

SOLUTION CONCENTRATIONS

- The amount of solute in a solution (concentration) is an important property of the solution. A dilute solution contains small quantities of solute relative to the solvent, while a concentrated solution contains large quantities of solute relative to the solvent.
- The concentration of a solution can be expressed in various ways, such as: molarity, molality, mass percent and mole fraction. Molarity was discussed earlier in Chapter 4. The other methods of expressing concentration will be discussed in this section.

Mass Percent:

- Concentration can be expressed as *mass percent* defined as:

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

- Mass of solution is defined as mass of solute + mass of solvent.

Mole Fraction:

- For some applications, it is more convenient to express concentration as *mole fraction*. Mole fraction of solute (X_{solute}) is defined as:

$$X_{\text{solute}} = \frac{\text{amount of solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Molality:

- A concentration unit that is independent of temperature is molality (m). Molality is defined as:

$$\text{Molality (m)} = \frac{\text{amount of solute (in mol)}}{\text{mass of solvent (in kg)}}$$

SOLUTION CONCENTRATIONS

- Examples that follow show how various concentration units can be calculated and their interconversions.

Examples:

1. A solution is prepared by dissolving 17.2 g of ethylene glycol ($C_2H_6O_2$) in 0.500 kg of water. The final volume of solution is 515 mL. Calculate the concentration of this solution in units of:
 - a) molarity
 - b) molality
 - c) mass percent of solute
 - d) mole fraction of solute

SOLUTION CONCENTRATIONS

Examples (cont'd):

2. What is the molarity of a 6.56% by mass glucose ($C_6H_{12}O_6$) solution? The density of the solution is 1.03 g/mL.

3. What is the molality of a 10.5% by mass glucose ($C_6H_{12}O_6$) solution? The density of the solution is 1.03 g/mL.

COLLIGATIVE PROPERTIES

- Properties of solution that depends on the number of particles dissolved in solution are called *colligative properties*. Some important colligative properties are vapor pressure lowering, freezing point depression and boiling point elevation.
- Since these properties depend on the number of particles in solution, nonelectrolytes are treated slightly differently than electrolytes when determining colligative properties. Recall that when one mol of nonelectrolyte dissolves in water, it produces one mol of particles.
- By contrast, when one mol of electrolyte dissolves in water, it produces more than one mol of particles. For example, when one mol of NaCl dissolves in water, it produces two mol of ions (particles).



Freezing Point Depression

- Addition of a nonvolatile solute to a solvent lowers its freezing point.
- This freezing point depression is proportional to the amount of solute in a solution.

$$\Delta T_f = m K_f$$

ΔT_f = freezing point depression

K_f = freezing point depression constant

m = molality of solution

Boiling Point Elevation

- Addition of a nonvolatile solute to a solvent increases its boiling point.
- This boiling point elevation is proportional to the amount of solute in a solution.

$$\Delta T_b = m K_b$$

ΔT_b = boiling point elevation

K_b = boiling point elevation constant

m = molality of solution

COLLIGATIVE PROPERTIES OF IONIC SOLUTIONS

- When evaluating colligative properties of ionic solutions, the total concentration of the ions must be considered.
- The number of ions produced from each formula unit is designated (*i*).



- The colligative properties of ionic solutions can be calculated with the following modifications:

$$\Delta T_b = i m K_b$$

$$\Delta T_f = i m K_f$$

Examples:

1. Calculate the freezing point of 0.010 m solution of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$. (K_f for water = $1.86 \text{ m}^\circ\text{C}$)



$$\Delta T_f =$$

$$T_f =$$

2. Which of the following solutions will have the lowest freezing point?

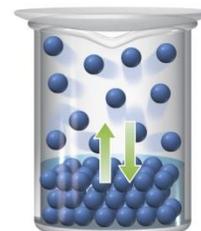
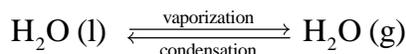
0.15 m NaCl

0.25 m $\text{C}_6\text{H}_{12}\text{O}_6$

0.10 m $\text{Fe}(\text{NO}_3)_3$

VAPOR PRESSURE LOWERING

- The pressure of a gas above a liquid at a particular temperature is defined as its vapor pressure. At a particular temperature, gas and liquid molecules for a substance are in dynamic equilibrium (meaning rate of vaporization equals the rate of condensation).



Dynamic equilibrium

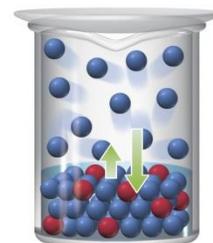
- What is the effect of a nonvolatile solute on the vapor pressure of a the liquid into which it dissolves?
- When a nonvolatile solute is added to a liquid, the solute particles (red) interfere with the ability of the solvent particles (blue) to vaporize. As a result, the vapor pressure of the liquid is lowered by addition of the solute.
- The vapor pressure of a solution can be quantified with **Raoult's Law**:

$$P_{\text{solution}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

P_{solution} = vapor pressure of solution

X_{solvent} = mole fraction of solvent

$P^{\circ}_{\text{solvent}}$ = vapor pressure of pure solvent at the same T



Rate of vaporization reduced by solute

- For example, for an aqueous solution at 25°C that contains 0.90 mol water and 0.10 mol of a non-volatile solute (such as sucrose), the vapor pressure can be calculated as shown below:

$$\begin{aligned} P_{\text{solution}} &= X_{\text{solvent}} P^{\circ}_{\text{solvent}} \\ &= (0.90)(23.8 \text{ mmHg}) = 21.4 \text{ mmHg} \end{aligned}$$

- Vapor pressure lowering (ΔP) is defined as the difference in vapor pressure between the pure solvent and the solution, and can be shown to be equal to:

$$\Delta P = X_{\text{solute}} P^{\circ}_{\text{solvent}}$$

- For example, for the aqueous solution described above, ΔP can be calculated by two different methods:

$$\Delta P = P^{\circ} - P_{\text{solution}} = 23.8 \text{ mmHg} - 21.4 \text{ mmHg} = 2.4 \text{ mmHg}$$

$$\Delta P = X_{\text{solute}} P^{\circ}_{\text{solvent}} = (0.10)(23.8 \text{ mmHg}) = 2.4 \text{ mmHg}$$

**VAPOR PRESSURE OF SOLUTIONS CONTAINING
VOLATILE (NONELECTROLYTE) SOLUTE**

- The previous examples consisted of solutions containing nonvolatile solutes. Some solutions contain a *volatile solvent* and a *volatile solute*. In these solutions, both the solute and the solvent contribute to the overall vapor pressure of the solution.
- A solution as described above may be an *ideal solution* (one that follows Raoult's law) or it may be *non-ideal solution* (one that does not follow Raoult's law).
- Similar to an ideal gas (which follows the ideal gas law exactly, an ideal solution follows Raoult's law exactly because the solute–solvent interactions are similar in magnitude to solute–solute and solvent–solvent interactions.
- In an ideal solution, the vapor pressure of each of the solution components is described by Raoult's law throughout the entire composition range of the solution. For example, for a two component solution containing liquids A and B, the vapor pressure of each component can be calculated as shown below:

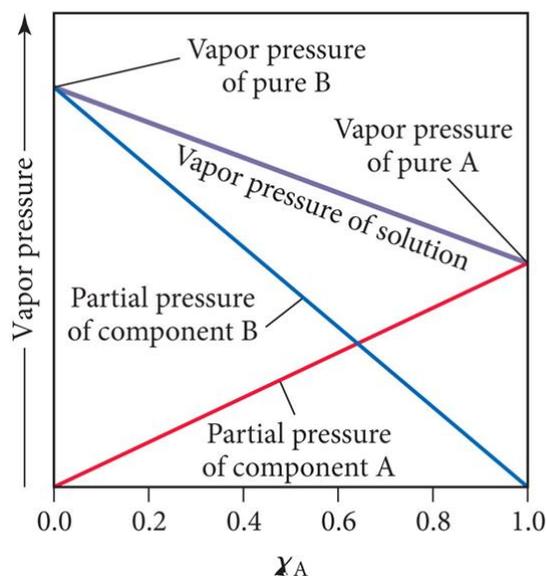
$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

- The total pressure above the solution is the sum of the partial pressure of the components. Therefore,

$$P_{\text{tot}} = P_A + P_B$$

- The graph below is a plot of vapor pressure versus solution composition for an ideal 2-component system.



Examples:

1. A solution contains 3.95 g of CS₂ and 2.43 g of acetone (CH₃COCH₃). The vapore pressure at 35°C of pure CS₂ and pure acetone are 515 mmHg and 332 mmHg, respectively. Assuming ideal behavior, calculate the vapor pressure of each of the components and the total pressure above the solution.

Step 1: Calculate mole fraction of each solution component:

Step 2: Calculate the partial pressure of each component:

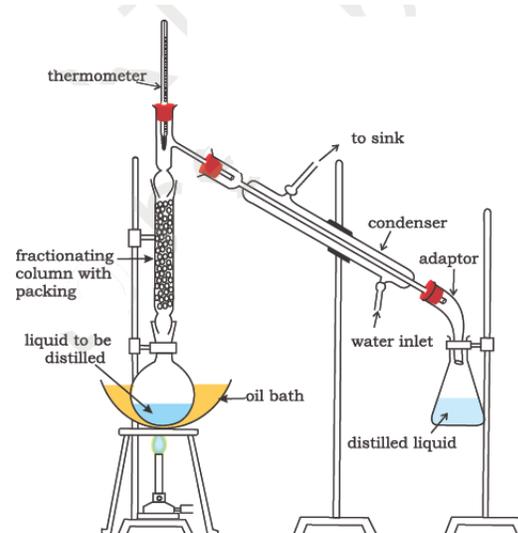
Step 3: Calculate the total vapor pressure of solution:

IDEAL SOLUTIONS WITH 2 OR MORE VOLATILE COMPONENTS

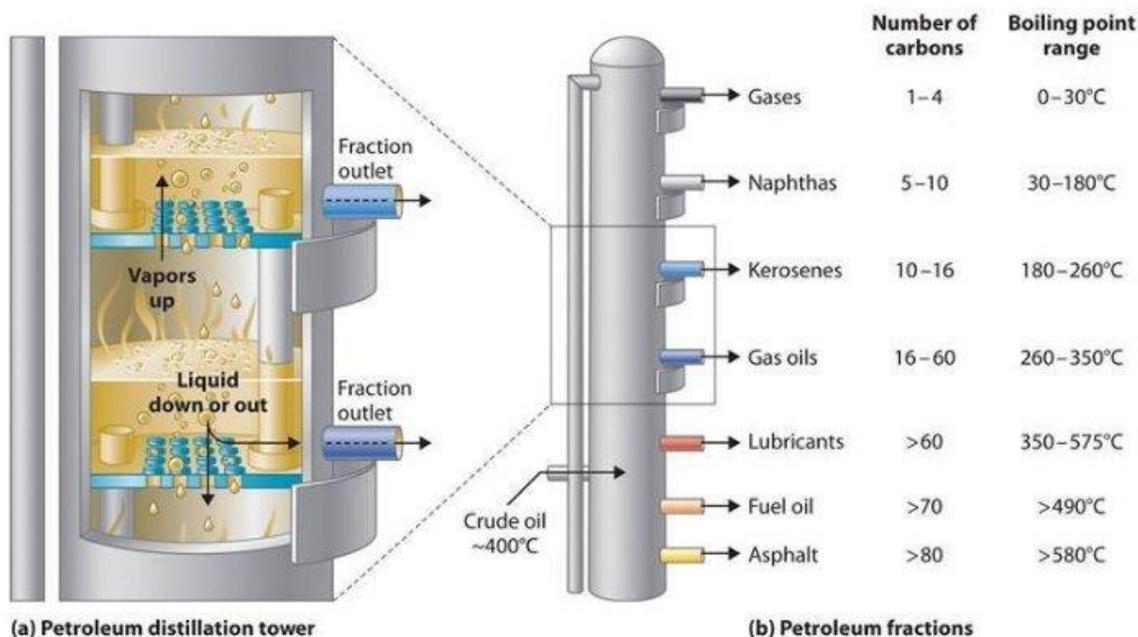
- Solutions sometimes have 2 or more volatile components. For example, gasoline is a complex solution containing several volatile substances.
- Assuming ideal behavior, we used Raoult's law to calculate the vapor pressure of the mixture based on mole fraction of each component and the vapor pressure of each in the pure state.
- These calculations indicated that the vapor in equilibrium above each mixture is richer in the more volatile component. Therefore, we can generalize the following statement:

The vapor in equilibrium above an ideal solution is richer in the more volatile component compared to the original mixture.

- This fact forms the basis of an important technique, called **distillation**. Distillation is used to separate (or partially separate) mixtures containing several volatile components.
- Distillation is the procedure by which a moonshiner obtains whiskey using a still, and by which petrochemical plants achieve the separation of crude petroleum into gasoline, diesel, lubricating oil and so on. Shown below are laboratory and industrial uses of this technique.



Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.



**COLLIGATIVE PROPERTIES OF STRONG ELECTROLYTES
VAN'T HOFF FACTOR**

- We have already discussed that when determining the colligative properties of solutions containing an ionic solid, one must consider the total concentration of dissolved particles. Earlier we used the term (*i*) to designate the number of particles formed in solution when an ionic solid dissolves.
- The ratio of the moles of dissolved particles in solution to the moles of formula units dissolved (*i*) is called the **Van't Hoff factor**:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

- Since 1 mol of NaCl produces 2 mol of particles in solution, we expect the van't Hoff factor for NaCl to be exactly 2. In reality, this expected factor occurs only in very dilute solutions. For example, the van't Hoff factor for 0.10 m NaCl is 1.87 and that for 0.010 m NaCl is 1.94. The van't Hoff factor approaches the expected value at infinite dilution.
- The table below shows the actual and the expected van't Hoff factors for a number of solutes:

TABLE 12.9 Van't Hoff Factors at 0.05 m Concentration in Aqueous Solution		
Solute	<i>i</i> Expected	<i>i</i> Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO ₄	2	1.3
MgCl ₂	3	2.7
K ₂ SO ₄	3	2.6
FeCl ₃	4	3.4

- The reason the van't Hoff factors do not exactly equal expected values is that some ions effectively pair in solution, slightly reducing the number of particles in solution.
- The diagram to the right shows how some hydrated anions and cations can get close enough to effectively pair and reduced the number of particles in solution.



Examples:

1. The freezing point of an aqueous 0.050 m CaCl_2 solution is -0.27°C . What is the van't Hoff factor for CaCl_2 at this concentration? (K_f for water = $1.86^\circ\text{C}/\text{m}$)

2. Calculate the freezing point of an aqueous 0.10 m FeCl_3 solution using a van't Hoff factor of 3.2.

3. A solution is prepared from 4.5701 g of magnesium chloride and 43.238 g of water. The vapor pressure of water above this solution is 0.3624 atm at 348 K. The vapor pressure of pure water at this temperature is 0.3804 atm. Find the value of the van't Hoff factor for magnesium chloride in this solution.

ANSWERS TO IN-CHAPTER PROBLEMS:

<i>Page</i>	<i>Example No.</i>	<i>Answer</i>
2	1	a) Molarity = 0.538 M b) Molality = 0.554 m c) Mass percent of solute = 3.33% d) Mole fraction of solute = 0.0989
3	2	Molarity = 0.375 M
	3	Molality = 0.651 m
5	1	$T_f = -8.11\text{ }^\circ\text{C}$
	2	$T_b = 102.23\text{ }^\circ\text{C}$
	3	$T_f = -15.6\text{ }^\circ\text{C}$
	4	610 g
6	1	$T_f = -0.093\text{ }^\circ\text{C}$
	2	0.10 m $\text{Fe}(\text{NO}_3)_3$
8	1	$P_{\text{soln}} = 23.4\text{ mmHg}$
	2	$P_{\text{soln}} = 22.5\text{ mmHg}$
	3	$X_{\text{EG}} = 0.144$
10	1	a) $X_A = 0.5535$; $X_B = 0.4465$ b) $P_A = 285\text{ mmHg}$; $P_B = 148\text{ mmHg}$ c) $P_{\text{tot}} = 433\text{ mmHg}$
11	2	a) $P_A = 26.6\text{ mmHg}$; $P_B = 20.4\text{ mmHg}$ b) $P_{\text{tot}} = 47.0\text{ mmHg}$ c) % A = 52.5%; % B = 47.5%
	3	$X_{\text{pentane}} = 0.391$; $X_{\text{hexane}} = 0.609$
13	1	$P_{\text{soln}} = 88.8\text{ mmHg}$
	2	$P_{\text{soln}} = 23.0\text{ mmHg}$
15	1	$i = 2.9$
	2	$T_f = -0.60\text{ }^\circ\text{C}$
	3	$i = 2.484$