



Solutions and Their Physical Properties

References : 1. General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette)
2. Chemistry-10th Edition (Raymond Chang)

Chemical Reactions in Solution

Most reactions in the general chemistry laboratory are carried out in solution. This is partly because mixing the reactants in solution helps to achieve the close contact between atoms, ions, or molecules necessary for a reaction to occur.



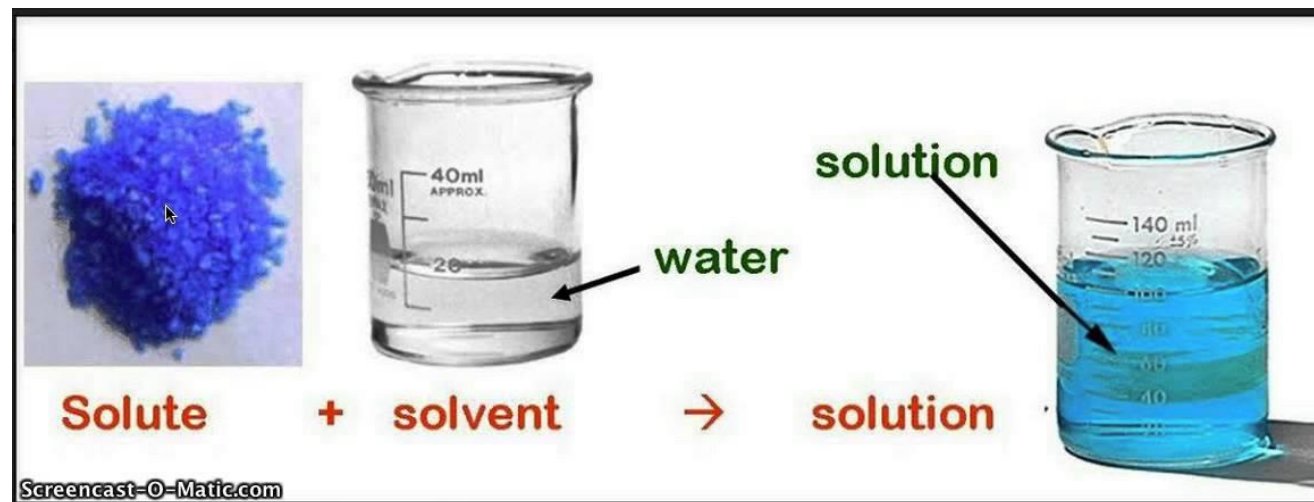
A solution is a **homogeneous mixture**.

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.



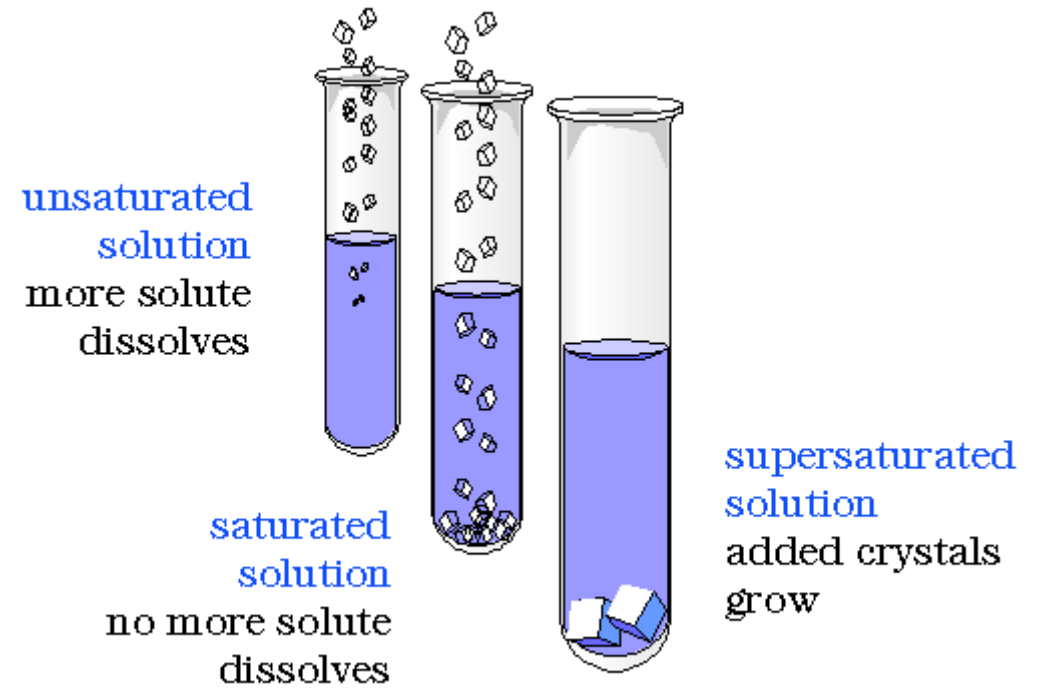
We can distinguish six types of solutions, depending on the original states (solid, liquid, or gas) of the solution components.

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.

Because liquid volumes are so easily measured, some solutions are prepared on a volume percent basis. For example, a handbook lists a freezing point of for a methyl alcohol–water antifreeze solution that is 25.0% by volume. Such a solution could be prepared by dissolving with water until the total solution volume is 100.0 mL.

Another possibility is to express the mass of solute and volume of solution. An aqueous solution with 0.9 g NaCl in 100.0 mL of solution is said to be 0.9% NaCl (mass/volume). Mass/volume percent is extensively used in the medical and pharmaceutical fields.

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).

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

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

Molarity (M)

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

Molality (m)

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



Comparison of Concentration Units

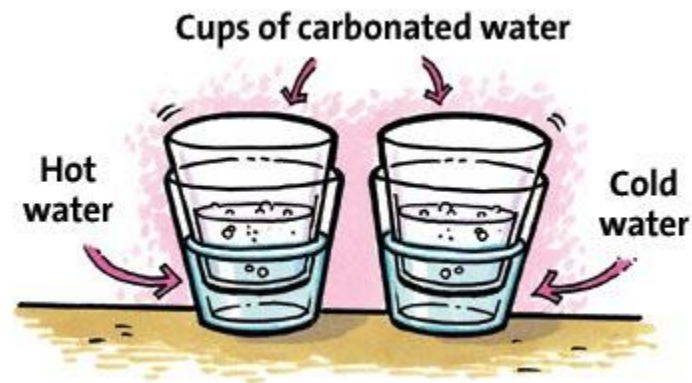
The choice of a concentration unit is based on the purpose of the experiment. For instance, the mole fraction is not used to express the concentrations of solutions for titrations and gravimetric analyses, but it is appropriate for calculating partial pressures of gases and for dealing with vapor pressures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

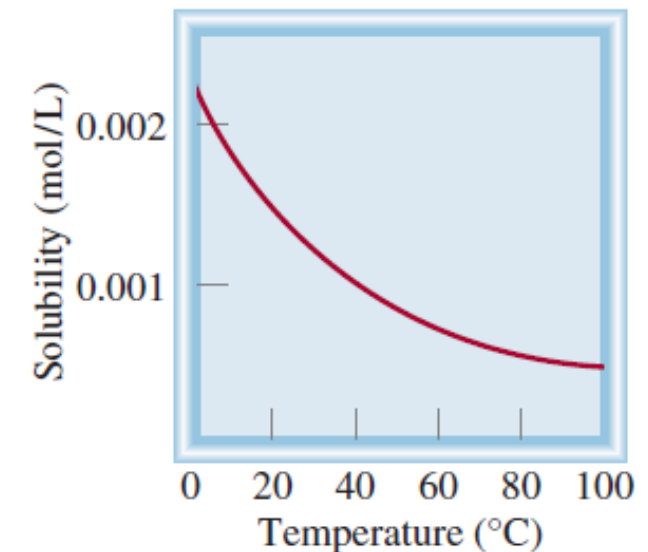
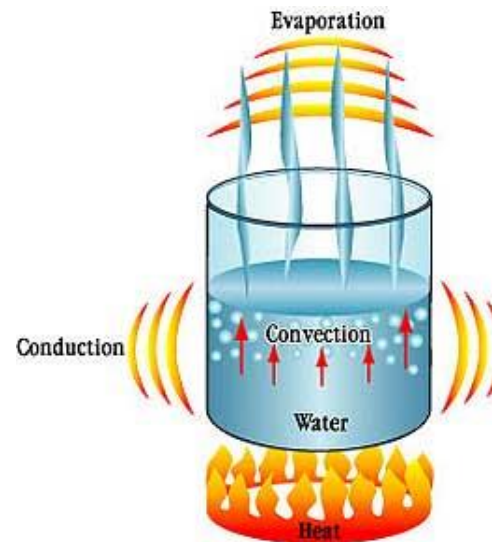


Figure 12.5 Dependence on temperature of the solubility of O₂ gas in water. Note that the solubility decreases as temperature increases.

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:**

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

$$c \propto P$$

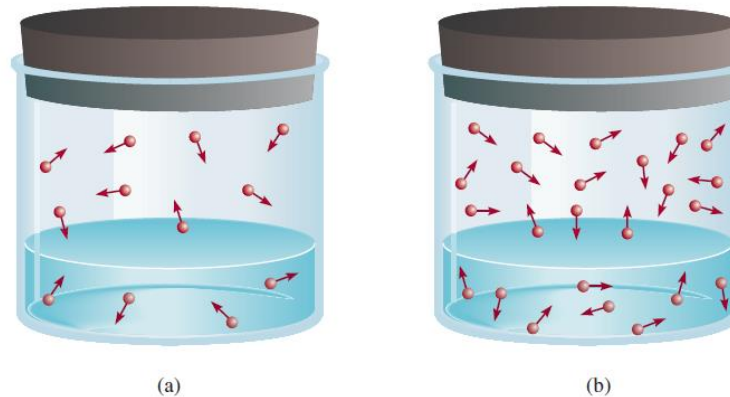
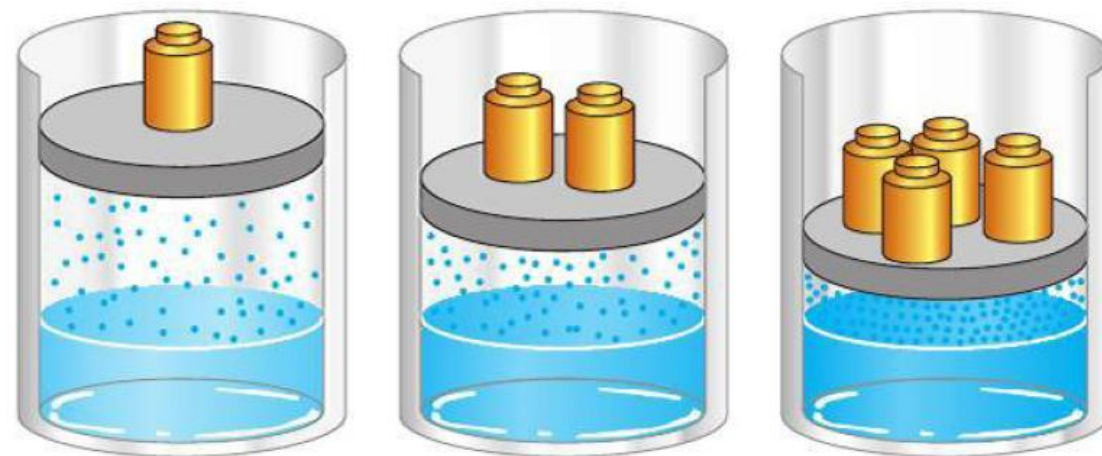


Figure 12.6 A molecular interpretation of Henry's law. When the partial pressure of the gas over the solution increases from (a) to (b), the concentration of the dissolved gas also increases according to Equation (12.3).

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).

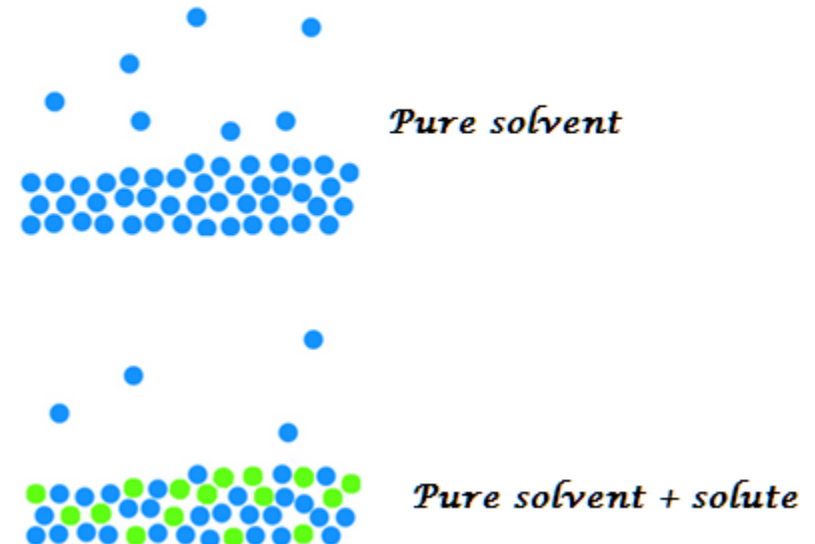
Vapor Pressures of Solutions

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

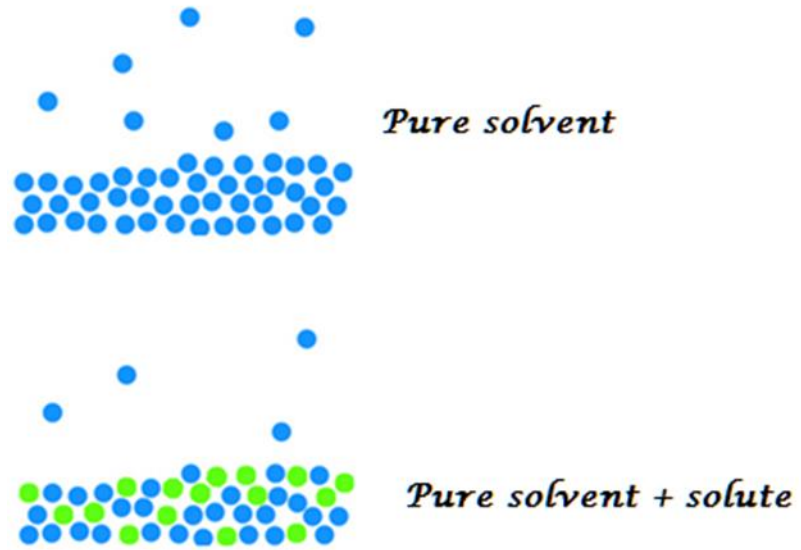
Raoult's law states that the partial pressure exerted by solvent vapor above an ideal solution, P_A , is the product of the mole fraction of solvent in the solution, x_A , and the vapor pressure of the pure solvent at the given temperature,

P_A° .

$$P_A = x_A P_A^\circ$$



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



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.*

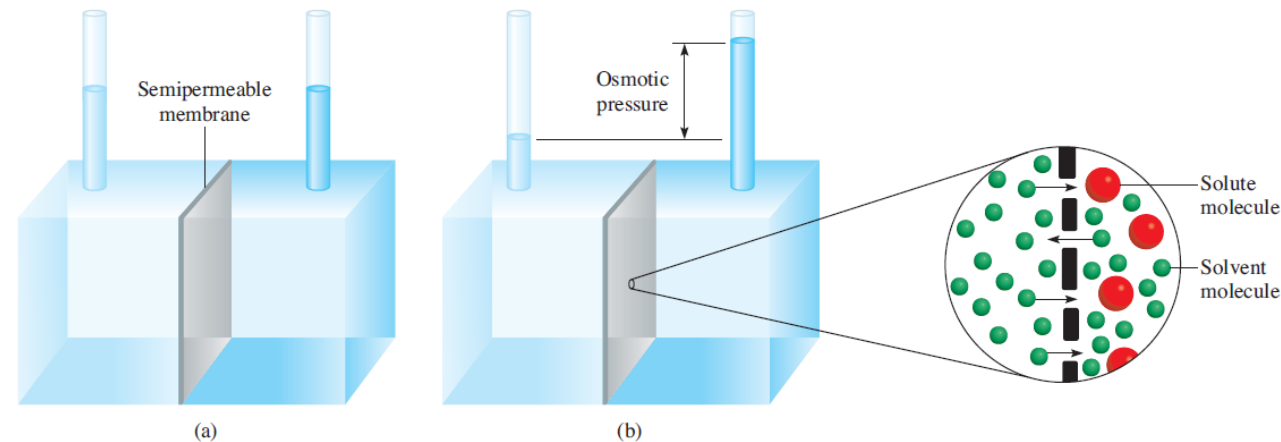
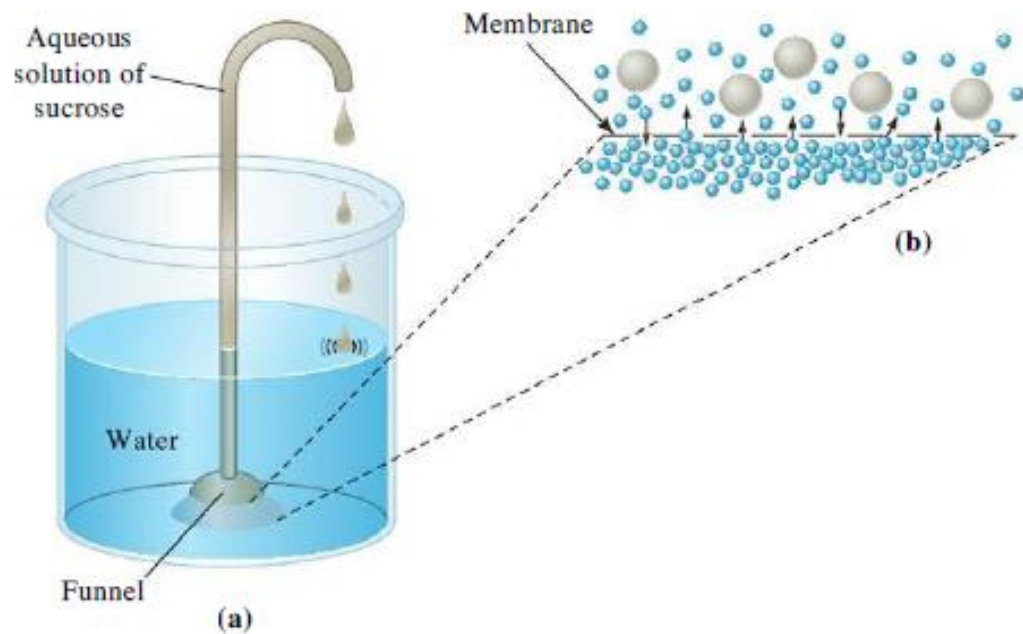


Figure 12.11 Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted 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.*

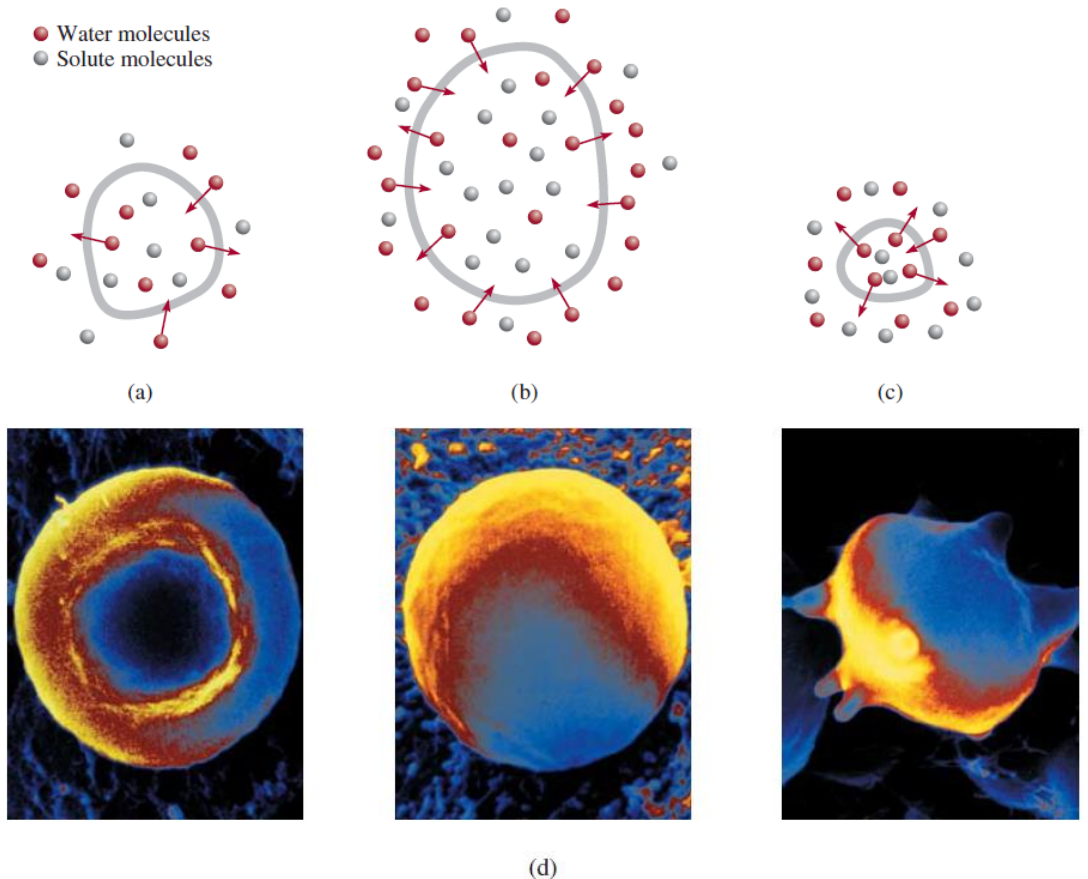
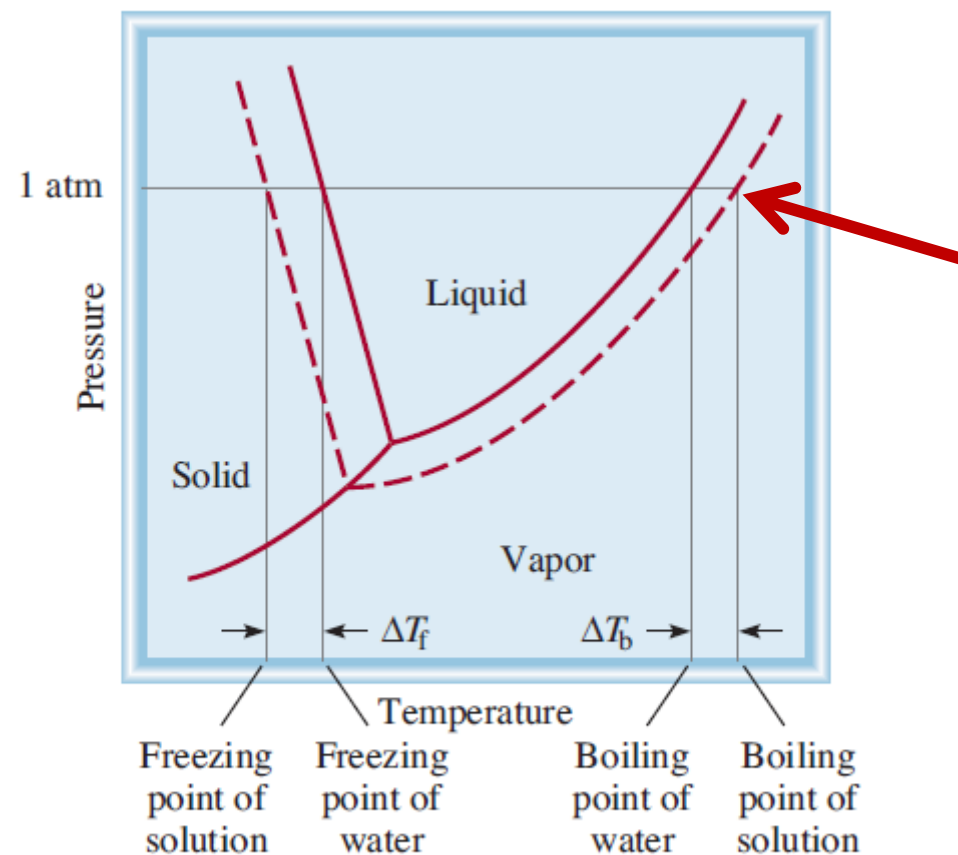


Figure 12.13 A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.

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 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,

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

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:

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

