

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:

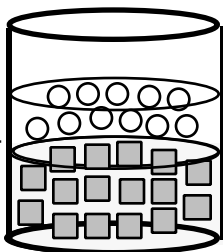
1. separation of solvent molecules
2. separation of solute molecules
3. mixing of solvent and solute molecules

So why don't all liquids mix and all solids dissolve in liquids?

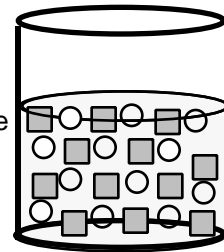
- If solvent-solute interaction can't compete with solute-solute and solvent-solvent interactions, they remain separated.

○=solute
■=solvent

When solute-solute or solvent-solvent interactions are stronger than solute-solvent interactions, solute and solvent stay separated.



When solute-solvent interactions are as strong as solute-solute and solvent-solvent interactions, solute and solvent mix.



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!

solid solute	polar solvent	nonpolar solvents
polar	soluble	insoluble
nonpolar	insoluble	soluble
ionic	Check Solubility Rules	insoluble

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 $NaCl$ $Mg(OH)_2$ $CCl_4(l)$ NH_3 $C_{diamond}$

Example 2: Which of the following will be soluble in or miscible with hexane, C_6H_{14} , a nonpolar liquid?(Circle all that apply)

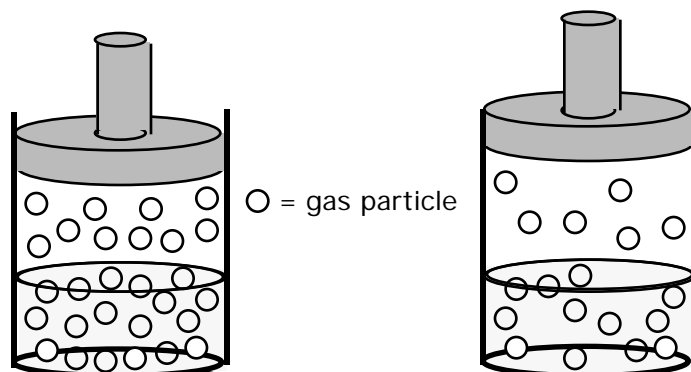
I_2 $NaCl$ $Mg(OH)_2$ $CCl_4(l)$ NH_3 $C_{diamond}$

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 when partial pressure of gas above liquid

Why? Greater pressure over solution (See Fig. 13.14 on p. 479)
more gas molecules encounter liquid surface
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 ↑, solubility of a gas in a liquid ↓ (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 they have a higher tendency to find the surface (b/w liquid and air) they escape more quickly fewer gas molecules in the liquid!

Solid solubility and Temperature:

- As T ↑, solubility of a solid in a liquid ↑ (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)

$$\begin{aligned}\text{Mass percent of solute} &= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \\ &= \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%\end{aligned}$$

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?

$$\text{Parts per Million (ppm) solute} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^6$$

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

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.

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

For **dilution** problems, use $M_1V_1 = M_2V_2$ where **M=molarity, V=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

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

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% HC₂H₃O₂ (MM of HC₂H₃O₂ = 60.06 g/mol) by mass.

2. Calculate the molarity of a 0.417 *m* glucose ($C_6H_{12}O_6$, 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)

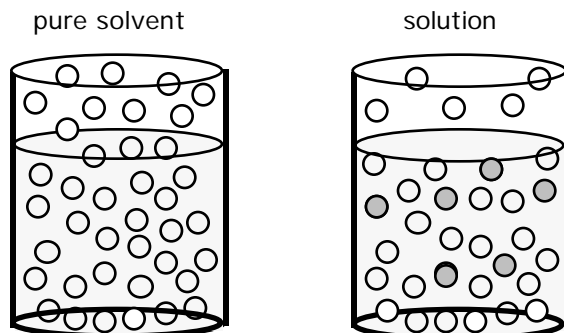
electrolytes: exist as ions in solution

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)

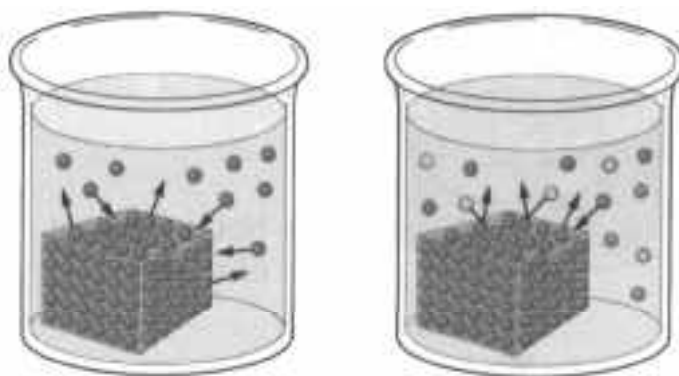
Boiling-Point Elevation:

- 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: $T_b = T_b^\circ + \Delta T_b$
where T_b =boiling point of solution, T_b° =b. p. of pure solvent, ΔT_b =b.p. increase
- ΔT_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 $K_b=0.52^\circ\text{C}/m$.

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:

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

where T_f =freezing point of solution, T_f° =freezing point of pure solvent, and ΔT_f =freezing point depression

- ΔT_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 $K_f=1.86^\circ\text{C}/m$.

Osmotic Pressure (Nonelectrolytes)

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

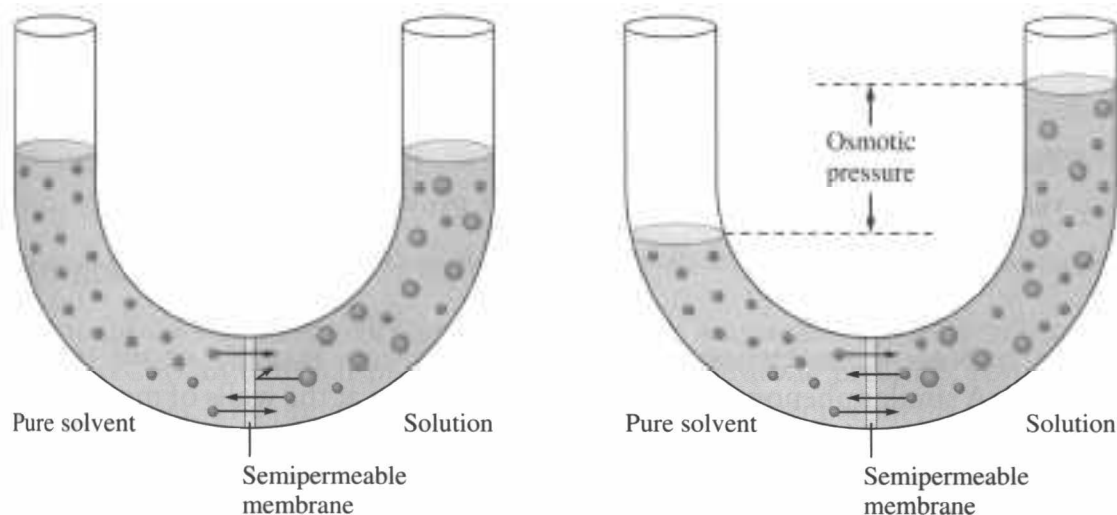
osmosis: net movement of solvent molecules through semipermeable membrane from pure solvent or more dilute solution to more concentrated solution
— result of differences in vapor pressure due to differences in concentrations

osmotic pressure (π): 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

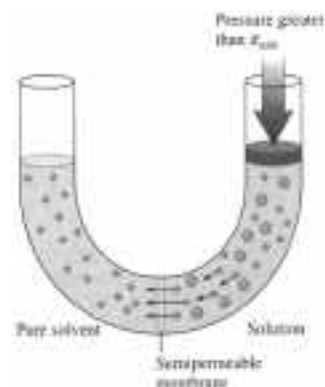


Example: We often hear the phrase "learning by osmosis." If we consider the head to be a semipermeable membrane, information the solute, and one actually tries to learn by osmosis by sleeping on a textbook, what would actually happen?

We can calculate **osmotic pressure ()** at a given temperature: $\pi = MRT$
where M =molarity of solute, $R=0.0821$ 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 = number of moles of ions per mole of electrolyte

$$i = \frac{\text{actual number of particles in solution after dissociation}}{\text{number of compounds dissolved before dissociation}}$$

Example: Give i for each of the following solutions:

a. Na_3PO_4 : $i =$

b. CaCl_2 and KOH : $i =$

c. $\text{Al}(\text{NO}_3)_3$ and H_2SO_4 : $i =$

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

$$T_b = i K_b m \quad \text{and} \quad T_f = i K_f m \quad \text{and} \quad \Delta T = i M R T$$

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 KNO_3 .

Ex. 2: Estimate the boiling point of 0.25 m solutions of 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 . $K_f=1.86^{\circ}\text{C}/m$.