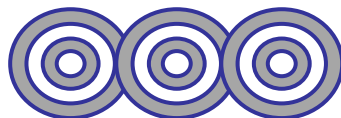*Chemistry, Raymond Chang*
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Chapter 12
Physical Properties of Solutions

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12.1
Types of solutions

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

In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

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.
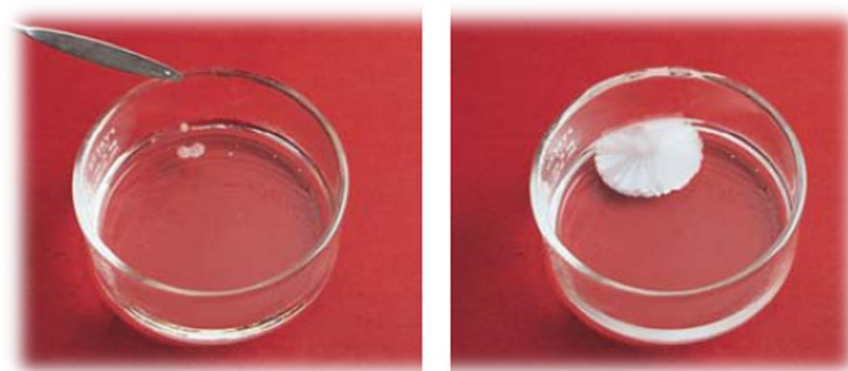
In a supersaturated sodium acetate solution, sodium acetate crystals rapidly form when a small seed crystal is added.

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)

12.2
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.

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
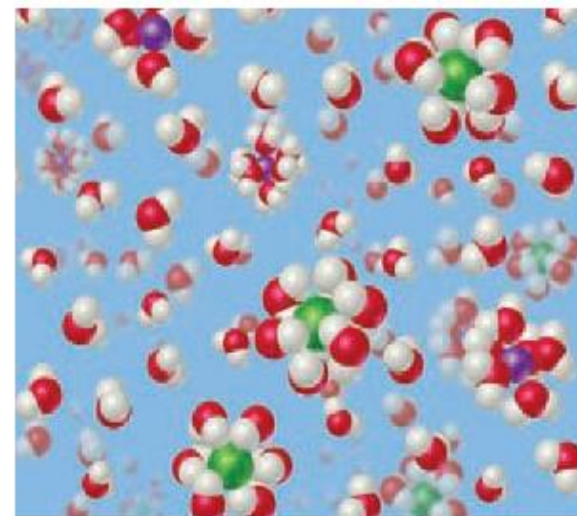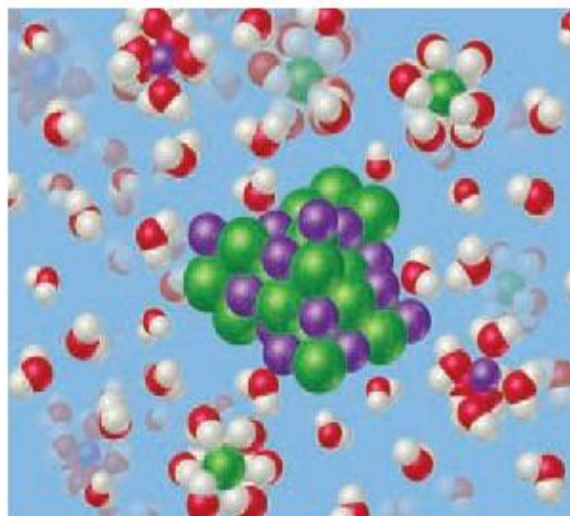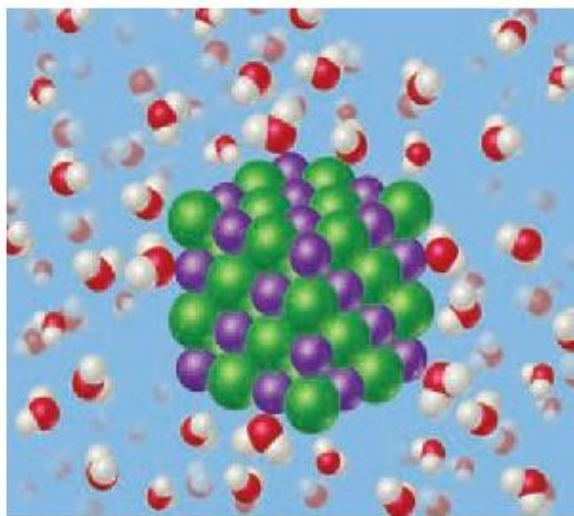
The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.

Three processes affect the energetics of solution:

Step 1 ΔH_1

Solvent

Step 2 ΔH_2

Solute

separation of solvent particles
(breaking solvent-solvent interactions)

separation of solute particles
(breaking solute-solute interactions)

Step 3 ΔH_3

Solution

new interactions between solute and solvent (forming the solute-solvent interactions)
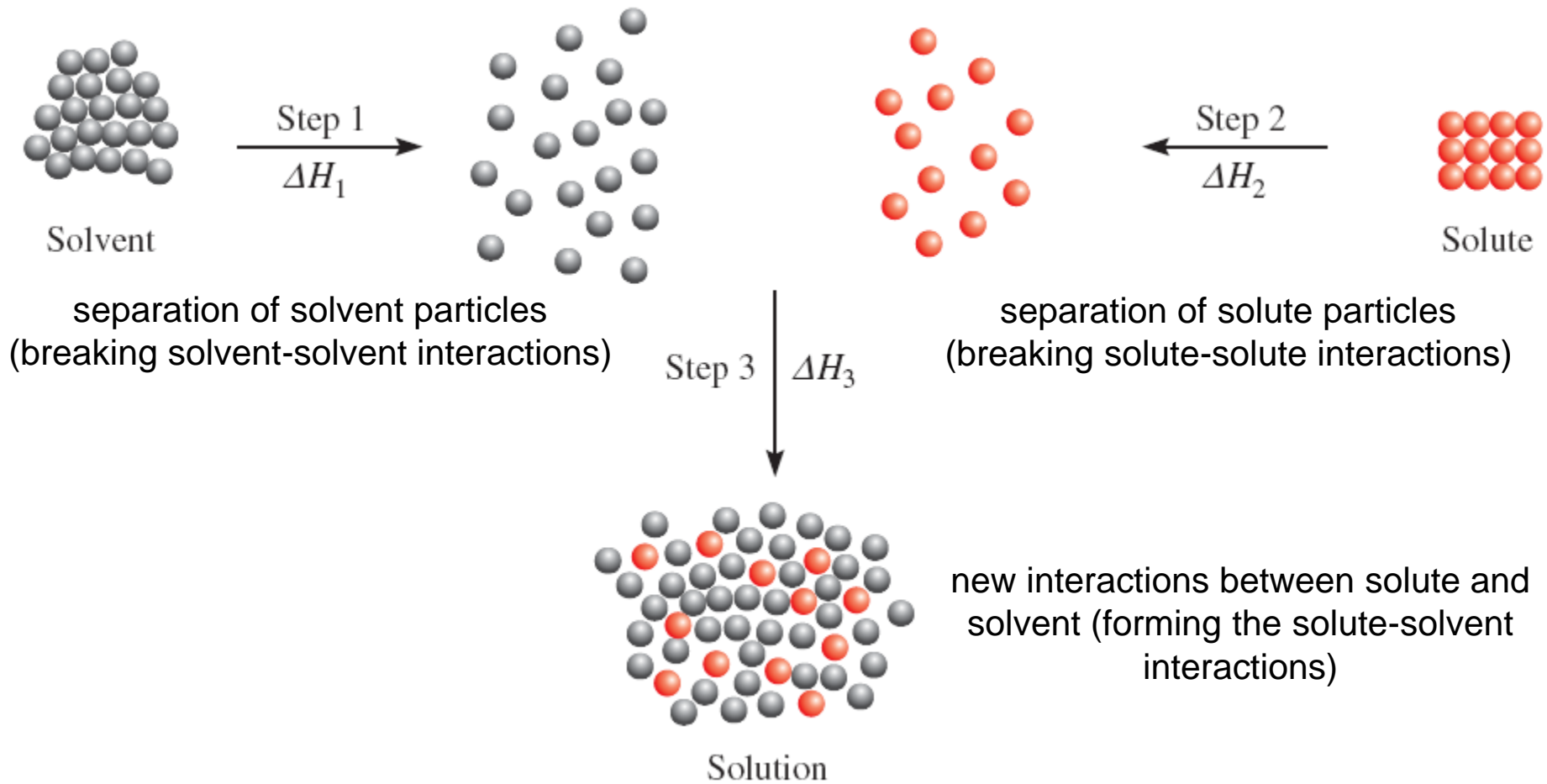
The overall enthalpy change in forming a solution, ΔH_{soln}, is the sum of the three associated processes:

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

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

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

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

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

Chemists use the axiom "**like dissolves like**".

-Polar substances tend to dissolve in polar solvents.
-Nonpolar substances tend to dissolve in nonpolar solvents.

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

The stronger the intermolecular attractions between solute and solvent, the more likely the solute will dissolve.

Examples,,,

Carbon tetrachloride (CCl_4) and benzene (C_6H_6) are readily dissolve in each other. Both CCl_4 and C_6H_6 are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces.

Nonpolar hydrocarbons such as hexane (C_6H_{14}) and octane (C_8H_{18}) dissolve in another nonpolar one like CCl_4.

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

methanol   ethanol   1,2-ethylene glycol
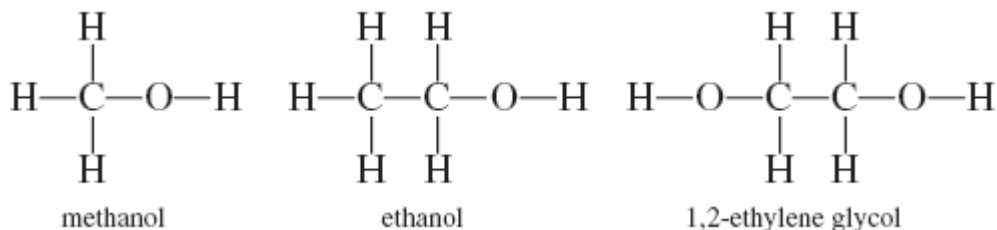
Acetone has a strongly polar **C=O** bond and pairs of nonbonding electrons on the **O** atom that can form hydrogen bonds with water.
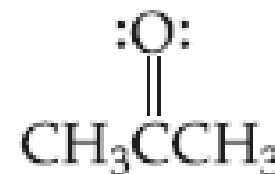

Sodium chloride (**NaCl**) dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction. In general, ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as **benzene** and CCl_4.

Two liquids are said to be **miscible** if they are completely soluble in each other in all proportions.

When **NaCl** is added to **H_2O**, **H_2O** molecules orient themselves on the surface of the **NaCl** crystals.

The +ve end of **H_2O** dipole is oriented toward the **Cl^-** ions, and the −ve end of the **H_2O** dipole is oriented toward the Na^+ ions. The attractions are strong enough to pull the ions from their positions in the crystal. Once separated from the crystal, the **Na^+** and **Cl^-** ion are surrounded by **H_2O** molecules.

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.
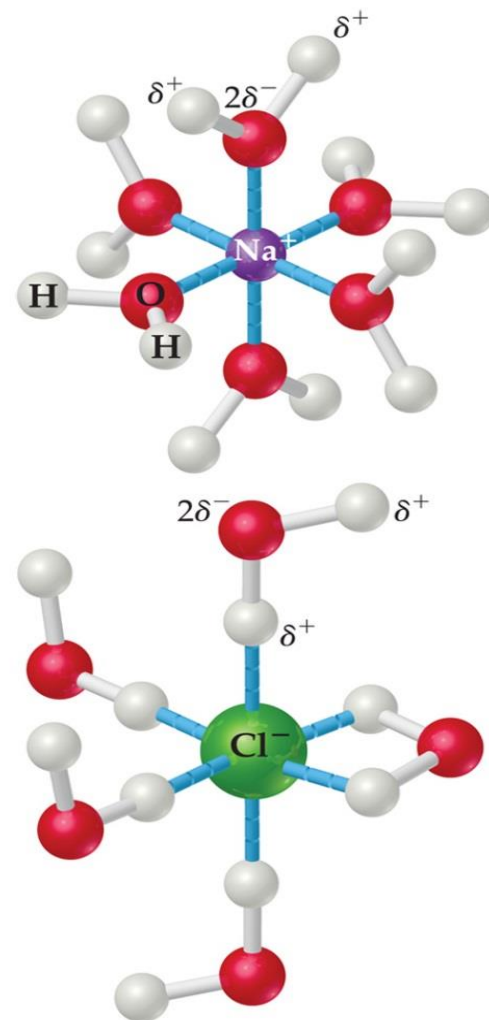
EXAMPLE

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 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.

(a) Br_2 is a nonpolar molecule and therefore should be more soluble in C_6H_6, which is also nonpolar, than in water.

(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 water.

Example

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride (CCl_4) or in water:
(a) C_7H_{16}, (b) Na_2SO_4, (c) HCl, and (d) I_2.

Solution

- C_7H_{16}: hydrocarbon, so it is molecular and nonpolar.
- Na_2SO_4: compound containing a metal and nonmetals, is ionic.
- HCl: containing two nonmetals that differ in electronegativity, is polar.
- I_2: diatomic molecule with atoms of equal electronegativity, is nonpolar.

Therefore,
C_7H_{16} and I_2 (the nonpolar solutes) would be more soluble in the nonpolar CCl_4 than in polar H_2O
Whereas water would be the better solvent for Na_2SO_4 and HCl (the ionic and polar covalent solutes).

12.3
Concentration units

Quantitative study of a solution requires knowing its concentration.

Concentration is the amount of solute present in a given amount of solvent or solution.

Chemists use several different concentration units (different expressions), each of which has advantages as well as limitations.

The most four common units of concentration:
- **percent by mass**,
- **mole fraction**,
- **molarity**,
- **molality**.

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:

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

The percent by mass is a unitless.

EXAMPLE

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

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

$$= \frac{0.892\ \text{g}}{0.892\ \text{g} + 54.6\ \text{g}} \times 100\%$$

$$= 1.61\%$$

Practice Exercise

A sample of 6.44 g of naphthalene ($C_{10}H_8$) is dissolved in 80.1 g of benzene (C_6H_6). Calculate the percent by mass of naphthalene in this solution.

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 unitless.

Molarity (*M*)

Molarity is the number of moles of solute in 1 L of solution.

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

the units of molarity are mol/L.

Molality (*m*)

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

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

the units of molality are mol/kg.

Molarity is generally easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent. On the other hand, molality is independent of temperature; 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.

EXAMPLE

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.

$$\text{moles of } H_2SO_4 = 24.4 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } H_2SO_4}$$

$$= 0.249 \text{ mol } H_2SO_4$$

$$m = \frac{0.249 \text{ mol } H_2SO_4}{0.198 \text{ kg } H_2O}$$

$$= 1.26 \ m$$

Practice Exercise

What is the molality of a solution containing 7.78 g of urea $[(NH_2)_2CO]$ in 203 g of water?

EXAMPLE

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.

Suppose that you start with a 100.0 g of the solution, then the mass of phosphoric acid is 35.4 percent, or 35.4 g, and mass of water must be 100.0% − 35.4% = 64.6% or 64.6 g.

$$\text{moles of } H_3PO_4 = 35.4 \text{ g } H_3PO_4 \times \frac{1 \text{ mol } H_3PO_4}{97.99 \text{ g } H_3PO_4}$$
$$= 0.361 \text{ mol } H_3PO_4$$

The mass of water is 64.6 g, or 0.0646 kg.

$$\text{molality} = \frac{0.361 \text{ mol } H_3PO_4}{0.0646 \text{ kg } H_2O}$$
$$= 5.59 \, m$$

Practice Exercise

Calculate the molality of a 44.6 percent (by mass) aqueous solution of sodium chloride.

EXAMPLE

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.

The total mass of 1 L of a 2.45 M solution of methanol is

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

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

mass of H_2O = mass of soln − mass of solute

$$= 976 \text{ g} - \left(2.45 \text{ mol CH}_3\text{OH} \times \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) = 898 \text{ g}$$

$$\text{molality} = \frac{2.45 \text{ mol CH}_3\text{OH}}{0.898 \text{ kg H}_2\text{O}}$$

$$= 2.73 \ m$$

Practice Exercise

Calculate the molality of a 5.86 M ethanol (C_2H_5OH) solution whose density is 0.927 g/mL.

Example

A solution is made by dissolving 4.35 g glucose ($C_6H_{12}O_6$) in 25.0 mL of water at 25 °C. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

Solution

Use the molar mass of glucose, 180.2 g/mL, to convert grams to moles:

$$\text{Mol } C_6H_{12}O_6 = (4.35 \text{ g } C_6H_{12}O_6)\left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6}\right) = 0.0241 \text{ mol } C_6H_{12}O_6$$

Because water has a density of 1.00 g/mL, the mass of the solvent is

$$(25.0 \text{ mL})(1.00 \text{ g/mL}) = 25.0 \text{ g} = 0.0250 \text{ kg}$$

Finally, the molality:

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.0241 \text{ mol } C_6H_{12}O_6}{0.0250 \text{ kg } H_2O} = 0.964 \text{ } m$$

Practice Exercise

What is the molality of a solution made by dissolving 36.5 g of naphthalene ($C_{10}H_8$) in 425 g of toluene (C_7H_8)?
Answer: 0.670 *m*

Example

An aqueous solution of hydrochloric acid contains 36% HCl by mass. **(a)** Calculate the mole fraction of HCl in the solution. **(b)** Calculate the molality of HCl in the solution.

Solution

(a) To calculate the mole fraction of HCl, we convert the masses of HCl and H_2O to moles:

$$\text{Moles HCl} = (36 \text{ g HCl})\left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}}\right) = 0.99 \text{ mol HCl}$$

$$\text{Moles } H_2O = (64 \text{ g } H_2O)\left(\frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O}\right) = 3.6 \text{ mol } H_2O$$

$$X_{HCl} = \frac{\text{moles HCl}}{\text{moles } H_2O + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

(b) To calculate the molality of HCl in the solution, We use the calculated number of moles of HCl in part (a), and the mass of solvent is $64 \text{ g} = 0.064 \text{ kg}$:

$$\text{Molality of HCl} = \frac{0.99 \text{ mol HCl}}{0.064 \text{ kg } H_2O} = 15 \, m$$

Practice Exercise

A commercial bleach solution contains 3.62 mass % NaOCl in water. Calculate **(a)** the mole fraction and **(b)** the molality of NaOCl in the solution.

Answer: **(a)** 9.00×10^{-3}, **(b)** $0.505 \, m$.

Example

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C_7H_8) and 225 g of benzene. Calculate the molarity of the solution.

Solution

The volume of the solution is obtained from the mass of the solution (mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

$$\text{Moles } C_7H_8 = (5.0 \text{ g } C_7H_8)\left(\frac{1 \text{ mol } C_7H_8}{92 \text{ g } C_7H_8}\right) = 0.054 \text{ mol}$$

The density of the solution is used to convert the mass of the solution to its volume:

$$\text{Milliliters soln} = (230 \text{ g})\left(\frac{1 \text{ mL}}{0.876 \text{ g}}\right) = 263 \text{ mL}$$

Molarity is moles of solute per liter of solution:

$$\text{Molarity} = \left(\frac{\text{moles } C_7H_8}{\text{liter soln}}\right) = \left(\frac{0.054 \text{ mol } C_7H_8}{263 \text{ mL soln}}\right)\left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}}\right) = 0.21 \text{ M}$$

Comment: Because the mass of the solvent (0.225 kg) and the volume of the solution (0.263 L) are similar in magnitude, the molarity and molality are also similar in magnitude:

$$(0.054 \text{ mol } C_7H_8)/(0.225 \text{ kg solvent}) = 0.24 \text{ m}$$

Practice Exercise

A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate **(a)** the molality of glycerol, **(b)** the mole fraction of glycerol, **(c)** the molarity of glycerol in the solution.
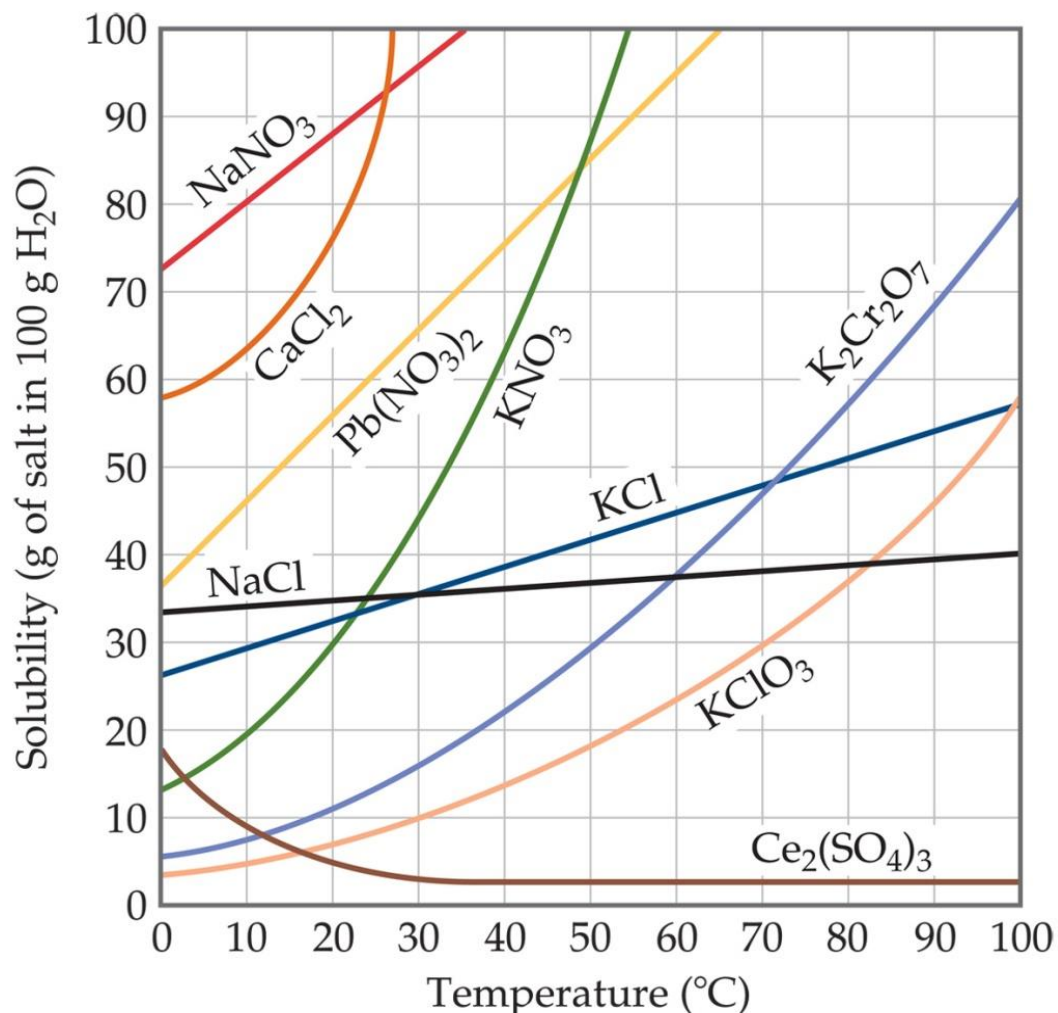***Answer:*** **(a)** 10.9 m, **(b)** X_{C3H8O3}= 0.163, **(c)** 5.97 M

12.4
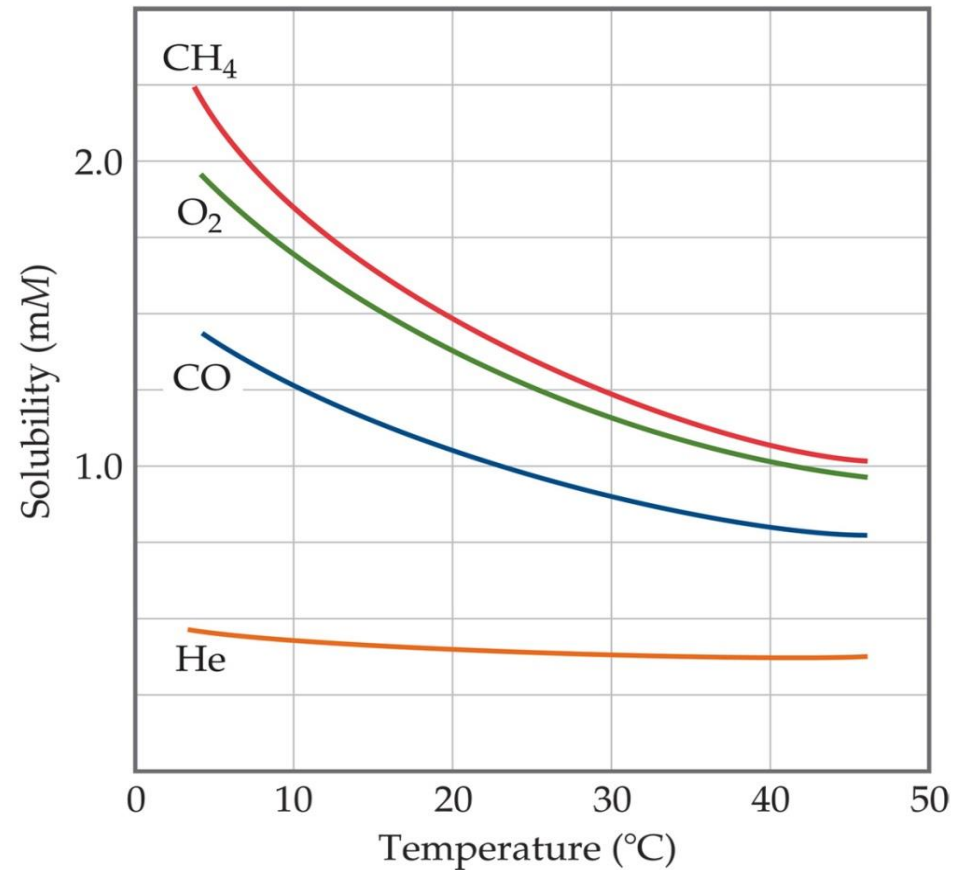# The effect of temperature on solubility

Solid Solubility and Temperature

In most but certainly not all cases, the solubility of a solid substance increases with temperature.

Gas Solubility and Temperature

The solubility of gases in water usually decreases with increasing temperature

12.5
The effect of pressure on the solubility of gases

Henry's Law

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

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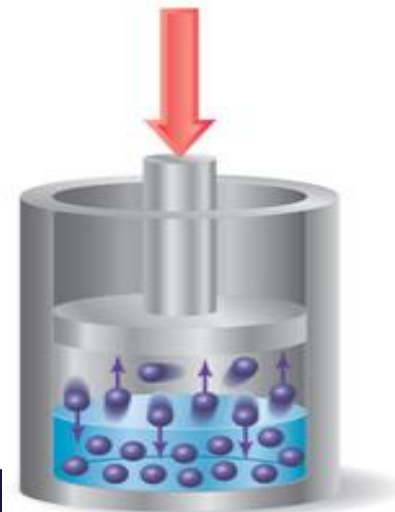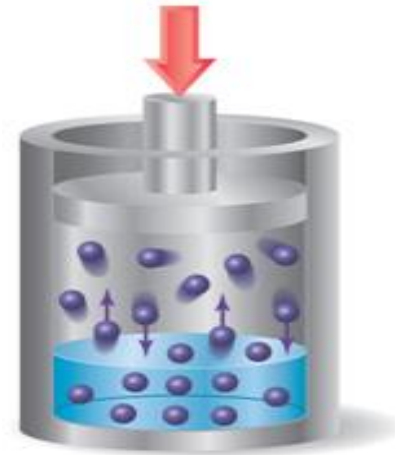
$$c \propto P$$

$$c = kP$$

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; and,
k: is a constant (for a given gas) that depends only on temperature. The constant k has the units mol/L·atm.

EXAMPLE

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

The first step is to calculate the quantity k

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

Therefore, the solubility of nitrogen gas in water is

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

Practice Exercise

Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's law constant for oxygen is 1.3 x 10^{-3} mol/L·atm.

12.6
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.

The colligative properties are:

- Vapor pressure lowering.
- Boiling point elevation.
- Melting point depression.
- Osmotic pressure.

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.

The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration. This relationship is expressed by **Raoult's law**.

$$P_1 = X_1 P_1^{\circ}$$

where:
X_1 : is the mole fraction of a solvent in a solution.
P_1^{o} : is the vapor pressure of pure solvent at that temperature.
P_1 : is the vapor pressure of a solvent over a solution (above the solution).

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

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

$$P_1 = P_1^{\circ} - X_2 P_1^{\circ} \qquad P_1^{\circ} - P_1 = \Delta P = X_2 P_1^{\circ}$$

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

EXAMPLE

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 = 31.82 mmHg. Assume the density of the solution is 1.00 g/mL.

First we calculate the number of moles of glucose and water in the solution:

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

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

The mole fraction of water, X_1,

$$X_1 = \frac{n_1}{n_1 + n_2}$$

$$= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955$$

Therefore, the vapor pressure of the glucose solution is

$$P_1 = X_1 P_1^{\circ} \qquad P_1 = 0.955 \times 31.82 \text{ mmHg}$$
$$= 30.4 \text{ mmHg}$$

Finally, the vapor-pressure lowering is (31.82 - 30.4) = 1.4 mmHg.

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

As solute molecules are added to a solution, the solvent become less volatile (decreased vapor pressure).

Solute-solvent interactions contribute to this effect, because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.
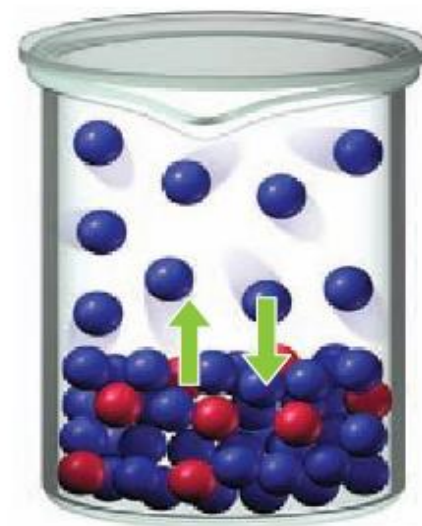
Solvent alone   Solvent + solute

The greater the disorder, the more favorable the process; a solution is more disordered than a pure solvent.

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^0 and P_B^0 are the vapor pressures of the pure substances;
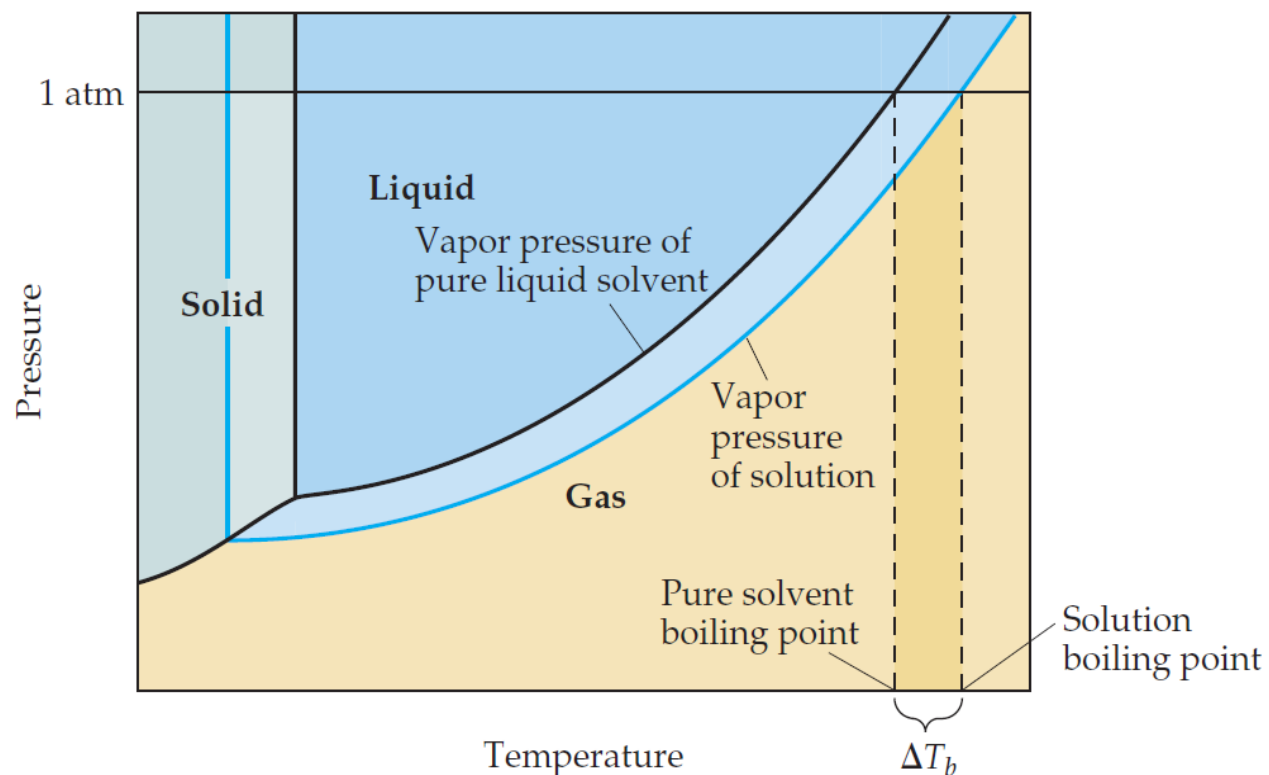- X_A and X_B are their mole fractions.

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

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

Boiling-Point Elevation

The **boiling point** of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points than the pure solvent.

Phase diagram for a pure solvent and for a solution of a nonvolatile solute.

At the normal boiling point of the pure liquid, the vapor pressure of the solution will be less than 1 atm. Therefore, a higher temperature is required to attain a vapor pressure of 1 atm. Thus, the boiling point of the solution is higher than that of the pure liquid.

The change in boiling point is proportional to the **molality** (**m**) of the solution:

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b \, m$$

where:
K_b is the molal boiling point elevation constant, a property of the solvent.
ΔT_b is added to the normal boiling point of the solvent.

The increase in boiling point relative to that of the pure solvent, ΔT_b is a +ve quantity obtained by subtracting the boiling point of the pure solvent from the boiling point of the solution.
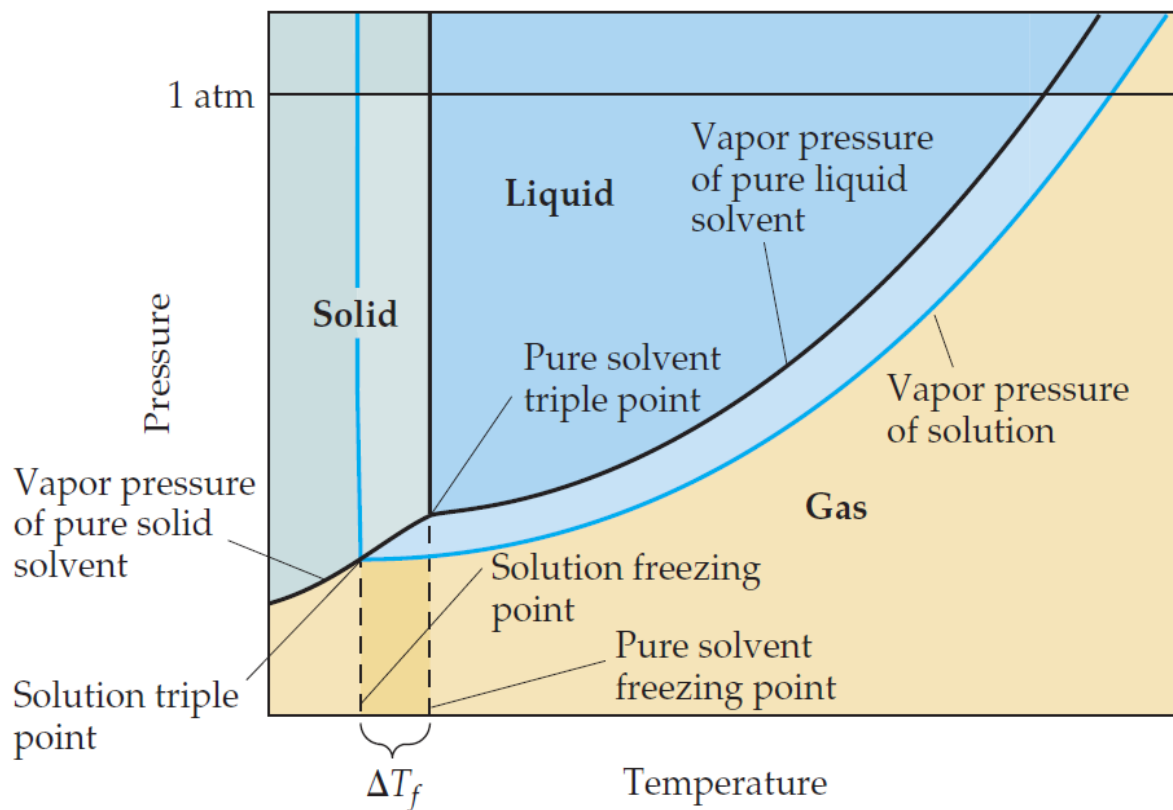
$$\Delta T_b = T_{soln} - T_{pure\ solvent} \qquad (T_{soln} > T_{pure\ solvent})$$

Freezing-Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have lower freezing points than the pure solvent.
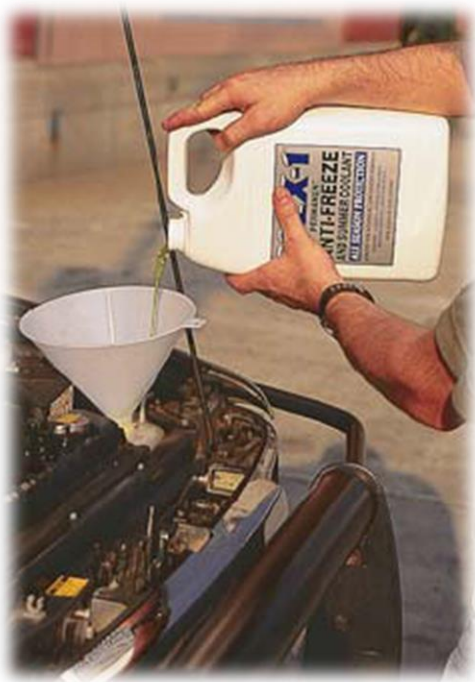
e.g., Antifreeze being added to an automobile radiator. Antifreeze consists of an aqueous solution of ethylene glycol, $CH_2(OH)CH_2(OH)$.

Phase diagram for a pure solvent and for a solution of a nonvolatile solute

Boiling Point Elevation and Freezing Point Depression

$$\Delta T_b = K_b\ m$$

$$\Delta T_f = K_f\ m$$

Molal boiling-point elevation and freezing-point depression constants of several common liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/m)	Normal Boiling Point (°C)*	K_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

For water,

K_b is 0.52 °C/m; therefore, a 1 m aqueous solution of sucrose or any other aqueous solution that is 1 m in nonvolatile solute particles will boil 0.52 °C higher than pure water (100.52°C).

K_f is 1.86 °C/m; therefore, a 1 m aqueous solution of sucrose or any other aqueous solution that is 1 m in nonvolatile solute particles will freeze 1.86 °C lower than pure water (-1.86°C).

EXAMPLE

Ethylene glycol, $CH_2(OH)CH_2(OH)$, is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C). Calculate the freezing point of a solution containing 651 g of this substance 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.

$$651 \text{ g EG} \times \frac{1 \text{ mol EG}}{62.07 \text{ g EG}} = 10.5 \text{ mol EG}$$

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

$$= \frac{10.5 \text{ mol EG}}{2.505 \text{ kg H}_2\text{O}} = 4.19 \text{ mol EG/kg H}_2\text{O}$$

$$= 4.19 \; m$$

$$\Delta T_f = K_f m$$
$$= (1.86°C/m)(4.19 \; m)$$
$$= 7.79°C$$

Because pure water freezes at 0°C, the solution will freeze at (0 - 7.79) = -7.79°C.

We can calculate boiling-point elevation in the same way as follows:

$$\Delta T_b = K_b m$$
$$= (0.52°C/m)(4.19 \; m)$$
$$= 2.2°C$$

Because the solution will boil at (100 + 2.2) = 102.2°C, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

Example

Automotive antifreeze consists of ethylene glycol, $CH_2(OH)CH_2(OH)$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass % solution of ethylene glycol in water.

Solution

The molality of the solution is calculated as follows:

$$\text{Molality} = \frac{\text{moles } C_2H_6O_2}{\text{kilograms } H_2O} = \left(\frac{250 \text{ g } C_2H_6O_2}{750 \text{ g } H_2O}\right)\left(\frac{1 \text{ mol } C_2H_6O_2}{62.1 \text{ g } C_2H_6O_2}\right)\left(\frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O}\right)$$

$$= 5.37 \; m$$

We can now use Equations to calculate the changes in the boiling and freezing points:

$$\Delta T_b = K_b m = (0.51 \,°C/m)(5.37 \; m) = 2.7 \,°C$$

$$\Delta T_f = K_f m = (1.86 \,°C/m)(5.37 \; m) = 10.0 \,°C$$

Hence, the boiling and freezing points of the solution are

$$\text{Boiling point} = (\text{normal bp of solvent}) + \Delta T_b$$
$$= 100.0 \,°C + 2.7 \,°C = 102.7 \,°C$$

$$\text{Freezing point} = (\text{normal fp of solvent}) - \Delta T_f$$
$$= 0.0 \,°C - 10.0 \,°C = -10.0 \,°C$$

Comment: Notice that the solution is a liquid over a larger temperature range than the pure solvent.

Practice Exercise

Calculate the boiling point and freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.

Answer:

T_b: **101.3°C.**

T_f: **-4.48°C.**

Osmotic Pressure

The pressure required to stop or to prevent osmosis by pure solvent, known as **osmotic pressure**, π, of the solution.

The osmotic pressure obeys a law similar in form to the ideal gas law:

$$\pi = MRT$$

where: M is the molarity of solution, R is the gas constant (0.0821 L atm/K mol), and T is the absolute temperature. The osmotic pressure, π, is expressed in atm.
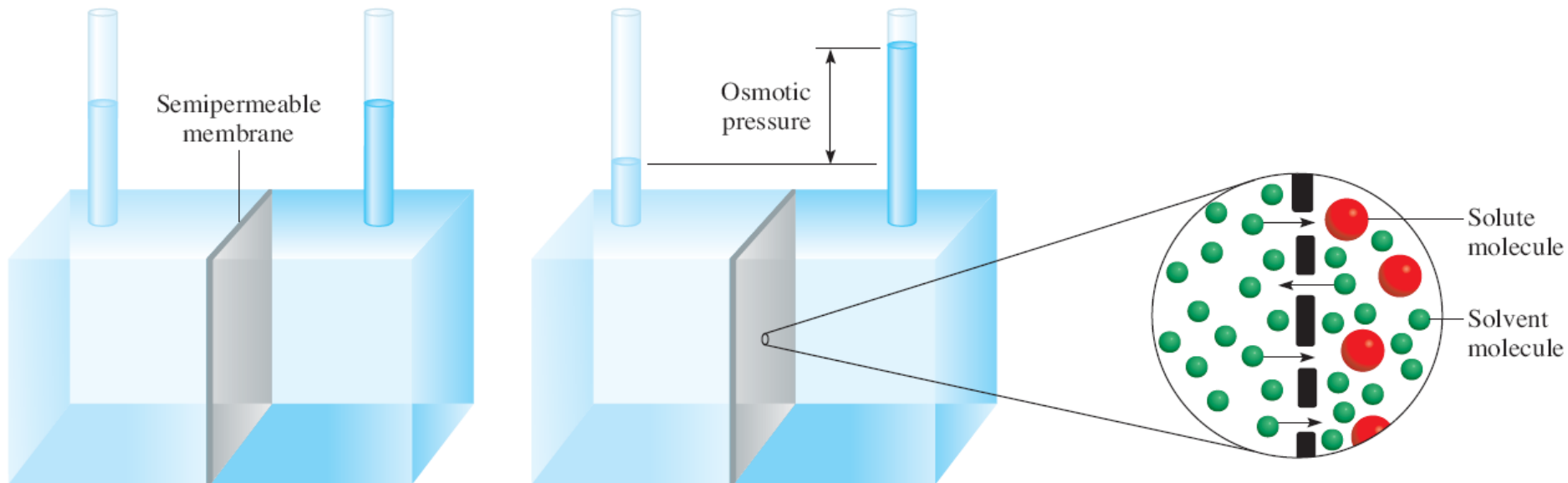

The levels of the pure solvent (left) and of the solution (right) are equal at the start.

During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium.

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**.

Osmosis plays a very important role in living systems.

The membranes of red blood cells, for example, are semipermeable.
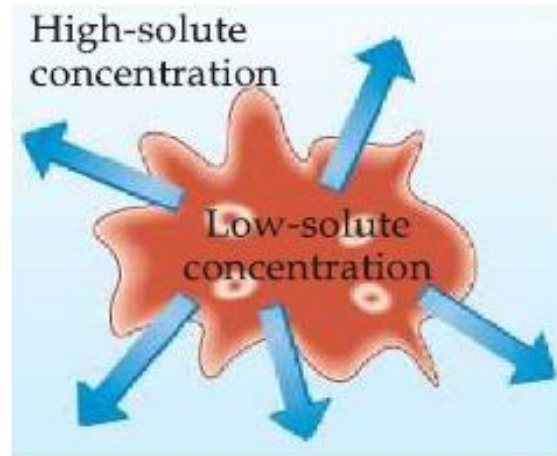
(a) Crenation
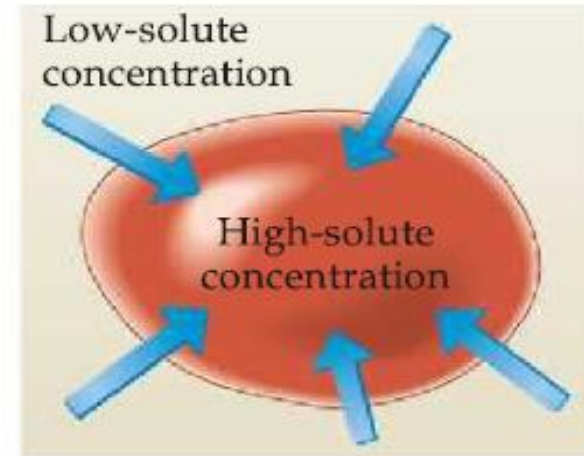
(b) Hemolysis

The blue arrows represent the net movement of water molecules.

Water will flow out of the cell, and **crenation** results (causes the cell to **shrivel**).
Water will flow into the cell, and **hemolysis** results (causes the cell to **rupture**).

EXAMPLE

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

$$\pi = MRT$$

$$M = \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

$$= 1.23 \text{ mol/L}$$

$$= 1.23 \text{ } M$$

Practice Exercise

What is the osmotic pressure (in atm) of a 0.884 M urea solution at 16°C?

Using Colligative Properties to Determine Molar Mass

The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute. Theoretically, any of the four colligative properties is suitable for this purpose. In practice, however, only freezing-point depression and osmotic pressure are used because they show the most pronounced changes.

freezing-point depression → molality → number of moles → molar mass

osmotic pressure → molarity → number of moles → molar mass

EXAMPLE

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene. The freezing point of the solution is 1.05°C below that of pure benzene. What are the molar mass and molecular formula of this compound?

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

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

$$\text{molar mass} = \frac{\text{grams of compound}}{\text{moles of compound}}$$
$$= \frac{7.85\ \text{g}}{0.0617\ \text{mol}} = \boxed{127\ \text{g/mol}}$$

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127\ \text{g/mol}}{64\ \text{g/mol}} \approx 2$$

Therefore, the molecular formula is $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

EXAMPLE

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

$$\pi = MRT$$

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

$$= \frac{10.0 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$

$$= 5.38 \times 10^{-4} \, M$$

The volume of the solution is 1 L, so it must contain 5.38 x 10⁻⁴ mol of Hb.

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$

$$\text{molar mass of Hb} = \frac{\text{mass of Hb}}{\text{moles of Hb}}$$

$$= \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}}$$

$$= 6.51 \times 10^4 \text{ g/mol}$$