10 Solutions

Collecting maple sap and converting it to maple syrup utilize many of the chemical principles found in this chapter.

Sugaring Off, c.1865 (oil on canvas), Johnson, Eastman (1824–1906) / Huntington Library and Art Gallery, San Marino, CA, USA/©The Huntington Library, Art Collections & Botanical Gardens/The Bridgeman Art Library

Water, water, everywhere,
And all the boards did shrink;
Water, water, everywhere,
Nor any drop to drink.

—SAMUEL TAYLOR COLERIDGE
From *The Rime of the Ancient Mariner*

Chapter Outline

In the course of a day, you use or make solutions many times. Your morning cup of coffee is a solution of solids (sugar and coffee) in a liquid (water). The gasoline you fill your gas tank with is a solution of several different liquid hydrocarbons. The soda you drink at a study break is a solution containing a gas (carbon dioxide) in a liquid (water).

A solution is a homogeneous mixture of a **solute** (substance being dissolved) distributed through a **solvent** (substance doing the dissolving). Solutions exist in any of the three physical states: gas, liquid, or solid. Air, the most common gaseous solution, is a mixture of nitrogen, oxygen, and lesser amounts of other gases. Many metal alloys are solid solutions. An example is the U.S. "nickel" coin (25% Ni, 75% Cu). The most familiar solutions are those in the liquid state, especially ones in which water is the solvent. Aqueous solutions are most important for our purposes in chemistry and will be emphasized in this chapter.

This chapter covers several of the physical aspects of solutions, including

- methods of expressing solution concentrations by specifying the relative amounts of solute and solvent (Section 10-1).
- factors affecting solubility, including the nature of the solute and the solvent, the temperature, and the pressure (Section 10-2).
- the effect of solutes on such solvent properties as vapor pressure, freezing point, and boiling point (Sections 10-3 and 10-4).

10-1 Concentration Units

Several different methods are used to express relative amounts of solute and solvent in a solution. Two concentration units, *molarity* and *mole fraction,* were referred to in previous chapters. Two others, *mass percent* and *molality,* are considered for the first time.

Molarity (*M*)

In Chapter 4, **molarity** was the concentration unit of choice in dealing with solution stoichiometry. You will recall that molarity is defined as

$$\text{molarity } (M) = \frac{\text{moles solute}}{\text{liters solution}}$$

A solution can be prepared to a specified molarity by weighing out the calculated mass of solute and dissolving in enough solvent to form the desired volume of solution. Alternatively, you can start with a more concentrated solution and dilute with water to give a solution of the desired molarity (Figure 10.1). The calculations are straightforward if you keep a simple point in mind: Adding solvent cannot change the number of moles of solute. That is,

It's easier to dilute a concentrated solution than to start from "scratch."

$$n_{\text{solute}} \text{ (concentrated solution)} = n_{\text{solute}} \text{ (dilute solution)}$$

In both solutions, n can be found by multiplying the molarity, M, by the volume in liters, V. Hence

$$M_c V_c = M_d V_d \qquad (10.1)$$

where the subscripts c and d stand for concentrated and dilute solutions, respectively.

The advantage of preparing solutions by the method illustrated in Figure 10.1 is that only volume measurements are necessary. If you wander into the general chemistry storeroom, you're likely to find concentrated "stock" solutions of various chemicals. Storeroom personnel prepare the more dilute solutions that you use in the laboratory on the basis of calculations like those in the following example.

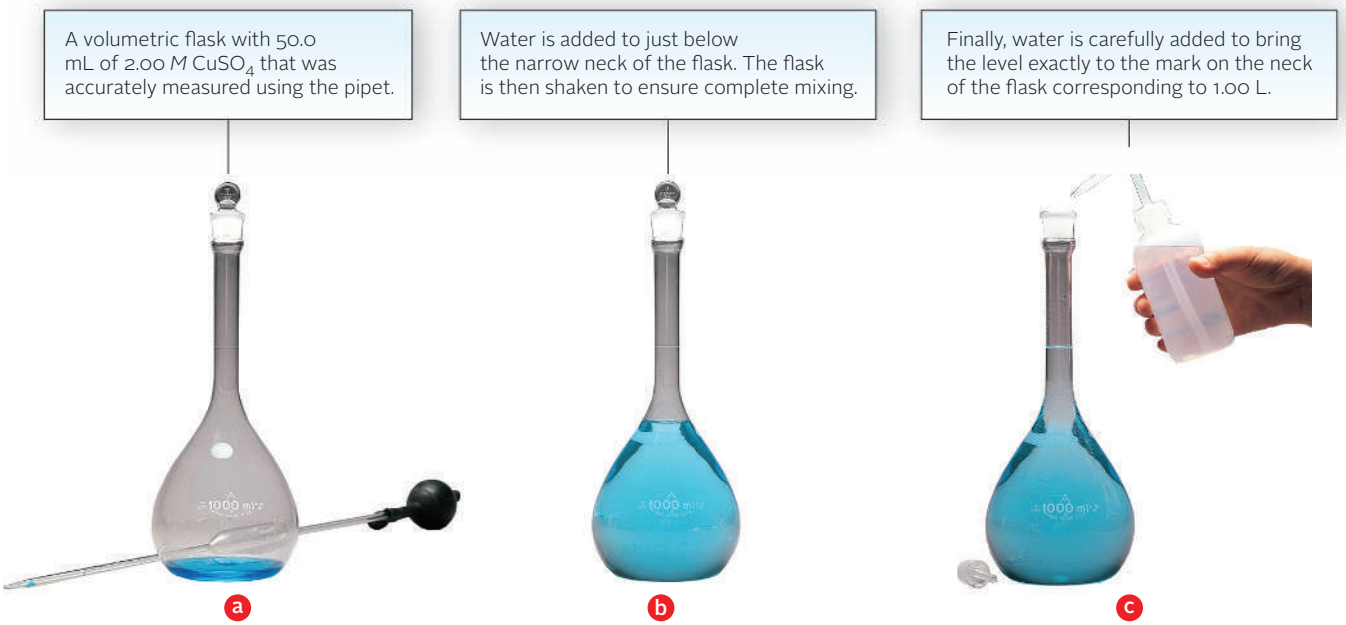

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Figure 10.1 Preparation of one liter of 0.100 *M* $CuSO_4$ by dilution.

EXAMPLE 10.1

Copper sulfate is widely used as a dietary supplement for animal feed. A lab technician prepares a "stock" solution of $CuSO_4$ by adding 40.00 g of $CuSO_4$ to enough water to make 500.0 mL of solution. An experiment requires a 0.1000 *M* solution of $CuSO_4$.

a What is the molarity of the $CuSO_4$ "stock" solution prepared by the technician?

ANALYSIS

Information given:	mass $CuSO_4$ (40.00 g); $V_{solution}$ (500.0 mL)
Information implied:	molar mass of $CuSO_4$
Asked for:	molarity of stock solution

STRATEGY

Recall (from Chapter 3) the definition of molarity:

$$M = \frac{\text{moles solute}}{\text{volume of solution (L)}}$$

SOLUTION

n_{CuSO_4}

$$40.00 \text{ g } CuSO_4 \times \frac{1 \text{ mol}}{159.6 \text{ g}} = 0.2506 \text{ mol}$$

$M_{\text{stock solution}}$

$$\frac{0.2506 \text{ mol}}{0.5000 \text{ L}} = 0.5013 \ M$$

b How would you prepare 1.500 L of 0.1000 *M* solution from the stock solution?

ANALYSIS

Information given:	for stock solution from part (a): M_c (0.5013 *M*) for diluted solution: M_d (0.1000 *M*); V_d (1.500 L)
Asked for:	how to prepare 1.500 L of 0.1000 *M* $CuSO_4$ from the stock solution

STRATEGY

1. The question really is: What volume of "stock" solution needs to be diluted to give the desired volume and molarity?
2. Substitute into Equation 10.1 to calculate V_c, the volume of the concentrated or stock solution.

$$M_c V_c = M_d V_d$$

SOLUTION

V_c

$$V_c = \frac{M_d V_d}{M_c} = \frac{(0.1000 \ M)\ (1.500 \text{ L})}{0.5013 \ M} = 0.2992 \text{ L}$$

Directions

Measure out 299.2 mL of the stock solution and dilute with enough water to make 1.500 L of solution.

END POINT

The molarity of the $CuSO_4$ stock solution (0.5013 *M*) is about five times what you need (0.1000 *M*), so it is reasonable to use only one fifth of the volume of the stock solution ($\approx$ 0.3 L $\rightarrow$ 1.500 L).

Mole Fraction (X)

Recall from Chapter 5 the defining equation for **mole fraction** (X) of a component A:

$$X_A = \frac{\text{moles A}}{\text{total moles}} = \frac{n_A}{n_{tot}}$$

The mole fractions of all components of a solution (A, B, . . .) must add to unity:

$$X_A + X_B + \cdots = 1$$

EXAMPLE 10.2

Hydrogen peroxide is used by some water treatment systems to remove the disagreeable odor of sulfides in drinking water. It is available commercially in a 30.0% by mass aqueous solution. What is the mole fraction of H_2O_2?

ANALYSIS

Information given:	mass percent of H_2O_2 (30.0%)
Information implied:	molar masses of H_2O_2 and H_2O
Asked for:	mol fraction (X) of H_2O_2

STRATEGY

1. Start with a fixed mass of solution such as one hundred grams.
2. Calculate moles H_2O_2 ($n_{H_2O_2}$), moles H_2O (n_{H_2O}), and find total moles (n_{tot}).
3. Substitute into the equation:

$$X_A = \frac{n_A}{n_{tot}}$$

SOLUTION

1. Assume 100.0 g of solution	mass H_2O_2 = 30.0 g; mass H_2O = 70.0 g
2. n_{H_2O}	$n_{H_2O} = \frac{70.0\text{ g}}{18.02\text{ g/mol}} = 3.88\text{ mol}$
$n_{H_2O_2}$	$n_{H_2O_2} = \frac{30.0\text{ g}}{34.02\text{ g/mol}} = 0.882\text{ mol}$
n_{tot}	$n_{tot} = n_{H_2O_2} + n_{H_2O} = 0.882\text{ mol} + 3.88\text{ mol} = 4.76\text{ mol}$
3. $X_{H_2O_2}$	$X_{H_2O_2} = \frac{n_{H_2O_2}}{n_{tot}} = \frac{0.882\text{ mol}}{4.76\text{ mol}} = 0.185$

END POINTS

1. Multiplying the mol fraction of H_2O_2 by 100% gives the mol percent of H_2O_2 in the solution (18.5%).
2. Notice that the mole percent (18.5) is considerably less than the mass percent (30.0) of H_2O_2 in solution. That is because the molar mass of H_2O_2 is larger than that of H_2O.

Mass Percent; Parts per Million; Parts per Billion

The **mass percent** of solute in solution is expressed quite simply:

$$\text{mass percent of solute} = \frac{\text{mass solute}}{\text{total mass solution}} \times 100\%$$

In a solution prepared by dissolving 24 g of NaCl in 152 g of water,

$$\text{mass percent of NaCl} = \frac{24\text{ g}}{24\text{ g} + 152\text{ g}} \times 100\% = \frac{24}{176} \times 100\% = 14\%$$

When the amount of solute is very small, as with trace impurities in water, concentration is often expressed in **parts per million** (ppm) or **parts per billion** (ppb).

In the United States, by law, drinking water cannot contain more than 5×10^{-8} g of arsenic per gram of water:

$$\text{ppm As} = \frac{5 \times 10^{-8}\text{ g}}{\text{g sample}} \times 10^6 = 0.05; \qquad \text{ppb As} = \frac{5 \times 10^{-8}\text{ g}}{\text{g sample}} \times 10^9 = 50$$

For very dilute aqueous solutions, 1 ppm is approximately equivalent to 1 mg/L. This is because the density of water at 25°C is 1.0 g/mL, and very dilute solutions have a density almost equal to that of pure water (1 g = 1 mL). Thus

$$1\text{ ppm} = \frac{1\text{ g solute}}{1 \times 10^6\text{ g solution}} = \frac{1\text{ g solute}}{1 \times 10^6\text{ mL solution}}$$

Converting g to mg and mL to L we get

$$\frac{1\text{ g solute}}{1 \times 10^6\text{ mL solution}} \times \frac{1000\text{ mg}}{1\text{ g}} \times \frac{1000\text{ mL}}{1\text{ L}} = 1\text{ mg/L}$$

Molality (*m*)

Molality and molarity are concentration units; morality is something else.

The concentration unit **molality,** symbol *m*, is the number of moles of solute per kilogram (1000 g) of solvent.

$$\text{molality } (m) = \frac{\text{moles solute}}{\text{kilograms solvent}}$$

You can readily calculate the molality of a solution if you know the masses of solute and solvent (Example 10.3).

EXAMPLE 10.3

Glucose, $C_6H_{12}O_6$, in water is often used for intravenous feeding. Sometimes sodium ions are added to the solution. A pharmacist prepares a solution by adding 2.0 mg of sodium ions (in the form of NaCl), 6.00 g of glucose, and 112 g of water.

a What is the molality of the glucose in solution?

ANALYSIS

Information given:	mass of glucose (6.00 g) mass of water (112 g)
Information implied:	molar mass of glucose
Asked for:	*m* of glucose

STRATEGY

1. Recall the definition of molality and identify the solute and solvent.

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

2. Find the numerator (moles of solute). Find the denominator (kg of solvent).
3. Substitute into the definition of *m*.

continued

SOLUTION

numerator

$$\text{moles solute (glucose)} = \frac{6.00 \text{ g glucose}}{180.16 \text{ g/mol}} = 0.0333$$

denominator

$$\text{mass of solvent } (H_2O) \text{ in kg} = 112 \text{ g}/1000 = 0.112 \text{ kg}$$

m

$$m = \frac{\text{moles glucose}}{\text{kg } H_2O} = \frac{0.0333 \text{ mol}}{0.112 \text{ kg}} = 0.297\ m$$

b How many ppm of Na^+ does the solution contain?

ANALYSIS

Information given: mass of Na^+ ions (2.0 mg), mass of glucose (6.00 g), mass of water (112 g)

Asked for: ppm Na^+

STRATEGY

Subsitute into the equation: $\text{ppm of } Na^+ = \frac{\text{mass } Na^+ \text{ (in grams)}}{\text{mass solution}} \times 10^6$

SOLUTION

mass of solution

$$\text{mass of solution} = \text{mass } Na^+ + \text{mass glucose} + \text{mass water}$$

$$\text{mass of solution} = \left(2.00 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}}\right) + 6.00 \text{ g} + 112 \text{ g} = 118 \text{ g}$$

ppm Na^+

$$\text{ppm} = \frac{\text{mass } Na^+}{\text{mass solution}} \times 10^6 = \frac{0.00200 \text{ g}}{118 \text{ g}} \times 10^6 = 17$$

END POINT

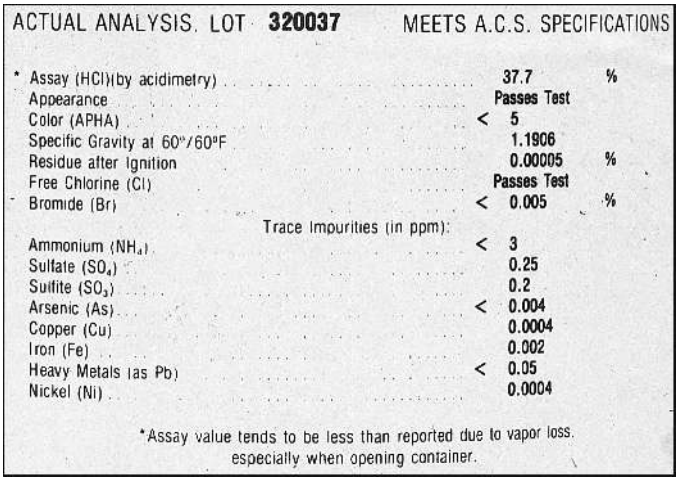
Theoretically, you would also need to calculate the mass of Cl^- ions and add that to the mass of Na^+, glucose, and water. Practically, the mass of Cl^- ions (like the mass of Na^+ ions) is negligible when compared with the mass of the solution.

Conversions Between Concentration Units

It is frequently necessary to convert from one concentration unit to another. This problem arises, for example, in making up solutions of hydrochloric acid. Typically, the analysis or assay that appears on the label (Figure 10.2) does not give the molarity or molality of the acid. Instead, it lists the mass percent of solute and the density of the solution.

Conversions between concentration units are relatively straightforward provided you *first decide on a fixed amount of solution*. The amount chosen depends on the unit in which concentration is originally expressed. Some suggested starting quantities are listed below.

When the Original Concentration Is	Start With
Mass percent	100 g solution
Molarity (M)	1.00 L solution
Molality (m)	1000 g solvent
Mole fraction (X)	1 mol (solute + solvent)


ACTUAL ANALYSIS. LOT 320037 MEETS A.C.S. SPECIFICATIONS

* Assay (HCl)(by acidimetry)	37.7	%
Appearance	Passes Test	
Color (APHA)	< 5	
Specific Gravity at 60°/60°F	1.1906	
Residue after Ignition	0.00005	%
Free Chlorine (Cl)	Passes Test	
Bromide (Br)	< 0.005	%
Trace Impurities (in ppm):		
Ammonium (NH_4)	< 3	
Sulfate (SO_4)	0.25	
Sulfite (SO_3)	0.2	
Arsenic (As)	< 0.004	
Copper (Cu)	0.0004	
Iron (Fe)	0.002	
Heavy Metals (as Pb)	< 0.05	
Nickel (Ni)	0.0004	

*Assay value tends to be less than reported due to vapor loss, especially when opening container.

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Figure 10.2 The label on a bottle of concentrated hydrochloric acid. The label gives the mass percent of HCl in the solution (known as the *assay*) and the density (or *specific gravity*) of the solution. The molality, molarity, and mole fraction of HCl in the solution can be calculated from this information.

Complex problems can usually be solved if you know where to start.

In these kinds of calculations, there can be many different types of concentration units that you need to obtain from one given concentration unit. To keep your data organized, it is best to prepare and fill in a table like the one below.

	moles	← MM → mass	density → volume
Solute			
Solvent			
Solution			


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Molarity and molality. On the left is a 0.10 *M* solution of potassium chromate. On the right is a 0.10 *m* solution that contains the same amount of potassium chromate (19.4 g, in dish). The 0.10 *M* solution was made by placing the solid in the flask and adding water to give 1 L of solution. The 0.10 *m* solution was prepared by placing the solid in the flask and adding 1000 g of water. You can see that the 0.10 *m* solution has a slightly larger volume.

Here is an illustration of how you can fill in and use the table. Suppose that you want to find the molality (*m*) of a solution X (MM = 100.0 g/mol) that is 1.35 *M* and has a density of 1.28 g/mL. The given concentration unit is molarity. Recall the definition of molarity (1.35 moles solute in 1000 mL of solution) and fill in the table accordingly. The concentration unit asked for is molality (moles solute in 1 kg of solvent). The table shown below has the given data filled in the appropriate spaces and the spots needed for the molality are shaded. Your table now looks like this:

	moles	← MM → mass	density → volume
Solute	1.35		
Solvent			
Solution			1000 mL

You can calculate the mass of the solvent if you know the mass of the solution and the mass of the solute. Since the density and the volume of the solution are known, the mass of the solution is 1280 g [(1.28 g/mL)(1000 mL)]. The mass of the solute is 135 g [(1.35 mol)(100.0 g/mol)]. Thus the mass of the solvent is 1145 g (1280 g − 135 g) or 1.145 kg.

Your table now looks like this:

	moles	← MM	mass	density →	volume
Solute	1.35		135 g		
Solvent			1145 g		
Solution			1280 g		1000 mL

Finding the molality is now simply a matter of using the data in the shaded spaces to fit the defintion of molality.

$$\text{molality } (m) = \frac{n_{\text{solute}}}{\text{mass solvent (kg)}} = \frac{1.35 \text{ mol}}{1.145 \text{ kg}} = 1.18\ m$$

EXAMPLE 10.4 GRADED

Consider the information given on the label of the bottle of HCl shown in Figure 10.2 (page 252).

a What is the mass percent of water in the bottle?

ANALYSIS

Information given:	from the label: mass % of HCl (37.7%)
Asked for:	mass % of H_2O

SOLUTION

mass % H_2O	100% = mass % HCl + mass % H_2O mass % H_2O = 100% − 37.7% = 62.3%

b What is the molality of HCl?

ANALYSIS

Information given:	from label: mass % of HCl (37.7%), from part (a): mass % of H_2O (62.3%)
Asked for:	molality m

STRATEGY

1. Assume 100.0 g of solution.
2. Draw the table, fill in the mass of solute and solvent, and shade in the spots needed for molality: moles of solute and mass of solvent in kg.
3. Find the moles of solute and add to the table.
4. Substitute values into the defining equation for molality.

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

SOLUTION

2. Table

	moles	← MM	mass	density →	volume
Solute			37.7 g		
Solvent			62.3 g		
Solution			100.0 g		

continued

3. moles solute

$$37.7 \text{ g HCl} \times \frac{1 \text{ mol}}{36.46 \text{ g}} = 1.03 \text{ g}$$

Table

	moles ← MM	mass	density → volume
Solute	1.03	37.7 g	
Solvent		0.0623 kg	
Solution		100.0 g	

4. m

$$\frac{1.03 \text{ mol}}{0.0623 \text{ kg}} = 16.5\ m$$

c What is the molarity of the HCl in the bottle?

ANALYSIS

Information given:	from label: mass % of HCl (37.7%) from part (a): mass % of H_2O (62.3%) from part (b): moles of solute (1.03)
Asked for:	M

STRATEGY

1. Draw the table as in part (b). Shade in the spots needed for molarity: moles of solute and volume of solution.

2. Find the volume of solution and fill in the table with that information.

3. Substitute values into the defining equation for molarity.

$$M = \frac{\text{moles solute}}{\text{volume solution (L)}}$$

SOLUTION

1. Table

	moles ← MM	mass	density → volume
Solute	1.03	37.7 g	
Solvent		0.0623 kg	
Solution		100.0 g	

2. $V_{solution}$

$$V_{solution} = \frac{\text{mass}}{\text{density}} = \frac{100.0 \text{ g}}{1.19 \text{ g/ml}} = 84.0 \text{ mL} = 0.0840 \text{ L}$$

Table

	moles ← MM	mass	density → volume
Solute	1.03	37.7 g	
Solvent		0.0623 kg	
Solution		100.0 g	0.0840 L

3. M

$$M = \frac{\text{mol solute}}{V_{solution}\text{ (L)}} = \frac{1.03 \text{ mol}}{0.0840 \text{ L}} = 12.3\ M$$

10-2 Principles of Solubility

The extent to which a solute dissolves in a particular solvent depends on several factors. The most important of these are

- the nature of solvent and solute particles and the interactions between them.
- the temperature at which the solution is formed.
- the pressure of a gaseous solute.

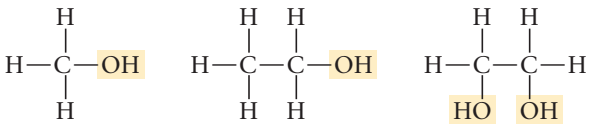
In this section we consider in turn the effect of each of these factors on **solubility**.

Solute-Solvent Interactions

In discussing solubility, it is sometimes stated that "like dissolves like." A more meaningful way to express this idea is to say that two substances with intermolecular forces of about the same type and magnitude are likely to be very soluble in one another (Figure 10.3). To illustrate, consider the hydrocarbons pentane, C_5H_{12}, and hexane, C_6H_{14}, which are completely soluble in each other. Molecules of these nonpolar substances are held together by dispersion forces of about the same magnitude. A pentane molecule experiences little or no change in intermolecular forces when it goes into solution in hexane.

Most nonpolar substances have very small water solubilities. Petroleum, a mixture of hydrocarbons, spreads out in a thin film on the surface of a body of water rather than dissolving. The mole fraction of pentane, C_5H_{12}, in a saturated water solution is only 0.0001. These low solubilities are readily understood in terms of the structure of liquid water, which you will recall (Chapter 9) is strongly hydrogen-bonded. Dissimilar intermolecular forces between C_5H_{12} (dispersion) and H_2O (H bonds) lead to low solubility.

Of the relatively few organic compounds that dissolve readily in water, many contain —OH groups. Three familiar examples are methyl alcohol, ethyl alcohol, and ethylene glycol, all of which are infinitely soluble in water.



In these compounds, as in water, the principal intermolecular forces are hydrogen bonds. When a substance like methyl alcohol dissolves in water, it forms hydrogen bonds with H_2O molecules. These hydrogen bonds, joining a CH_3OH molecule to an H_2O molecule, are about as strong as those in the pure substances.

Not all organic compounds that contain —OH groups are soluble in water (Table 10.1). As molar mass increases, the polar —OH group represents an increasingly smaller portion of the molecule. At the same time, the nonpolar hydrocarbon portion becomes larger. As a result, solubility decreases with increasing molar mass. Butanol, $CH_3CH_2CH_2CH_2OH$, is much less soluble in water than methyl alcohol, CH_3OH. The hydrocarbon portion, shaded in gold, is much larger in butanol.

The solubility (or insolubility) of different vitamins is of concern in nutrition. Molecules of vitamins B and C contain several —OH groups that can form hydrogen bonds with water (Figure 10.4). As a result, they are water-soluble, readily excreted by the body, and must be consumed daily. In contrast, vitamins A, D, E, and K, whose molecules are relatively nonpolar, are water-insoluble. These vitamins are not so readily excreted; they tend to stay behind in fatty tissues. This means that the body can draw on its reservoir of vitamins A, D, E, and K to deal with sporadic deficiencies. Conversely, megadoses of these vitamins can lead to very high, possibly toxic, concentrations in the body.

You can't remove the "hot" taste of chili peppers by drinking water because the compound responsible is nonpolar and water-insoluble.

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Figure 10.3 Solubility and intermolecular forces. Oil *(left)* is made up of nonpolar molecules. It does not mix well with water because water is polar. Ethylene glycol *(right)*, commonly used as antifreeze, mixes with water in all proportions because both form hydrogen bonds.

Table 10.1 Solubilities of Alcohols in Water

Substance	Formula	Solubility (g solute/L H_2O)
Methyl alcohol	CH_3OH	Completely soluble
Ethyl alcohol	CH_3CH_2OH	Completely soluble
Propanol	$CH_3CH_2CH_2OH$	Completely soluble
Butanol	$CH_3CH_2CH_2CH_2OH$	74
Pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	27
Hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	6.0
Heptanol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$	1.7

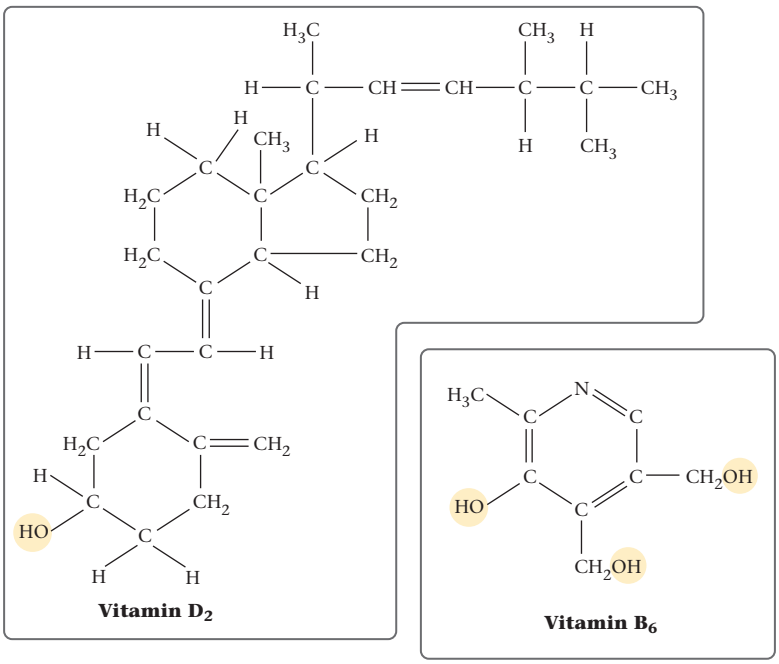

Figure 10.4 Molecular structures of vitamin D_2 and vitamin B_6. Polar groups are shown in color. Vitamin D_2 is water-insoluble and vitamin B_6 is water-soluble.

As we noted in Chapter 4, the solubility of ionic compounds in water varies tremendously from one solid to another. The extent to which solution occurs depends on a balance between two forces, both electrical in nature:

We can't predict which factor will predominate, so we can't predict solubility.

1. The force of attraction between H_2O molecules and the ions, which tends to bring the solid into solution. If this factor predominates, the compound is very soluble in water, as is the case with NaCl, NaOH, and many other ionic solids.
2. The force of attraction between oppositely charged ions, which tends to keep them in the solid state. If this is the major factor, the water solubility is very low. The fact that $CaCO_3$ and $BaSO_4$ are almost insoluble in water implies that interionic attractive forces predominate with these ionic solids.

Effect of Temperature on Solubility

When an excess of a solid such as sodium nitrate, $NaNO_3$, is shaken with water, an equilibrium is established between ions in the solid state and in solution:

$$NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq)$$

At 20°C, the saturated solution contains 87.6 g of $NaNO_3$ per one hundred grams of water.

A similar type of equilibrium is established when a gas such as oxygen is bubbled through water.

$$O_2(g) \rightleftharpoons O_2(aq)$$

At 20°C and 1 atm, 0.00138 mol of O_2 dissolves per liter of water.

The effect of a temperature change on solubility equilibria such as these can be predicted by applying a simple principle. ***An increase in temperature always shifts the position of an equilibrium to favor an endothermic process.*** This means that if the solution process absorbs heat ($\Delta H_{soln.} > 0$), an increase in temperature increases the solubility. Conversely, if the solution process is exothermic ($\Delta H_{soln.} < 0$), an increase in temperature decreases the solubility.

Dissolving a solid in a liquid is usually an endothermic process; heat must be absorbed to break down the crystal lattice.

$$\text{solid} + \text{liquid} \rightleftharpoons \text{solution} \qquad \Delta H_{soln.} > 0$$

For example, for sodium nitrate,

$$\Delta H_{soln.} = \Delta H_f^\circ\ Na^+(aq) + \Delta H_f^\circ\ NO_3^-(aq) - \Delta H_f^\circ\ NaNO_3(s) = +22.8\ kJ$$

Consistent with this effect, the solubility of $NaNO_3$ and most (but not all) other solids increases with temperature (Figure 10.5).

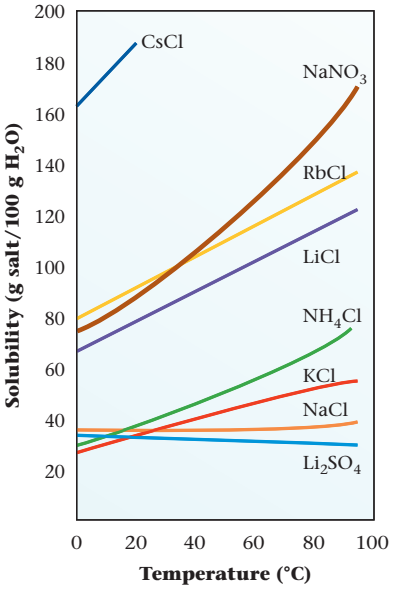

Figure 10.5 Solubility of ionic compounds vs. temperature.

Gases behave quite differently from solids. When a gas condenses to a liquid, heat is always evolved. By the same token, heat is usually evolved when a gas dissolves in a liquid:

$$\text{gas} + \text{liquid} \rightleftharpoons \text{solution} \qquad \Delta H_{soln.} < 0$$

This means that the reverse process (gas coming out of solution) is endothermic. Hence, it is favored by an increase in temperature; typically, gases become less soluble as the temperature rises. This rule is followed by all gases in water. You have probably noticed this effect when opening carbonated drinks (Figure 10.6). Cold drinks produce fewer bubbles than warm drinks because carbon dioxide is less soluble at higher temperature. For the same reason, warm carbonated beverages go flat faster than cold ones. You have probably noticed this effect when heating water in an open pan or beaker. Bubbles of air are driven out of the water by an increase in temperature. The reduced solubility of oxygen in water at high temperatures (Figure 10.7a) may explain why trout congregate at the bottom of deep pools on hot summer days when the surface water is depleted of dissolved oxygen.

Figure 10.6 Gas solubility and temperature. The two bottles of carbonated water show the dramatic difference between the solubility of carbon dioxide at low temperature *(left)* and room temperature *(right)*.

Effect of Pressure on Solubility

Pressure has a major effect on solubility only for gas-liquid systems. At a given temperature, raising the pressure increases the solubility C_g, of a gas. Indeed, at low to moderate pressures, gas solubility is directly proportional to pressure (Figure 10.7b).

$$C_g = kP_g \qquad (10.2)$$

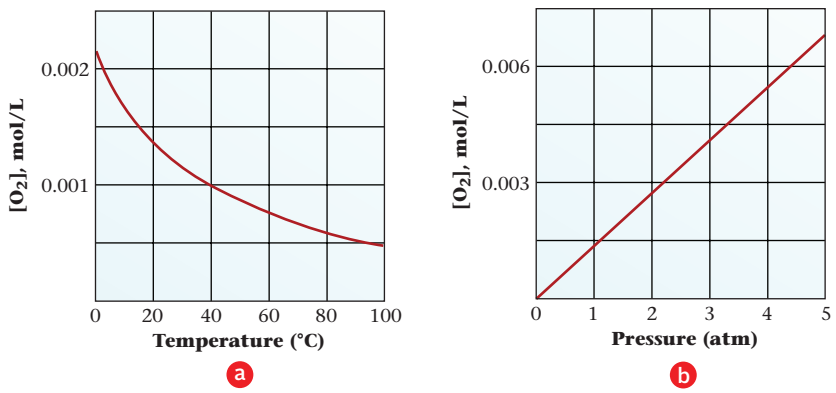

Figure 10.7 Oxygen solubility. The solubility of $O_2(g)$ in water decreases as temperature rises (a) and increases as pressure increases (b). In (a), the pressure is held constant at 1 atm; in (b), the temperature is held constant at 25°C.

where P_g is the partial pressure of the gas over the solution, C_g is its concentration in the solution, and k is a constant characteristic of the particular gas-liquid system. This relation is called **Henry's law** after its discoverer, William Henry (1775–1836), a friend of John Dalton.

Henry's law arises because increasing the pressure raises the concentration of molecules in the gas phase. To balance this change and maintain equilibrium, more gas molecules enter the solution, increasing their concentration in the liquid phase (Figure 10.8).

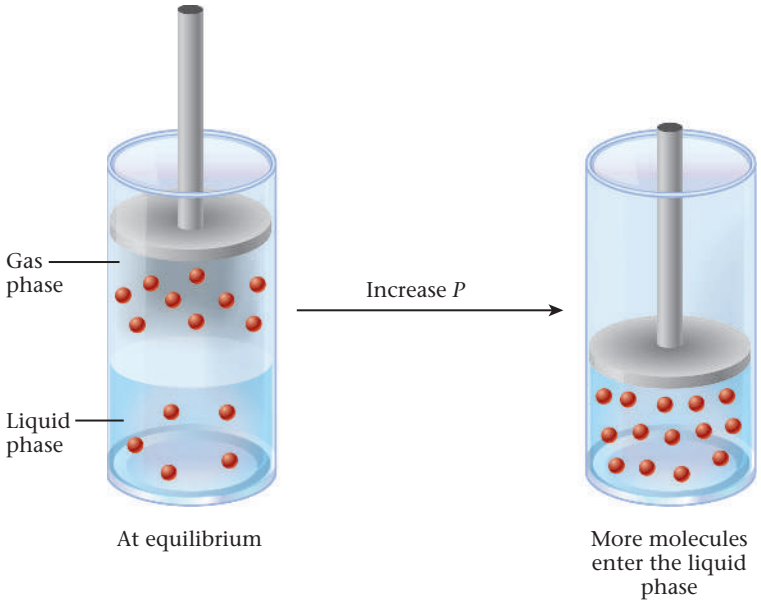

Figure 10.8 Henry's law at work. An increase in pressure, caused by a decrease in volume for the gas phase, causes the O_2 molecules to enter the liquid phase, resulting in more O_2 dissolved.

EXAMPLE 10.5

The solubility of pure nitrogen in blood at body temperature, 37°C, and one atmosphere is 6.2×10^{-4} M. If a diver breathes air ($X_{N_2} = 0.78$) at a depth where the total pressure is 2.5 atm, calculate the concentration of nitrogen in his blood.

ANALYSIS

Information given:	solubility of N_2 (C_{N_2}) (6.2×10^{-4} M) at 1.00 atm X_{N_2} (0.78) P_{tot} (2.5 atm)
Information implied:	k for N_2 in blood P_{N_2}
Asked for:	solubility of N_2 (C_{N_2}) at 2.50 atm

STRATEGY

1. At a given temperature, k is dependent only on the nature of the gas-liquid system. Find k using Henry's law and the solubility for pure N_2 at 1.00 atm.

   $$C_{N_2} = kP_{N_2}$$

2. Find P_{N_2} when P_{tot} is 2.5 atm using the relationship between mol fraction and partial pressure (Chapter 5).

   $$P_{N_2} = X_{N_2} P_{tot}$$

3. Substitute into Henry's law to get C_{N_2} at the higher pressure.

continued

SOLUTION	
1. k	$k = \dfrac{C_{N_2}}{P_{N_2}} = \dfrac{6.2 \times 10^{-4}\ M}{1.00\ \text{atm}} = 6.2 \times 10^{-4}\ M/\text{atm}$
2. P_{N_2}	$P_{N_2} = X_{N_2} P_{\text{tot}} = (0.78)(2.5\ \text{atm}) = 2.0\ \text{atm}$
3. C_{N_2}	$C_{N_2} = kP_{N_2} = 6.2 \times 10^{-4}\ \dfrac{M}{\text{atm}} \times 2.0\ \text{atm} = 1.2 \times 10^{-3}\ M$

The influence of partial pressure on gas solubility is used in making carbonated beverages such as beer, sparkling wines, and many soft drinks. These beverages are bottled under pressures of CO_2 as high as 4 atm. When the bottle or can is opened, the pressure above the liquid drops to 1 atm, and the carbon dioxide rapidly bubbles out of solution (Figure 10.9). Pressurized containers for shaving cream, whipped cream, and cheese spreads work on a similar principle. Pressing a valve reduces the pressure on the dissolved gas, causing it to rush from solution, carrying liquid with it as a foam.

Another consequence of the effect of pressure on gas solubility is the painful, sometimes fatal, affliction known as the "bends." This occurs when a person goes rapidly from deep water (high pressure) to the surface (lower pressure), where gases are less soluble. The rapid decompression causes air, dissolved in blood and other body fluids, to bubble out of solution. These bubbles impair blood circulation and affect nerve impulses (Figure 10.10). To minimize these effects, deep-sea divers and aquanauts breathe a helium-oxygen mixture rather than compressed air (nitrogen-oxygen). Helium is only about one-third as soluble as nitrogen, and hence much less gas comes out of solution on decompression.

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Figure 10.9 Henry's law. As soon as the pressure is released, carbon dioxide begins to bubble out of solution in a carbonated beverage.

SCUBA divers have to worry about this.

SCUBA divers must pay attention to the solubility of gases in the blood and the fact that solubility increases with pressure.

A hyperbaric chamber. People who have problems breathing can be placed in a hyperbaric chamber where they are exposed to a higher partial pressure of oxygen.

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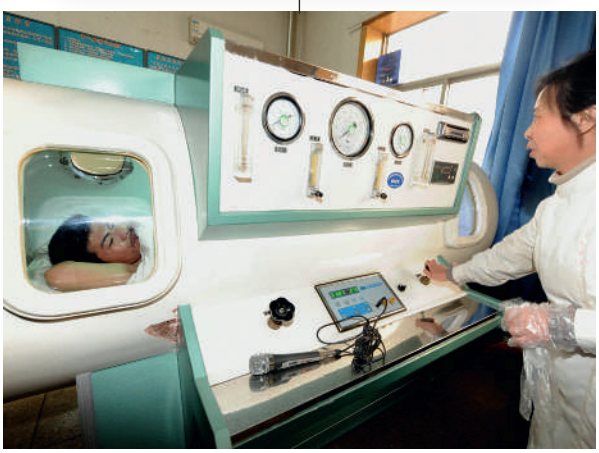


Jin Liangkuai/Xinhua/Zumapress/Newscom

b

Figure 10.10 Solubility affected by pressure.

10-3 Colligative Properties of Nonelectrolytes

The properties of a solution differ considerably from those of the pure solvent. Those solution properties that depend primarily on the *concentration of solute particles* rather than their nature are called **colligative properties.** Such properties include vapor pressure lowering, osmotic pressure, boiling point elevation, and freezing point depression. This section considers the relations between colligative properties and solute concentration, with nonelectrolytes that exist in solution as molecules.

The relationships among colligative properties and solute concentration are best regarded as limiting laws. They are approached more closely as the solution becomes more dilute. In practice, the relationships discussed in this section are valid, for nonelectrolytes, to within a few percent at concentrations as high as 1 *M*. At higher concentrations, solute-solute interactions lead to larger deviations.

Vapor Pressure Lowering

You may have noticed that concentrated aqueous solutions evaporate more slowly than does pure water. This reflects the fact that the vapor pressure of water over the solution is less than that of pure water (Figure 10.11).

Vapor pressure lowering is a true colligative property; that is, it is independent of the nature of the solute but directly proportional to its concentration. For example, the vapor pressure of water above a 0.10 *M* solution of either glucose or sucrose at 0°C is the same, about 0.008 mm Hg less than that of pure water. In a 0.30 *M* solution, the vapor pressure lowering is almost exactly three times as great, 0.025 mm Hg.

Vapor pressure lowering is directly proportional to solute mole fraction.

The relationship between solvent vapor pressure and concentration is ordinarily expressed as

$$P_1 = X_1 P_1^\circ \qquad (10.3)$$

In this equation, P_1 is the vapor pressure of solvent over the solution, P_1° is the vapor pressure of the pure solvent at the same temperature, and X_1 is the mole fraction of solvent. Note that because X_1 in a solution must be less than 1, P_1 must be less than P_1°. This relationship is called **Raoult's law;** François Raoult (1830–1901) carried out a large number of careful experiments on vapor pressures and freezing point lowering.

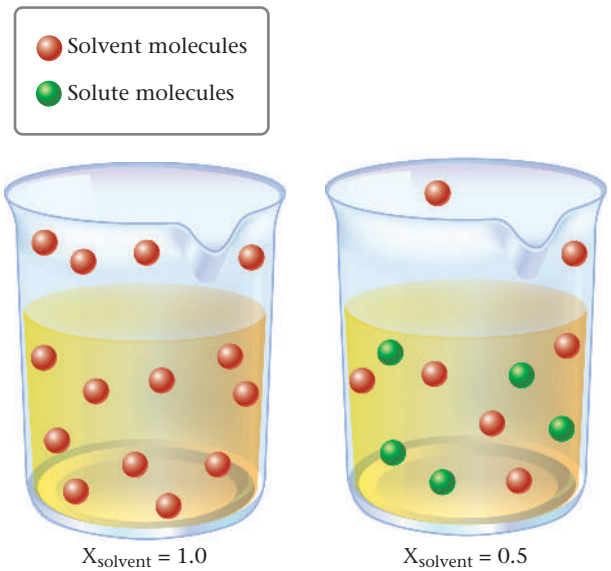


Figure 10.11 Raoult's law. Adding a solute lowers the concentration of solvent molecules in the liquid phase. To maintain equilibrium, the concentration of solvent molecules in the gas phase must decrease, thereby lowering the solvent vapor pressure.

To obtain a direct expression for vapor pressure lowering, note that $X_1 = 1 - X_2$, where X_2 is the mole fraction of solute. Substituting $1 - X_2$ for X_1 in Raoult's law,

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

Rearranging,

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

The quantity $(P_1^\circ - P_1)$ is the vapor pressure lowering (ΔP). It is the difference between the solvent vapor pressure in the pure solvent and in solution.

$$\Delta P = X_2 P_1^\circ \qquad (10.4)$$

EXAMPLE 10.6

A solution contains 82.0 g of glucose, $C_6H_{12}O_6$, in 322 g of water. Calculate the vapor pressure of the solution at 25°C (vapor pressure of pure water at 25°C = 23.76 mm Hg).

ANALYSIS

Information given:	mass of solute, glucose (82.0 g) mass of solvent, H_2O (322 g) vapor pressure of pure water at 25°C (23.76 mm Hg)
Information implied:	molar masses of glucose and water
Asked for:	vapor pressure of the solution at 25°C

STRATEGY

1. Find moles of solute, moles of solvent, and mole fraction of solvent.
2. Substitute into Equation 10.3, where the subscript 1 refers to the solvent (in this case, water).

$$P_1 = X_1 P_1^\circ$$

SOLUTION

1. moles solute

$$n_{\text{glucose}} = 82.0\text{ g} \times \frac{1\text{ mol glucose}}{180.2\text{ g}} = 0.455\text{ mol}$$

moles solvent

$$n_{H_2O} = 322\text{ g} \times \frac{1\text{ mol } H_2O}{18.02\text{ g}} = 17.9\text{ mol}$$

mole fraction of solvent

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{\text{glucose}}} = \frac{17.9\text{ mol}}{(17.9 + 0.455)\text{ mol}} = 0.975$$

2. P_{H_2O}

$$P_{H_2O} = (X_{H_2O})(P^\circ_{H_2O}) = (0.975)(23.76\text{ mm Hg}) = 23.17\text{ mm Hg}$$

END POINT

The vapor pressure of water in the solution decreases only by 0.589 mm Hg. This is because there is a relatively small amount of solute (glucose) in the solution.

Boiling Point Elevation and Freezing Point Lowering

When a solution of a nonvolatile solute is heated, it does not begin to boil until the temperature exceeds the boiling point of the solvent. The difference in temperature is called the **boiling point elevation,** ΔT_b.

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

where T_b and T_b° are the boiling points of the solution and the pure solvent, respectively. As boiling continues, pure solvent distills off, the concentration of solute increases, and the boiling point continues to rise (Figure 10.12).

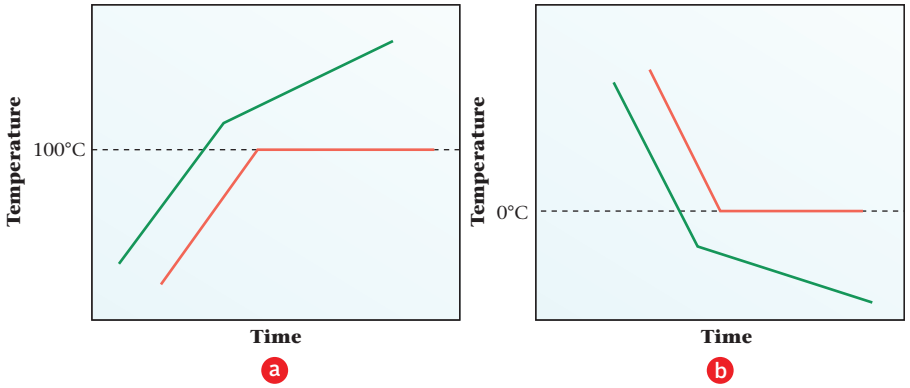


Figure 10.12 Boiling (a) and freezing (b) curves for pure water (red) and an aqueous solution (green). For pure water, the temperature remains constant during boiling or freezing. For the solution, the temperature changes steadily during the phase change because water is being removed, increasing the concentration of solute.

When a solution is cooled, it does not begin to freeze until a temperature below the freezing point of the pure solvent is reached. The **freezing point lowering,** ΔT_f, is defined to be a positive quantity:

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

where T_f°, the freezing point of the solvent, lies above T_f, the freezing point of the solution. As freezing takes place, pure solvent freezes out, the concentration of solute increases, and the freezing point continues to drop. This is what happens with "ice beer." When beer is cooled below 0°C, pure ice separates and the percentage of ethyl alcohol increases.

Boiling point elevation is a direct result of vapor pressure lowering. At any given temperature, a solution of a nonvolatile solute* has a vapor pressure *lower* than that of the pure solvent. Hence a *higher* temperature must be reached before the solution boils, that is, before its vapor pressure becomes equal to the external pressure. Figure 10.13 illustrates this reasoning graphically.

The freezing point lowering, like the boiling point elevation, is a direct result of the lowering of the solvent vapor pressure by the solute. Notice from Figure 10.13 that the freezing point of the solution is the temperature at which the solvent in solution has the same vapor pressure as the pure solid solvent. This implies that it is pure solvent (e.g., ice) that separates when the solution freezes.

Solutes raise the boiling point and lower the freezing point.

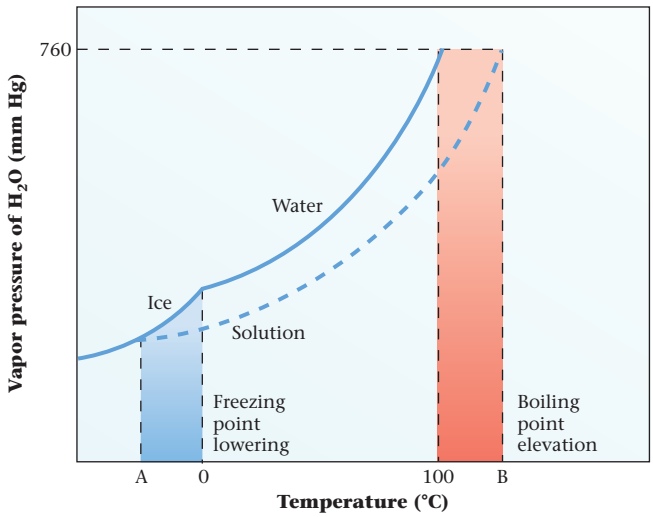


Figure 10.13 Effects of vapor pressure lowering. Because a nonvolatile solute lowers the vapor pressure of a solvent, the boiling point of a solution will be higher and the freezing point lower than the corresponding values for the pure solvent. Water solutions freeze *below* 0°C at point A and boil *above* 100°C at point B.

*Volatile solutes ordinarily lower the boiling point because they contribute to the total vapor pressure of the solution.

Boiling point elevation and freezing point lowering, like vapor pressure lowering, are colligative properties. They are directly proportional to solute concentration, generally expressed as molality, m. The relevant equations are

$$\Delta T_b = k_b \text{ (molality)}$$

$$\Delta T_f = k_f \text{ (molality)}$$

The proportionality constants in these equations, k_b and k_f, are called the *molal boiling point constant* and the *molal freezing point constant,* respectively. Their magnitudes depend on the nature of the solvent (Table 10.2). Note that when the solvent is water,

$$k_b = 0.52°C/m \qquad k_f = 1.86°C/m$$

EXAMPLE 10.7

An antifreeze solution is prepared containing 50.0 cm^3 of ethylene glycol, $C_2H_6O_2$ (d = 1.12 g/cm^3), in 50.0 g of water. Calculate the freezing point of this 50-50 mixture.

ANALYSIS

Information given:	volume of ethylene glycol (50.0 cm^3) density of ethylene glycol (1.12 g/cm^3) mass of water (50.0 g)
Information implied:	mass of ethylene glycol molar mass of ethylene glycol k_f for water (Table 10.2) freezing point of water
Asked for:	freezing point of the solution

STRATEGY

1. Determine the number of moles of ethylene glycol in solution. Use the following plan:

$$\text{Volume} \xrightarrow{\text{density}} \text{mass} \xrightarrow{\text{MM}} \text{moles}$$

2. Find the molality m of the solution by using the defining equation for molality.

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

3. Find ΔT_f.

$$\Delta T_f = k_f(m)$$

4. Find $T_{solution}$.

$$\Delta T_f = T°_{solvent} - T_{solution}$$

SOLUTION

1. mol ethylene glycol

$$50.0 \text{ cm}^3 \times \frac{1.12 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol}}{62.04 \text{ g}} = 0.903 \text{ mol}$$

2. m

$$m = \frac{\text{mol solute}}{\text{mass solvent (kg)}} = \frac{0.903 \text{ mol}}{0.05000 \text{ kg}} = 18.1\ m$$

3. ΔT_f

$$\Delta T_f = k_f(m) = (1.86°C/m)(18.1\ m) = 33.7°C$$

4. $T_{solution}$

$$T_{solution} = T°_{solvent} - \Delta T_f = 0°C - 33.7°C = -33.7°C$$

END POINT

Actually, the freezing point is somewhat lower, about −37°C (−35°F), which reminds us that the equation used, $\Delta T_f = k_f(m)$, is a limiting law, strictly valid only in very dilute solutions.

Table 10.2 Molal Freezing Point and Boiling Point Constants

Solvent	fp (°C)	k_f (°C/m)	bp (°C)	k_b (°C/m)
Water	0.00	1.86	100.00	0.52
Acetic acid	16.66	3.90	117.90	2.53
Benzene	5.50	5.10	80.10	2.53
Cyclohexane	6.50	20.2	80.72	2.75
Camphor	178.40	40.0	207.42	5.61
p-Dichlorobenzene	53.1	7.1	174.1	6.2
Naphthalene	80.29	6.94	217.96	5.80

You take advantage of freezing point lowering when you add antifreeze to your automobile radiator in winter. Ethylene glycol, $HO(CH_2)_2OH$, is the solute commonly used. It has a high boiling point (197°C), is virtually nonvolatile at 100°C, and raises the boiling point of water. Hence antifreeze that contains ethylene glycol does not boil away in summer driving.

Propylene glycol, HO—$(CH_2)_3$—OH, is much less toxic.

Osmotic Pressure

One interesting effect of vapor pressure lowering is shown at the left of Figure 10.14. We start with two beakers, one containing pure water and the other containing a sugar solution. These are placed next to each other under a bell jar (Figure 10.14a). As time passes, the liquid level in the beaker containing the solution rises. The level of pure water in the other beaker falls. Eventually, by evaporation and condensation, all the water is transferred to the solution (Figure 10.14b). At the end of the experiment, the beaker that contained pure water is empty. The driving force behind this process is the difference in vapor pressure of water in the two beakers. *Water moves from a region where its vapor pressure or mole fraction is high ($X_1 = 1$ in pure water) to one in which its vapor pressure or mole fraction is lower ($X_1 < 1$ in sugar solution).*

The apparatus shown in Figure 10.14c and d can be used to achieve a result similar to that found in the bell jar experiment. In this case, a sugar solution is

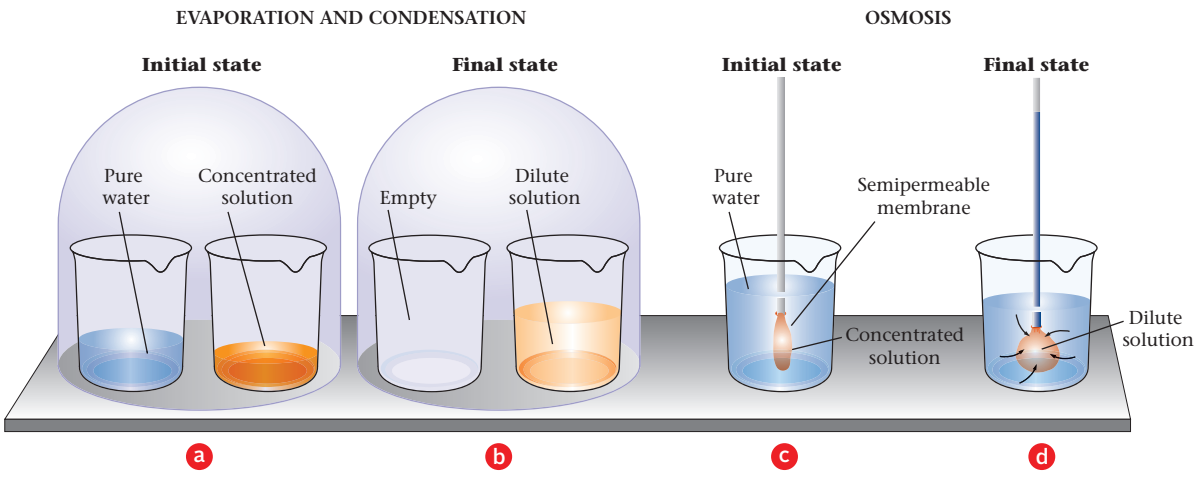


Figure 10.14 Evaporation and condensation (a and b); osmosis (c and d). Water tends to move spontaneously from a region where its vapor pressure is high to a region where it is low. In a → b, movement of water molecules occurs through the air trapped under the bell jar. In c → d, water molecules move by osmosis through a semipermeable membrane. The driving force is the same in the two cases, although the mechanism differs.

separated from water by a semipermeable membrane. This may be an animal bladder, a slice of vegetable tissue, or a piece of parchment. The membrane, by a mechanism that is not well understood, allows water molecules to pass through it, but not sugar molecules. As before, water moves from a region where its mole fraction is high (pure water) to a region where it is lower (sugar solution). This process, taking place through a membrane permeable only to the solvent, is called **osmosis.** As a result of osmosis, the water level rises in the tube and drops in the beaker (Figure 10.14d).

The semipermeable membranes act like molecular sieves.

The osmotic pressure, π, is equal to the external pressure, P, just sufficient to prevent osmosis (Figure 10.15). If P is less than π, osmosis takes place in the normal way, and water moves through the membrane into the solution (Figure 10.15a). By making the external pressure large enough, it is possible to reverse this process (Figure 10.15b). When $P > \pi$, water molecules move through the membrane from the solution to pure water. This process, called *reverse osmosis,* is used to obtain fresh water from seawater in arid regions of the world, including Saudi Arabia. It is also used to concentrate the sap from which maple syrup is made.

Reverse osmosis absorbs energy, but there's plenty of that in Saudi Arabia.

Osmotic pressure, like vapor pressure lowering, is a colligative property. For any nonelectrolyte, π is directly proportional to molarity, M. The equation relating these two quantities is very similar to the ideal gas law:

$$\pi = \frac{nRT}{V} = MRT \qquad (10.5)$$

where R is the gas law constant, 0.0821 L · atm/mol · K, and T is the Kelvin temperature. Even in dilute solution, the osmotic pressure is quite large. Consider, for example, a 0.10 M solution at 25°C:

$$\pi = (0.10 \text{ mol/L})\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K}) = 2.4 \text{ atm}$$

A pressure of 2.4 atm is equivalent to that of a column of water 25 m (more than 80 ft) high.

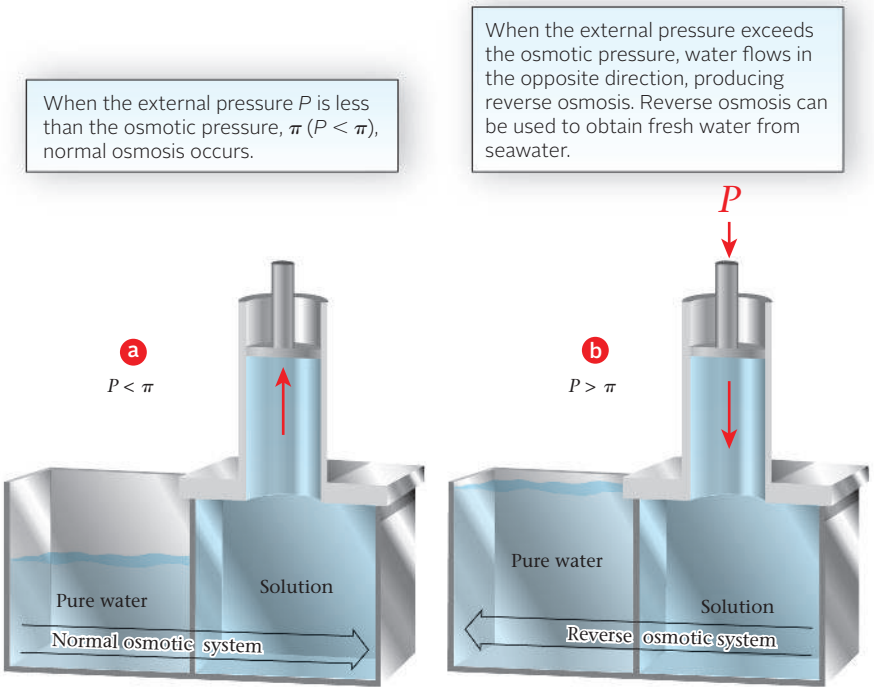


Figure 10.15 Reverse osmosis.

EXAMPLE 10.8

Calculate the osmotic pressure at 15°C of a solution prepared by dissolving 50.0 g of sugar, $C_{12}H_{22}O_{11}$, in enough water to form one liter of solution.

ANALYSIS

Information given:	T (15°C) mass of sugar (50.0 g) volume of solution (1.00 L)
Information implied:	molar mass of sugar R value
Asked for:	Osmotic pressure of the solution (π)

STRATEGY

1. Determine the molarity M of the solution using the following plan:

$$\text{mass of solute} \xrightarrow{\text{MM}} \text{moles of solute} \xrightarrow{V \text{ of solution}} (M)$$

2. Substitute into Equation 10.5 to determine the osmotic pressure, π. Use the R value 0.0821 L · atm/mol · K.

SOLUTION

1. mol solute

$$50.0 \text{ g} \times \frac{1 \text{ mol}}{342.3 \text{ g}} = 0.146 \text{ mol}$$

M

$$M = \text{mol solute/volume solution (L)} = 0.146 \text{ mol}/1.000 \text{ L} = 0.146\ M$$

2. π

$$\pi = MRT = 0.146 \frac{\text{mol}}{\text{L}} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 15)\text{K} = 3.45 \text{ atm}$$

Mama G. Clarke

Figure 10.16 Effect of osmosis on cucumbers and prunes. When a cucumber is pickled, water moves out of the cucumber by osmosis into the concentrated brine solution. A prune placed in pure water swells as water moves into the prune, again by osmosis.

Dishwashers' hands get wrinkled too.

If a cucumber is placed in a concentrated brine solution, it shrinks and assumes the wrinkled skin of a pickle. The skin of the cucumber acts as a semipermeable membrane. The water solution inside the cucumber is more dilute than the solution surrounding it. As a result, water flows out of the cucumber into the brine (Figure 10.16).

When a dried prune is placed in water, the skin also acts as a semipermeable membrane. This time the solution inside the prune is more concentrated than the water, so that water flows into the prune, making the prune less wrinkled.

Nutrient solutions used in intravenous feeding must be *isotonic* with blood; that is, they must have the same osmotic pressure as blood. If the solution is too

dilute, its osmotic pressure will be less than that of the fluids inside blood cells; in that case, water will flow into the cell until it bursts. Conversely, if the nutrient solution has too high a concentration of solutes, water will flow out of the cell until it shrivels and dies.

Determination of Molar Masses from Colligative Properties

Colligative properties, particularly freezing point depression, can be used to determine molar masses of a wide variety of nonelectrolytes. The approach used is illustrated in Examples 10.9 and 10.10.

EXAMPLE 10.9

A student is directed to determine the molar mass of 1.00 g of an unknown solid dissolved in cyclohexane. She is given the following pertinent information about the solvent:

volume of solvent in solution: 225 mL
freezing point: 6.50°C
freezing point constant: 20.2°C/*m*
density: 0.779 g/mL

She does a freezing point determination and finds the freezing point of the solution to be 6.18°C. What is the molar mass of the solute?

ANALYSIS

Information given:	mass of solute (1.00 g) volume of solvent (225 mL) freezing point of solution, T_f (6.18°C) solvent—cyclohexane: freezing point, T_f° (6.50°C), k_f (20.2°C/*m*), density (0.779 g/mL)
Information implied:	mass of solvent ΔT_f
Asked for:	molar mass of solute

STRATEGY

1. Determine the freezing point depression.
   $\Delta T_f = T_f^\circ - T_f$
2. Find the molality of the solution.
   $\Delta T_f = mk_f$
3. Find the mass of the solvent in kg using the density.
4. Using the defining equation for molality, find the moles of solute.
5. Find the molar mass using the mass and number of moles of solute.

SOLUTION

1. ΔT_f	$\Delta T_f = T_f^\circ - T_f = 6.50°C - 6.18°C = 0.32°C$
2. m	$m = \dfrac{\Delta T_f}{k_f} = \dfrac{0.32°C}{20.2°C/m} = 0.016$
3. mass of solvent	$225\ mL \times 0.779\ \dfrac{g}{mL} \times \dfrac{1\ kg}{1000\ g} = 0.175\ kg$
4. moles of solute	moles solute $= (m)$(mass of solvent) $= (0.016)(0.175) = 2.8 \times 10^{-3}$
5. molar mass	$\text{molar mass} = \dfrac{\text{mass}}{\text{moles}} = \dfrac{1.00\ g}{2.8 \times 10^{-3}\ mol} = 3.6 \times 10^2\ g/mol$

In carrying out a molar mass determination by freezing point depression, we must choose a solvent in which the solute is readily soluble. Usually, several such solvents are available. Of these, we tend to pick one that has the largest k_f. This makes ΔT_f large and thus reduces the percent error in the freezing point measurement. From this point of view, cyclohexane or other organic solvents are better choices than water, because their k_f values are larger.

Molar masses can also be determined using other colligative properties. Osmotic pressure measurements are often used, particularly for solutes of high molar mass, where the concentration is likely to be quite low. The advantage of using osmotic pressure is that the effect is relatively large. Consider, for example, a 0.0010 *M* aqueous solution, for which

$$\pi \text{ at } 25^\circ\text{C} = 0.024 \text{ atm} = 18 \text{ mm Hg}$$
$$\Delta T_f \approx 1.86 \times 10^{-3} \,^\circ\text{C}$$
$$\Delta T_b \approx 5.2 \times 10^{-4} \,^\circ\text{C}$$

A pressure of 18 mm Hg can be measured relatively accurately; temperature differences of the order of 0.001°C are essentially impossible to measure accurately.

EXAMPLE 10.10

A solution made up of 2.00 g of an unknown solute and 275 mL of water (d = 1.00 g/mL) has an osmotic pressure of 0.872 atm at 25°C. What is the molar mass of the unknown solute?

ANALYSIS

Information given:	mass of solute (2.00 g) volume of solvent (275 mL) π (0.872 atm); T (25°C) density of solvent (1.00 g/mL); density of solution (1.00 g/mL)
Information implied:	mass of solution volume of solution R value
Asked for:	molar mass of solute

STRATEGY

1. Find the molarity *M*, by substituting into Equation 10.5.
   $\pi = MRT$
2. Determine the volume of the solution by first finding its mass.
   mass of solution = mass of solute + mass of water
   volume of solution = mass/density
3. Find the moles of solute using the defining equation for molarity.
   M = moles solute/volume of solution (L)
4. Find the molar mass; molar mass = mass/moles

SOLUTION

1. M

$$M = \frac{\pi}{RT} = \frac{0.872 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.0356 \text{ mol/L}$$

2. Volume of solution

$$\text{mass of solution} = \text{mass of solute} + \text{mass of solvent}$$
$$= 2.00 \text{ g} + (275 \text{ mL} \times 1.00 \text{ g/mL}) = 277 \text{ g}$$

$$\text{volume of solution} = \frac{277 \text{ g}}{1.00 \text{ g/mL}} = 277 \text{ mL} = 0.277 \text{ L}$$

continued

3. Moles of solute	mol solute = MV = (0.0356 mol/L)(0.277 L) = 0.00987
4. Molar mass	molar mass = mass/moles = 2.00 g/0.00987 mol = 203 g/mol

10-4 Colligative Properties of Electrolytes

As noted earlier, colligative properties of solutions are directly proportional to the concentration of solute *particles*. On this basis, it is reasonable to suppose that, at a given concentration, an electrolyte should have a greater effect on these properties than does a nonelectrolyte. When one mole of a nonelectrolyte such as glucose dissolves in water, one mole of solute molecules is obtained. On the other hand, one mole of the electrolyte NaCl yields two moles of ions (1 mol of Na^+, 1 mol of Cl^-). With $CaCl_2$, three moles of ions are produced per mole of solute (1 mol of Ca^{2+}, 2 mol of Cl^-).

This reasoning is confirmed experimentally. Compare, for example, the vapor pressure lowerings for 1.0 *M* solutions of glucose, sodium chloride, and calcium chloride at 25°C.

	Glucose	NaCl	$CaCl_2$
ΔP	0.42 mm Hg	0.77 mm Hg	1.3 mm Hg

With many electrolytes, ΔP is so large that the solid, when exposed to moist air, picks up water *(deliquesces)*. This occurs with calcium chloride, whose saturated solution has a vapor pressure only 30% that of pure water. If dry $CaCl_2$ is exposed to air in which the relative humidity is greater than 30%, it absorbs water and forms a saturated solution. Deliquescence continues until the vapor pressure of the solution becomes equal to that of the water in the air.

The freezing points of electrolyte solutions, like their vapor pressures, are lower than those of nonelectrolytes at the same concentration. Sodium chloride and calcium chloride are used to lower the melting point of ice on highways; their aqueous solutions can have freezing points as low as −21 and −55°C, respectively (Figure 10.17).

Potassium chloride is sold for home use because it's kinder to the environment.

© Peter Gudella/Shutterstock.com

Figure 10.17 Truck applying salt, NaCl, on a snow-packed road.

To calculate the freezing point lowering of an electrolyte in water, we use the general equation

$$\Delta T_f = i \times 1.86°C/m \times \text{molality} \qquad (10.6)$$

the multiplier i in this equation is known as the *Van't Hoff factor*. It tells us the number of moles of particles in solution (molecules or ions) per mole of solute. For sugar or other nonelectrolytes, i is 1:

$$C_{12}H_{22}O_{11}(s) \longrightarrow C_{12}H_{22}O_{11}(aq); \qquad 1 \text{ mol sugar} \longrightarrow 1 \text{ mol molecules}$$

For NaCl and $CaCl_2$, i should be 2 and 3, respectively.

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq); \qquad 1 \text{ mol NaCl} \longrightarrow 2 \text{ mol ions}$$
$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq); \qquad 1 \text{ mol } CaCl_2 \longrightarrow 3 \text{ mol ions}$$

Similar equations apply for other colligative properties.

$$\Delta T_b = i \times 0.52°C/m \times \text{molality} \qquad (10.7)$$
$$\pi = i \times \text{molarity} \times RT$$

EXAMPLE 10.11

Estimate the freezing points of 0.20 *m* aqueous solutions of KNO_3 and $Cr(NO_3)_3$. Assume that *i* is the number of moles of ions formed per mole of electrolyte.

ANALYSIS

Information given:	molality of solutions
Information implied:	i; k_f; T_f°
Asked for:	T_f

STRATEGY

1. Determine *i* by counting the moles of ions present after the solute dissociates.
2. Apply Equation 10.6 to find ΔT; then find the freezing point of the solution, T_f.

SOLUTION

KNO_3: i	$KNO_3(s) \longrightarrow K^+(aq) + NO_3^-(aq)$
	2 ions: 1 K^+ and NO_3^-; $i = 2$
T_f	$\Delta T = ik_f m = 2(1.86°C/m)(0.20\ m) = 0.74°C$
	$T_f = T_f^\circ - \Delta T = 0°C - 0.74°C =$ $-0.74°C$
$Cr(NO_3)_3$: i	$Cr(NO_3)_3(s) \longrightarrow Cr^{3+}(aq) + 3NO_3^-(aq)$
	4 ions: 1 Cr^{3+} and 3 NO_3^-; $i = 4$
T_f	$\Delta T = ik_f m = 4(1.86°C/m)(0.20\ m) = 1.5°C$
	$T_f = T_f^\circ - \Delta T = 0°C - 1.5°C =$ $-1.5°C$

The data in Table 10.3 suggest that the situation is not as simple as this discussion implies. The observed freezing point lowerings of NaCl and $MgSO_4$ are smaller than would be predicted with $i = 2$. For example, 0.50 *m* solutions of NaCl and $MgSO_4$ freeze at −1.68 and −0.995°C, respectively; the predicted freezing point is −1.86°C. Only in very dilute solution does the multiplier *i* approach the predicted value of 2.

Table 10.3 Freezing Point Lowerings of Solutions

	ΔT_f Observed (°C)		*i* (Calc from ΔT_f)	
Molality	**NaCl**	**$MgSO_4$**	**NaCl**	**$MgSO_4$**
0.00500	0.0182	0.0160	1.96	1.72
0.0100	0.0360	0.0285	1.94	1.53
0.0200	0.0714	0.0534	1.92	1.44
0.0500	0.176	0.121	1.89	1.30
0.100	0.348	0.225	1.87	1.21
0.200	0.685	0.418	1.84	1.12
0.500	1.68	0.995	1.81	1.07

This behavior is generally typical of electrolytes. Their colligative properties deviate considerably from ideal values, even at concentrations below 1 *m*. There are at least a couple of reasons for this effect.

1. Because of electrostatic attraction, an ion in solution tends to surround itself with more ions of opposite than of like charge (Figure 10.18). The existence of this *ionic atmosphere*, first proposed in 1923 by Peter Debye (1884–1966), a Dutch physical chemist, prevents ions from acting as completely independent solute particles. The result is to make an ion somewhat less effective than a nonelectrolyte molecule in its influence on colligative properties.
2. Oppositely charged ions may interact strongly enough to form a discrete species called an *ion pair*. This effect is essentially nonexistent with electrolytes such as NaCl, in which the ions have low charges (+1, −1). However, with $MgSO_4$ (+2, −2 ions), ion pairing plays a major role. Even at concentrations as low as 0.1 *m*, there are more $MgSO_4$ ion pairs than free Mg^{2+} and SO_4^{2-} ions.

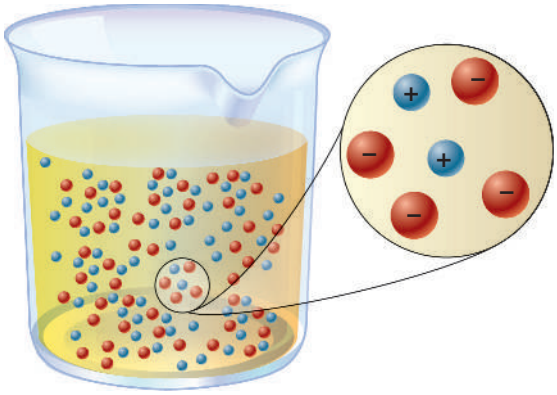


Figure 10.18 Ionic atmosphere. An ion, on the average, is surrounded by more ions of opposite charge than of like charge.

Freezing point lowering (or other colligative properties) can be used to determine the extent of dissociation of a weak electrolyte in water. The procedure followed is illustrated in Example 10.12.

EXAMPLE 10.12 CONCEPTUAL

The freezing point of a 0.50 *m* solution of oxalic acid, $H_2C_2O_4$, in water is −1.12°C. Which of the following equations best represents what happens when oxalic acid dissolves in water?

(1) $H_2C_2O_4(s) \longrightarrow H_2C_2O_4(aq)$

(2) $H_2C_2O_4(s) \longrightarrow H^+(aq) + HC_2O_4^-(aq)$

(3) $H_2C_2O_4(s) \longrightarrow 2H^+(aq) + C_2O_4^{2-}(aq)$

ANALYSIS

Information given:	*m* (0.50) $T_f = -1.12°C$
Information implied:	k_f; $T_f°$
Asked for:	Which equation best represents the dissociation of oxalic acid?

STRATEGY

1. Find *i* for all 3 equations using Equation 10.6.

2. The calculated *i* values should be 1 for equation (1), 2 for equation (2), and 3 for equation (3).

SOLUTION

i

$$i = \frac{\Delta T}{k_f m} = \frac{0°C - (-1.12°C)}{(1.86°C/m)(0.50\ m)} = 1.2$$

Equation (1) gives the value closest to 1.2.

END POINT

Actually about 20% of the oxalic acid is ionized via Equation (2).

Maple Syrup

The collection of maple sap and its conversion to syrup or sugar illustrate many of the principles covered in this chapter. Moreover, in northern New England, making maple syrup is an interesting way to spend the month of March (Figure A), which separates midwinter from "mud season."

The driving force behind the flow of maple sap is by no means obvious. The calculated osmotic pressure of sap, a 2% solution of sucrose (MM = 342 g/mol), is

$$\pi = \frac{20/342 \text{ mol}}{1 \text{ L}} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 280 \text{ K} = 1.3 \text{ atm}$$

This is sufficient to push water to a height of about 45 ft; many maple trees are taller than that. Besides, a maple tree continues to bleed sap for several days after it has been cut down. An alternative theory suggests that sap is forced out of the tree by bubbles of $CO_2(g)$, produced by respiration. When the temperature drops at night, the carbon dioxide goes into solution, and the flow of sap ceases. This would explain the high sensitivity of sap flow to temperature; the aqueous solubility of carbon dioxide doubles when the temperature falls by 15°C.

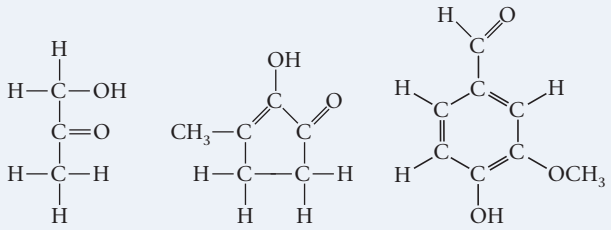
If you want to make your own maple syrup on a small scale, perhaps 10 to 20 L per season, there are a few principles to keep in mind.

1. Make sure the trees you tap are *maples;* hemlocks would be a particularly poor choice. Identify the trees to be tapped in the fall, before the leaves fall. If possible, select sugar maples, which produce about one liter of maple syrup per tree per season. Other types of maples are less productive.

William L. Masterton

Figure A William L. Masterton collecting sap from red maple trees. (WLM made delicious maple syrup—CNH)

2. It takes 20 to 40 L of sap to yield one liter of maple syrup. To remove the water, you could freeze the sap, as the Native Americans did 300 years ago. The ice that forms is pure water; by discarding it, you increase the concentration of sugar in the remaining solution. Large-scale operators today use reverse osmosis to remove about half of the water. The remainder must be boiled off. The characteristic flavor of maple syrup is caused by compounds formed on heating, such as



acetol cyclotene vanillin

It's best to boil off the water outdoors. If you do this in the kitchen, you may not be able to open the doors and windows for a couple of weeks. Wood tends to swell when it absorbs a few hundred liters of water.

3. When the concentration of sugar reaches 66%, you are at the maple syrup stage. The calculated boiling point elevation (660 g of sugar, 340 g of water)

$$\Delta T_b = 0.52°\text{C} \times \frac{660/342}{0.340} = 3.0°\text{C}$$

is somewhat less than the observed value, about 4°C. The temperature rises very rapidly around 104°C (Figure B), which makes thermometry the method of choice for detecting the end point. Shortly before that point, add a drop or two of vegetable oil to prevent foaming; perhaps this is the source of the phrase "spreading oil on troubled waters."

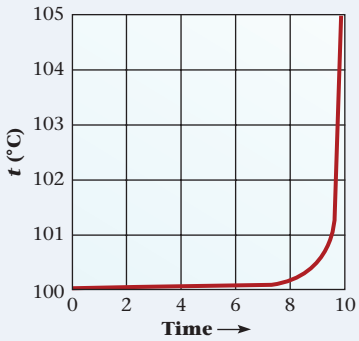


Figure B Boiling maple sap. It seems to take forever to boil down maple sap until you reach 101°C. Then the temperature rises rapidly to the end point, 104°C. Further *careful* heating produces maple sugar.

Key Concepts

1. Make dilution calculations. **(Example 10.1; Problems 11–14, 16)**
2. Calculate a concentration (*M*, *X*, mass %, *m*, ppm). **(Examples 10.2, 10.3; Problems 1–8)**
3. Convert from one concentration unit to another. **(Example 10.4; Problems 9, 10, 15–20)**
4. Apply Henry's law to relate gas solubility to partial pressure. **(Example 10.5; Problems 27–30)**

5. Apply Raoult's law to calculate vapor pressure lowering. **(Example 10.6; Problems 33–36)**
6. Relate freezing point, boiling point, osmotic pressure to solute concentration. **(Examples 10.7, 10.8, 10.10; Problems 31, 32, 37–44, 53–56)**
7. Use colligative properties to determine molar mass of a solute. **(Example 10.9; Problems 45–52)**
8. Use colligative properties to determine extent of ionization. **(Example 10.11; Problems 57, 58)**

Key Equations

Dilution of solution	$M_c V_c = M_d V_d$
Henry's law	$C_g = kP_g$
Raoult's law	$P_1 = X_1 P_1°$; $\Delta P = X_2 P_1°$
Osmotic pressure	$\pi = MRT \times i$
Boiling point	$\Delta T_b = k_b \times m \times i$ ($k_b = 0.52°C/m$ for water) (i = no. of moles of particles per mole of solute)
Freezing point	$\Delta T_f = k_f \times m \times i$ ($k_f = 1.86°C/m$ for water)

Key Terms

boiling point elevation
colligative properties
freezing point lowering
mass percent
molality
molarity
mole fraction
osmosis
osmotic pressure
parts per billion
parts per million

Summary Problem

Consider naphthalene, $C_{10}H_8$, the active ingredient of moth balls. A solution of naphthalene is prepared by mixing 25.0 g of naphthalene with 0.750 L of carbon disulfide, CS_2 (d = 1.263 g/mL). Assume that the volume of the solution is the same as that of the solvent after the solution is prepared.

(a) What is the mass percent of naphthalene in the solution?

(b) What is the concentration of naphthalene in parts per million?

(c) What is the density of the solution?

(d) What is the molarity of the solution?

(e) What is the molality of the solution?

(f) The vapor pressure of pure CS_2 at 25°C is 358 mm Hg. Assume that the vapor pressure exerted by naphthalene is negligible. (It is 1 mm Hg at 50°C.) What is the vapor pressure of the solution at this temperature?

(g) What is the osmotic pressure of the solution at 25°C?

(h) The normal boiling point of CS_2 is 46.13°C ($k_b = 2.34°C/m$). What is the normal boiling point of the solution?

(i) Vasopressin is a hormone secreted by the pituitary gland to regulate the rate at which water is reabsorbed by the kidneys. To determine its molar mass, 10.00 g of vasopressin is dissolved in 50.00 g of naphthalene ($k_f = 6.94°C/m$). The freezing point of the mixture is determined to be 79.01°C; that of pure naphthalene is 80.29°C. What is the molar mass of vasopressin?

Answers

(a) 2.57%
(b) 2.57×10^4 ppm
(c) 1.30 g/mL
(d) 0.260 *M*
(e) 0.206 *m*
(f) 352 mm Hg
(g) 6.36 atm
(h) 46.61°C
(i) 1.08×10^3 g/mol

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

10-1 Concentration Units

1. A solution is prepared by dissolving 12.15 g of nickel(II) nitrate in 175 mL of water (d = 1.00 g/mL). Calculate
(**a**) the mass percent of nickel(II) nitrate in the solution.
(**b**) the mole fraction of nickel(II) ions in the solution.

2. Acetone, C_3H_6O, is the main ingredient of nail polish remover. A solution is made up by adding 35.0 mL of acetone (d = 0.790 g/mL) to 50.0 mL of ethyl alcohol, C_2H_6O (d = 0.789 g/mL). Assuming volumes are additive, calculate
(**a**) the mass percent of acetone in the solution.
(**b**) the volume percent of ethyl alcohol in the solution.
(**c**) the mole fraction of acetone in the solution.

3. For a solution of acetic acid (CH_3COOH) to be called "vinegar," it must contain 5.00% acetic acid by mass. If a vinegar is made up only of acetic acid and water, what is the molarity of acetic acid in the vinegar? The density of the vinegar is 1.006 g/mL.

4. Solutions introduced directly into the bloodstream have to be "isotonic" with blood; that is, they must have the same osmotic pressure as blood. An aqueous NaCl solution has to be 0.90% by mass to be isotonic with blood. What is the molarity of the sodium ions in solution? Take the density of the solution to be 1.00 g/mL.

5. Silver ions can be found in some of the city water piped into homes. The average concentration of silver ions in city water is 0.028 ppm.
(**a**) How many milligrams of silver ions would you ingest daily if you drank eight glasses (eight oz/glass) of city water daily?
(**b**) How many liters of city water are required to recover 1.00 g of silver chemically?

6. Lead is a poisonous metal that especially affects children because children retain a larger fraction of lead than adults do. To date, there is no "safe" concentration of lead in blood. Research shows that 100 μg/L (2 significant figures) of lead in the blood of young children can cause delayed cognitive development. How many moles of lead per liter in a child's blood does 100 μg Pb/L represent? How many ppm? Assume the density of blood is 1.00 g/mL.

7. Complete the following table for aqueous solutions of copper(II) sulfate.

	Mass of Solute	Volume of Solution	Molarity
(a)	12.50 g	478 mL	_____
(b)	_____	283 mL	0.299 *M*
(c)	4.163 g	_____	0.8415 *M*

8. Complete the following table for aqueous solutions of aluminum nitrate.

	Mass of Solute	Volume of Solution	Molarity
(a)	1.672 g	145.0 mL	_____
(b)	2.544 g	_____	1.688 *M*
(c)	_____	894 mL	0.729 *M*

9. Complete the following table for aqueous solutions of caffeine, $C_8H_{10}O_2N_4$.

	Molality	Mass Percent Solvent	Ppm Solute	Mole Fraction Solvent
(a)	_____	_____	_____	0.900
(b)	_____	_____	1269	_____
(c)	_____	85.5	_____	_____
(d)	0.2560	_____	_____	_____

10. Complete the following table for aqueous solutions of theobromine, $C_7H_8N_4O_2$, the alkaloid present in chocolate and cocoa.

	Molality	Mass Percent Solute	Ppm Solvent	Mole Fraction Solute
(a)	_____	_____	_____	0.0542
(b)	_____	_____	557,169	_____
(c)	_____	17.4	_____	_____
(d)	0.8341	_____	_____	_____

11. Describe how you would prepare 465 mL of 0.3550 *M* potassium dichromate solution starting with
(**a**) solid potassium dichromate.
(**b**) 0.750 *M* potassium dichromate solution.

12. Describe how you would prepare 750.0 mL of 0.362 *M* barium hydroxide solution starting with
(**a**) solid barium hydroxide.
(**b**) 4.93 *M* barium hydroxide solution.

13. A solution is prepared by diluting 225 mL of 0.1885 *M* aluminum sulfate solution with water to a final volume of 1.450 L. Calculate
(**a**) the number of moles of aluminum sulfate before dilution.
(**b**) the molarities of the aluminum sulfate, aluminum ions, and sulfate ions in the diluted solution.

14. A solution is prepared by diluting 0.7850 L of 1.262 *M* potassium sulfide solution with water to a final volume of 2.000 L.

(**a**) How many grams of potassium sulfide were dissolved to give the original solution?

(**b**) What are the molarities of the potassium sulfide, potassium ions, and sulfide ions in the diluted solution?

15. A bottle of phosphoric acid is labeled "85.0% H_3PO_4 by mass; density = 1.689 g/cm^3." Calculate the molarity, molality, and mole fraction of the phosphoric acid in solution.

16. A bottle of concentrated aqueous ammonia is labelled "29.8% NH_3 by mass; density = 0.8960 g/mL."

(**a**) What is the molarity of the ammonia solution?

(**b**) If 300.0 mL of the commercial ammonia is diluted with water to make 2.50 L of solution, what is the molarity of the diluted solution?

17. Complete the following table for aqueous solutions of potassium hydroxide.

	Density (g/mL)	Molarity	Molality	Mass Percent of Solute
(a)	1.05	1.13	_____	_____
(b)	1.29	_____	_____	30.0
(c)	1.43	_____	14.2	_____

18. Complete the following table for aqueous solutions of potassium carbonate.

	Density	Molarity	Molality	Mass Percent of Solute
(a)	1.02 g/mL	0.632	_____	_____
(b)	1.16 g/mL	_____	_____	28.5
(c)	1.20 g/mL	_____	5.11	_____

19. Assume that 30 L of maple sap yields one kilogram of maple syrup (66% sucrose, $C_{12}H_{22}O_{11}$). What is the molality of the sucrose solution after one fourth of the water content of the sap has been removed?

20. Juice (d = 1.0 g/mL) from freshly harvested grapes has about 24% sucrose by mass. What is the molality of sucrose, $C_{12}H_{22}O_{11}$, in the grape juice after 25% (by mass) of the water content has been removed? Assume a volume of 15.0 L.

10-2 Principles of Solubility

21. Which of the following is more likely to be soluble in benzene (C_6H_6)? In each case, explain your answer.

(**a**) CCl_4 or NaCl

(**b**) hexane (C_6H_{14}) or glycerol ($CH_2OHCHOHCH_2OH$)

(**c**) acetic acid (CH_3COOH) or heptanoic acid ($C_6H_{13}COOH$)

(**d**) HCl or propylchloride ($CH_3CH_2CH_2Cl$)

22. Which of the following is more likely to be soluble in CCl_4? In each case explain your answer.

(**a**) benzene or KCl (**b**) octane or glycerol

(**c**) $CHCl_3$ or $C_6H_{11}Cl_3$ (**d**) CBr_4 or $CHBr_3$

23. Choose the member of each set that you would expect to be more soluble in water. Explain your answer.

(**a**) naphthalene, $C_{10}H_8$, or hydrogen peroxide, H—O—O—H

(**b**) silicon dioxide or sodium hydroxide

(**c**) chloroform, $CHCl_3$, or hydrogen chloride

(**d**) methyl alcohol, CH_3OH, or methyl ether, $H_3C—O—CH_3$

24. Choose the member of each set that you would expect to be more soluble in water.

(**a**) ethyl chloride (C_2H_5Cl) or ethanol (C_2H_5OH)

(**b**) ammonia (NH_3) or phosphine (PH_3)

(**c**) heptanoic acid ($CH_3(CH_2)_5COOH$) or propionic acid (CH_3CH_2COOH)

(**d**) iodine trichloride or sodium iodide

25. Consider the process by which lead chloride dissolves in water:

$$PbCl_2(s) \longrightarrow Pb^{2+}(aq) + 2Cl^-(aq)$$

(**a**) Using data from tables in Chapter 8, calculate ΔH for this reaction.

(**b**) Based only on thermodynamic data, would you expect the solubility of $PbCl_2$ to increase if the temperature is increased?

26. Consider the process by which calcium carbonate dissolves in water:

$$CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

(**a**) Using data from tables in Chapter 8, calculate ΔH for this reaction.

(**b**) Based only on thermodynamic data, would you expect the solubility of $CaCO_3$ to increase when the temperature is increased?

27. The Henry's law constant for the solubility of helium gas in water is 3.8×10^{-4} *M*/atm at 25°C.

(**a**) Express the constant for the solubility of helium gas in *M*/mm Hg.

(**b**) If the partial pressure of He at 25°C is 293 mm Hg, what is the concentration of dissolved He in mol/L at 25°C?

(**c**) What volume of helium gas can be dissolved in 10.00 L of water at 293 mm Hg and 25°C? (Ignore the partial pressure of water.)

28. The Henry's law constant for the solubility of argon gas in water is 1.0×10^{-3} *M*/atm at 30°C.

(**a**) Express the constant in *M*/mm Hg.

(**b**) If the partial pressure of argon gas at 30°C is 693 mm Hg, what is the concentration (in *M*) of the dissolved argon gas at 30°C?

(**c**) How many grams of argon gas can be dissolved in 29 L of water at 693 mm Hg and 30°C? (Ignore the partial pressure of water.)

29. A carbonated beverage is made by saturating water with carbon dioxide at 0°C and a pressure of 3.0 atm. The bottle is then opened at room temperature (25°C), and comes to

equilibrium with air in the room containing CO_2 ($P_{CO_2} = 3.4 \times 10^{-4}$ atm). The Henry's law constant for the solubility of CO_2 in water is 0.0769 *M*/atm at 0°C and 0.0313 *M*/atm at 25°C.

(a) What is the concentration of carbon dioxide in the bottle before it is opened?

(b) What is the concentration of carbon dioxide in the bottle after it has been opened and come to equilibrium with the air?

30. Air contains 78% nitrogen. At 25°C, Henry's law constant for nitrogen is 6.8×10^{-4} *M*/atm, while at 37°C, it is 6.2×10^{-4} *M*/atm.

(a) How many milligrams of the nitrogen in the air will dissolve in 3.0 L of water at 25°C? The air in the head space above the water has a pressure of 1.38 atm.

(b) How many milligrams of the nitrogen in the air will dissolve in 3.0 L of water at 37°C? The air in the head space above the water has a pressure of 1.38 atm.

(c) How much more nitrogen is dissolved at the lower temperature in mass percent?

10-3 Colligative Properties of Nonelectrolytes

31. Vodka is advertised to be *80 proof*. That means that the ethanol (C_2H_5OH) concentration is 40% (two significant figures) by volume. Assuming the density of the solution to be 1.0 g/mL, what is the freezing point of vodka? The density of ethanol is 0.789 g/mL.

32. What is the freezing point of maple syrup (66% sucrose)? Sucrose is $C_{12}H_{22}O_{11}$.

33. Calculate the vapor pressure of water over each of the following ethylene glycol ($C_2H_6O_2$) solutions at 22°C (vp pure water = 19.83 mm Hg). Ethylene glycol can be assumed to be nonvolatile.

(a) $X_{\text{ethylene glycol}} = 0.288$

(b) percent ethylene glycol by mass = 39.0%

(c) 2.42 *m* ethylene glycol

34. Calculate the vapor pressure of water over each of the following solutions of glycerol, $C_3H_8O_3$, at 28°C (vapor pressure of pure water = 28.35 mm Hg). Glycerol can be assumed to be nonvolatile.

(a) percent glycerol by mass = 30.6%

(b) 2.74 *m*

(c) mole fraction of glycerol = 0.188

35. The vapor pressure of pure CCl_4 at 65°C is 504 mm Hg. How many grams of naphthalene ($C_{10}H_8$) must be added to 25.00 g of CCl_4 so that the vapor pressure of CCl_4 over the solution is 483 mm Hg? Assume that the vapor pressure of naphthalene at 65°C is negligible.

36. Consider an aqueous solution of urea, ($CO(NH_2)_2$) at 26°C. Its vapor pressure is 21.15 mm Hg (vapor pressure of pure H_2O = 25.21 mm Hg). How would you prepare 250.0 mL of this solution (d = 1.06 g/mL)?

37. Calculate the osmotic pressure of the following solutions of urea, $(NH_2)_2CO$, at 22°C.

(a) 0.217 *M* urea

(b) 25.0 g urea dissolved in enough water to make 685 mL of solution.

(c) 15.0% urea by mass (density of the solution = 1.12 g/mL)

38. Pepsin is an enzyme involved in the process of digestion. Its molar mass is about 3.50×10^4 g/mol. What is the osmotic pressure in mm Hg at 30°C of a 0.250-g sample of pepsin in 55.0 mL of an aqueous solution?

39. Calculate the freezing point and normal boiling points of each of the following aqueous solutions.

(a) 2.63 *m* acetic acid

(b) 33.0% by mass lactose, $C_{12}H_{22}O_{11}$

(c) 32.15 mL of ethylene glycol, $C_2H_6O_2$ (d = 1.113 g/mL) in 624 mL of water (d = 1.00 g/mL)

40. How many grams of the following nonelectrolytes would have to be mixed with 100.0 g of *p*-dichlorobenzene to increase the boiling point by 3.0°C? To decrease the freezing point by 2.0°C? (Use Table 10.2.)

(a) succinic acid ($C_4H_6O_4$)

(b) caffeine ($C_8H_{10}N_4O_2$)

41. What is the freezing point and normal boiling point of a solution made by adding 39 mL of acetone, C_3H_6O, to 225 mL of water? The densities of acetone and water are 0.790 g/cm^3 and 1.00 g/cm^3, respectively.

42. Antifreeze solutions are aqueous solutions of ethylene glycol, $C_2H_6O_2$ (d = 1.12 g/mL). In Connecticut, cars are "winterized" by filling radiators with an antifreeze solution that will protect the engine for temperatures as low as −20°F.

(a) What is the minimum molality of antifreeze solution required?

(b) How many milliliters of ethylene glycol need to be added to 250 mL of water to prepare the solution called for in (a)?

43. When 13.66 g of lactic acid, $C_3H_6O_3$, are mixed with 115 g of stearic acid, the mixture freezes at 62.7°C. The freezing point of pure stearic acid is 69.4°C. What is the freezing point constant of stearic acid?

44. A solution consisting of 4.50 g of propylene glycol, $C_3H_8O_2$, in 40.5 mL of t-butyl alcohol (d = 0.780 g/mL) freezes at 8.5°C. The freezing point of t-butyl alcohol is 25.5°C. What is its freezing point constant?

45. Insulin is a hormone responsible for the regulation of glucose levels in the blood. An aqueous solution of insulin has an osmotic pressure of 2.5 mm Hg at 25°C. It is prepared by dissolving 0.100 g of insulin in enough water to make 125 mL of solution. What is the molar mass of insulin?

46. Epinephrine (or adrenaline) is a hormone and neurotransmitter. It participates in the fight-or-flight response of the sympathetic nervous system. An aqueous solution of epinephrine is prepared by dissolving 0.250 g of the hormone in enough water to make 0.350 L of solution. The solution has an osmotic pressure of 71.8 mm Hg at 22°C. What is the molar mass of epinephrine?

47. Lauryl alcohol is obtained from the coconut and is an ingredient in many hair shampoos. Its empirical formula is $C_{12}H_{26}O$. A solution of 5.00 g of lauryl alcohol in 100.0 g of benzene boils at 80.78°C. Using Table 10.2, find the molecular formula of lauryl alcohol.

48. The Rast method uses camphor ($C_{10}H_{16}O$) as a solvent for determining the molar mass of a compound. When 2.50 g of cortisone acetate are dissolved in 50.00 g of camphor (k_f = 40.0°C/*m*), the freezing point of the mixture is 173.44°C; that of pure camphor is 178.40°C. What is the molar mass of cortisone acetate?

49. Caffeine is made up of 49.5% C, 5.2% H, 16.5% O, and 28.9% N. A solution made up of 8.25 g of caffeine and 100.0 mL of benzene (d = 0.877 g/mL) freezes at 3.03°C. Pure benzene (k_f = 5.10°C/m) freezes at 5.50°C. What are the simplest and molecular formulas for caffeine?

50. A compound contains 42.9% C, 2.4% H, 16.6% N, and 38.1% O. The addition of 3.16 g of this compound to 75.0 mL of cyclohexane (d = 0.779 g/cm^3) gives a solution with a freezing point at 0.0°C. Using Table 10.2, determine the molecular formula of the compound.

51. A biochemist isolates a new protein and determines its molar mass by osmotic pressure measurements. A 50.0-mL solution is prepared by dissolving 225 mg of the protein in water. The solution has an osmotic pressure of 4.18 mm Hg at 25°C. What is the molar mass of the new protein?

52. A new enzyme is isolated and purified. Its molar mass is determined by measuring the osmotic pressure of 0.850 L of an aqueous solution containing 7.89 g of the enzyme. The osmotic pressure of the solution is 1.14 mm Hg at 22°C. What is the molar mass of the enzyme?

10-4 Colligative Properties of Electrolytes

53. Estimate the freezing and normal boiling points of 0.25 m aqueous solutions of

(**a**) NH_4NO_3 (**b**) $NiCl_3$ (**c**) $Al_2(SO_4)_3$

54. Arrange 0.10 m aqueous solutions of the following solutes in order of decreasing freezing point and boiling point.

(**a**) $Al(ClO_3)_3$ (**b**) CH_3OH
(**c**) $(NH_4)_2Cr_2O_7$ (**d**) $MgSO_4$

55. Aqueous solutions introduced into the bloodstream by injection must have the same osmotic pressure as blood; that is, they must be "isotonic" with blood. At 25°C, the average osmotic pressure of blood is 7.7 atm. What is the molarity of an isotonic saline solution (NaCl in H_2O)? Recall that NaCl is an electrolyte; assume complete conversion to Na^+ and Cl^- ions.

56. What is the osmotic pressure of a 0.135 M solution of Na_2SO_4 at 20°C? (Assume complete dissociation.)

57. The freezing point of a 0.11 m solution of HNO_2 is −0.20°C.

(**a**) What is i for the solution?
(**b**) Is the solution made
(**i**) of HNO_2 molecules only?
(**ii**) of H^+ and NO_2^- only?
(**iii**) of more HNO_2 molecules than H^+ ions?
(**iv**) primarily of H^+ and NO_2^- ions with some HNO_2 molecules?

58. The freezing point of a 0.21 m aqueous solution of H_2SO_4 is −0.796°C.

(**a**) What is i?
(**b**) Is the solution made up primarily of
(**i**) H_2SO_4 molecules only?
(**ii**) H^+ and HSO_4^- ions?
(**iii**) 2 H^+ and 1 SO_4^{2-} ions?

59. An aqueous solution of LiX is prepared by dissolving 3.58 g of the electrolyte in 283 mL of H_2O (d = 1.00 g/mL). The solution freezes at −1.81°C. What is X^-? (Assume complete dissociation of LiX to Li^+ and X^-.)

60. An aqueous solution of M_2O is prepared by dissolving 10.91 g of the electrolyte in 435 mL of H_2O (d = 1.00 g/mL). The solution freezes at −4.68°C. What is M^+? (Assume complete dissociation of M_2O to M^+ and O^{2-}.)

Unclassified

61. A sucrose ($C_{12}H_{22}O_{11}$) solution that is 45.0% sucrose by mass has a density of 1.203 g/mL at 25°C. Calculate its

(**a**) molarity.
(**b**) molality.
(**c**) vapor pressure (vp H_2O at 25°C = 23.76 mm Hg).
(**d**) normal boiling point.

62. An aqueous solution made up of 32.47 g of iron(III) chloride in 100.0 mL of solution has a density of 1.249 g/mL at 25°C. Calculate its

(**a**) molarity.
(**b**) molality.
(**c**) osmotic pressure at 25°C (assume i = 4).
(**d**) freezing point.

63. How would you prepare 5.00 L of a solution that is 43.0% H_2SO_4 by mass if the resulting solution has a density of 1.329 g/mL? What is the molarity of the resulting solution?

64. Carbon tetrachloride (CCl_4) boils at 76.8°C and has a density of 1.59 g/mL.

(**a**) A solution prepared by dissolving 0.287 mol of a nonelectrolyte in 255 mL of CCl_4 boils at 80.3°C. What is the boiling point constant (k_b) for CCl_4?
(**b**) Another solution is prepared by dissolving 37.1 g of an electrolyte (MM = 167 g/mol) in 244 mL of CCl_4. The resulting solution boils at 85.2°C. What is i for the electrolyte?

65. Twenty-five milliliters of a solution (d = 1.107 g/mL) containing 15.25% by mass of sulfuric acid is added to 50.0 mL of 2.45 M barium chloride.

(**a**) What is the expected precipitate?
(**b**) How many grams of precipitate are obtained?
(**c**) What is the chloride concentration after precipitation is complete?

66. The Henry's law constant for the solubility of radon in water at 30°C is 9.57×10^{-6} M/mm Hg. Radon is present with other gases in a sample taken from an aquifer at 30°C. Radon has a mole fraction of 2.7×10^{-6} in the gaseous mixture. The gaseous mixture is shaken with water at a total pressure of 28 atm. Calculate the concentration of radon in the water. Express your answers using the following concentration units.

(**a**) molarity
(**b**) ppm (Assume that the water sample has a density of 1.00 g/mL.)

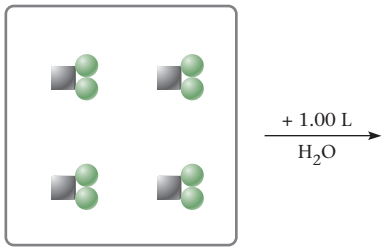
67. Pure bromobenzene, C_6H_5Br, boils at 156.0°C and has a boiling point constant of 6.26°C/m. A sample of bromobenzene is contaminated by anthracene, $C_{14}H_{10}$. The boiling point of the impure sample is 159.2°C. How pure is the sample? (Express your answer as mass percent bromobenzene.)

68. Consider two solutions at a certain temperature. Solution X has a nonelectrolyte as a solute and an osmotic pressure of 1.8 atm. Solution Y also has a nonelectrolyte as a solute and an osmotic pressure of 4.2 atm. What is the osmotic pressure of a solution made up of equal volumes of solutions X and Y at the same temperature? Assume that the volumes are additive.

Conceptual Problems

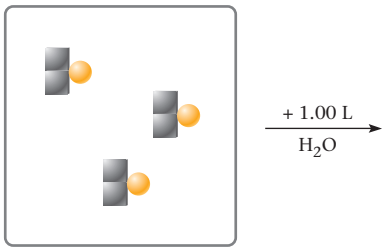
69. A pharmacist prepares an isotonic saline solution for intravenous infusion. Instead of preparing a 0.15 *M* solution, a 1.5 *M* solution is prepared. What would happen to the red blood cells if this erroneously prepared solution is infused?

70. One mole of $CaCl_2$ is represented as □⦙○ where □ represents Ca and ○ represents Cl. Complete the picture showing only the calcium and chloride ions. The water molecules need not be shown.



What is the molarity of Ca^{2+}? of Cl^-?

71. One mole of Na_2S is represented as ⦙○ where □ represents Na and ○ represents S. Complete the picture showing only the sodium and sulfide ions. The water molecules need not be shown.



What is the molarity of Na^+? of S^{2-}?

72. Consider two nonelectrolytes X and Y. X has a higher molar mass than Y. Twenty-five grams of X are dissolved in 100 g of solvent C and labeled solution 1. Twenty-five grams of Y are dissolved in 100 g of solvent C and labeled solution 2. Both solutions have the same density. Which solution has

(a) a higher molarity?
(b) a higher mass percent?
(c) a higher molality?
(d) a larger multiplier *i*?
(e) a larger mole fraction of solvent?

73. Consider three test tubes. Tube A has pure water. Tube B has an aqueous 1.0 *m* solution of ethanol, C_2H_5OH. Tube C has an aqueous 1.0 *m* solution of NaCl. Which of the following statements are true? (Assume that for these solutions 1.0 *m* = 1.0 *M*.)

(a) The vapor pressure of the solvent over tube A is greater than the solvent pressure over tube B.
(b) The freezing point of the solution in tube B is higher than the freezing point of the solution in tube A.
(c) The freezing point of the solution in tube B is higher than the freezing point of the solution in tube C.
(d) The boiling point of the solution in tube B is higher than the boiling point of the solution in tube C.
(e) The osmotic pressure of the solution in tube B is greater than the osmotic pressure of the solution in tube C.

74. The freezing point of 0.20 *m* HF is −0.38°C. Is HF primarily nonionized in this solution (HF molecules), or is it dissociated to H^+ and F^- ions?

75. A certain gaseous solute dissolves in water, evolving 12.0 kJ of heat. Its solubility at 25°C and 4.00 atm is 0.0200 *M*. Would you expect the solubility to be greater or less than 0.0200 *M* at

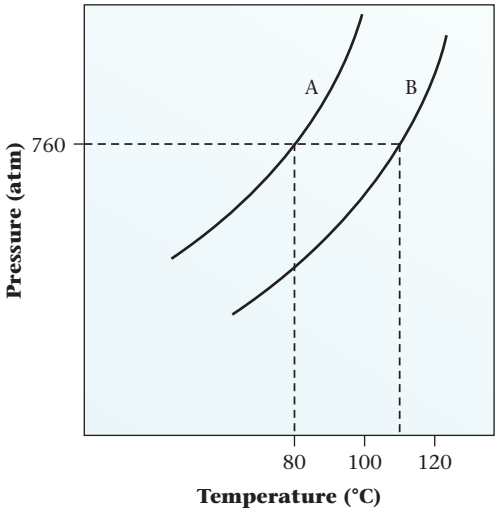
(a) 5°C and 6 atm? (b) 50°C and 2 atm?
(c) 20°C and 4 atm? (d) 25°C and 1 atm?

76. The freezing point of 0.10 *M* $KHSO_3$ is −0.38°C. Which of the following equations best represents what happens when $KHSO_3$ dissolves in water?

(a) $KHSO_3(s) \longrightarrow KHSO_3(aq)$
(b) $KHSO_3(s) \longrightarrow K^+(aq) + HSO_3^-(aq)$
(c) $KHSO_3(s) \longrightarrow K^+(aq) + SO_3^{2-}(aq) + H^+(aq)$

77. Consider 2 vapor pressure curves A and B. They are the vapor pressure curves of pure benzene and a contaminated solution of benzene with a nonvolatile solute.

(a) Which graph shows the vapor pressure curve for pure benzene?
(b) What is the boiling point of the contaminated benzene solution?
(c) Estimate the molality of the contaminated solution (k_b = 2.53°C/*m*).



78. A gaseous solute dissolves in water. The solution process has ΔH = −15 kJ. Its solubility at 22°C and 6.00 atm is 0.0300 *M*. Would you expect the solubility to be greater or less at

(a) 22°C and 1 atm?
(b) 18°C and 6 atm?
(c) 15°C and 10 atm?
(d) 35°C and 3 atm?

79. In your own words, explain

(a) why seawater has a lower freezing point than fresh water.
(b) why one often obtains a "grainy" product when making fudge (a supersaturated sugar solution).
(c) why the concentrations of solutions used for intravenous feeding must be controlled carefully.
(d) why fish in a lake (and fishermen) seek deep, shaded places during summer afternoons.
(e) why champagne "fizzes" in a glass.

80. Explain, in your own words,

(**a**) how to determine experimentally whether a pure substance is an electrolyte or a nonelectrolyte.

(**b**) why a cold glass of beer goes "flat" upon warming.

(**c**) why the molality of a solute is ordinarily larger than its mole fraction.

(**d**) why the boiling point is raised by the presence of a solute.

81. Beaker A has 1.00 mol of chloroform, $CHCl_3$, at 27°C. Beaker B has 1.00 mol of carbon tetrachloride, CCl_4, also at 27°C. Equal masses of a nonvolatile, nonreactive solute are added to both beakers. In answering the questions below, the following data may be helpful.

	$CHCl_3$ (A)	CCl_4 (B)
Vapor pressure at 27°C	0.276 atm	0.164 atm
Boiling point	61.26°C	76.5°C
k_b (°C/*m*)	3.63	5.03

Write <, >, =, or *more information needed* in the blanks provided.

(**a**) Vapor pressure of solvent over beaker B _____ vapor pressure of solvent over beaker A.

(**b**) Boiling point of solution in beaker A _____ boiling point of solution in beaker B.

(**c**) Vapor pressure of pure $CHCl_3$ _____ vapor pressure of solvent over beaker A.

(**d**) Vapor pressure lowering of solvent in beaker A _____ vapor pressure lowering of solvent in beaker B.

(**e**) Mole fraction of solute in beaker A _____ mole fraction of solute in beaker B.

Challenge Problems

82. What is the density of an aqueous solution of potassium nitrate that has a normal boiling point of 103.0°C and an osmotic pressure of 122 atm at 25°C?

83. A solution contains 158.2 g of KOH per liter; its density is 1.13 g/mL. A lab technician wants to prepare 0.250 *m* KOH, starting with 100.0 mL of this solution. How much water or solid KOH should be added to the 100.0-mL portion?

84. Consider a mixture of methyl alcohol (CH_3OH) and n-propyl alcohol ($CH_3CH_2CH_2OH$). A mixture of both alcohols with a mass of 14.2 g is stirred into 100.0 g of water. The freezing point of the new solution is depressed by 5.5°C. What is the mol percent of methyl alcohol in the mixture of both alcohols?

85. The water-soluble nonelectrolyte X has a molar mass of 410 g/mol. A 0.100-g mixture containing this substance and sugar (MM = 342 g/mol) is added to 1.00 g of water to give a solution whose freezing point is −0.500°C. Estimate the mass percent of X in the mixture.

86. A martini, weighing about 5.0 oz (142 g), contains 30.0% by mass of alcohol. About 15% of the alcohol in the martini passes directly into the bloodstream (7.0 L for an adult). Estimate the concentration of alcohol in the blood (g/cm^3) of a person who drinks two martinis before dinner. (A concentration of 0.00080 g/cm^3 or more is frequently considered indicative of intoxication in a "normal" adult.)

87. When water is added to a mixture of aluminum metal and sodium hydroxide, hydrogen gas is produced. This is the reaction used in commercial drain cleaners:

$$2Al(s) + 6H_2O(l) + 2OH^-(aq) \longrightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

A sufficient amount of water is added to 49.92 g of NaOH to make 0.600 L of solution; 41.28 g of Al is added to this solution and hydrogen gas is formed.

(**a**) Calculate the molarity of the initial NaOH solution.

(**b**) How many moles of hydrogen were formed?

(**c**) The hydrogen was collected over water at 25°C and 758.6 mm Hg. The vapor pressure of water at this temperature is 23.8 mm Hg. What volume of hydrogen was generated?

88. Consider an aqueous solution with a boiling point of 105.0°C. The solute in the solution is an ionic compound M_2X. What is the mol fraction of the solute in the mixture?

89. It is found experimentally that the volume of a gas that dissolves in a given amount of water is independent of the pressure of the gas; that is, if 5 cm^3 of a gas dissolves in 100 g of water at 1 atm pressure, 5 cm^3 will dissolve at a pressure of 2 atm, 5 atm, 10 atm, ... Show that this relationship follows logically from Henry's law and the ideal gas law.