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Chem 113: Chemistry

3.00 credits, 3 hours/week

Dr. Abu Bin Imran

Properties of solutions,
Colloid and Nanochemistry,
Introduction to computational chemistry;
Design of new molecules, materials and drug.

Professor Mominul Islam

Electrochemistry; electrolytic conduction, corrosion, devices for energy storage,
Phase rule and phase diagram;
Chemistry of biodegradable and conductive polymer; LED, LCD/touch screen,
Energy and chemistry,

Dr. Ayesha Akter

Quantum concept in atomic structure,
VSEPR; molecular geometry, Quantum concept in bonding; VBT and MOT,
Frontier MOT and electronic transition,
Silicon chemistry,
Chemistry of proteins, nucleic acids (DNA, RNA), carbohydrates and lipids;

References

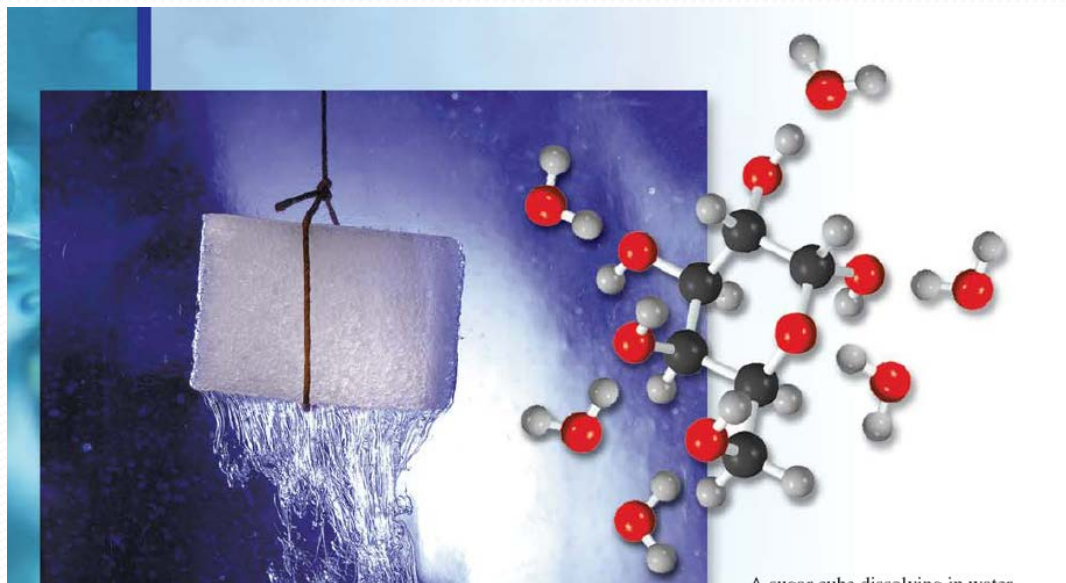
1. Chemistry by Raymond Chang, Kenneth A. Goldsby
2. General Chemistry
By Darrell D. Ebbing and Steven D. Gammon
3. Principles of Physical Chemistry by Kindle edition
by Maron, S. H., Prutton, C.F.



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Solution



A **solution** is a **homogeneous mixture of two or more substances**.

focus involving at least one liquid component—that is, gas-liquid, liquid-liquid, and solid-liquid solutions.

TABLE 12.1 Types of Solutions

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



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

An **unsaturated solution** contains less solute than it has the capacity to dissolve.

A **supersaturated solution**, contains more solute than is present in a saturated solution.

Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals.

Crystallization is the process in which dissolved solute comes out of solution and forms crystals.



Figure 12.1 In a supersaturated sodium acetate solution (left), sodium acetate crystals rapidly form when a small seed crystal is added.

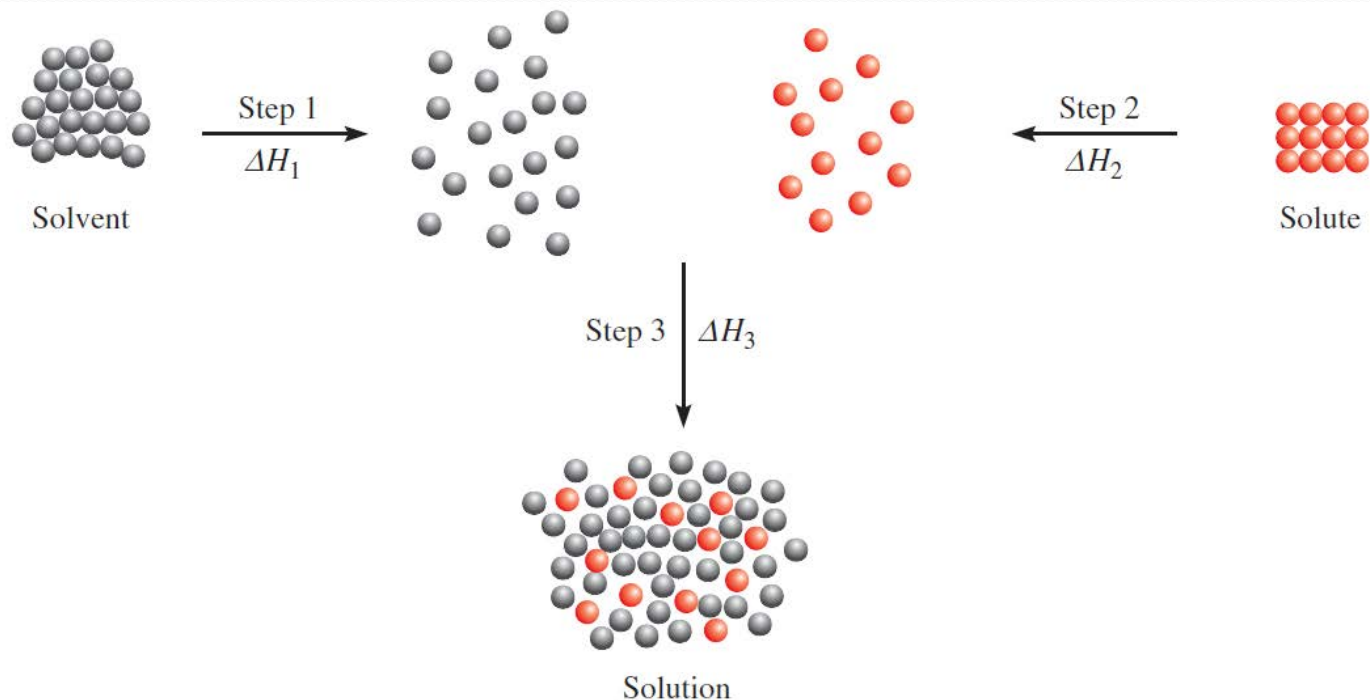
A Molecular View of the Solution Process

The intermolecular attractions that hold molecules together in liquids and solids also play a central role in the formation of solutions. When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules.

The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction

A Molecular View of the Solution Process



Steps 1 and 2 require energy input to **break attractive intermolecular forces**; therefore, they are endothermic. In step 3 the **solvent and solute molecules mix**. This process can be exothermic or endothermic.

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

A Molecular View of the Solution Process

If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favorable, or exothermic ($\Delta H_{\text{soln}} < 0$).

If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H_{\text{soln}} > 0$).

The solution process is governed by two factors. One is energy, which determines whether a solution process is exothermic or endothermic.

The second factor is disorder.

when solute and solvent molecules mix to form a solution, there is an increase in randomness, or disorder. In the pure state, the solvent and solute possess a fair degree of order. Much of this order is destroyed when the solute dissolves in the solvent.

Solubility

Solubility is a measure of **how much solute will dissolve in a solvent at a specific temperature.**

The saying “**like dissolves like**” is helpful in predicting the solubility of a substance in a given solvent.

Carbon tetrachloride (CCl_4) and benzene (C_6H_6) are nonpolar liquids. The **only intermolecular forces present in these substances are dispersion forces.**

When these two liquids are mixed, **they readily dissolve in each other, because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to the forces between CCl_4 molecules and between C_6H_6 molecules.** Two liquids are said to be ***miscible*** if *they are completely soluble in each other in all proportions.*

Solubility

Alcohols such as methanol, ethanol, and 1,2-ethylene glycol are miscible with water because they can form **hydrogen bonds with water molecules**:

When **sodium chloride** dissolves in water, the ions are stabilized in solution by **hydration**, which involves ion-dipole interaction. In general, we predict **that ionic compounds should be much more soluble in polar solvents**, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride. Because the molecules of nonpolar solvents lack a dipole moment, they cannot effectively solvate the Na^+ and Cl^- ions.

Solvation is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner.

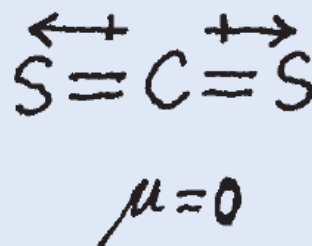
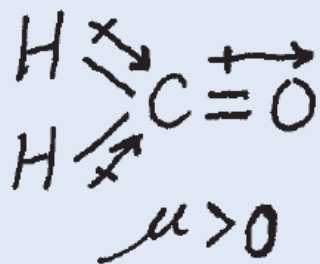
The process is called **hydration** when the **solvent is water**.

Predict the relative solubilities in the following cases: (a) Bromine (Br_2) in benzene (C_6H_6 , $\mu=0$ D) and in water ($\mu=1.87$ D), (b) KCl in carbon tetrachloride (CCl_4 , $\mu=0$ D) and in liquid ammonia (NH_3 , $\mu=1.46$ D), (c) formaldehyde (CH_2O) in carbon disulfide (CS_2 , $\mu=0$ D) and in water.

Solution (a) Br_2 is a nonpolar molecule and therefore should be more soluble in C_6H_6 , which is also nonpolar, than in water. The only intermolecular forces between Br_2 and C_6H_6 are dispersion forces.

(b) KCl is an ionic compound. For it to dissolve, the individual K^+ and Cl^- ions must be stabilized by ion-dipole interaction. Because CCl_4 has no dipole moment, KCl should be more soluble in liquid NH_3 , a polar molecule with a large dipole moment.

(c) Because CH_2O is a polar molecule and CS_2 (a linear molecule) is nonpolar,



the forces between molecules of CH_2O and CS_2 are dipole-induced dipole and dispersion. On the other hand, CH_2O can form hydrogen bonds with water, so it should be more soluble in that solvent.

Concentration Units

Percent by Mass

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

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

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

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

independent of temperature

Concentration Units

Mole Fraction (X)

The mole fraction of a component of a solution, say, component A, is written X_A and is defined as

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

The mole fraction is also unitless

Concentration Units

Molarity (M)

molarity is the number of **moles of solute** in **1 L of solution**;

the units of molarity are **mol/L**.

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

Concentration Units

Molality (m)

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

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

molality is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent. The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 M at 25°C may become 0.97 M at 45°C because of the increase in volume on warming. This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

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

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

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

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

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

Calculate the concentration of a 0.396 m glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution in molarity. Molar mass of glucose = 180.2 g and the density of the solution = 1.16 g/mL

Solⁿ

$$\left(0.396 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6} \times \frac{180.2 \text{ g}}{1 \cancel{\text{mol C}_6\text{H}_{12}\text{O}_6}} \right) + 1000 \text{ g H}_2\text{O} = 1071 \text{ g}$$

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

Finally, the molarity of the solution is given by

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

The density of a 2.45 M aqueous solution of methanol (CH_3OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

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

want to calculate

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

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

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

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

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

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

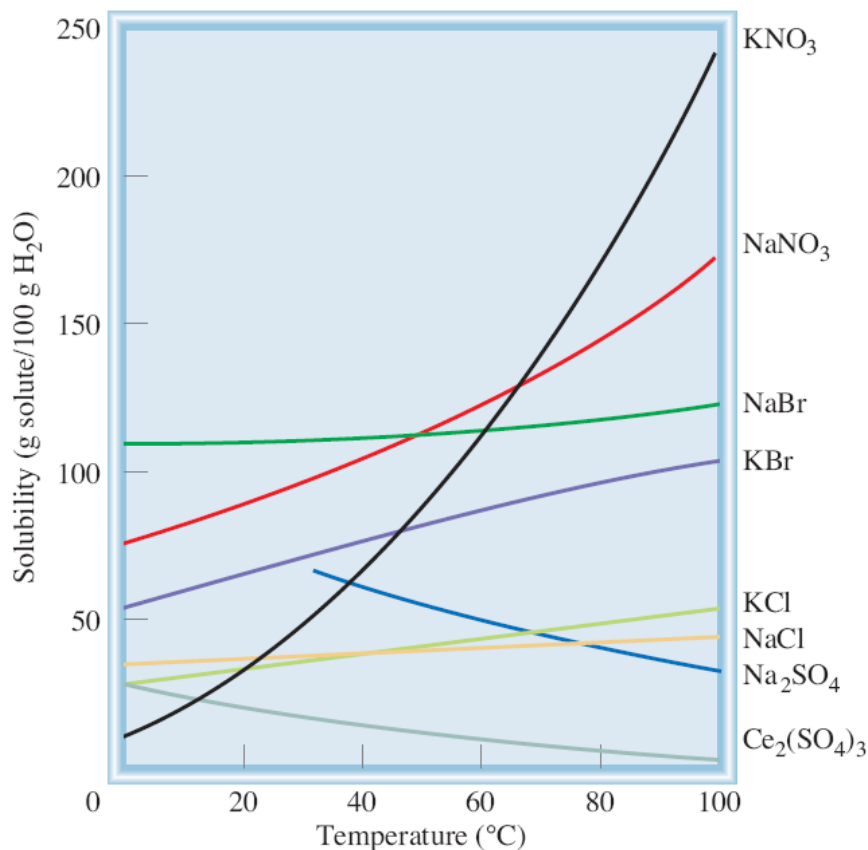
$$\begin{aligned}\text{moles of H}_3\text{PO}_4 &= 35.4 \text{ g H}_3\text{PO}_4 \times \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \\ &= 0.361 \text{ mol H}_3\text{PO}_4\end{aligned}$$

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

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

The Effect of Temperature on Solubility

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



Solid Solubility and Temperature

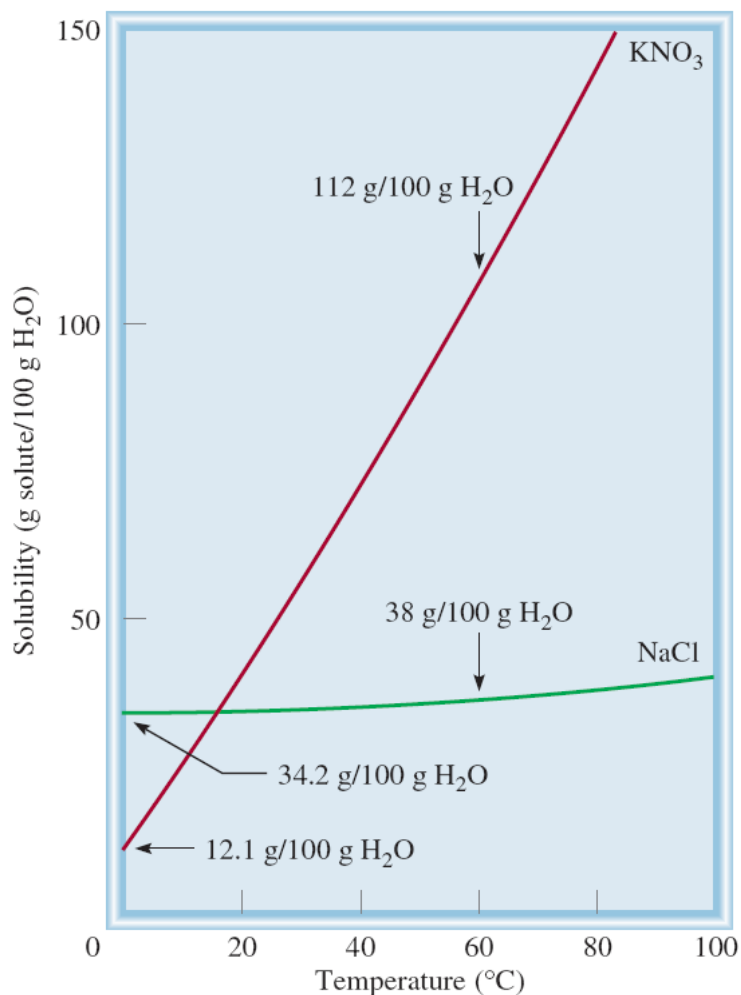
the solubility of a solid substance increases with temperature.

there is no clear correlation between the sign of ΔH_{soln} and the variation of solubility with temperature.

the solution process of CaCl_2 is exothermic, and that of NH_4NO_3 is endothermic

The Effect of Temperature on Solubility

Solid Solubility and Temperature



Fractional Crystallization

Fractional crystallization is the separation of a mixture of substances into pure components on the basis of their differing solubilities.

Many of the solid inorganic and organic compounds that are used in the laboratory were purified by fractional crystallization.

Figure 12.4 The solubilities of KNO₃ and NaCl at 0°C and 60°C. The difference in temperature dependence enables us to isolate one of these compounds from a solution containing both of them, through fractional crystallization.

The Effect of Temperature on Solubility

Gas Solubility and Temperature

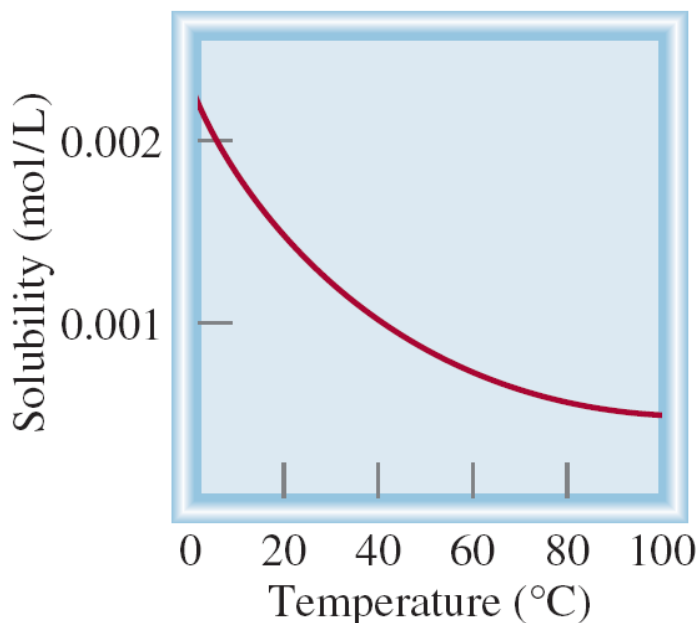


Figure 12.5 *Dependence on temperature of the solubility of O₂ gas in water. Note that the solubility decreases as temperature increases. The pressure of the gas over the solution is 1 atm.*

The solubility of gases in water usually decreases with increasing temperature

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



The Effect of Temperature on Solubility

Gas Solubility and Temperature



Thermal pollution

Every year in the United States some **100,000 billion gallons of water are used for industrial cooling, mostly in electric power and nuclear power production.** This process heats the water, which is then returned to the rivers and lakes from which it was taken.



An increase in water temperature accelerates their rate of metabolism, which generally doubles with each 10°C rise.

The speedup of metabolism increases the fish's need for oxygen at the same time that the supply of oxygen decreases because of its lower solubility in heated water.

The Effect of Temperature on Solubility

Gas Solubility and Temperature

Fishing on a hot summer day



an experienced fisherman usually picks a deep spot in the river or lake to cast the bait. Because the oxygen content is greater in the deeper, cooler region, most fish will be found there.

The Effect of Pressure on the Solubility of Gases

External pressure has **no influence on the solubilities of liquids and solids**, but it does greatly affect the solubility of gases. The quantitative relationship between gas solubility and pressure is given by *Henry's† law, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:*

William Henry (1775–1836). English chemist

$$c \propto P$$

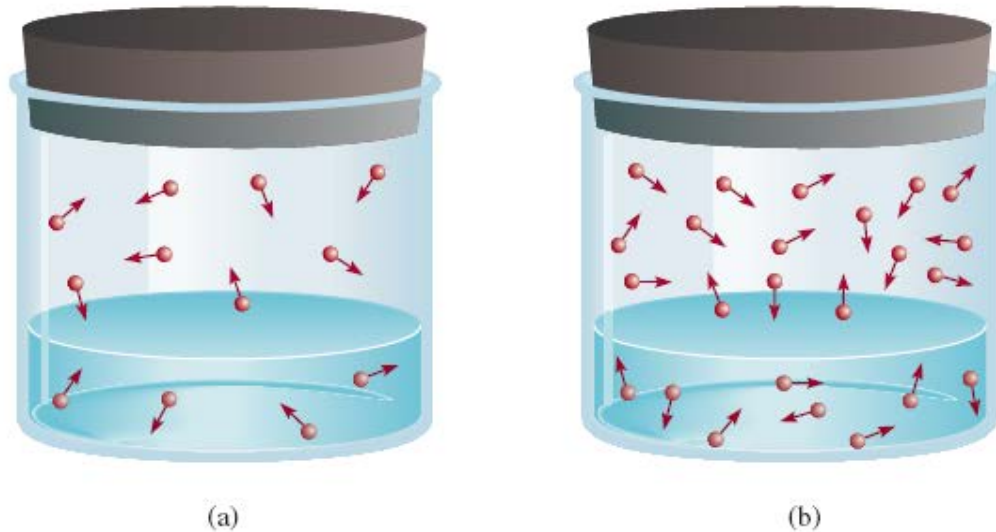
$$c = kP$$

c is the molar concentration (mol/L) of the dissolved gas;
 P is the pressure (in atm) of the gas over the solution at equilibrium;
 k is a constant that depends only on temperature. The constant k has the units mol/L.atm.



The effervescence of a soft drink. The bottle was shaken before being opened to dramatize the escape of CO₂.

The Effect of Pressure on the Solubility of Gases



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

The amount of gas that will dissolve in a solvent depends on how frequently the gas molecules collide with the liquid surface and become trapped by the condensed phase.

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

Solution

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

Therefore, the solubility of nitrogen gas in water is

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

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

The Effect of Pressure on the Solubility of Gases

Exception of Henry's law:

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



- ❑ Carbon dioxide also reacts with water, as follows:



- ❑ Oxygen gas is only sparingly soluble in water. However, its solubility in blood is dramatically greater because of the high content of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:



The Effect of Pressure on the Solubility of Gases



Deep waters in Lake Nyos are pumped to the surface to remove dissolved CO₂ gas.

- ❖ On August 21, 1986, Lake Nyos in Cameroon, a small nation on the west coast of Africa, suddenly belched a dense cloud of carbon dioxide. Speeding down a river valley, the cloud asphyxiated over 1700 people and many livestock.
- ❖ Lake Nyos is stratified into layers that do not mix. A boundary separates the freshwater at the surface from the deeper, denser solution containing dissolved minerals and gases, including CO₂. The CO₂ gas comes from springs of carbonated groundwater that percolate upward into the bottom.
- ❖ earthquake, landslide, or even strong winds may have upset the delicate balance within the lake, creating waves that overturned the water layers.

Colligative Properties of Nonelectrolyte Solutions

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

regardless of whether they are atoms, ions, or molecules.

The colligative properties are

- *vapor-pressure lowering,*
- *boiling-point elevation,*
- *freezing-point depression,*
- *and osmotic pressure.*

Relatively dilute solutions whose **concentrations are $\leq 0.2\text{ M}$.**

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

If a **solute is nonvolatile** (that is, it does not have a measurable vapor pressure),

the vapor pressure of its solution is always less than that of the pure solvent.

Thus, the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution.

This relationship is expressed by Raoult's law

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

Raoult's law: It states that *the vapor pressure of a solvent over a solution, P_1 , is given by the vapor pressure of the pure solvent, P_1° , times the mole fraction of the solvent in the solution, X_1 :*

$$P_1 = X_1 P_1^\circ$$

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

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

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

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

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



Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

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

One driving force in physical and chemical processes is an increase in disorder—the greater the disorder, the more favorable the process. Vaporization increases the disorder of a system because molecules in a vapor have less order than those in a liquid. Because a solution is more disordered than a pure solvent, the difference in disorder between a solution and a vapor is less than that between a pure solvent and a vapor.

The presence of solute particles disrupts the intermolecular forces between the solvent molecules, making it harder for them to escape into the vapor phase.

the vapor pressure of the solution will be lower than that of the pure solvent due to the reduction in the number of solvent molecules at the surface available to evaporate.

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

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

Raoult's law holds equally well in this case:

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

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

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

$$P_T = P_A + P_B$$

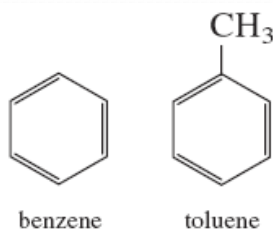
$$P_T = X_A P_A^\circ + X_B P_B^\circ$$

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

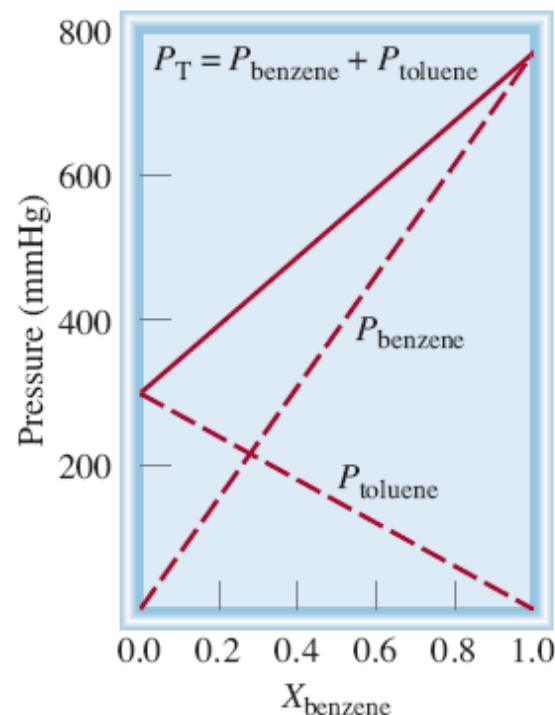
If both components of a solution are *volatile*

In a solution of benzene and toluene, the vapor pressure of each component obeys Raoult's law.



The benzene-toluene solution is one of the few examples of an *ideal solution*, which is any solution that obeys Raoult's law.

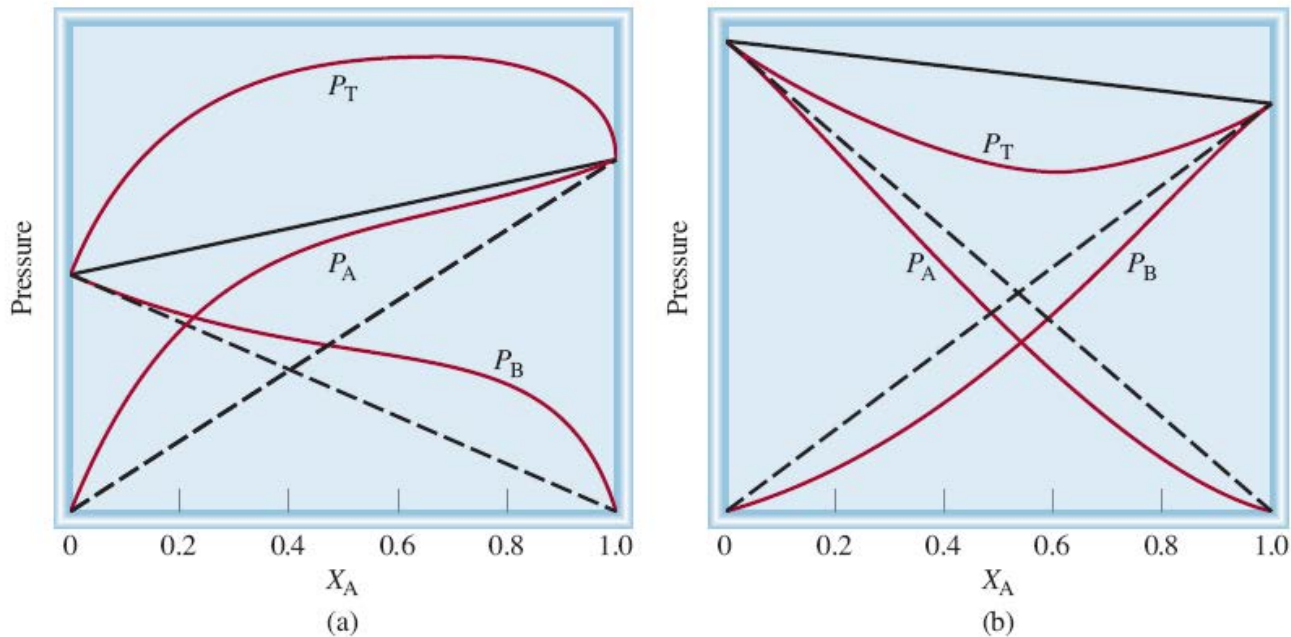
One characteristic of an ideal solution is that the heat of solution, ΔH_{soln} , is zero



The dependence of the partial pressures of benzene and toluene on their mole fractions in a benzene-toluene solution ($X_{\text{toluene}} = 1 - X_{\text{benzene}}$) at 80°C. This solution is said to be ideal because the vapor pressures obey Raoult's law.

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering



Nonideal solutions.

- (a) Positive deviation occurs when P_T is greater than that predicted by Raoult's law (the solid black line).
- (b) Negative deviation. Here, P_T is less than that predicted by Raoult's law (the solid black line).

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

Solution The vapor pressure of a solution (P_1) is

$$P_1 = X_1 P_1^\circ$$

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

the number of moles of glucose and water in the solution:

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

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

The mole fraction of water, X_1 , is given by

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

Therefore, the vapor pressure of the glucose solution is

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

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

Colligative Properties of Nonelectrolyte Solutions

Boiling-Point Elevation

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

The **boiling point elevation** (ΔT_b) is defined as *the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b°)*:

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

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

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

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

where m is the molality of the solution and K_b is the **molal boiling-point elevation constant**. The units of K_b are $^\circ\text{C}/m$.

Colligative Properties of Nonelectrolyte Solutions

Freezing-Point Depression

The **freezing point depression** (ΔT_f) is defined as *the freezing point of the pure solvent (T_f°) minus the freezing point of the solution (T_f)*:

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

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

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

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



Colligative Properties of Nonelectrolyte Solutions

Freezing-Point Depression

Freezing involves a transition from the disordered state to the ordered state.

For this to happen, energy must be removed from the system.

Because a solution has greater disorder than the solvent, more energy needs to be removed from it to create order than in the case of a pure solvent.

Therefore, the solution has a lower freezing point than its solvent.

Colligative Properties of Nonelectrolyte Solutions

Freezing-Point Depression

Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl_2 . This method of thawing succeeds because it depresses the freezing point of water.



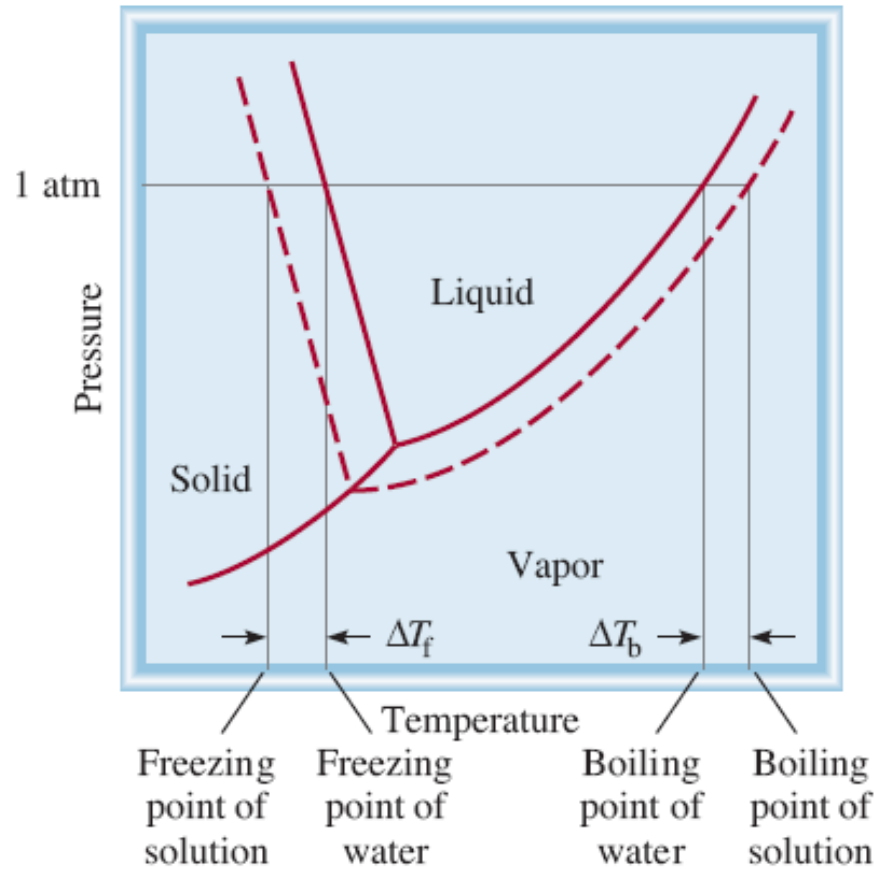
Sprinkling salt over ice



De-icing of airplanes is based on freezing-point depression.



Phase diagram



Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions. The *dashed curves pertain to the solution, and the solid curves to the pure solvent.*

boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water.

Calculate the freezing point of a solution containing 651 g of ethylene glycol in 2505 g of water. Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g and $k_f = 1.86^\circ\text{C}/m$, $K_b = 0.52^\circ\text{C}/m$.

$$\Delta T_f = K_f m$$

Diagram annotations:

- Red arrow pointing to ΔT_f : want to calculate
- Red arrow pointing to K_f : constant
- Red arrow pointing to m : need to find

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

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

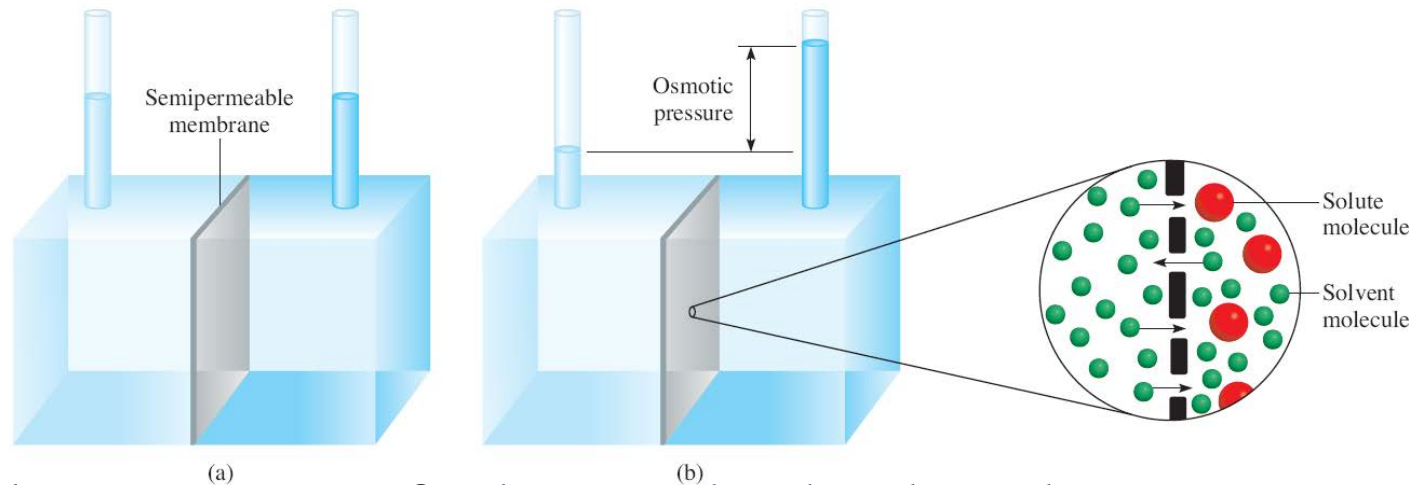
Because pure water freezes at 0°C , the solution will freeze at $(0 - 7.79)^\circ\text{C}$ or -7.79°C .

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

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

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure



The selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. a ***semipermeable membrane***, which *allows the passage of solvent molecules but blocks the passage of solute molecules*.

The **osmotic pressure** (p) of a solution is *the pressure required to stop osmosis*. The osmotic pressure of a solution is given by

$$\pi = MRT$$

where M is the molarity of solution, R is the gas constant ($0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$), and T is the absolute temperature. The osmotic pressure, π , is expressed in atm. Because osmotic pressure measurements are carried out at constant temperature, we express the concentration in terms of the more convenient units of molarity rather than molality.

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure

Osmotic pressure is directly proportional to the concentration of solution.

If two solutions are of equal concentration and, hence, have the same osmotic pressure, they are said to be *isotonic*.

If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic*

and the more dilute solution is described as *hypotonic*

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure

Hemolysis

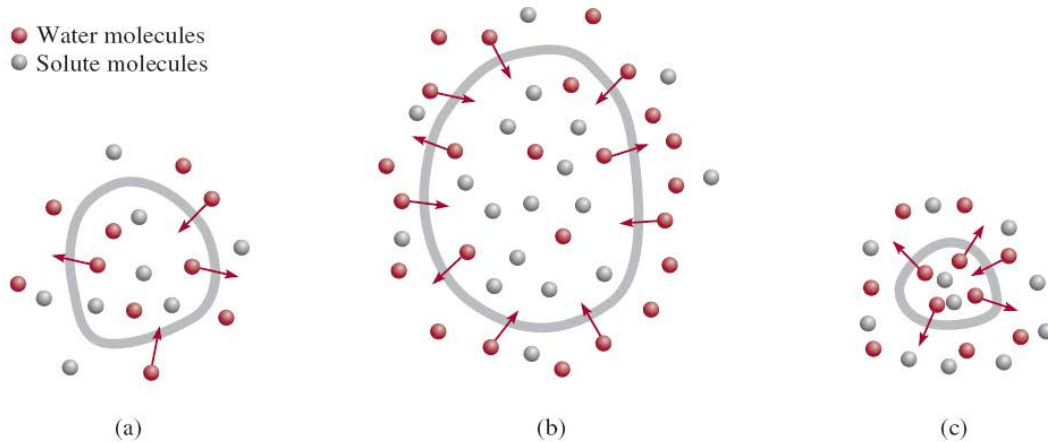
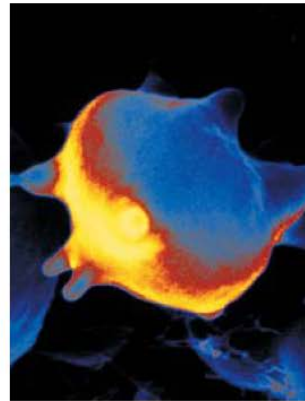
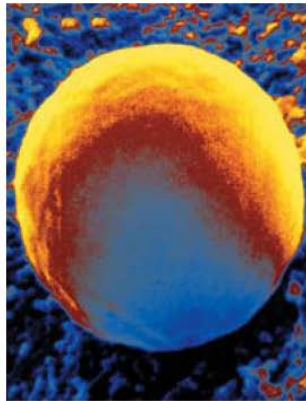
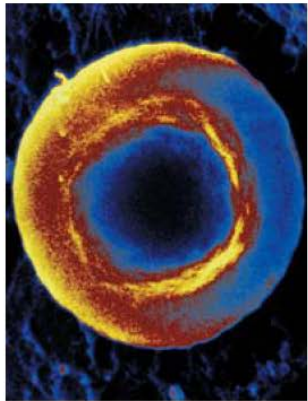


Figure 12.13 A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.



(d)

To study the contents of red blood cells, which are protected from the external environment by a semipermeable membrane, biochemists use a technique called **hemolysis**. The red blood cells are placed in a hypotonic solution. Because the hypotonic solution is less concentrated than the interior of the cell, water moves into the cells. The cells swell and

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure

Preservation of Jam and Jelly



A large quantity of sugar is actually essential to the preservation process because the sugar helps to kill bacteria that may cause botulism. When a bacterial cell is in a hypertonic (high-concentration) sugar solution, the intracellular water tends to move out of the bacterial cell to the more concentrated solution by osmosis. This process, known as *crenation*, causes the cell to shrink and, eventually, to cease functioning.

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure Transporting water upward in plants



Osmotic pressure also is the major mechanism for transporting water upward in plants. Because leaves constantly lose water to the air, in a process called transpiration, the solute concentrations in leaf fluids increase. Water is pulled up through the trunk, branches, and stems of trees by osmotic pressure. Up to 10 to 15 atm pressure is necessary to transport water to the leaves at the tops of California's redwoods, which reach about 120 m in height.

The formula for low-molecular-mass starch is $(C_6H_{10}O_5)_n$, where n averages 200. When 0.798 g of starch is dissolved in 100.0 mL of water solution, what is the osmotic pressure, in mmHg, at 25°C?

Solution The molecular mass of $(C_6H_{10}O_5)_{200}$ is 32,400 amu. The number of moles in 0.798 g of starch is

$$0.798 \text{ g starch} \times \frac{1 \text{ mol starch}}{32,400 \text{ g starch}} = 2.46 \times 10^{-5} \text{ mol starch}$$

The molarity of the solution is

$$\frac{2.46 \times 10^{-5} \text{ mol}}{0.1000 \text{ L solution}} = 2.46 \times 10^{-4} \text{ mol/L solution}$$

and the osmotic pressure at 25°C is

$$\begin{aligned}\pi &= MRT \\ &= 2.46 \times 10^{-4} \text{ mol/L} \times 0.0821 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol}) \times 298 \text{ K} \\ &= 6.02 \times 10^{-3} \text{ atm} = 6.02 \times 10^{-3} \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} \\ &= 4.58 \text{ mmHg}\end{aligned}$$



Using Colligative Properties to Determine Molar Mass

Camphor is a white solid that melts at 179.5°C and freezing-point-depression constant is $40^{\circ}\text{C}/m$. a. A 1.07-mg sample of a compound was dissolved in 78.1 mg of camphor. The solution melted at 176.0°C . What is the molecular mass of the compound? b. If the empirical formula of the compound is CH , what is the molecular formula?

Solution a. The freezing-point lowering is

$$\Delta T_f = (179.5 - 176.0)^{\circ}\text{C} = 3.5^{\circ}\text{C}$$

so the molality of the solution is

$$\frac{\Delta T_f}{K_f} = \frac{3.5^{\circ}\text{C}}{40^{\circ}\text{C}/m} = 0.088\text{ } m$$

moles of the compound that are dissolved in 78.1 mg of camphor

$$0.088\text{ mol/kg} \times 78.1 \times 10^{-6}\text{ kg} = 6.9 \times 10^{-6}\text{ mol}$$

The molar mass of the compound is

$$M_m = \frac{1.07 \times 10^{-3}\text{ g}}{6.9 \times 10^{-6}\text{ mol}} = 1.6 \times 10^2\text{ g/mol}$$

The molecular mass is **160 amu** (two significant figures).

b. The empirical formula mass of CH is 13 amu . Therefore, the number of CH units in the molecule is

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{1.6 \times 10^2\text{ amu}}{13\text{ amu}} = 12$$

The molecular formula is **$\text{C}_{12}\text{H}_{12}$** .

Colligative Properties of Electrolyte Solutions

Electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves. total number of solute particles that determines the colligative properties of a solution. 0.1 *m* CaCl₂ solution to depress the freezing point by three times as much as a 0.1 *m* sucrose solution because each CaCl₂ produces three ions. To account for this effect we define a quantity called the **van't Hoff factor**, given by

$$i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

Consequently, the equations for colligative properties must be modified as

$$\Delta T_b = iK_b m$$

$$\Delta T_f = iK_f m$$

$$\pi = iMRT$$

Colligative Properties of Electrolyte Solutions

In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated because at higher concentrations, electrostatic forces come into play and bring about the formation of ion pairs. An **ion pair** is **made up of one or more cations and one or more anions held together by electrostatic forces**. The presence of an ion pair reduces the number of particles in solution, causing a reduction in the colligative properties.

Electrolytes containing multicharged ions such as Mg^{2+} , Al^{3+} , SO_4^{2-} , and PO_4^{3-} have a greater tendency to form ion pairs than electrolytes such as NaCl and KNO_3 , which are made up of singly charged ions.

TABLE 12.3 The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

Electrolyte	<i>i</i> (Measured)	<i>i</i> (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO ₄	1.3	2.0
MgCl ₂	2.7	3.0
FeCl ₃	3.4	4.0

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

Estimate the freezing point of a 0.010 m aqueous solution of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$. Assume the value of i based on the formula of the compound.

Solution When aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, dissolves in water, it dissociates into five ions.



Therefore, you assume $i = 5$. The freezing-point depression is

$$\Delta T_f = iK_f c_m = 5 \times 1.86^\circ\text{C}/m \times 0.010 m = 0.093^\circ\text{C}$$

The estimated freezing point of the solution is $0.000^\circ\text{C} - 0.093^\circ\text{C} = -0.093^\circ\text{C}$.

