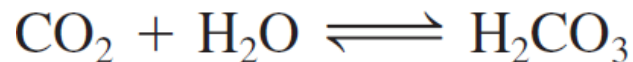


- Most gases obey Henry's law, but there are some important exceptions.
- For example, if the dissolved gas *reacts* with water, higher solubilities can result.

The solubility of **ammonia** is much higher than expected because of the reaction



Carbon dioxide also reacts with water, as follows:



Another interesting example is the dissolution of ***molecular oxygen in blood.***



EXAMPLE 12.6

The solubility of nitrogen gas at 25°C and 1 atm is 6.8×10^{-4} mol/L. What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

Solution The first step is to calculate the quantity k in Equation (12.3):

$$\begin{aligned}c &= kP \\6.8 \times 10^{-4} \text{ mol/L} &= k (1 \text{ atm}) \\k &= 6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm}\end{aligned}$$

Therefore, the solubility of nitrogen gas in water is

$$\begin{aligned}c &= (6.8 \times 10^{-4} \text{ mol/L} \cdot \text{atm})(0.78 \text{ atm}) \\&= 5.3 \times 10^{-4} \text{ mol/L} \\&= 5.3 \times 10^{-4} M\end{aligned}$$

Colligative Properties of Nonelectrolyte Solutions

Colligative 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,
 - freezing-point depression,
 - osmotic pressure.

Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

X_1 = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0 \quad X_2 = \text{mole fraction of the } \underline{\text{solute}}$$

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

EXAMPLE 12.7

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 is given in Table 5.3 (p. 200). Assume the density of the solution is 1.00 g/mL.

Solution

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 , is given by

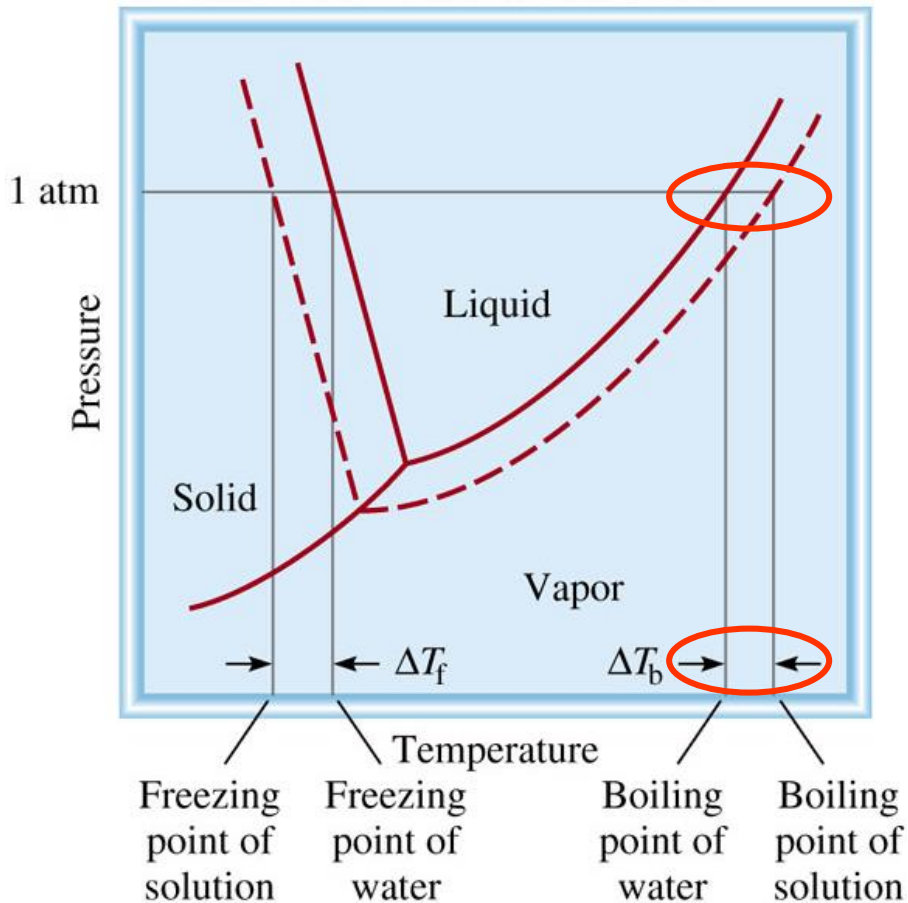
$$\begin{aligned} X_1 &= \frac{n_1}{n_1 + n_2} \\ &= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955 \end{aligned}$$

From Table 5.3, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

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

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

Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

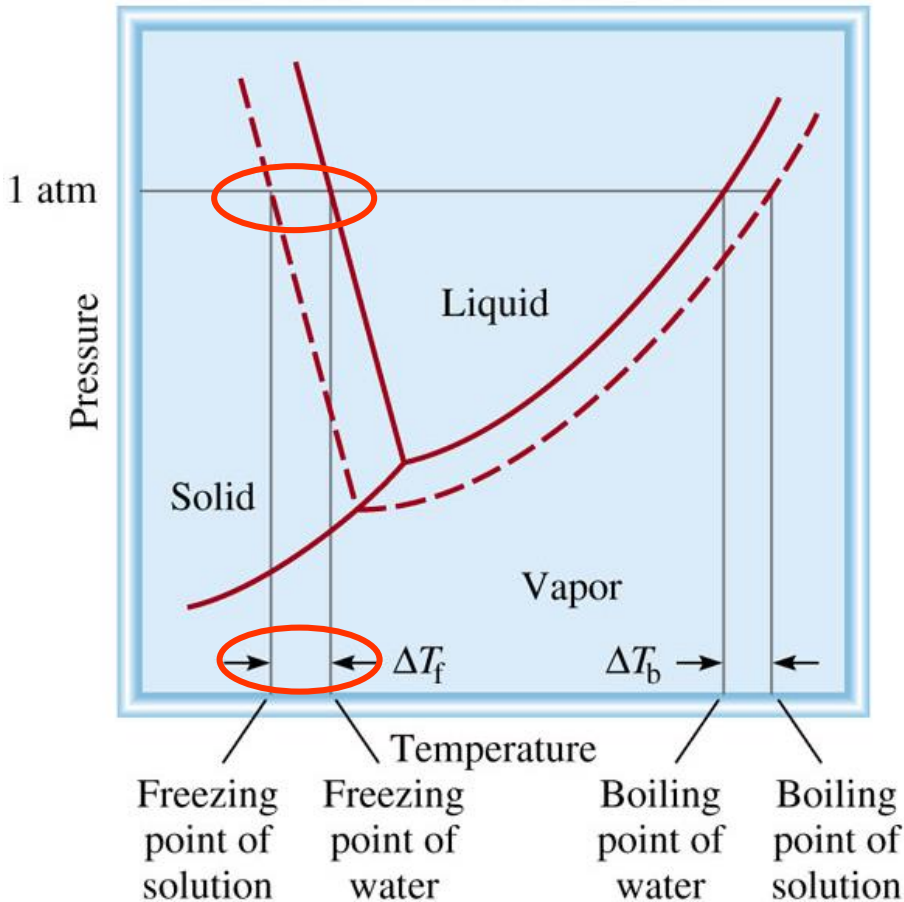
$$T_b > T_b^0 \quad \Delta T_b > 0$$

$$\Delta T_b = K_b m$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant ($^{\circ}\text{C}/m$) for a given solvent

Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$$T_f^0 > T_f \quad \Delta T_f > 0$$

$$\Delta T_f = K_f m$$

m is the molality of the solution

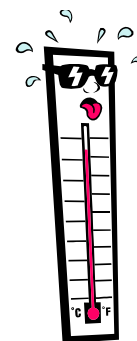
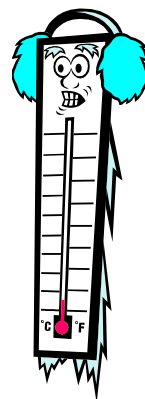
K_f is the molal freezing-point depression constant ($^{\circ}\text{C}/m$) for a given solvent

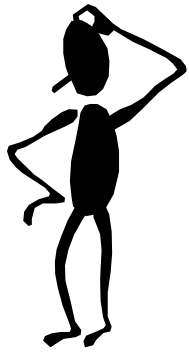
TABLE 12.2

Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point ($^{\circ}\text{C}$)*	K_f ($^{\circ}\text{C}/m$)	Normal Boiling Point ($^{\circ}\text{C}$)*	K_b ($^{\circ}\text{C}/m$)
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.





What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g/mol.

$$\Delta T_f = K_f m \quad K_f \text{ water} = 1.86 \text{ } ^\circ\text{C}/m$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478 \text{ g} \times \frac{1 \text{ mol}}{62.01 \text{ g}}}{3.202 \text{ kg solvent}} = 2.41 m$$

$$\Delta T_f = K_f m = 1.86 \text{ } ^\circ\text{C}/m \times 2.41 m = 4.48 \text{ } ^\circ\text{C}$$

$$\Delta T_f = T_f^0 - T_f$$

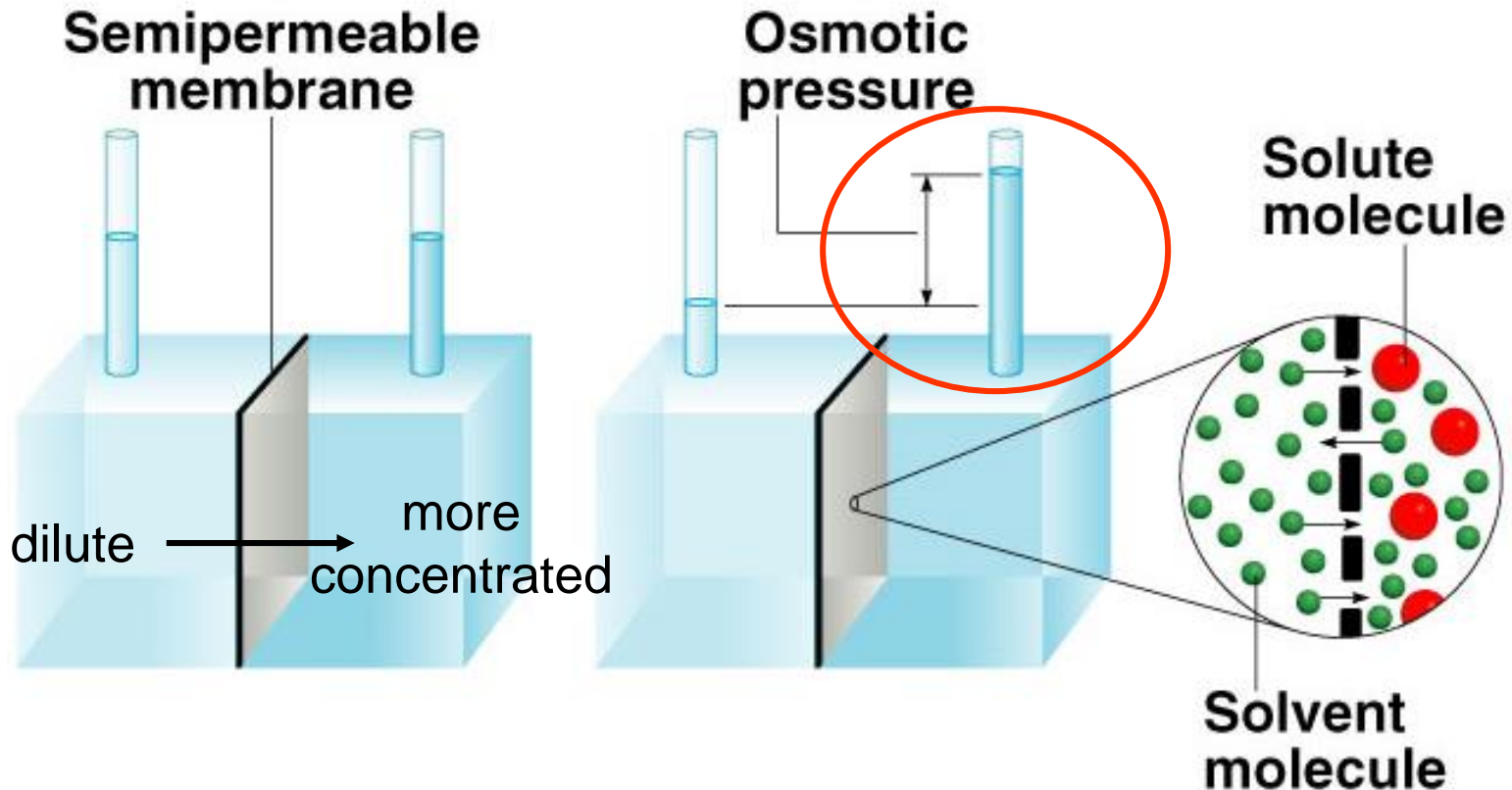
$$T_f = T_f^0 - \Delta T_f = 0.00 \text{ } ^\circ\text{C} - 4.48 \text{ } ^\circ\text{C} = -4.48 \text{ } ^\circ\text{C}$$

Osmotic Pressure (π)

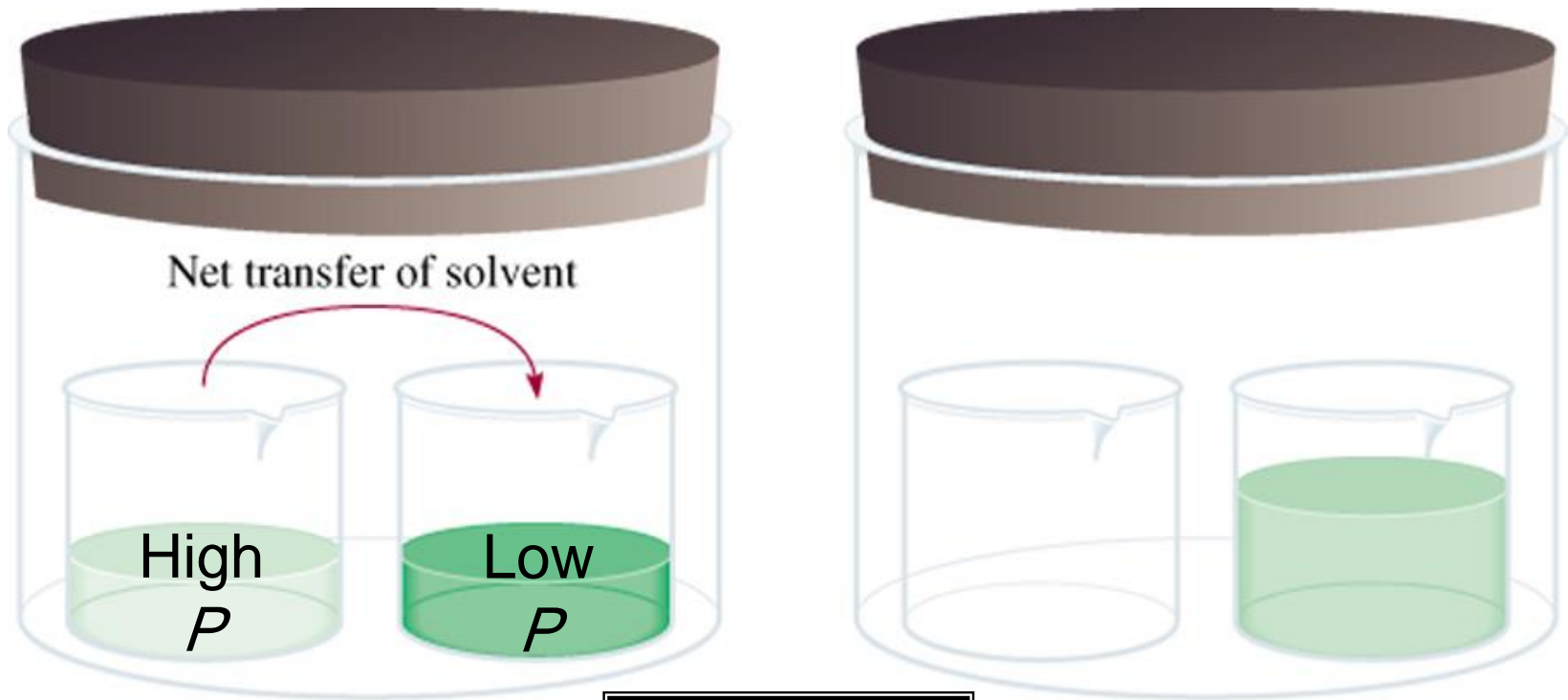
Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A **semipermeable membrane** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



Osmotic Pressure (π)



$$\pi = MRT$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

EXAMPLE 12.9

The average osmotic pressure of seawater, measured in the kind of apparatus shown in Figure 12.11, is about 30.0 atm at 25°C. Calculate the molar concentration of an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) that is isotonic with seawater.

Solution A solution of sucrose that is isotonic with seawater must have the same osmotic pressure, 30.0 atm. Using Equation (12.8).

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

Summary - Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

Boiling-Point Elevation $\Delta T_b = K_b m$

Freezing-Point Depression $\Delta T_f = K_f m$

Osmotic Pressure (π) $\pi = MRT$

Using Colligative Properties to Determine Molar Mass

From the experimentally determined freezing-point depression or osmotic pressure, We can calculate the molality or molarity of the solution. Knowing the mass of the solute, we can readily determine its molar mass,

EXAMPLE 12.10

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?

Solution The sequence of conversions for calculating the molar mass of the compound is

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

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

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

Thus, the molar mass of the solute is

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

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 12.11

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.

Solution The sequence of conversions is as follows:

$$\pi = MRT$$

$$M = \frac{\pi}{RT}$$

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

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb. We use this quantity to calculate the molar mass:

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