



Solutions and Their Physical Properties

References : General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette).

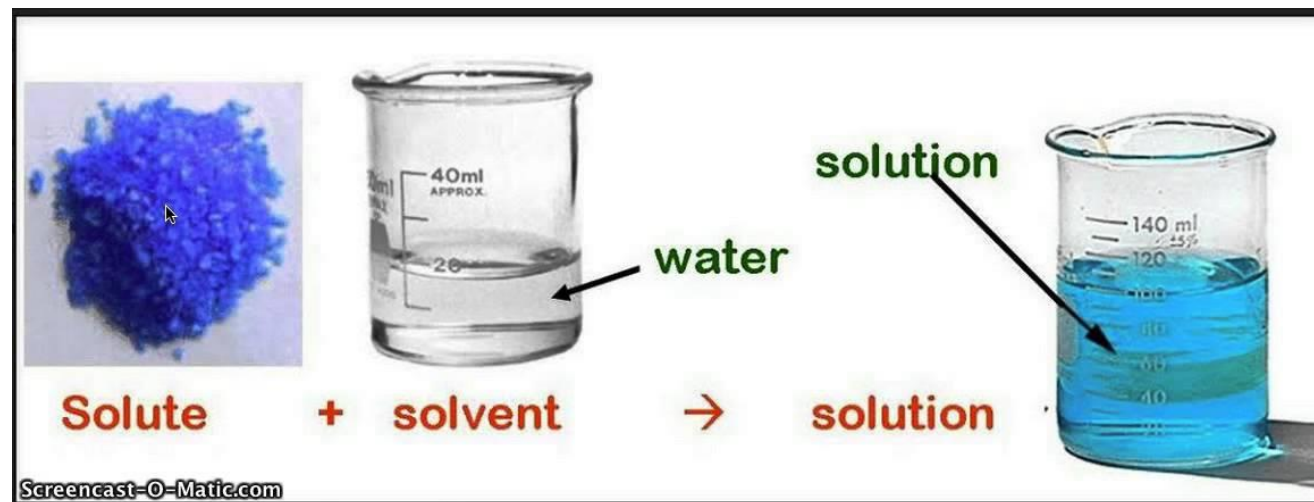
A solution is a **homogeneous mixture**.

It is **homogeneous** because its composition and properties are uniform, and **it is a mixture** because it contains two or more substances in proportions that can be varied.

- A solution is composed of a solvent and one or more solutes.

The solvent is the component that is present in the greatest quantity or that determines the state of matter in which the solution exists.

A solute is said to be dissolved in the solvent. A concentrated solution has a relatively large quantity of dissolved solute(s), and a dilute solution has only a small quantity.



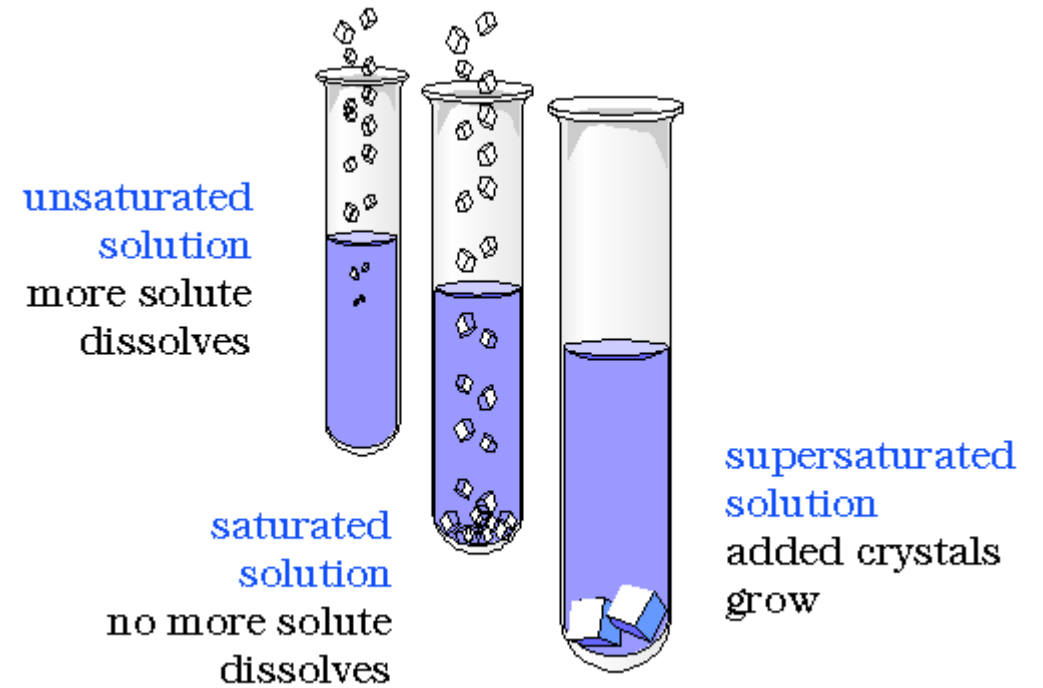
We can distinguish six types of solutions, depending on the original states (solid, liquid, or gas) of the solution components.

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)

Solutions are also characterized by their capacity to dissolve solute:

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 it has the capacity to dissolve. A third type, a **supersaturated solution**, contains more solute than is present in a saturated solution. Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals. Crystallization is the process in which dissolved solute comes out of solution and forms crystals.



Solution Concentration

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

The concentration of a solution can be expressed in many different ways. Chemists use several different concentration units, each of which has advantages as well as limitations. Let us examine the four most common units of concentration: percent by mass, mole fraction, molarity, and molality.

Mass Percent, Volume Percent, and Mass/Volume Percent

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

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$

**The percent by mass is a unitless number because it is a ratio of two similar quantities.

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?

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Solution We write

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

Parts per Million, Parts per Billion, and Parts per Trillion

In solutions where the mass or volume percent of a component is very low, we often switch to other units to describe solution concentration.

For example, 1 mg solute/L solution amounts to only 0.001 g/L. A solution that is this dilute will have the same density as water, approximately 1 g/mL; therefore, the solution concentration is 0.001 g solute/100 g solution, which is the same as 1 g solute/1000000 g solution. We can describe the solute concentration more succinctly as **1 part per million (ppm)**. For a solution with only 1 μg solute/ L solution, the situation is 1×10^{-6} g solute/100 g solution, or 1 g solute/ 1×10^9 g solution. Here, the solute concentration is **1 part per billion (ppb)**. If the solute concentration is 1 ng solute/ L solution, the concentration is **1 part per trillion (ppt)**.

$$ppm = \frac{1 \text{ g solute}}{10^6 \text{ g of solution}} \approx \frac{1 \text{ mg solute}}{\text{L solution}}$$

$$ppb = \frac{1 \text{ g solute}}{10^9 \text{ g of solution}} \approx \frac{1 \mu\text{g solute}}{\text{L solution}}$$

$$ppt = \frac{1 \text{ g solute}}{10^{12} \text{ g of solution}} \approx \frac{1 \text{ ng solute}}{\text{L solution}}$$

Mole Fraction and Mole Percent

To relate certain physical properties (such as vapor pressure) to solution concentration, we need a unit in which all solution components are expressed on a mole basis.

We can do this with the mole fraction. The mole fraction of component i , designated x_i , is the fraction of all the molecules in a solution that are of type i . The mole fraction of component j is x_j and so on. The mole fraction of a solution component is defined as;

$$x_i = \frac{\text{amount of component } i \text{ (in moles)}}{\text{total amount of all solution components (in moles)}}$$

The sum of the mole fractions of all the solution components is 1.

$$x_i + x_j + x_k + \cdots = 1$$

The mole percent of a solution component is the percent of all the molecules in solution that are of a given type.

Mole percents are mole fractions multiplied by 100%

Molarity

The composition of a solution may be specified by giving its molar concentration (or molarity), which is defined as the number of moles of solute in 1 L of solution;

that is,

$$\text{molarity} = \frac{\text{amount of solute (in moles)}}{\text{volume of solution (in liters)}}$$

The expression above can be written more compactly as

$$c = \frac{n}{V}$$

where c is the molarity in moles per liter (mol/L), n is the amount of solute in moles (mol), and V is the volume of the solution in liters (L).

If 0.440 mol urea, is dissolved in enough water to make 1.000 L of solution, the solution concentration, or molarity, is

$$\frac{0.440 \text{ mol CO(NH}_2)_2}{1.000 \text{ L soln}} = 0.440 \text{ M CO(NH}_2)_2$$

EXAMPLE 4-7**Calculating Molarity from Measured Quantities**

A solution is prepared by dissolving 25.0 mL ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ ($d = 0.789 \text{ g/mL}$), in enough water to produce 250.0 mL solution. What is the molarity of ethanol in the solution?

The molar mass of EtOH=46.07 g/mol

EXAMPLE 4-7 Calculating Molarity from Measured Quantities

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The number of moles of ethanol in a 25.0 mL sample of pure ethanol is calculated below in a single line.

$$\begin{aligned} ? \text{ mol CH}_3\text{CH}_2\text{OH} &= 25.0 \text{ mL CH}_3\text{CH}_2\text{OH} \times \frac{0.789 \text{ g CH}_3\text{CH}_2\text{OH}}{1 \text{ mL CH}_3\text{CH}_2\text{OH}} \times \frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \\ &= 0.428 \text{ mol CH}_3\text{CH}_2\text{OH} \end{aligned}$$

To apply the definition of molarity given in expression (4.3), note that $250.0 \text{ mL} = 0.2500 \text{ L}$.

$$\text{molarity} = \frac{0.428 \text{ mol CH}_3\text{CH}_2\text{OH}}{0.2500 \text{ L soln}} = 1.71 \text{ M CH}_3\text{CH}_2\text{OH}$$

Molality is the number of moles of solute dissolved in 1 kg (1000 g) of solvent—that is,

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

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.

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Strategy To calculate the molality, we need to know the number of moles of methanol and the mass of solvent in kilograms. We assume 1 L of solution, so the number of moles of methanol is 2.45 mol.

$$m = \frac{\text{moles of solute} \leftarrow \text{given}}{\text{mass of solvent (kg)} \leftarrow \text{need to find}}$$

want to calculate \nearrow

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

$$\begin{aligned} \text{mass of H}_2\text{O} &= \text{mass of soln} - \text{mass of solute} \\ &= 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) \\ &= 898 \text{ g} \end{aligned}$$

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

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

Practice Exercise Calculate the molality of a 5.86 *M* ethanol (C₂H₅OH) solution whose density is 0.927 g/mL.

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.

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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.

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

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

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

Molarity (M)

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

Molality (m)

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



EXAMPLE 14-1 Expressing a Solution Concentration in Various Units

An ethanol–water solution is prepared by dissolving 10.00 mL of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ ($d = 0.789 \text{ g/mL}$), in a sufficient volume of water to produce 100.0 mL of a solution with a density of 0.982 g/mL (Fig. 14-1). What is the concentration of ethanol in this solution expressed as (a) volume percent; (b) mass percent; (c) mass/volume percent; (d) mole fraction; (e) mole percent; (f) molarity; (g) molality?

(The molar mass of $\text{EtOH} = 46.07 \text{ g/mol}$, $\text{H}_2\text{O} = 18 \text{ g/mol}$)

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Analyze

Each part of this problem uses an equation presented in the text. Expressing concentrations in these different units will illustrate the similarities and differences among volume percent, mass percent, mass/volume percent, mole fraction, mole percent, molarity, and molality.

Solve

- (a) Volume percent ethanol

$$\text{volume percent ethanol} = \frac{10.00 \text{ mL ethanol}}{100.0 \text{ mL solution}} \times 100\% = 10.00\%$$

- (b) Mass percent ethanol

$$\begin{aligned} \text{mass ethanol} &= 10.00 \text{ mL ethanol} \times \frac{0.789 \text{ g ethanol}}{1.00 \text{ mL ethanol}} \\ &= 7.89 \text{ g ethanol} \end{aligned}$$

$$\text{mass soln} = 100.0 \text{ mL soln} \times \frac{0.982 \text{ g soln}}{1.0 \text{ mL solution}} = 98.2 \text{ g soln}$$

$$\text{mass percent ethanol} = \frac{7.89 \text{ g ethanol}}{98.2 \text{ g solution}} \times 100\% = 8.03\%$$

- (c) Mass/volume percent ethanol

$$\text{mass/volume percent ethanol} = \frac{7.89 \text{ g ethanol}}{100.0 \text{ mL solution}} \times 100\% = 7.89\%$$

(d) Mole fraction of ethanol

Convert the mass of ethanol from part (b) to an amount in moles.

$$\begin{aligned} ? \text{ mol CH}_3\text{CH}_2\text{OH} &= 7.89 \text{ g CH}_3\text{CH}_2\text{OH} \times \frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \\ &= 0.171 \text{ mol CH}_3\text{CH}_2\text{OH} \end{aligned}$$

Determine the mass of water present in 100.0 mL of solution.

$$98.2 \text{ g soln} - 7.89 \text{ g ethanol} = 90.3 \text{ g water}$$

Convert the mass of water to the number of moles present.

$$\begin{aligned} ? \text{ mol H}_2\text{O} &= 90.3 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 5.01 \text{ mol H}_2\text{O} \\ x_{\text{CH}_3\text{CH}_2\text{OH}} &= \frac{0.171 \text{ mol CH}_3\text{CH}_2\text{OH}}{0.171 \text{ mol CH}_3\text{CH}_2\text{OH} + 5.01 \text{ mol H}_2\text{O}} = \frac{0.171}{5.18} = 0.0330 \end{aligned}$$

(e) Mole percent ethanol

$$\text{mole percent CH}_3\text{CH}_2\text{OH} = x_{\text{CH}_3\text{CH}_2\text{OH}} \times 100\% = 0.0330 \times 100\% = 3.30\%$$

(f) Molarity of ethanol

Divide the number of moles of ethanol from part (d) by the solution volume, 100.0 mL = 0.1000 L.

$$\text{molarity} = \frac{0.171 \text{ mol CH}_3\text{CH}_2\text{OH}}{0.1000 \text{ L soln}} = 1.71 \text{ M}$$

(g) Molality of ethanol

First, convert the mass of water present in 100.0 mL of solution [from part (d)] to the unit kg.

$$? \text{ kg H}_2\text{O} = 90.3 \text{ g H}_2\text{O} \times \frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} = 0.0903 \text{ kg H}_2\text{O}$$

Use this result and the number of moles of CH₃CH₂OH from part (d) to establish the molality.

$$\text{molality} = \frac{0.171 \text{ mol CH}_3\text{CH}_2\text{OH}}{0.0903 \text{ kg H}_2\text{O}} = 1.89 \text{ mol kg}^{-1}$$

EXAMPLE 14-2 Converting Molarity to Mole Fraction

Laboratory ammonia is 14.8 M $\text{NH}_3(\text{aq})$ with a density of 0.8980 g/mL. What is x_{NH_3} in this solution?

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Analyze

In this problem we note that no volume of solution is stated, suggesting that our calculation can be based on any fixed volume of our choice. A convenient volume to work with is one liter. We need to determine the number of moles of NH_3 and of H_2O in one liter of the solution.

Solve

Find the number of moles of NH_3 by using the definition of molarity.

$$\text{moles of NH}_3 = 1.00 \text{ L} \times \frac{14.8 \text{ mol NH}_3}{1 \text{ L}} = 14.8 \text{ mol NH}_3$$

For moles of H_2O , first find mass of the solution by using solution density.

$$\text{mass of soln} = 1000.0 \text{ mL soln} \times \frac{0.8980 \text{ g soln}}{1.0 \text{ mL solution}} = 898.0 \text{ g soln}$$

Then use moles of NH_3 and molar mass to find the mass of NH_3 .

$$\text{mass of NH}_3 = 14.8 \text{ mol NH}_3 \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} = 252 \text{ g NH}_3$$

Find the mass of H_2O by subtracting the mass of NH_3 from the solution mass.

$$\text{mass of H}_2\text{O} = 898.0 \text{ g soln} - 252 \text{ g NH}_3 = 646 \text{ g H}_2\text{O}$$

Find moles of H_2O by multiplying by the inverse of the molar mass for H_2O .

$$\text{moles of H}_2\text{O} = 646 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 35.8 \text{ mol H}_2\text{O}$$

Find the mole fraction of ammonia x_{NH_3} by dividing moles NH_3 by the total number of moles of NH_3 and H_2O in the solution.

$$x_{\text{NH}_3} = \frac{14.8 \text{ mol NH}_3}{14.8 \text{ mol NH}_3 + 35.8 \text{ mol H}_2\text{O}} = 0.292$$

PRACTICE EXAMPLE A: A 16.00% aqueous solution of glycerol, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, by mass, has a density of 1.037 g/mL. What is the mole fraction of glycerol in this solution?

PRACTICE EXAMPLE B: A 10.00% aqueous solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, by mass, has a density of 1.040 g/mL. What is (a) the molarity; (b) the molality; and (c) the mole fraction of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in this solution?

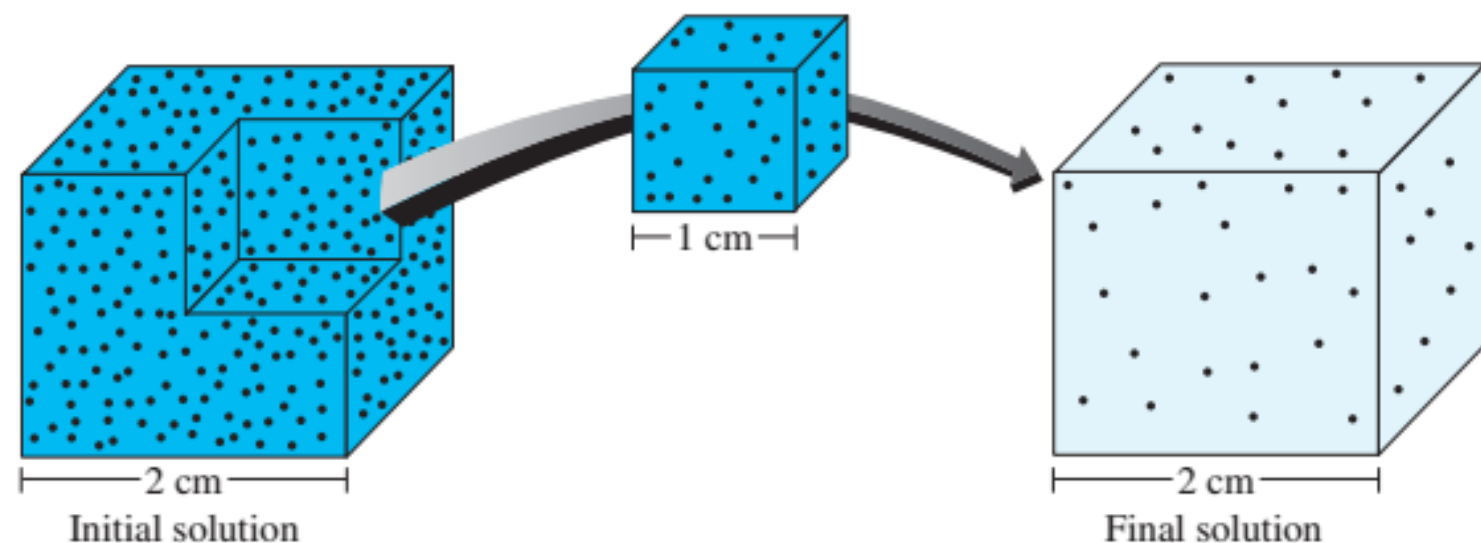
Solution Dilution

A common sight in chemistry storerooms and laboratories is rows of bottles containing solutions for use in chemical reactions. It is not practical, however, to store solutions of every possible concentration. Instead, most labs store fairly concentrated solutions, so-called *stock solutions*, which can then be used to prepare more dilute solutions by adding water. The principle of dilution, which you have probably already inferred, is that the same solute that was present in a sample of stock solution is distributed throughout the larger volume of a diluted solution (see Figure 4-6).

When a volume of a solution is diluted, the amount of solute *remains constant*. If we write equation (4.4) for the initial (i) undiluted solution, we obtain $n_i = c_i V_i$; for the final (f) diluted solution, we obtain $n_f = c_f V_f$. Because n_i is equal to n_f , we obtain the following result:

$$c_i V_i = c_f V_f \quad (4.5)$$

Figure 4-7 illustrates the laboratory procedure for preparing a solution by dilution. Example 4-9 explains the necessary calculation.



▲ FIGURE 4-6

Visualizing the dilution of a solution

The final solution is prepared by extracting $\frac{1}{8}$ of the initial solution— 1 cm^3 —and diluting it with water to a volume of 8 cm^3 . The number of dots in the 8 cm^3 of final solution, representing the number of solute particles, is the same as in the 1 cm^3 of initial solution.

KEEP IN MIND

that equation (4.5) applies only to dilution problems. An alternative expression uses the subscripts 1 and 2 in place of *i* and *f*: $c_1V_1 = c_2V_2$. Some students mistakenly use $c_1V_1 = c_2V_2$ to convert from moles of substance 1 to moles of substance 2 when doing stoichiometry problems. To avoid making this mistake, always use the subscripts “*i*” and “*f*” when using equation (4.5), or even better, use the subscripts “dil” (for diluted) and “conc” (for concentrated):

$$c_{\text{dil}}V_{\text{dil}} = c_{\text{conc}}V_{\text{conc}}$$

EXAMPLE 4-9 Preparing a Solution by Dilution

A particular analytical chemistry procedure requires 0.0100 M K_2CrO_4 . What volume of 0.250 M K_2CrO_4 must be diluted with water to prepare 0.2500 L of 0.0100 M K_2CrO_4 ?

First, calculate the amount of solute that must be present in the final solution.

$$? \text{ mol K}_2\text{CrO}_4 = 0.2500 \text{ L soln} \times \frac{0.0100 \text{ mol K}_2\text{CrO}_4}{1 \text{ L soln}} = 0.00250 \text{ mol K}_2\text{CrO}_4$$

Second, calculate the volume of 0.250 M K_2CrO_4 that contains 0.00250 mol K_2CrO_4 .

$$? \text{ L soln} = 0.00250 \text{ mol K}_2\text{CrO}_4 \times \frac{1 \text{ L soln}}{0.250 \text{ mol K}_2\text{CrO}_4} = 0.0100 \text{ L soln}$$

$$V_i = V_f \times \frac{c_f}{c_i} = 250.0 \text{ mL} \times \frac{0.0100 \text{ M}}{0.250 \text{ M}} = 10.0 \text{ mL}$$

Comparison of Concentration Units

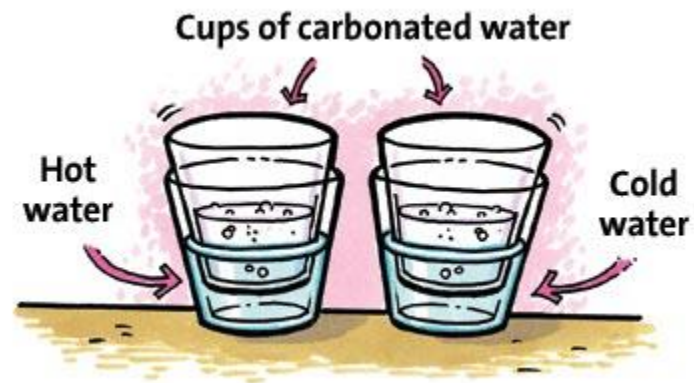
The choice of a concentration unit is based on the purpose of the experiment. For instance, the mole fraction is not used to express the concentrations of solutions for titrations and gravimetric analyses, but it is appropriate for calculating partial pressures of gases and for dealing with vapor pressures of solutions.

Suppose we prepare a solution at 20 by using a volumetric flask calibrated at 25. Then suppose we warm this solution to 25. As the temperature increases from 20 to 25 the amount of solute remains constant, but the solution volume increases slightly (by about 0.1%). The number of moles of solute per liter—the molarity—*decreases* slightly (by about 0.1%). This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

The Effect of Temperature on Solubility

Solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent at a specific temperature.

➤ Temperature affects the solubility of most substances.



Solubilities of Gases

Why does a freshly opened can of soda pop fizz, and why does the soda go flat after a time? To answer questions like these requires an understanding of the solubilities of gases. As discussed in this section, the effect of temperature on the solubility of gases is generally different from that on solid solutes. Additionally, the pressure of a gas strongly affects its solubility.

The solubility of gases in water usually decreases with increasing temperature. When water is heated in a beaker, you can see bubbles of air forming on the side of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.

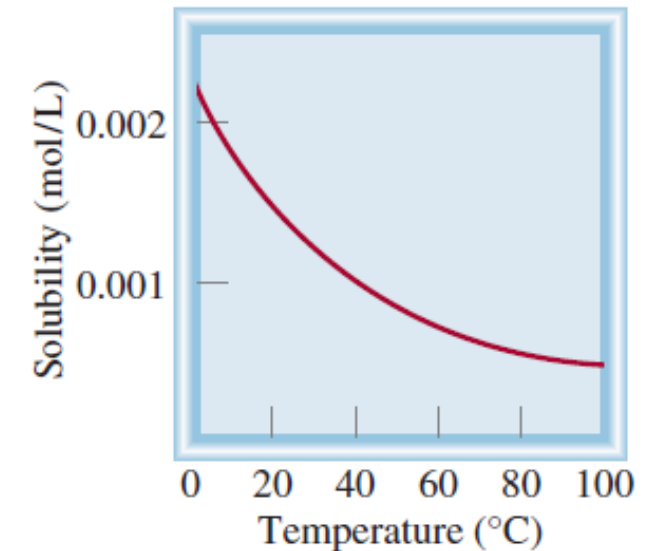
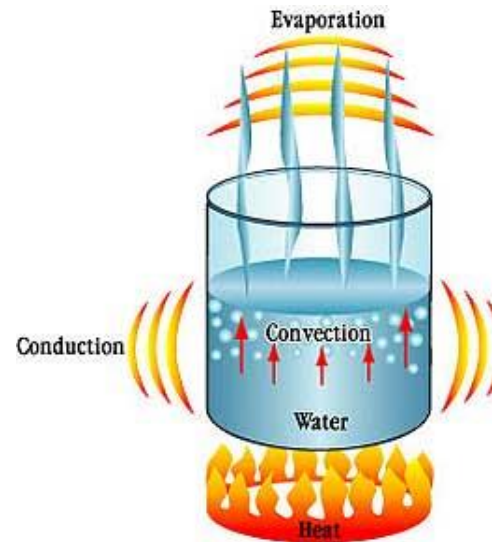


Figure 12.5 Dependence on temperature of the solubility of O₂ gas in water. Note that the solubility decreases as temperature increases.

The Effect of Pressure on the Solubility of Gases

For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases.

The quantitative relationship between gas solubility and pressure is given by **Henry's† law, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:**

$$C = k \times P_{\text{gas}}$$

$$c \propto P$$

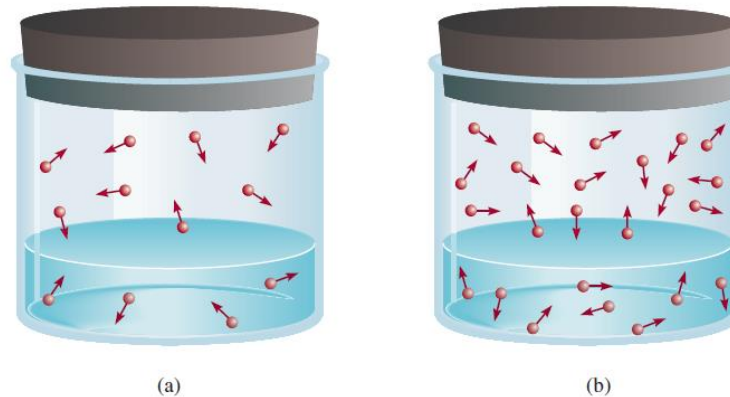
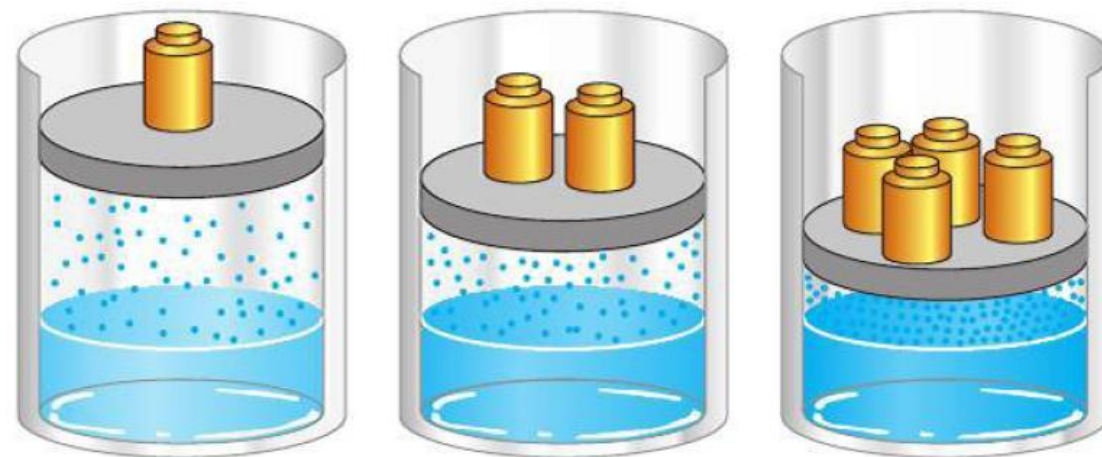


Figure 12.6 A molecular interpretation of Henry's law. When the partial pressure of the gas over the solution increases from (a) to (b), the concentration of the dissolved gas also increases according to Equation (12.3).

Here C is the molar concentration (mol/L) of the dissolved gas; P is the pressure (in atm) of the gas over the solution at equilibrium; and, for a given gas, k is a constant that depends only on temperature.

We can rationalize Henry's law as follows: In a saturated solution, the rate of evaporation of gas molecules from solution and the rate of condensation of gas molecules into the solution are equal. Both of these rates depend on the number of molecules per unit volume.

With increasing pressure on the system, the number of molecules per unit volume in the gaseous state increases (through an increase in the gas pressure), and the number of molecules per unit volume must also increase in the solution (through an increase in concentration).



Effect of pressure on the solubility of a gas

The concentration of dissolved gas (suggested by the depth of color) is proportional to the pressure of the gas above the solution (suggested by the density of the dots).

We see a practical application of Henry's law in carbonated beverages. The dissolved gas is carbon dioxide, and the higher the gas pressure maintained above the soda pop, the more that dissolves. When a bottle of soda is opened, some gas is released. As the gas pressure above the solution drops, dissolved is expelled, usually fast enough to cause fizzing.



▲ The unopened bottle of soda water is under a high pressure of $\text{CO}_2(\text{g})$. When a similar bottle is opened, the pressure quickly drops and some of the $\text{CO}_2(\text{g})$ is released from solution (bubbles).

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.

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Strategy The given solubility enables us to calculate Henry's law constant (k), which can then be used to determine the concentration of the solution.

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

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

The decrease in solubility is the result of lowering the pressure from 1 atm to 0.78 atm.

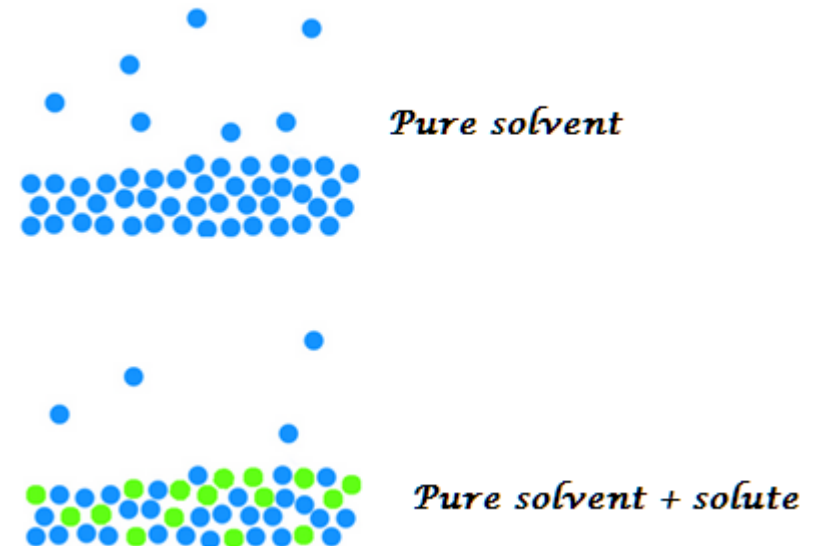
Vapor Pressures of Solutions

In the 1880s, the French chemist F. M. Raoult found that a dissolved solute *lowers the vapor pressure of the solvent*.

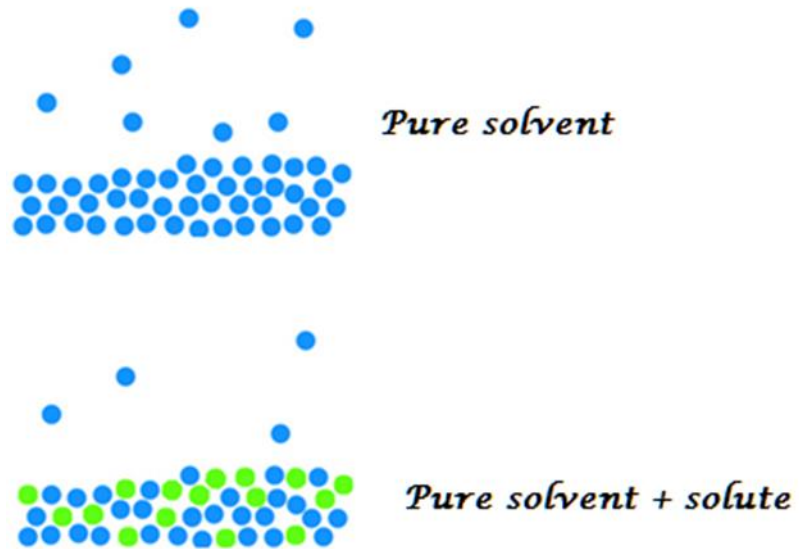
Raoult's law states that the partial pressure exerted by solvent vapor above an ideal solution, P_A , is the product of the mole fraction of solvent in the solution, x_A , and the vapor pressure of the pure solvent at the given temperature,

P_A° .

$$P_A = x_A P_A^\circ$$



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



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.

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$$P_1 = X_1 P_1^\circ$$

want to calculate \nearrow P_1 \nwarrow need to find
 \nwarrow X_1 \nearrow given

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 .

Osmotic Pressure

Many chemical and biological processes depend on *osmosis, the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.*

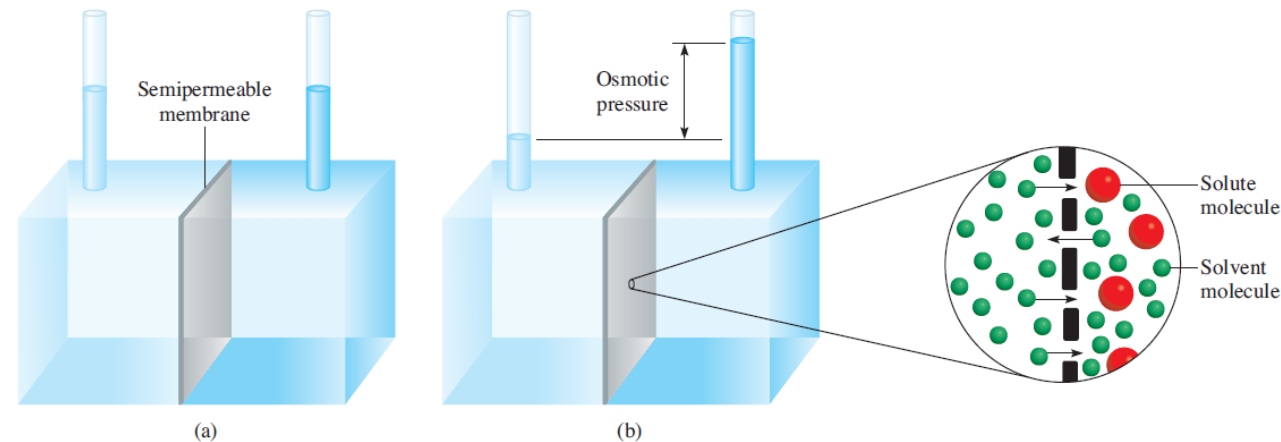
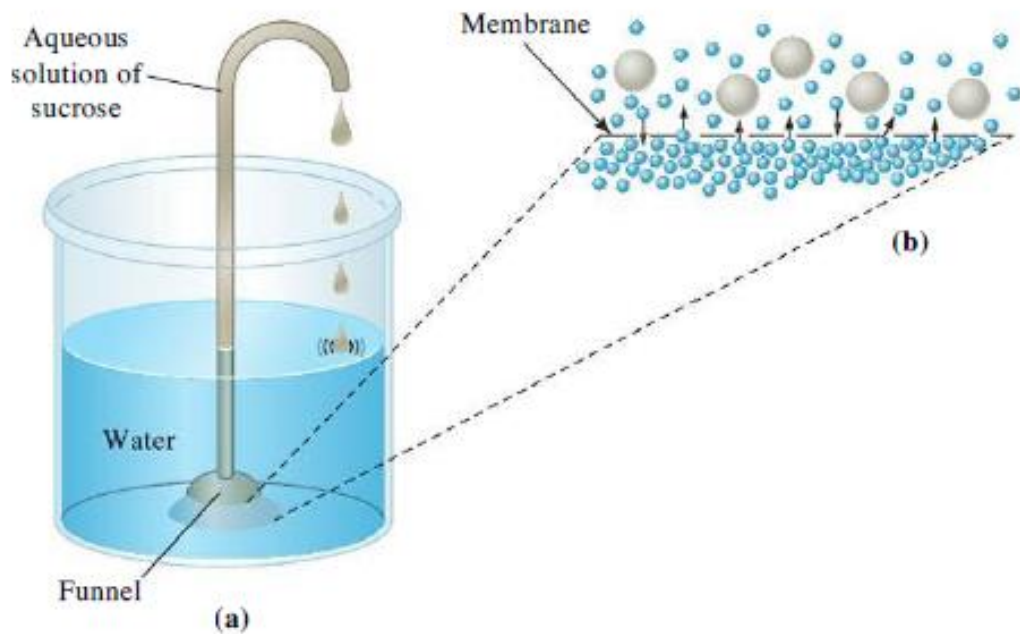


Figure 12.11 Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium. Basically, the same effect occurs when the pure solvent is replaced by a more dilute solution than that on the right.

An aqueous sucrose (sugar) solution in a long glass tube is separated from pure water by a semipermeable membrane (permeable to water only). Water molecules can pass through the membrane in either direction, and they do. But because the concentration of water molecules is greater in the pure water than in the solution, there is a net flow from the pure water into the solution. This net flow, called **osmosis**, causes the solution to rise in the tube. The more **concentrated** the sucrose solution, the higher the solution level rises.



Applying pressure to the sucrose solution slows down the net flow of water across the membrane into the solution. With a sufficiently high pressure, the net influx of water can be stopped altogether. The necessary pressure to stop osmotic flow is called the **osmotic pressure of the solution**.

The osmotic pressure of a solution is given by

$$\pi V = nRT$$

$$\pi = \frac{n}{V}RT = M \times RT$$

$$\pi = MRT$$

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, p , is expressed in atm.

- Osmotic pressure is directly proportional to the concentration of solution. This is what we would expect, because all colligative properties depend only on the number of solute particles in solution.
- 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.*

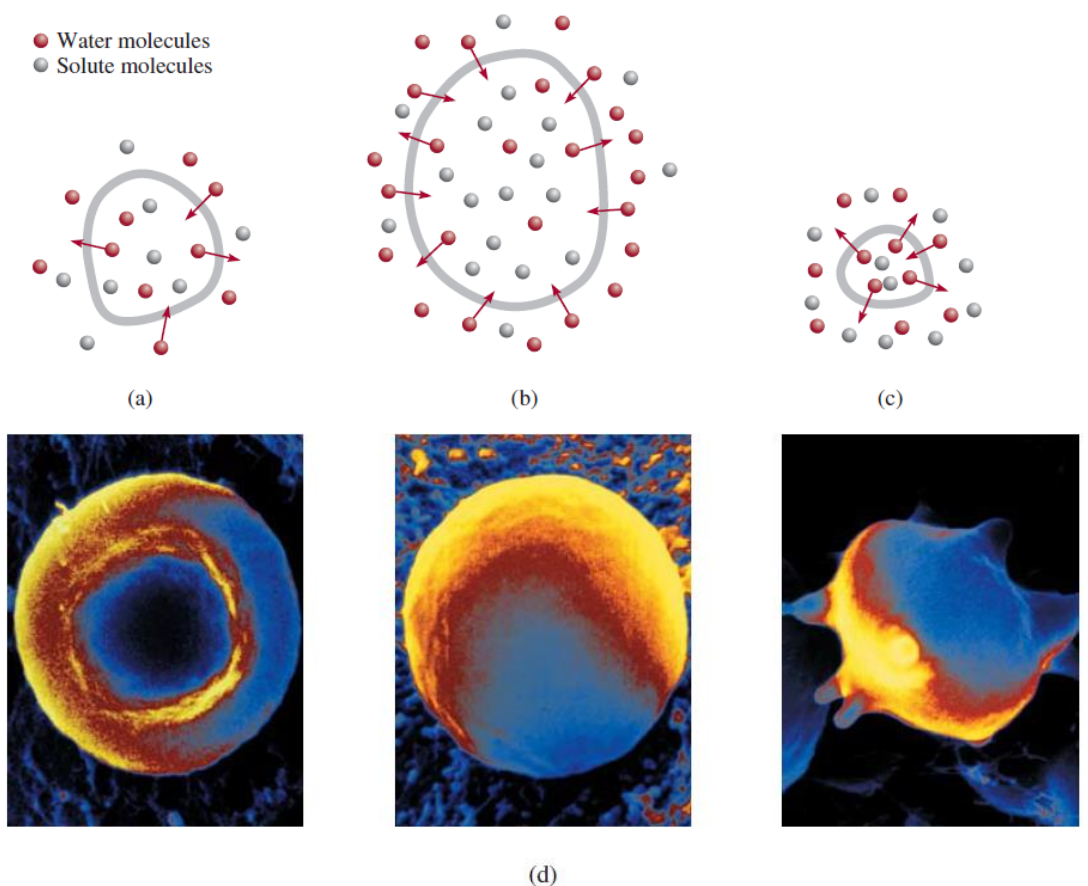


Figure 12.13 A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.

EXAMPLE 13-8 **Calculating Osmotic Pressure**

What is the osmotic pressure at 25 °C of an aqueous solution that is 0.0010 M $C_{12}H_{22}O_{11}$ (sucrose)?

EXAMPLE 13-8 Calculating Osmotic Pressure

What is the osmotic pressure at 25 °C of an aqueous solution that is 0.0010 M $C_{12}H_{22}O_{11}$ (sucrose)?

Analyze

We just need to substitute the data into equation (13.4).

Solve

$$\pi = \frac{0.0010 \text{ mol} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ L}}$$

$$\pi = 0.024 \text{ atm (18 mmHg)}$$

PRACTICE EXAMPLE A: What is the osmotic pressure at 25°C of an aqueous solution that contains 1.50 g $C_{12}H_{22}O_{11}$ in 125 mL of solution?

PRACTICE EXAMPLE B: What mass of urea [$CO(NH_2)_2$] would you dissolve in 225 mL of solution to obtain an osmotic pressure of 0.015 atm at 25 °C?

EXAMPLE 13-9 Establishing a Molar Mass from a Measurement of Osmotic Pressure

A 50.00 mL sample of an aqueous solution contains 1.08 g of human serum albumin, a blood-plasma protein. The solution has an osmotic pressure of 5.85 mmHg at 298 K. What is the molar mass of the albumin?

EXAMPLE 13-9 Establishing a Molar Mass from a Measurement of Osmotic Pressure

A 50.00 mL sample of an aqueous solution contains 1.08 g of human serum albumin, a blood-plasma protein. The solution has an osmotic pressure of 5.85 mmHg at 298 K. What is the molar mass of the albumin?

$$\pi = 5.85 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 7.70 \times 10^{-3} \text{ atm}$$

$$\pi V = nRT \quad \pi V = \frac{m}{M}RT \quad M = \frac{mRT}{\pi V}$$

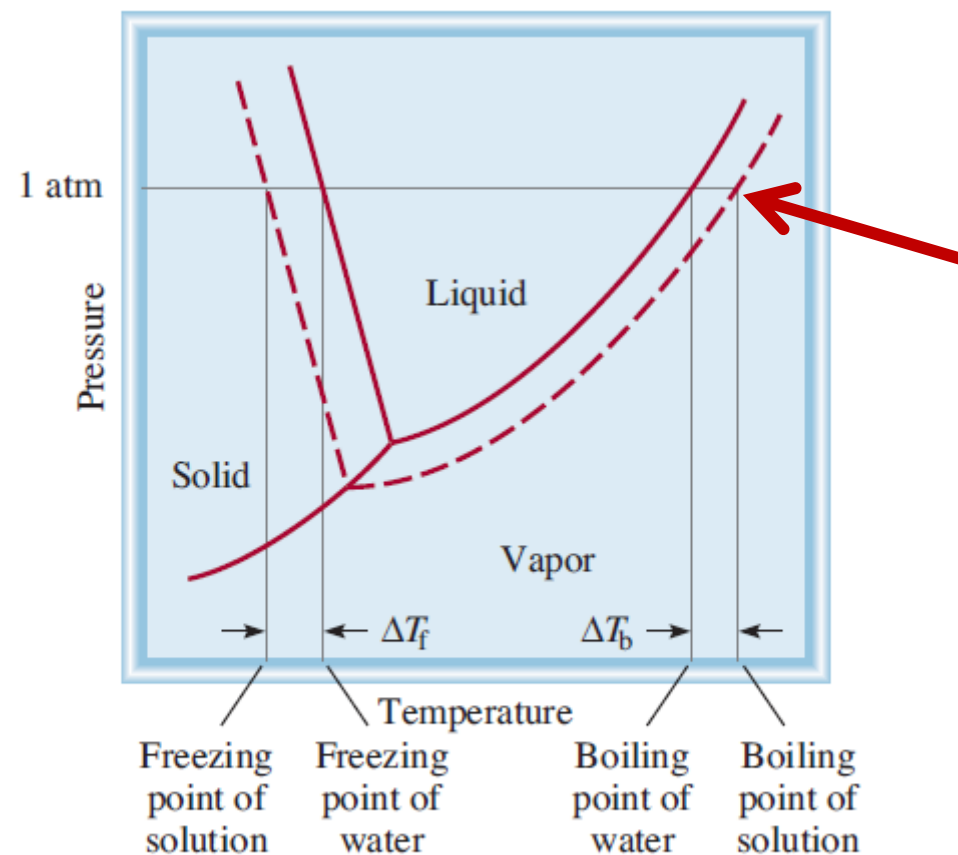
$$M = \frac{1.08 \text{ g} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{7.70 \times 10^{-3} \text{ atm} \times 0.0500 \text{ L}} = 6.86 \times 10^4 \text{ g/mol}$$

PRACTICE EXAMPLE A: Creatinine is a by-product of nitrogen metabolism and can be used to provide an indication of renal function. A 4.04 g sample of creatinine is dissolved in enough water to make 100.0 mL of solution. The osmotic pressure of the solution is 8.73 mmHg at 298 K. What is the molar mass of creatinine?

Boiling-Point Elevation

The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure. Because the presence of a nonvolatile solute lowers the vapor pressure of a solution, it must also affect the boiling point of the solution.

Figure shows the phase diagram of water and the changes that occur in an aqueous solution. Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent regardless of temperature, the liquid vapor curve for the solution lies below that for the pure solvent. Consequently, the dashed solution curve intersects the horizontal line that marks $P = 1 \text{ atm}$ at a *higher* temperature than the normal boiling point of the pure solvent. **This graphical analysis shows that the boiling point of the solution is higher than that of water.**



This graphical analysis;

shows that the boiling point of the solution is higher than that of water. The **boiling-point elevation** (ΔT_b) is defined as *the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°)*:

$$\Delta T_b = T_b - T_b^\circ$$

Because $T_b > T_b^\circ$, ΔT_b is a positive quantity.

The value of ΔT_b is proportional to the vapor-pressure lowering, and so it is also proportional to the concentration (molality) of the solution. That is,

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

where m is the molality of the solution and K_b is the *molal boiling-point elevation constant*. The units of K_b are $^\circ\text{C}/m$. It is important to understand the choice of concentration unit here. We are dealing with a system (the solution) whose temperature is *not* constant, so we cannot express the concentration units in molarity because molarity changes with temperature.

Freezing-Point Depression

A nonscientist may remain forever unaware of the boiling-point elevation phenomenon, but a careful observer living in a cold climate is familiar with freezing-point depression. Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl₂. This method of thawing succeeds because it depresses the freezing point of water.

Figure 12.10 shows that lowering the vapor pressure of the solution shifts the solid-liquid curve to the left. Consequently, this line intersects the horizontal line at a temperature *lower* than the freezing point of water. The **freezing point depression** (ΔT_f) is defined as *the freezing point of the pure solvent (T_f°) minus the freezing point of the solution (T_f)*:

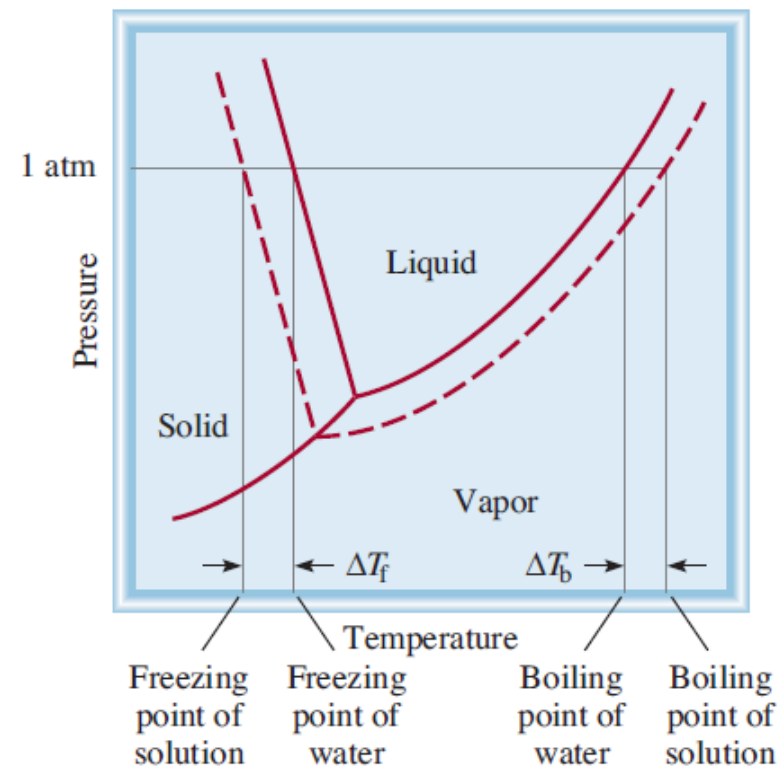
$$\Delta T_f = T_f^\circ - T_f$$

Because $T_f^\circ > T_f$, ΔT_f is a positive quantity. Again, ΔT_f is proportional to the concentration of the solution:

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where m is the concentration of the solute in molality units, and K_f is the *molal freezing-point depression constant* (see Table 12.2). Like K_b , K_f has the units $^\circ\text{C}/m$.



Freezing involves a transition from the disordered state to the ordered state. For this to happen, energy must be removed from the system. Because a solution has greater disorder than the solvent, more energy needs to be removed from it to create order than in the case of a pure solvent. Therefore, the solution has a lower freezing point than its solvent. Note that when a solution freezes, the solid that separates is the pure solvent component.

EXAMPLE 14-11 Predicting Colligative Properties for Electrolyte Solutions

Predict the freezing point of aqueous $0.00145 \text{ mol kg}^{-1} \text{ MgCl}_2$.

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Predict the freezing point of aqueous $0.00145 \text{ mol kg}^{-1} \text{ MgCl}_2$.

Analyze

We will use a modified freezing-point depression equation in which the van't Hoff factor i is included. We first note that MgCl_2 is a salt that completely dissociates when it is dissolved in water. So we determine the value of i for MgCl_2 . We can do this by writing an equation to represent the dissociation of $\text{MgCl}_2(\text{s})$. Then we use the appropriate freezing-point depression expression.

Solve



Because *three* moles of ions are obtained per mole of formula units dissolved, we expect the value $i = 3$.

Now use the expression

$$\begin{aligned} \Delta T_f &= -i \times K_f \times m \\ &= -3 \times 1.86 \text{ }^\circ\text{C mol}^{-1} \text{ kg} \times 0.00145 \text{ mol}^{-1} \text{ kg} \\ &= -0.0081 \text{ }^\circ\text{C} \end{aligned}$$

The predicted freezing point is $-0.0081 \text{ }^\circ\text{C}$.