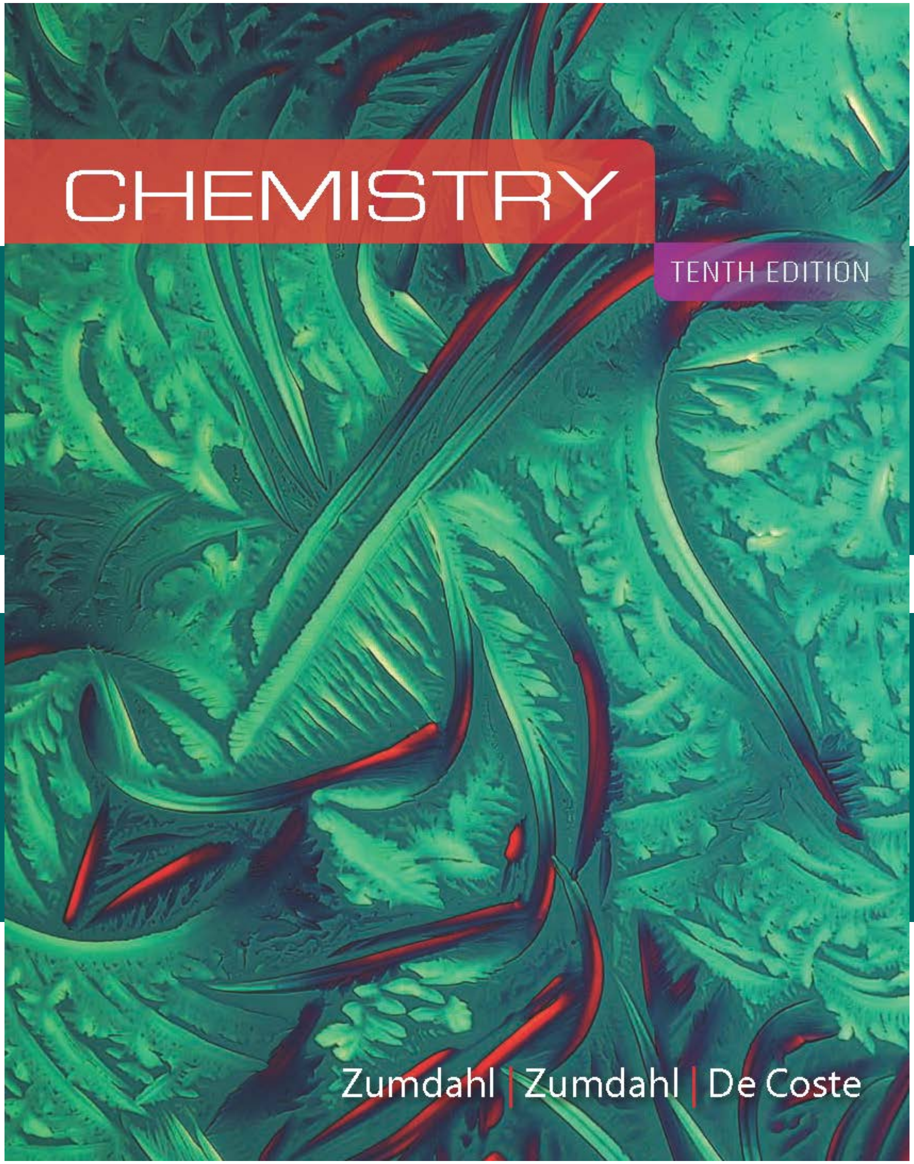

Chapter 11

Properties of Solutions

Chapter 11

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Table 11.1 - Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

Solution Composition

- As mixtures have variable compositions, relative amounts of substances in a solution must be specified
  - Qualitative terms - Dilute and concentrated
  - **Molarity** (*M*): Number of moles of solute per liter of solution

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

Solution Composition (continued)

- **Mass percent** (weight percent)

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 100\%$$

- **Mole fraction** (χ)

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B}$$

- **Molality** (m)

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Interactive Example 11.1 - Various Methods for Describing Solution Composition

- A solution is prepared by mixing 1.00 g ethanol (C_2H_5OH) with 100.0 g water to give a final volume of 101 mL
  - Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution

Interactive Example 11.1 - Solution

- Molarity
  - The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 2.17 \times 10^{-2} \text{ mol } C_2H_5OH$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

Interactive Example 11.1 - Solution (Continued 1)

$$\text{Molarity of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}}$$

$$\text{Molarity of } C_2H_5OH = 0.215\ M$$

- Mass percent

$$\text{Mass percent } C_2H_5OH = \left(\frac{\text{mass of } C_2H_5OH}{\text{mass of solution}}\right) \times 100\%$$

$$= \left(\frac{1.00 \text{ g } C_2H_5OH}{100.0 \text{ g } H_2O + 1.00 \text{ g } C_2H_5OH}\right) \times 100\% = 0.990\%\ C_2H_5OH$$

Interactive Example 11.1 - Solution (Continued 2)

- Mole fraction

$$\text{Mole fraction of } C_2H_5OH = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{H_2O}}$$

$$n_{H_2O} = 100.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 5.56 \text{ mol}$$

$$\chi_{C_2H_5OH} = \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}} = \frac{2.17 \times 10^{-2}}{5.58} = 0.00389$$

Interactive Example 11.1 - Solution (Continued 3)

- Molality

$$\text{Molality of } C_2H_5OH = \frac{\text{moles of } C_2H_5OH}{\text{kilogram of } H_2O} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}}$$

$$= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}} = 0.217\ m$$

Critical Thinking

- You are given two aqueous solutions with different ionic solutes (Solution A and Solution B)
  - What if you are told that Solution A has a greater concentration than Solution B by mass percent, but Solution B has a greater concentration than Solution A in terms of molality?
    - Is this possible?
      - If not, explain why not
      - If it is possible, provide example solutes for A and B and justify your answer with calculations

Normality (*N*)

- Measure of concentration
- Number of equivalents per liter of solution
  - Definition of an equivalent depends on the reaction that takes place in a solution
    - For acid–base reactions, the equivalent is the mass of acid or base that can accept or provide exactly 1 mole of protons
    - For oxidation–reduction reactions, the equivalent is the quantity of oxidizing or reducing agent that can accept or provide 1 mole of electrons

Interactive Example 11.2 - Calculating Various Methods of Solution Composition from the Molarity

- The electrolyte in automobile lead storage batteries is a 3.75 *M* sulfuric acid solution that has a density of 1.230 g/mL
  - Calculate the mass percent, molality, and normality of the sulfuric acid

Interactive Example 11.2 - Solution

- What is the density of the solution in grams per liter?

$$1.230\frac{\text{g}}{\text{mL}} \times \frac{1000\text{ mL}}{1\text{ L}} = 1.230 \times 10^3 \text{ g/L}$$

- What mass of H_2SO_4 is present in 1.00 L of solution?
  - We know 1 liter of this solution contains 1230 g of the mixture of sulfuric acid and water

Interactive Example 11.2 - Solution (Continued 1)

- Since the solution is 3.75 *M*, we know that 3.75 moles of H_2SO_4 is present per liter of solution
- The number of grams of H_2SO_4 present is

$$3.75\text{ mol} \times \frac{98.0\text{ g H}_2\text{SO}_4}{1\text{ mol}} = 368\text{ g H}_2\text{SO}_4$$

Interactive Example 11.2 - Solution (Continued 2)

- How much water is present in 1.00 L of solution?
  - The amount of water present in 1 liter of solution is obtained from the difference

$$1230 \text{ g solution} - 368 \text{ g } H_2SO_4 = 862 \text{ g } H_2O$$

- What is the mass percent?
  - Since we now know the masses of the solute and solvent, we can calculate the mass percent

Interactive Example 11.2 - Solution (Continued 3)

$$\text{Mass percent } H_2SO_4 = \frac{\text{mass of } H_2SO_4}{\text{mass of solution}} \times 100\%$$

$$= \frac{368 \text{ g}}{1230 \text{ g}} \times 100\% = 29.9\%\ H_2SO_4$$

- What is the molality?
  - From the moles of solute and the mass of solvent, we can calculate the molality

Interactive Example 11.2 - Solution (Continued 4)

$$\text{Molality of } H_2SO_4 = \frac{\text{moles } H_2SO_4}{\text{kilogram of } H_2O}$$

$$= \frac{3.75 \text{ mol } H_2SO_4}{862 \text{ g } H_2O \times \dfrac{1 \text{ kg } H_2O}{1000 \text{ g } H_2O}} = 4.35\ m$$

Interactive Example 11.2 - Solution (Continued 5)

- What is the normality?
  - Since each sulfuric acid molecule can furnish two protons, 1 mole of H_2SO_4 represents 2 equivalents
  - Thus, a solution with 3.75 moles of H_2SO_4 per liter contains $2 \times 3.75 = 7.50$ equivalents per liter
    - The normality is 7.50 *N*

Steps Involved in the Formation of a Liquid Solution

1. Expand the solute
   - Separate the solute into its individual components
2. Expand the solvent
   - Overcome intermolecular forces in the solvent to make room for the solute
3. Allow the solute and solvent to interact to form the solution

Steps Involved in the Formation of a Liquid Solution
(continued)

- Steps 1 and 2 are endothermic
  - Forces must be overcome to expand the solute and solvent
- Step 3 is often exothermic

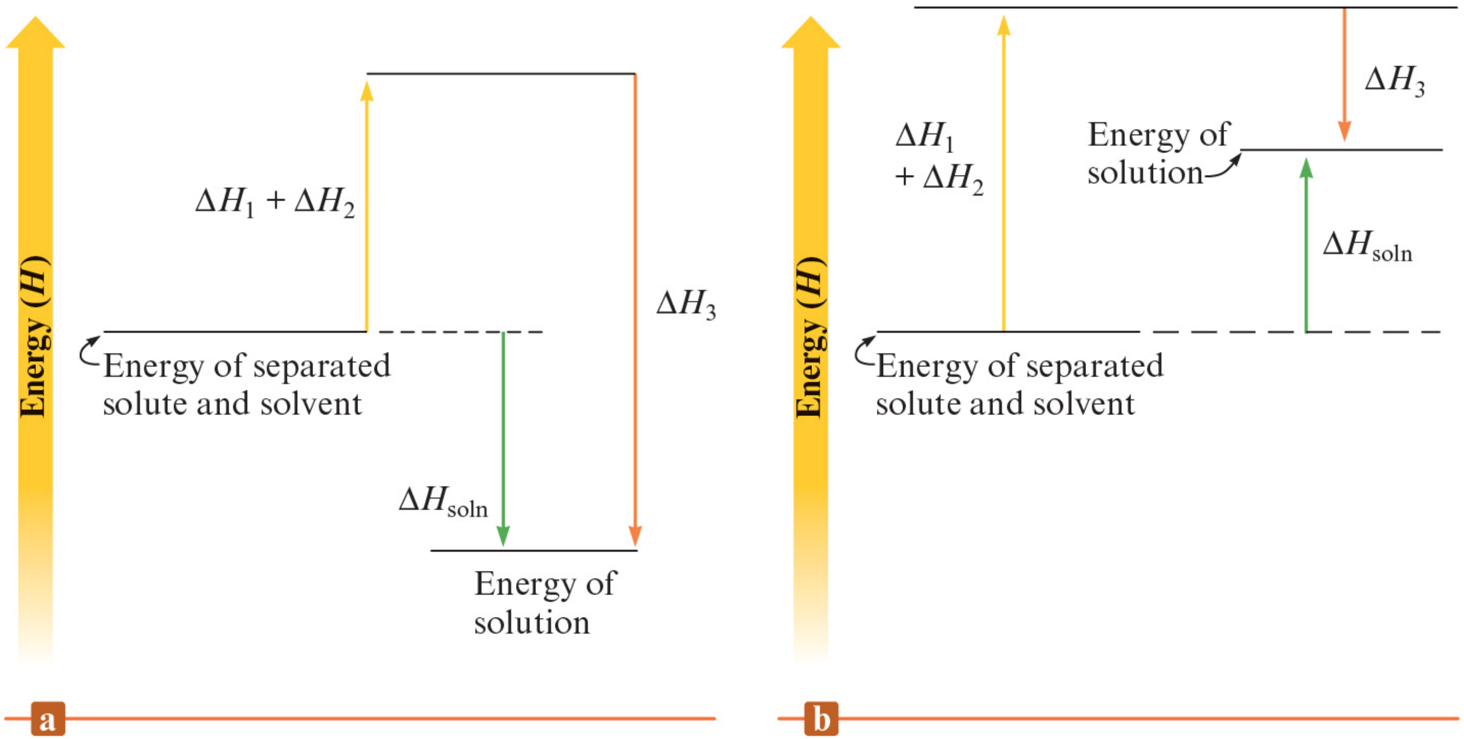
Enthalpy (Heat) of Solution (ΔH_{soln})

- Enthalpy change associated with the formation of the solution is the sum of the ΔH values for the steps:

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

  - ΔH_{soln} can have a positive sign when energy is absorbed or a negative sign when energy is released

Figure 11.2 - Heat of Solution



ΔH_{soln} has a negative sign if Step 3 releases more energy than that required by Steps 1 and 2

ΔH_{soln} has a positive sign if Steps 1 and 2 require more energy than is released in Step 3

Factors That Favor a Process

- Increase in probability of the mixed state when the solute and solvent are placed together
- Processes that require large amounts of energy tend not to occur
- Like dissolves like

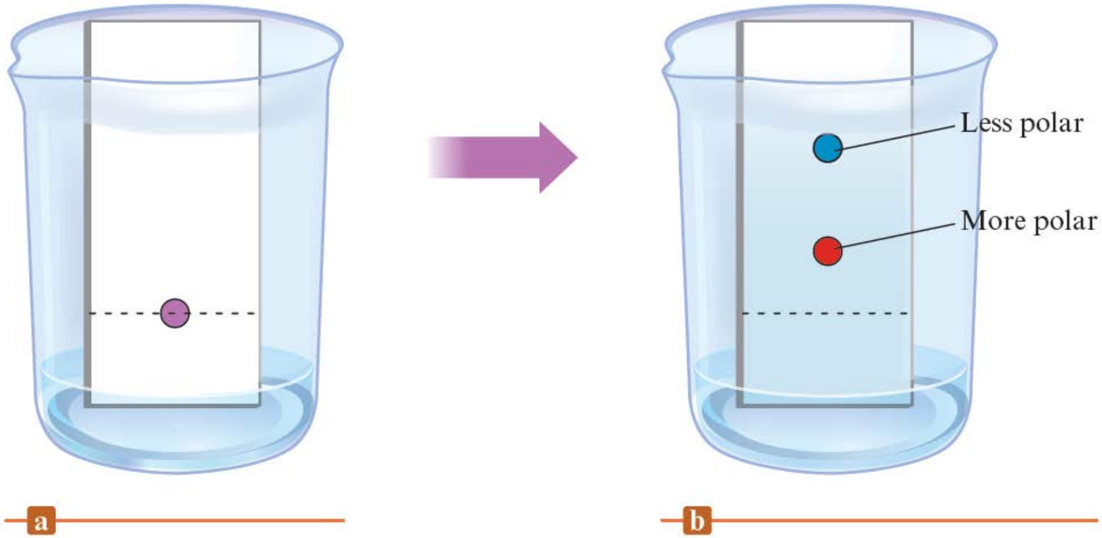
Table 11.3 - The Energy Terms for Various Types of Solutes and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

Thin Layer Chromatography (TLC)

- Uses a TLC plate as the stationary phase
  - TLC plate consists of a plastic sheet covered with a thin layer of silica gel
    - Silica gel is very polar and is capable of hydrogen bonding
- Mixture to be analyzed is placed on the plate, and the plate is dipped into a solvent (the mobile phase)
- Solvent travels up the plate due to capillary action

Figure 11.4 - Thin Layer Chromatography



(a) The plate is spotted and placed into the solvent

(b) After some time, the solvent (mobile phase) will travel up the plate and the less polar component travels farther than the more polar component

Critical Thinking

- You and a friend are studying for a chemistry exam
  - What if your friend tells you, "Since exothermic processes are favored and the sign of the enthalpy change tells us whether or not a process is endothermic or exothermic, the sign of ΔH_{soln} tells us whether or not a solution will form"?
    - How would you explain to your friend that this conclusion is not correct? What part, if any, of what your friend says is correct?

Interactive Example 11.3 - Differentiating Solvent Properties

- Decide whether liquid hexane (C_6H_{14}) or liquid methanol (CH_3OH) is the more appropriate solvent for the substances grease ($C_{20}H_{42}$) and potassium iodide (KI)

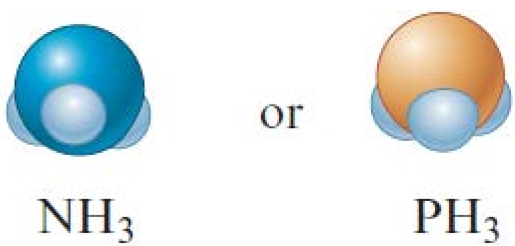
Interactive Example 11.3 - Solution

- Hexane is a nonpolar solvent because it contains C—H bonds
  - Hexane will work best for the nonpolar solute grease
- Methanol has an O—H group that makes it significantly polar
  - Will serve as the better solvent for the ionic solid KI

Exercise

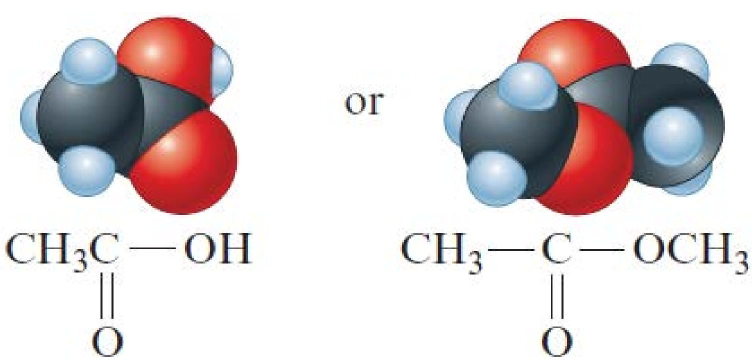
- For each of the following pairs, predict which substance would be more soluble in water

a.



NH_3

b.



CH_3COOH

Join In (2)

- Which of the following chemical or physical changes is an endothermic process?
  a. Combustion of gasoline
  b. Evaporation of water
  c. Freezing of water
  d. Mixing of sulfuric acid and water

Structure Effects

- Vitamins can be used to study the relationship among molecular structure, polarity, and solubility
  - Fat-soluble vitamins (A, D, E, and K) are nonpolar
    - Considered to be hydrophobic (water-fearing)
    - Can build up in the fatty tissues of the body
  - Water-soluble vitamins (B and C) are polar
    - Considered to be hydrophilic (water-loving)
    - Must be consumed regularly as they are excreted

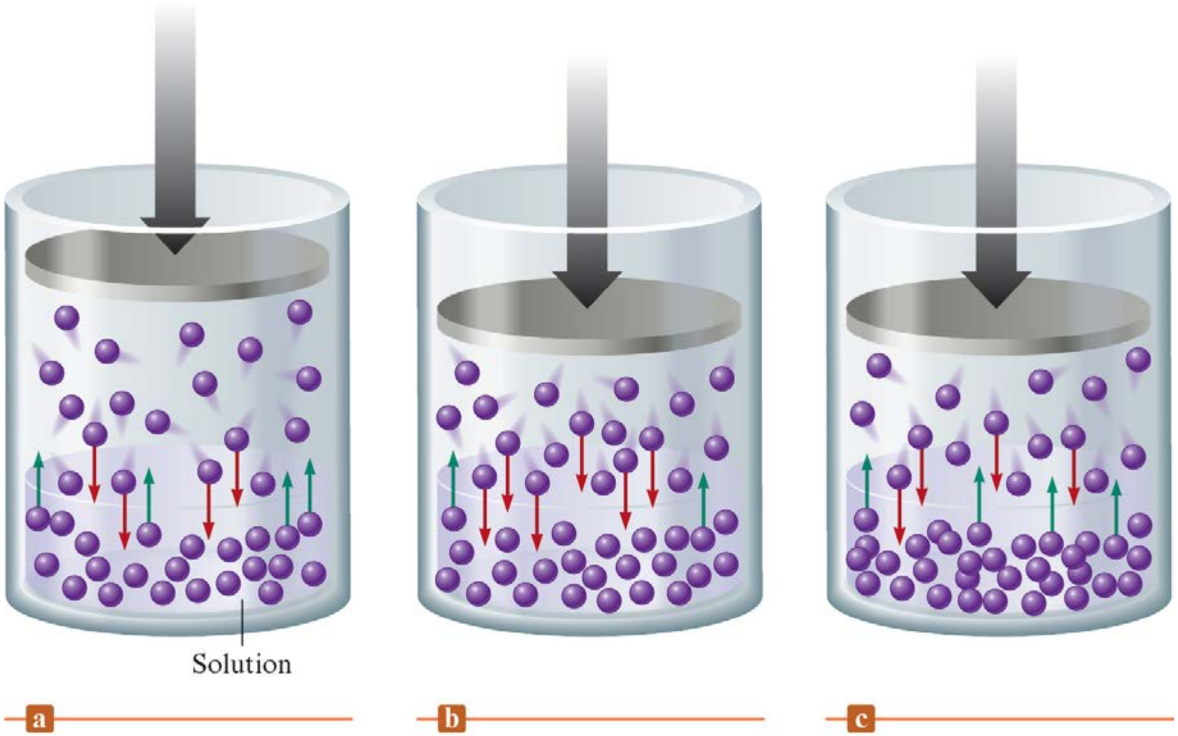
Pressure Effects

- Pressure increases the solubility of a gas
  - **Henry's law**: Amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution

$$C = kP$$

    - *C* - Concentration of the dissolved gas
    - *k* - Constant
    - *P* - Partial pressure of the gaseous solute above the solution

Figure 11.6 - Schematic Diagram That Depicts the Increase in Gas Solubility with Pressure



Interactive Example 11.4 - Calculations Using Henry's Law

- A certain soft drink is bottled so that a bottle at 25° C contains CO_2 gas at a pressure of 5.0 atm over the liquid
  - Assuming that the partial pressure of CO_2 in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO_2 in the soda both before and after the bottle is opened
    - The Henry's law constant for CO_2 in aqueous solution is 3.1×10^{-2} mol/L · atm at 25° C

Interactive Example 11.4 - Solution

- What is Henry's law for CO_2?
  - $C_{CO_2} = k_{CO_2} P_{CO_2}$
    - Where $k_{CO_2} = 3.1 \times 10^{-2}$ mol/L · atm
- What is the C_{CO_2} in the unopened bottle?
  - In the unopened bottle, $P_{CO_2} = 5.0$ atm

$$C_{CO_2} = k_{CO_2} P_{CO_2}$$

$$= \left(3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm}\right)\left(5.0 \text{ atm}\right) = 0.16 \text{ mol/L}$$

Interactive Example 11.4 - Solution (continued)

- What is the C_{CO_2} in the opened bottle?
  - In the opened bottle, the CO_2 in the soda eventually reaches equilibrium with the atmospheric CO_2, so P_{CO_2} = 4.0×10^{-4} atm and

$$C_{CO_2} = k_{CO_2} P_{CO_2} = \left(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)\left(4.0 \times 10^{-4} \text{ atm}\right)$$

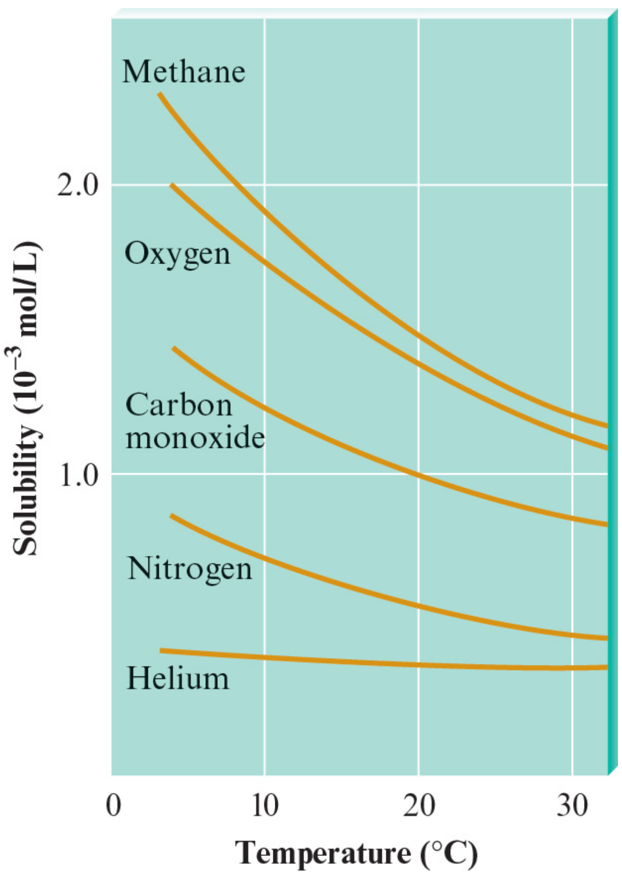
$$= 1.2 \times 10^{-5} \text{ mol/L}$$

  - Note the large change in concentration of CO_2
    - This is why soda goes “flat” after being open for a while

Temperature Effects (for Aqueous Solutions)

- Solids dissolve rapidly at higher temperatures
  - Amount of solid that can be dissolved may increase or decrease with increasing temperature
  - Solubilities of some substances decrease with increasing temperature
- Predicting temperature dependence of solubility is very difficult

Figure 11.8 - Solubilities of Several Gases in Water



Solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution

Temperature Effects (for Aqueous Solutions) (continued)

- Solubility of a gas in water decreases with increasing temperature
  - Water used for industrial cooling is returned to its natural source at higher than ambient temperatures
    - Causes **thermal pollution**
    - Warm water tends to float over the colder water, blocking oxygen absorption
  - Leads to the formation of boiler scale

Join In (3)

- Rank the following compounds according to increasing solubility in water
  I. $CH_3–CH_2–CH_2–CH_3$
  II. $CH_3–CH_2–O–CH_2–CH_3$
  III. $CH_3–CH_2–OH$
  IV. $CH_3–OH$

Join In (3) (continued)

a. I < III < IV < II

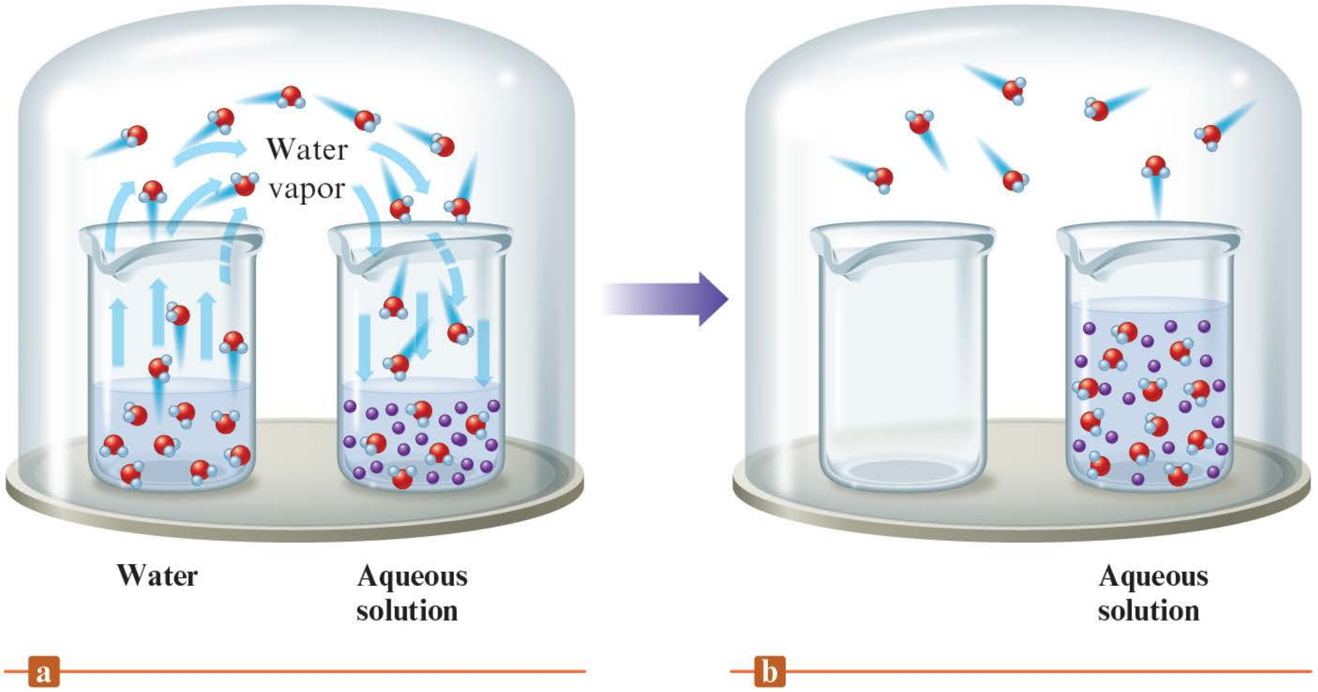
b. I < II < IV < III

c. III < IV < II < I

d. I < II < III < IV

e. IV < II < I < III

Figure 11.10 - An Aqueous Solution and Pure Water in a Closed Environment



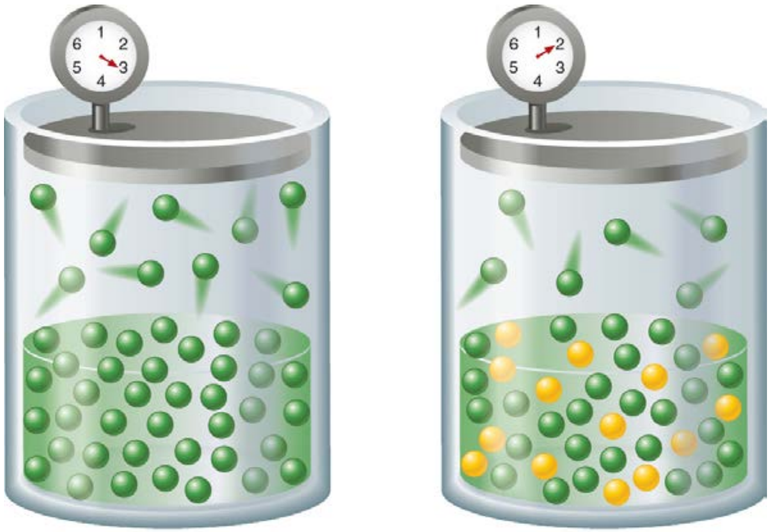
An aqueous solution and pure water in a closed environment

(a) Initial stage

(b) After a period of time, the water is transferred to the solution

Vapor Pressures of Solutions

- Presence of a nonvolatile solute lowers the vapor pressure of a solvent
  - Inhibits the escape of solvent molecules from the liquid



Pure solvent

Solution with a nonvolatile solute

Raoult's Law

$$P_{\text{soln}} = \chi_{\text{solvent}} P^{0}_{\text{solvent}}$$

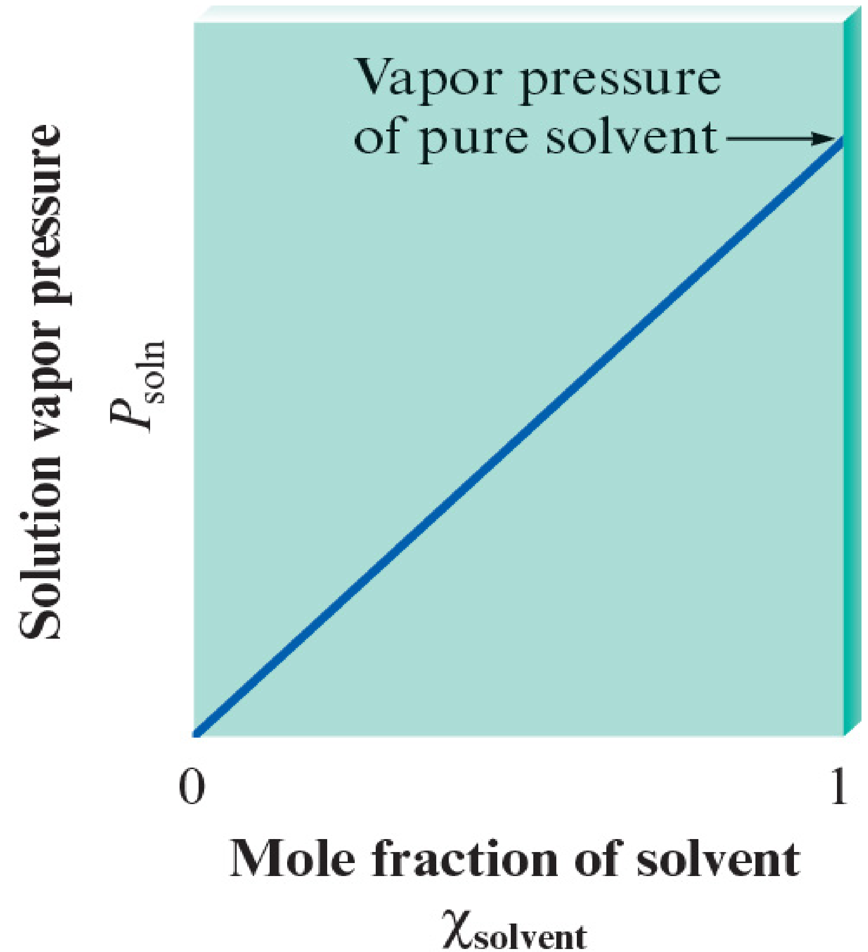
- P_{soln} - Observed vapor pressure of the solution
- χ_{solvent} - Mole fraction of the solvent
- P^{0}_{solvent} - Vapor pressure of the pure solvent

- Nonvolatile solute simply dilutes the solvent

Graphical Representation of Raoult's Law

- Can be represented as a linear equation of the form $y = mx + b$
  - $y = P_{soln}$
  - $x = \chi_{solvent}$
  - $m = P^0_{solvent}$
  - $b = 0$
- Slope of the graph is a straight line with a slope equal to $P^0_{solvent}$

Figure 11.12 - Plot of Raoult's Law



Interactive Example 11.5 - Calculating the Vapor Pressure of a Solution

- Calculate the expected vapor pressure at 25° C for a solution prepared by dissolving 158.0 g common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm^3 of water
  - At 25° C, the density of water is 0.9971 g/cm^3 and the vapor pressure is 23.76 torr

Interactive Example 11.5 - Solution

- What is Raoult's law for this case?

$$P_{\mathrm{soln}} = \chi_{\mathrm{H_2O}} P^0_{\mathrm{H_2O}}$$

  - To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose and the moles of water present

Interactive Example 11.5 - Solution (Continued 1)

- What are the moles of sucrose?

$$\text{Moles of sucrose} = 158.0\ \text{g sucrose} \times \frac{1\ \text{mol sucrose}}{342.3\ \text{g sucrose}} = 0.4616\ \text{mol sucrose}$$

- What are the moles of water?
  - To determine the moles of water present, we first convert volume to mass using the density:

$$643.5\ \text{cm}^3\ \text{H}_2\text{O} \times \frac{0.9971\ \text{g H}_2\text{O}}{\text{cm}^3\ \text{H}_2\text{O}} = 641.6\ \text{g H}_2\text{O}$$

Interactive Example 11.5 - Solution (Continued 2)

- The number of moles of water

$$641.6 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 35.60 \text{ mol } H_2O$$

- What is the mole fraction of water in the solution?

$$\chi_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol sucrose}} = \frac{35.60 \text{ mol}}{35.60 \text{ mol} + 0.4616 \text{ mol}}$$

$$= \frac{35.60 \text{ mol}}{36.06 \text{ mol}} = 0.9873$$

Interactive Example 11.5 - Solution (Continued 3)

- The vapor pressure of the solution is:

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P^0_{\text{H}_2\text{O}}$$

$$= (0.9872)(23.76 \text{ torr}) = 23.46 \text{ torr}$$

- The vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution
  - The vapor pressure has been lowered by 0.30 torr

Lowering of the Vapor Pressure

- Helps in counting molecules
  - Provides a means to experimentally determine molar masses
  - Raoult's law helps ascertain the number of moles of solute present in a solution
- Helps characterize solutions
  - Provides valuable information about the nature of the solute after it dissolves

Nonideal Solutions

- Both components are volatile in liquid–liquid solutions
  - Contribute to the total vapor pressure
  - Modified Raoult's law is applied here

$$P_{\mathrm{TOTAL}} = P_{\mathrm{A}} + P_{\mathrm{B}} = \chi_{\mathrm{A}} P_{\mathrm{A}}^{0} + \chi_{\mathrm{B}} P_{\mathrm{B}}^{0}$$

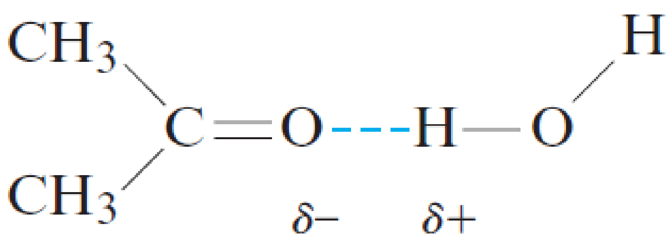
- P_{TOTAL} - Total vapor pressure of a solution containing A and B
- χ_{A} and χ_{B} - Mole fractions of A and B

Nonideal Solutions (continued)

  - P^0_A and P^0_B - Vapor pressures of pure A and pure B
  - P_A and P_B - Partial pressures resulting from molecules of A and of B in the vapor above the solution
- **Ideal solution**: Liquid–liquid solution that obeys Raoult's law
  - Nearly ideal behavior is observed when solute–solute, solvent–solvent, and solute–solvent interactions are similar

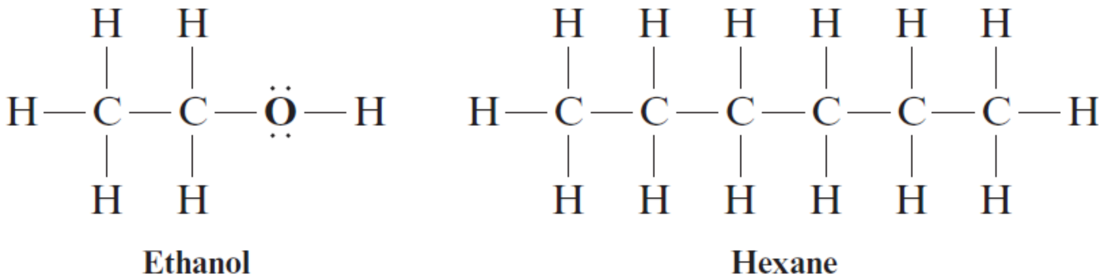
Behavior of Various Types of Solutions

- When ΔH_{soln} is large and negative:
  - Strong interactions exist between the solvent and solute
  - A negative deviation is expected from Raoult's law
    - Both components have low tendency to escape in the solution than in pure liquids
  - Example - Acetone–water solution



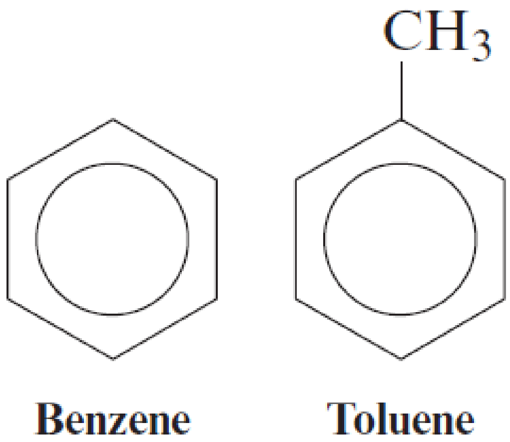
Behavior of Various Types of Solutions (Continued 1)

- When ΔH_{soln} is positive (endothermic), solute–solvent interactions are weaker
  - Molecules in the solution have a higher tendency to escape, and there is positive deviation from Raoult's law
  - Example - Solution of ethanol and hexane



Behavior of Various Types of Solutions (Continued 2)

- In a solution of very similar liquids:
  - ΔH_{soln} is close to zero
  - Solution closely obeys Raoult's law
  - Example - Benzene and toluene



Interactive Example 11.7 - Calculating the Vapor Pressure of a Solution Containing Two Liquids

- A solution is prepared by mixing 5.81 g acetone (C_3H_6O, molar mass = 58.1 g/mol) and 11.9 g chloroform ($HCCl_3$, molar mass = 119.4 g/mol)
  - At 35° C, this solution has a total vapor pressure of 260 torr
    - Is this an ideal solution?
    - The vapor pressures of pure acetone and pure chloroform at 35° C are 345 and 293 torr, respectively

Interactive Example 11.7 - Solution

- To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\mathrm{TOTAL}} = \chi_{\mathrm{A}} P_{\mathrm{A}}^{0} + \chi_{\mathrm{C}} P_{\mathrm{C}}^{0}$$

  - A stands for acetone, and C stands for chloroform
    - The calculated value can then be compared with the observed vapor pressure

Interactive Example 11.7 - Solution (Continued 1)

- First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

Interactive Example 11.7 - Solution (Continued 2)

- The solution contains equal numbers of moles of acetone and chloroform

$$\chi_A = 0.500 \text{ and } \chi_C = 0.500$$

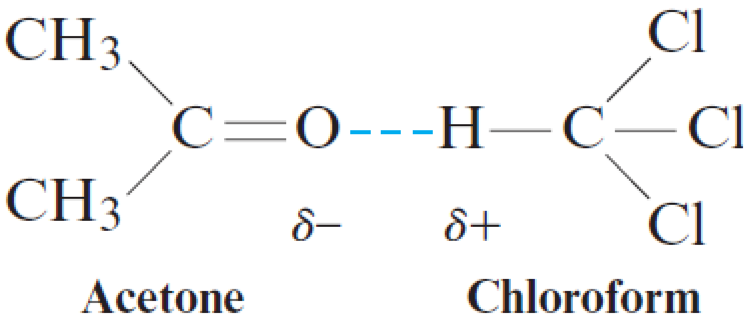
  - The expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$

  - Comparing this value with the observed pressure of 260 torr shows that the solution does not behave ideally

Interactive Example 11.7 - Solution (Continued 3)

- The observed value is lower than that expected
- This negative deviation from Raoult's law can be explained in terms of the hydrogen-bonding interaction which lowers the tendency of these molecules to escape from the solution



Homework

- A solution is made by mixing hexane (C_6H_{14}) and chloroform ($CHCl_3$)
  - What type of deviation from Raoult's law is expected for this solution?
    a. Positive deviation
    b. Negative deviation
    c. No deviation
- A solution of two liquids, A and B, shows negative deviation from Raoult's law
  - What does this mean?
    a. Molecules of A interact strongly with other A-type molecules
    b. The two liquids have a positive heat of solution
    c. Molecules of A interact weakly, if at all, with B-type molecules
    d. Molecules of A hinder the strong interaction between B-type molecules
    e. Molecules of A interact more strongly with B-type molecules than with A or B with B

Thank you