General Chemistry

CHEM 101
(3+1+0)

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Chapter 4
Physical Properties of Solutions

Types of Solutions

A *solution* is a homogenous mixture of 2 or more substances.

The *solute* is(are) the substance(s) present in the smaller amount(s).

The *solvent* is the substance present in the larger amount.

Types of solutions, depending on the original states (solid, liquid, or gas) of the solution components.

TABLE 12.1 Types of Solutions			
Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

Types of Solutions

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 the solvent has the capacity to dissolve at a specific temperature.

A *supersaturated solution* contains more solute than is present in a saturated solution at a specific temperature.

Crystallization is *the process in which dissolved solute comes out of solution and forms crystals*
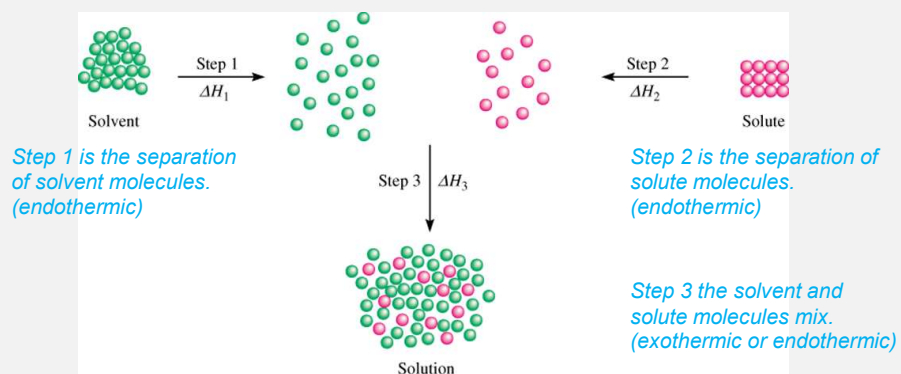
Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.

A Molecular View of the Solution Process

Three types of interactions in the solution process:
o solvent-solvent interaction
o solute-solute interaction
o solvent-solute interaction

Step 1 is the separation of solvent molecules. (endothermic)

Step 2 is the separation of solute molecules. (endothermic)

Step 3 the solvent and solute molecules mix. (exothermic or endothermic)

The heat of solution ΔH_{soln} is given by

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

A Molecular View of the Solution Process

o If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction,

The solution process is favorable, or exothermic (ΔH_{soln} = 0).

o If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions,

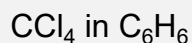*The solution process is endothermic (ΔH_{soln} = 0).*

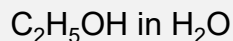## A Molecular View of the Solution Process

"**like dissolves like**"

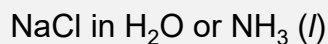Two substances with similar *intermolecular* forces are likely to be soluble in each other.

- o non-polar molecules are soluble in non-polar solvents

    CCl_4 in C_6H_6

- o polar molecules are soluble in polar solvents

    C_2H_5OH in H_2O

- o ionic compounds are more soluble in polar solvents

    $NaCl$ in H_2O or NH_3 (*l*)

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

Concentration Units

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

Types of 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:*

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

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

Concentration Units

EXAMPLE 12.2

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?

Strategy We are given the mass of a solute dissolved in a certain amount of solvent. Therefore, we can calculate the mass percent of KCl using Equation (12.1).

Solution We write

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

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

$$= 1.61\%$$

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.

Concentration Units

Types of 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

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

Concentration Units

Types of Concentration Units

Molarity (*M*)

Molarity was defined as the number of moles of solute in 1 L of solution

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

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*

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

Concentration Units

EXAMPLE 12.3

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.

Strategy To calculate the molality of a solution, we need to know the number of moles of solute and the mass of the solvent in kilograms.

Solution The definition of molality (*m*) is

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

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor.

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

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

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

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

$$= 1.26 \, m$$

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

Concentration Units

Comparison of Concentration Units

For example;

o The ***mole fraction*** is not used to express the concentrations of solutions for titrations and gravimetric analyses.

o It is appropriate for calculating partial pressures of gases and for dealing with vapor pressures of solutions.

o ***Percent by mass*** is similar to molality in that it is independent of temperature.

o It is defined in terms of ratio of mass of solute to mass of solution, We do not need to know the molar mass of the solute in order to calculate the percent by mass.

Concentration Units

Comparison of Concentration Units

o The advantage of ***molarity*** is that it is generally easier to measure the volume of a solution.

For this reason, molarity is often preferred over molality.

o ***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.

o This concentration dependence on temperature can significantly affect the accuracy of an experiment.

Therefore, it is sometimes preferable to use molality instead of molarity.

Concentration Units

Comparison of Concentration Units

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

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

Assume 1 L of solution:
  5.86 moles ethanol = 270 g ethanol
  927 g of solution (1000 mL x 0.927 g/mL)

mass of solvent = mass of solution – mass of solute
$$= 927 \text{ g} - 270 \text{ g} = 657 \text{ g} = 0.657 \text{ kg}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92 \ m$$

Concentration Units

Comparison of Concentration Units

To convert one concentration unit of a solution to another;

Example;

Express the concentration of a 0.396 m glucose ($C_6H_{12}O_6$) solution in molarity.

0.396 m glucose ($C_6H_{12}O_6$) i.e. there is 0.396 mole of glucose in 1000 g of the solvent.

To calculate molarity; we need to determine the volume of this solution.

First, we calculate the mass of the solution from the molar mass of glucose:

$$\left(0.396 \text{ mol } C_6H_{12}O_6 \times \frac{180.2 \text{ g}}{1 \text{ mol } C_6H_{12}O_6}\right) + 1000 \text{ g } H_2O = 1071 \text{ g}$$

Concentration Units

Comparison of Concentration Units

Determine the density of the solution, which is found to be 1.16 g/mL.

We can now calculate the volume of the solution in liters

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

The molarity of the solution is given by

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

Concentration Units

EXAMPLE 12.4

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.

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

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

want to calculate — given — need to find

Solution Our first step is to calculate the mass of water in one liter of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 M solution of methanol is

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

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

$$\text{mass of } H_2O = \text{mass of soln} - \text{mass of solute}$$
$$= 976 \text{ g} - \left(2.45 \text{ mol } CH_3OH \times \frac{32.04 \text{ g } CH_3OH}{1 \text{ mol } CH_3OH}\right)$$

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

$$\text{molality} = \frac{2.45 \text{ mol } CH_3OH}{0.898 \text{ kg } H_2O}$$
$$= 2.73 \ m$$

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

Concentration Units

EXAMPLE 12.5

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.

Strategy In solving this type of problem, it is convenient to assume that we start with a 100.0 g of the solution. If the mass of phosphoric acid is 35.4 percent, or 35.4 g, the percent by mass and mass of water must be $100.0\% - 35.4\% = 64.6\%$ and 64.6 g.

Solution From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

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

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

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

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

The Effect of Temperature on Solubility

Solid solubility and temperature

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

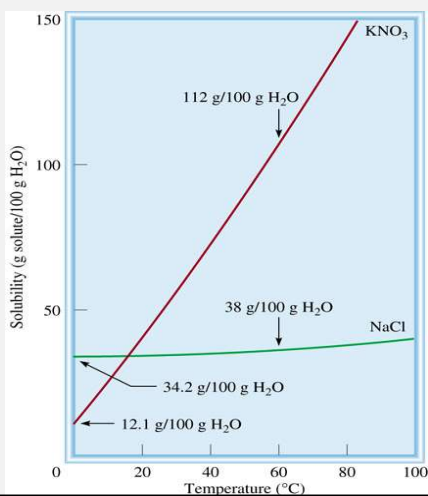○ Temperature affects the solubility of most substances.
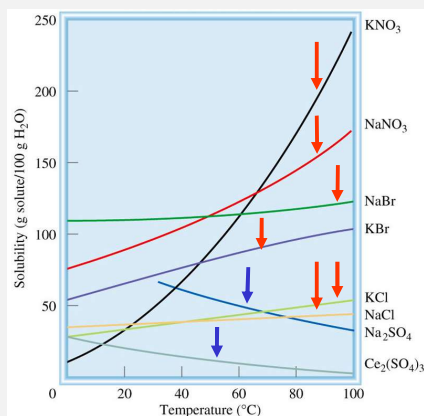
solubility increases with increasing temperature

solubility decreases with increasing temperature

The Effect of Temperature on Solubility

Solid solubility and temperature

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

Suppose you have 90 g KNO_3 contaminated with 10 g NaCl.

Fractional crystallization:

1. Dissolve sample in 100 mL of water at 60^0C

2. Cool solution to 0^0C

3. All NaCl will stay in solution (s = 34.2g/100g)

4. 78 g of PURE KNO_3 will precipitate (s = 12 g/100g). 90 g – 12 g = 78 g

The Effect of Temperature on Solubility

Gas Solubility and Temperature

The solubility of gases in water usually decreases with increasing temperature.

O_2 gas solubility and temperature
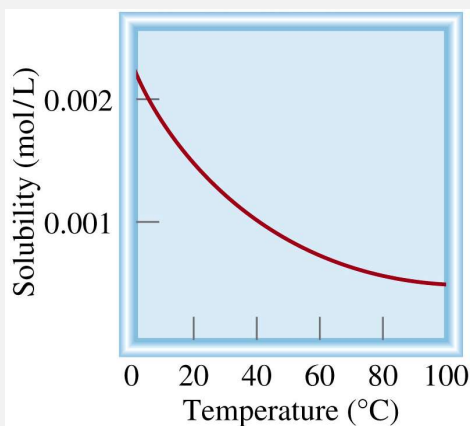
solubility usually decreases with increasing temperature

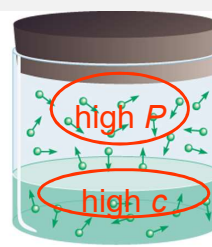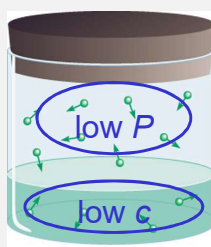## The Effect of Pressure on the Solubility of Gases

The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (*Henry's law*).

$$c = k_H P$$

c is the concentration (*M*) of the dissolved gas

P is the pressure of the gas over the solution

k_H is a constant for each gas (mol/L•atm) that depends only on temperature

A practical demonstration of Henry's law is the effervescence of a soft drink when the cap of the bottle is removed (air and CO_2 saturated with water vapor).

The Effect of Pressure on the Solubility of Gases

EXAMPLE 12.6

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

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

Solution The first step is to calculate the quantity *k* in Equation (12.3):

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

Therefore, the solubility of nitrogen gas in water is

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

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

Check The ratio of the concentrations $[(5.3 \times 10^{-4} \, M/6.8 \times 10^{-4} \, M) = 0.78]$ should be equal to the ratio of the pressures (0.78 atm/1.0 atm = 0.78).

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 1.3×10^{-3} mol/L · atm.

The Effect of Pressure on the Solubility of Gases

o Most gases obey Henry's law, <u>but there are some important exceptions</u>.

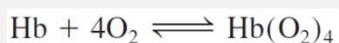o For example, if the dissolved gas *reacts* with water, higher solubilities can result.

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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Carbon dioxide also reacts with water, as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Another interesting example is the dissolution of *molecular oxygen in blood*.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

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.

o **The colligative properties are**

➢ vapor-pressure lowering,

➢ boiling-point elevation,

➢ freezing-point depression,

➢ osmotic pressure.

we are talking about relatively dilute solutions, that is, solutions whose concentrations are ≤ 0.2 *M*.

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering

Raoult's₁ law, which 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:*

$$\boxed{P_1 = X_1 P_1^0}$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

X_1 = mole fraction of the <u>solvent</u>

If the solution contains only one solute:

$$X_1 = 1 - X_2 \qquad P_1 = (1-X_2)P_1^0 \qquad P_1 = P_1^0 - X_2 P_1^0$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0 \qquad X_2 = \text{mole fraction of the } \underline{\text{solute}}$$

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

Colligative Properties of Nonelectrolyte Solutions

EXAMPLE 12.7

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30°C is given in Table 5.3 (p. 200). Assume the density of the solution is 1.00 g/mL.

Strategy We need Raoult's law [Equation (12.4)] to determine the vapor pressure of a solution. Note that glucose is a nonvolatile solute.

Solution The vapor pressure of a solution (P_1) is

$$P_1 = X_1 P_1°$$

want to calculate — need to find — given

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

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

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

The mole fraction of water, X_1, is given by

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

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

From Table 5.3, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

$$P_1 = 0.955 \times 31.82 \text{ mmHg}$$
$$= 30.4 \text{ mmHg}$$

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

Check We can also calculate the vapor pressure lowering by using Equation (12.5). Because the mole fraction of glucose is (1 − 0.955), or 0.045, the vapor pressure lowering is given by (0.045)(31.82 mmHg) or 1.4 mmHg.

Practice Exercise Calculate the vapor pressure of a solution made by dissolving 82.4 g of urea (molar mass = 60.06 g/mol) in 212 mL of water at 35°C. What is the vapor-pressure lowering?

Colligative Properties of Nonelectrolyte Solutions

Boiling-Point Elevation

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

o Because the presence of a nonvolatile solute lowers the vapor pressure of a solution, it must also affect the boiling point of the solution.

o At any temperature the vapor pressure of the solution is lower than that of the pure solvent regardless of temperature.

o The boiling point of the solution is higher than that of water.
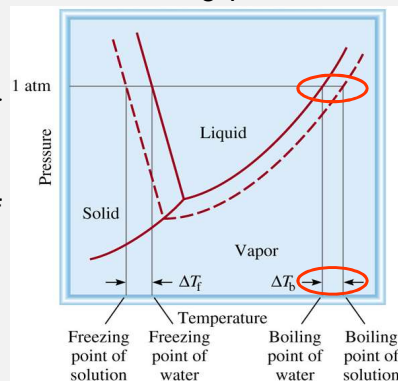
Colligative Properties of Nonelectrolyte Solutions

Boiling-Point Elevation

o The ***boiling point elevation (△T_b)*** is defined as *the boiling point of the solution (T_b) minus the boiling point of the pure solvent ($T°_b$):*

$$\Delta T_b = T_b - T_b^0$$

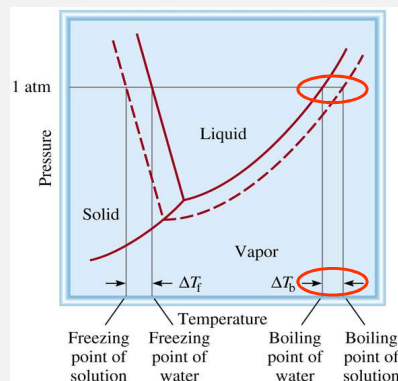T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

$$T_b > T_b^0 \qquad \Delta T_b > 0$$

$$\boxed{\Delta T_b = K_b\, m}$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant (^{0}C/*m*) for a given solvent
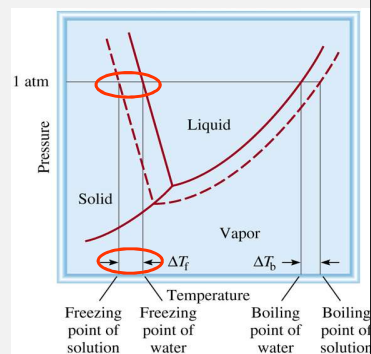
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Colligative Properties of Nonelectrolyte Solutions
Freezing-Point Depression

o 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.

o Lowering the vapor pressure of the solution shifts the solid-liquid curve to the left

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Colligative Properties of Nonelectrolyte Solutions
Freezing-Point Depression

The *freezing point depression (DT_f)* is defi ned as *the freezing point of the pure solvent (T $_f$°) minus the freezing point of the solution (T_f):*

$$\Delta T_f = T_f^0 - T_f$$
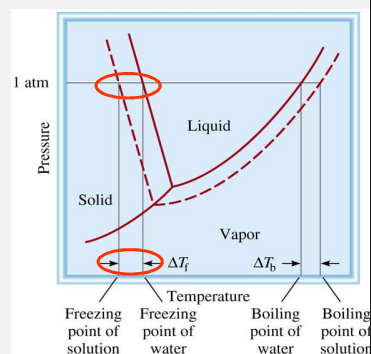
T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$$T_f^0 > T_f \qquad \Delta T_f > 0$$

$$\boxed{\Delta T_f = K_f\, m}$$

m is the molality of the solution

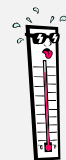K_f is the molal freezing-point depression constant (^{0}C/*m*) for a given solvent

Colligative Properties of Nonelectrolyte Solutions

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

TABLE 12.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

*Measured at 1 atm.

Colligative Properties of Nonelectrolyte Solutions

What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g/mol.

$\Delta T_f = K_f\, m$ K_f water = 1.86 ^{0}C/m

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478\ g \times \dfrac{1\ mol}{62.01\ g}}{3.202\ kg\ solvent} = 2.41\ m$$

$\Delta T_f = K_f\, m = 1.86\ ^0C/m \times 2.41\ m = 4.48\ ^0C$

$\Delta T_f = T_f^0 - T_f$

$T_f = T_f^0 - \Delta T_f = 0.00\ ^0C - 4.48\ ^0C = -4.48\ ^0C$

Colligative Properties of Nonelectrolyte Solutions
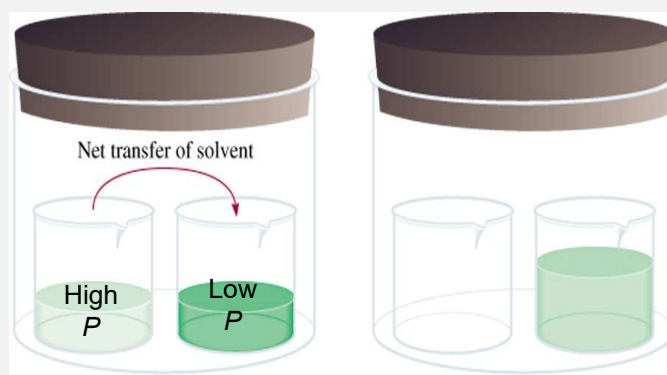
Osmotic Pressure (π)

Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A *semipermeable membrane* allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure (π)

$$\pi = MRT$$

M is the molarity of the solution
R is the gas constant (0.0821 L . atm/K . mol)
T is the temperature (in K)

Colligative Properties of Nonelectrolyte Solutions

Osmotic Pressure (π)

EXAMPLE 12.9

The average osmotic pressure of seawater, measured in the kind of apparatus shown in Figure 12.11, 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.

Strategy When we say the sucrose solution is isotonic with seawater, what can we conclude about the osmotic pressures of these two solutions?

Solution A solution of sucrose that is isotonic with seawater must have the same osmotic pressure, 30.0 atm. Using Equation (12.8).

$$\pi = MRT$$
$$M = \frac{\pi}{RT} = \frac{30.0 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$
$$= 1.23 \text{ mol/L}$$
$$= 1.23 \, M$$

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

Colligative Properties of Nonelectrolyte Solutions

Summary - Colligative Properties of Nonelectrolyte Solutions

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

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

Boiling-Point Elevation $\Delta T_b = K_b \, m$

Freezing-Point Depression $\Delta T_f = K_f \, m$

Osmotic Pressure (π) $\pi = MRT$

Colligative Properties of Nonelectrolyte Solutions
Using Colligative Properties to Determine Molar Mass

From the experimentally determined freezing-point depression or osmotic pressure,

We can calculate the molality or molarity of the solution.

Knowing the mass of the solute, we can readily determine its molar mass,

Colligative Properties of Nonelectrolyte Solutions
Using Colligative Properties to Determine Molar Mass

EXAMPLE 12.10

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?

Strategy Solving this problem requires three steps. First, we calculate the molality of the solution from the depression in freezing point. Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass. Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

Solution The sequence of conversions for calculating the molar mass of the compound is

freezing-point depression $\longrightarrow$ molality $\longrightarrow$ number of moles $\longrightarrow$ molar mass

Our first step is to calculate the molality of the solution. From Equation (12.7) and Table 12.2 we write

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

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

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

Thus, the molar mass of the solute is

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

Now we can determine the ratio

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

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

Practice Exercise A solution of 0.85 g of an organic compound in 100.0 g of benzene has a freezing point of 5.16°C. What are the molality of the solution and the molar mass of the solute?

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Colligative Properties of Nonelectrolyte Solutions

Using Colligative Properties to Determine Molar Mass

EXAMPLE 12.11

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.

Strategy We are asked to calculate the molar mass of Hb. The steps are similar to those outlined in Example 12.10. From the osmotic pressure of the solution, we calculate the molarity of the solution. Then, from the molarity, we determine the number of moles in 35.0 g of Hb and hence its molar mass. What units should we use for π and temperature?

Solution The sequence of conversions is as follows:

$$\text{osmotic pressure} \longrightarrow \text{molarity} \longrightarrow \text{number of moles} \longrightarrow \text{molar mass}$$

First we calculate the molarity using Equation (12.8)

$$\pi = MRT$$
$$M = \frac{\pi}{RT}$$
$$= \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}$$
$$= 5.38 \times 10^{-4} M$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb. We use this quantity to calculate the molar mass:

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$
$$\text{molar mass of Hb} = \frac{\text{mass of Hb}}{\text{moles of Hb}}$$
$$= \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}}$$
$$= 6.51 \times 10^4 \text{ g/mol}$$

Practice Exercise A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21°C. Calculate the molar mass of the polymer.