Chapter 13: Properties of Solutions

Problems: 9-10, 13-17, 21-42, 44, 49-60, 71-72, 73 (a,c), 77-79, 84(a-c), 91

**solution:** homogeneous mixture of a **solute** dissolved in a **solvent**

- **solute:** component(s) present in *smaller* amount
- **solvent:** component present in *greatest* amount
  - unless otherwise stated, assume the solvent is water

### 13.1 THE SOLUTION PROCESS

As a solute crystal is dropped into a solvent, the solvent molecules begin to attack and pull apart the solute molecules
→ solvent molecules surround the solute molecules, forming a solvent cage
→ solute dissolves in the solvent (See Fig. 13.1, p. 470)

#### Energy Changes and Solution Formation

**Three types of interactions to consider for solutions:**
1. solvent-solvent interaction
2. solute-solute interaction
3. solvent-solute interaction

**Consider the solution process taking place in three distinct steps:**
1. separation of solvent molecules
2. separation of solute molecules
3. mixing of solvent and solute molecules

So why don't all liquids mix and all solids dissolve in liquids?
- If solvent-solute interaction can’t compete with solute-solute and solvent-solvent interactions, they remain separated.

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[Diagram of solution process with solvent-solute interactions vs. solute-solute interactions]
13.2 SATURATED SOLUTIONS AND SOLUBILITY

**solubility:** Maximum amount of solute dissolved in solvent at specific temp.

**unsaturated:** contains less than the maximum amount of solute that a solvent can hold at specific temperature

**saturated:** contains the maximum amount of solute that a solvent can hold at specific temperature

**supersaturated:** contains more than the maximum amount of solute that a solvent can hold at specific temperature

How? At higher temperatures, solvents can hold more solute than at lower temperatures. If a given amount of solute is dissolved in a solvent at a higher temperature, then allowed to cool without being disturbed, the solute will remain in solution.

The solution is unstable, though, and the solute will crystallize if disturbed. (See Fig. 13.10, p. 475)

13.3 FACTORS AFFECTING SOLUBILITY

**Liquid-Liquid Solutions**

"Like dissolves like" rule
- polar molecules will mix (be miscible with) other polar molecules
- nonpolar molecules will mix (be miscible with) other nonpolar molecules
- polar molecules will not mix (be immiscible with) nonpolar molecules

**Solid-Liquid Solutions**

**Ionic and Molecular Compounds**
- “Like dissolves like” rule applies!

<table>
<thead>
<tr>
<th>solid solute</th>
<th>polar solvent</th>
<th>nonpolar solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>polar</td>
<td>soluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>nonpolar</td>
<td>insoluble</td>
<td>soluble</td>
</tr>
<tr>
<td>ionic</td>
<td>Check Solubility Rules</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

Note: Be able to determine whether a compound is polar or nonpolar given only its formula—i.e. get the Lewis structure, use VSEPR to get shape, and electronegativity differences to determine dipoles, and finally polarity.
Some solids do not dissolve in any solvent
1. **network covalent solids** (eg. graphite, quartz) never dissolve in any solvent
2. **metals** do not "dissolve"—they may react but don’t dissolve—in any solvent

Example 1: Determine whether the following are ionic, polar, or nonpolar. Determine which will be soluble in or miscible with water? (Circle all that apply)

$I_2$  $\text{NaCl}$  $\text{Mg(OH)}_2$  $\text{CCl}_4$ (l)  $\text{NH}_3$  $\text{C}_\text{diamond}$

Example 2: Which of the following will be soluble in or miscible with hexane, $\text{C}_6\text{H}_{14}$, a nonpolar liquid? (Circle all that apply)

$I_2$  $\text{NaCl}$  $\text{Mg(OH)}_2$  $\text{CCl}_4$ (l)  $\text{NH}_3$  $\text{C}_\text{diamond}$

**GAS-LIQUID SOLUTIONS**

**Gas solubility and Pressure Effects:**

Henry’s Law: Solubility of gas is proportional to partial P of gas above liquid

- Solubility of gas $\uparrow$ when partial pressure of gas above liquid $\uparrow$

**Why?** Greater pressure over solution (See Fig. 13.14 on p. 479)

$\Rightarrow$ more gas molecules encounter liquid surface

$\Rightarrow$ more gas molecules go into the liquid phase!
Practical applications:
- Why sodas won't be as carbonated after being opened
- Why divers get the "bends" — air dissolved in blood and other bodily fluids bubbles out when divers go from deep water (high pressure) to the surface (low pressure). The bubbles affect nerve impulses, resulting in the "bends."

Gas solubility and Temperature:
— As \( T \uparrow \), solubility of a gas in a liquid \( \downarrow \) (in most cases)
— a glass of soda outside quickly goes flat if left out on a hot summer day
— why bubbles form when water heated in an open pan (dissolved air escaping)

Why? At higher temperatures, gas molecules are moving more quickly
\[ \Rightarrow \] they have a higher tendency to find the surface (b/w liquid and air)
\[ \Rightarrow \] they escape more quickly
\[ \Rightarrow \] fewer gas molecules in the liquid!

Solid solubility and Temperature:
— As \( T \uparrow \), solubility of a solid in a liquid \( \uparrow \) (in most cases)
— e.g. we can dissolve more sugar in a cup of hot tea than in a glass of iced tea

13.4 Ways of Expressing Concentration

Mass Percent, parts per million (ppm), parts per billion (ppb)

\[
\text{Mass percent of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100% \\
= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100%
\]

Example: A 1.215-g sample of NaCl is dissolved in 65.483 g of water. What is the mass percent of NaCl in the solution?
Parts per Million (ppm) solute = \( \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^6 \)

Parts per Billion (ppb) solute = \( \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^9 \)

Example: A 2.500-g sample of groundwater was found to contain 5.4 micrograms (µg) of Zn\(^{2+}\). What is the concentration of Zn\(^{2+}\) in parts per million?

Mole Fraction \((X)\): has no units since ratio of two similar quantities

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

Example: A solution consists of 2.50 moles of ethanol and 3.50 moles of water. Calculate the mole fractions of both components.

Molarity = \( \frac{\text{moles of solute}}{\text{liters of solution}} \) in units of M=mol/L

For dilution problems, use \( M_1V_1 = M_2V_2 \) where \( M= \text{molarity, } V= \text{volume} \)

Example 1: How would you prepare a 100.0 mL of 0.500 M KI starting with 2.00 M KI?
**Molality:** number of moles of solute dissolved in 1 kg (1000 g) of solvent

\[
\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (in kg)}} \quad \text{in units of } \text{molal} = m
\]

Example: Calculate the molality of a sulfuric acid (MW=98.08 g/mol) solution containing 25.6 g of sulfuric acid in 195 g of water.

**Comparison of Concentration Units:**

- **mole fractions:** used for partial pressures of gases and for dealing with vapor pressures of solutions
- **molarity:** preferred over molality because easier to measure volume of a solution using calibrated glassware than to weigh solvent
- **molality:** independent of temperature, whereas molarity varies with temperature since volume varies — useful when experiment carried out over a range of temperatures
- **mass percent:** independent of temperature; molar masses not needed
- **parts per million:** for very low concentrations of solute (impurities, pollutants)

**Examples for converting from one concentration unit to another:**

- **Use unit analysis!**

  1. Calculate the molarity of an aqueous vinegar solution, which is 5.0% \(\text{HC}_2\text{H}_3\text{O}_2\) (MM of \(\text{HC}_2\text{H}_3\text{O}_2\) = 60.06 g/mol) by mass.
2. Calculate the molarity of a 0.417 $m$ glucose (C$_6$H$_{12}$O$_6$, MW=180.2 g/mol) solution if glucose's density is 1.16 g/mL.

13.5 Colligative Properties

**colligative properties**: properties depending on the number of solute particles in solution and not on the nature of the solute particles

**nonelectrolytes**: exist as molecules in solution (do not dissociate into ions)

**electrolytes**: exist as ions in solution

**Lowering the Vapor Pressure (Nonelectrolytes)**

**vapor pressure**: pressure exerted by vapor in equilibrium with its liquid or solid

A substance that has no vapor pressure is **nonvolatile**, whereas one that exhibits a vapor pressure is **volatile**.
- e.g. honey is considered nonvolatile while gasoline is volatile
- Adding a solute lowers the concentration of solvent molecules in liquid phase since solute particles block solvent molecules from going to gas phase
Boiling-Point Elevation and Freezing Point Depression (Nonelectrolytes)

**Boiling-Point Elevation:**
- presence of solute lowers vapor pressure of a solution (since solute particles present at interface block solvent molecules from going to gas phase)
- e.g. add salt to water to increase boiling point of water
- The increased boiling point is determined as follows: \( T_b = T_b^* + \Delta T_b \)
  where \( T_b = \) boiling point of solution, \( T_b^* = b. p. of pure solvent, \Delta T_b = b.p. increase \)
- \( \Delta T_b \) can be calculated using \( \Delta T_b = K_b m \)
  where \( m = \) molal concentration of solute, \( K_b = \) molal boiling point constant

Example: Calculate the boiling point of a solution containing 1.25 mol of NaCl in 0.250 kg of water using \( K_b = 0.52^\circ C/m \).

**Freezing-Point Depression:**
- amount of impurity (or solute) determines how much freezing point is lowered
- In the first beaker shown, ice is in equilibrium with pure liquid water
- In the second beaker, there are dissolved solute particles (lighter color)
- doesn’t freeze as quickly since solute particles block water
- Practical example of freezing-point depression
  — e.g. adding salt to roads/sidewalks to prevent them from freezing in winter

The new freezing point is determined as follows:

\[ T_f = T_f^* - \Delta T_f \]

where \( T_f = \) freezing point of solution, \( T_f^* = \) freezing point of pure solvent, and \( \Delta T_f = \) freezing point depression
- \( \Delta T_f \) can be calculated using \( \Delta T_f = K_f m \)
  where \( m = \) molal concentration of solute, \( K_f = \) molal freezing point constant
Example: Calculate the freezing point of a solution containing 1.25 mol of NaCl in 0.250 kg of water using $K_f=1.86 \degree C/m$.

**Osmotic Pressure (Nonelectrolytes)**

**semipermeable membrane**: allows solvent molecules to pass through but blocks the passage of solute molecules

**osmosis**: net movement of solvent molecules through semipermeable membrane from pure solvent or more dilute solution to more concentrated solution — result of differences in vapor pressure due to differences in concentrations

**osmotic pressure ($\pi$)**: pressure required to stop osmosis

- **isotonic**: when two solutions have equal osmotic pressure
- **hypertonic**: the more concentrated solution given two solutions not isotonic
- **hypotonic**: the less concentrated solution given two solutions not isotonic
Example: We often hear the phrase "learning by osmosis." If we consider the head to be a semipermeable membrane, information the solute, and one actually tries to learn by osmosis by sleeping on a textbook, what would actually happen?

We can calculate **osmotic pressure (\( \pi \)) at a given temperature:** \( \pi = MRT \)

where \( M \)=molarity of solute, \( R=0.0821 \, \text{L·atm/mol·K} \), and \( T=\)absolute in Kelvins

Example: A 0.125 M sample of seawater was taken at 25˚C. Calculate the osmotic pressure of the seawater sample.

If we make the external pressure large enough (i.e. for \( P > \pi \)), we can make water molecules go from solution to pure water. This process is called **reverse osmosis**.

**Colligative Properties of Electrolyte Solutions** (See A Closer Look on p. 494)

For colligative properties,

— Electrolyte solutions vary from those of nonelectrolyte solutions
— electrolytes dissociate into ions in solutions

⇒ increasing the total number of particles in solution
⇒ Because NaCl dissociates into Na\(^+\) and Cl\(^-\) ions, the freezing-point depression for 0.1 \( m \) NaCl nearly double that for 0.1 \( m \) sucrose
van't Hoff factor = \( i = \frac{\text{number of moles of ions per mole of electrolyte}}{\text{actual number of particles in solution after dissociation}} = \frac{\text{number of compounds dissolved before dissociation}}{i} \)

Example: Give \( i \) for each of the following solutions:

a. \( \text{Na}_3\text{PO}_4: i = \)

b. \( \text{CaCl}_2 \) and \( \text{KOH}: i = \)

c. \( \text{Al(NO}_3\text{)}_3 \) and \( \text{H}_2\text{SO}_4: i = \)

For electrolyte solutions, the van't Hoff factor can be included in the following:

\[
\Delta T_b = i K_b m \quad \text{and} \quad \Delta T_f = i K_f m \quad \text{and} \quad \pi = iMRT
\]

We can also use these equations to determine the van't Hoff factor for a solution.

Ex. 1: Estimate the freezing point of a 0.055 m solution of \( \text{KNO}_3 \).

Ex. 2: Estimate the boiling point of 0.25 m solutions of \( \text{MgCl}_2 \).
Ex. 3: The osmotic pressure of 0.010 M KI solution at 25˚C is 0.465 atm. Calculate the van't Hoff factor for KI at this concentration.

Note: The van't Hoff factor is **not** as straightforward for some electrolyte solutions that form ion pairs (cation and anion held closely together by attractive forces with no solvent molecules between them). The extent that ion pair formation occurs can be determined by comparing the theoretical and actual van't Hoff factors.

**Determination of Molar Mass**

Example: Ethylene glycol (EG) is a common automobile antifreeze. It is water soluble and a nonelectrolyte. Calculate the molar mass of EG if 651g of EG was dissolved in 2505 g of water, and the freezing point for the solution is −7.79˚C. \( \Delta T_f = 1.86^\circ C/m \).