

Chapter 13

The Properties of Mixtures:

Solutions and Colloids



The Properties of Mixtures: Solutions and Colloids

13.1 Types of Solutions: Intermolecular Forces and Predicting Solubility

13.2 Why Substances Dissolve: Understanding the Solution Process

13.3 Solubility as an Equilibrium Process

13.4 Quantitative Ways of Expressing Concentration

13.5 Colligative Properties of Solutions



Table 13.1 Approximate Composition of a Bacterium

Substance	Mass % of Cell	Number of Types	Number of Molecules
Water	~70	1	5×10^{10}
Ions	1	20	?
Sugars*	3	200	3×10^8
Amino acids*	0.4	100	5×10^7
Lipids*	2	50	3×10^7
Nucleotides*	0.4	200	1×10^7
Other small molecules	0.2	~200	?
Macromolecules (proteins, nucleic acids, polysaccharides)	23	~5000	6×10^6

*Includes precursors and metabolites.

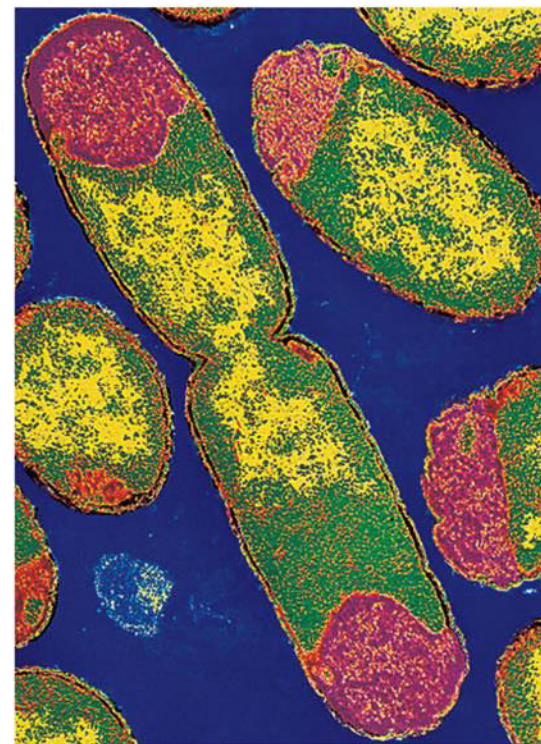
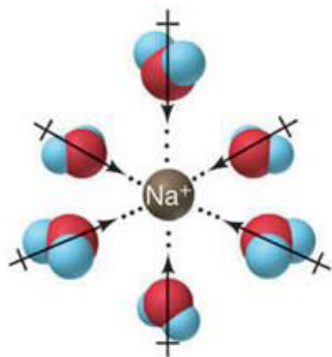
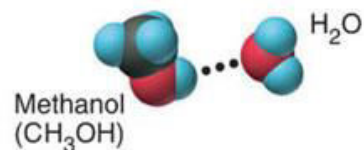


Figure 13.1 The major types of intermolecular forces in solutions.

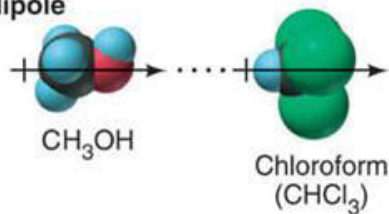
Ion-dipole
(40–600)



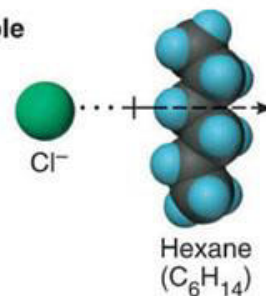
H bond
(10–40)



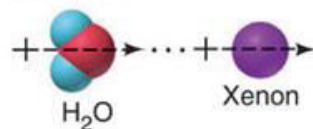
Dipole-dipole
(5–25)



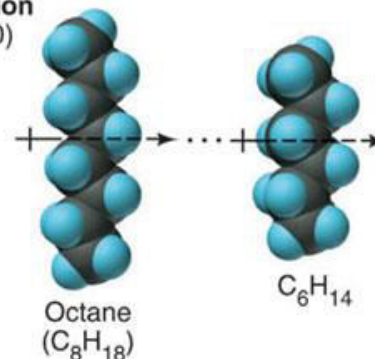
Ion-induced dipole
(3–15)



Dipole-induced dipole
(2–10)



Dispersion
(0.05–40)



LIKE DISSOLVES LIKE

Substances with similar types of intermolecular forces dissolve in each other.

When a solute dissolves in a solvent, solute-solute interactions and solvent-solvent interactions are being replaced with solute-solvent interactions. The forces must be comparable in strength in order to have a solution occur.



Figure 13.2

Hydration shells around an aqueous ion.

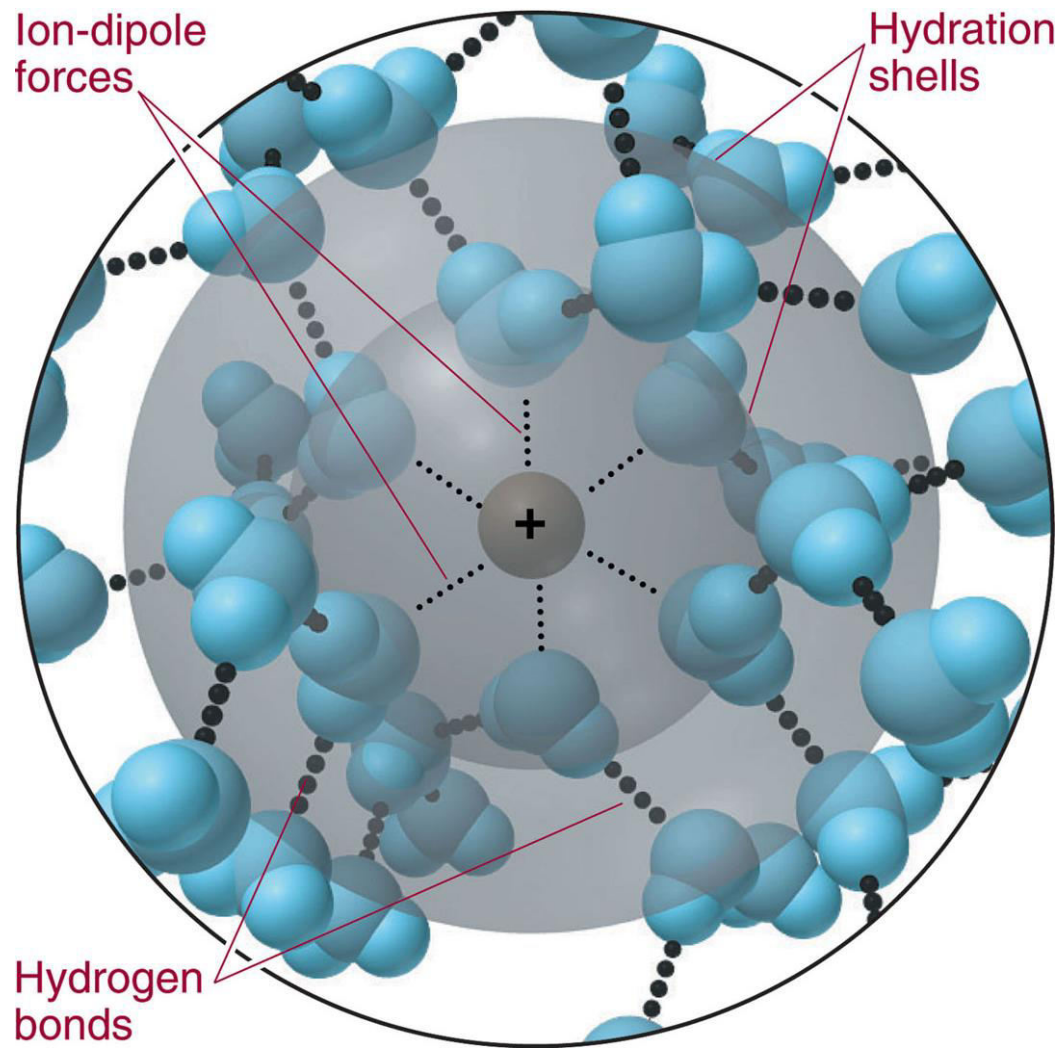


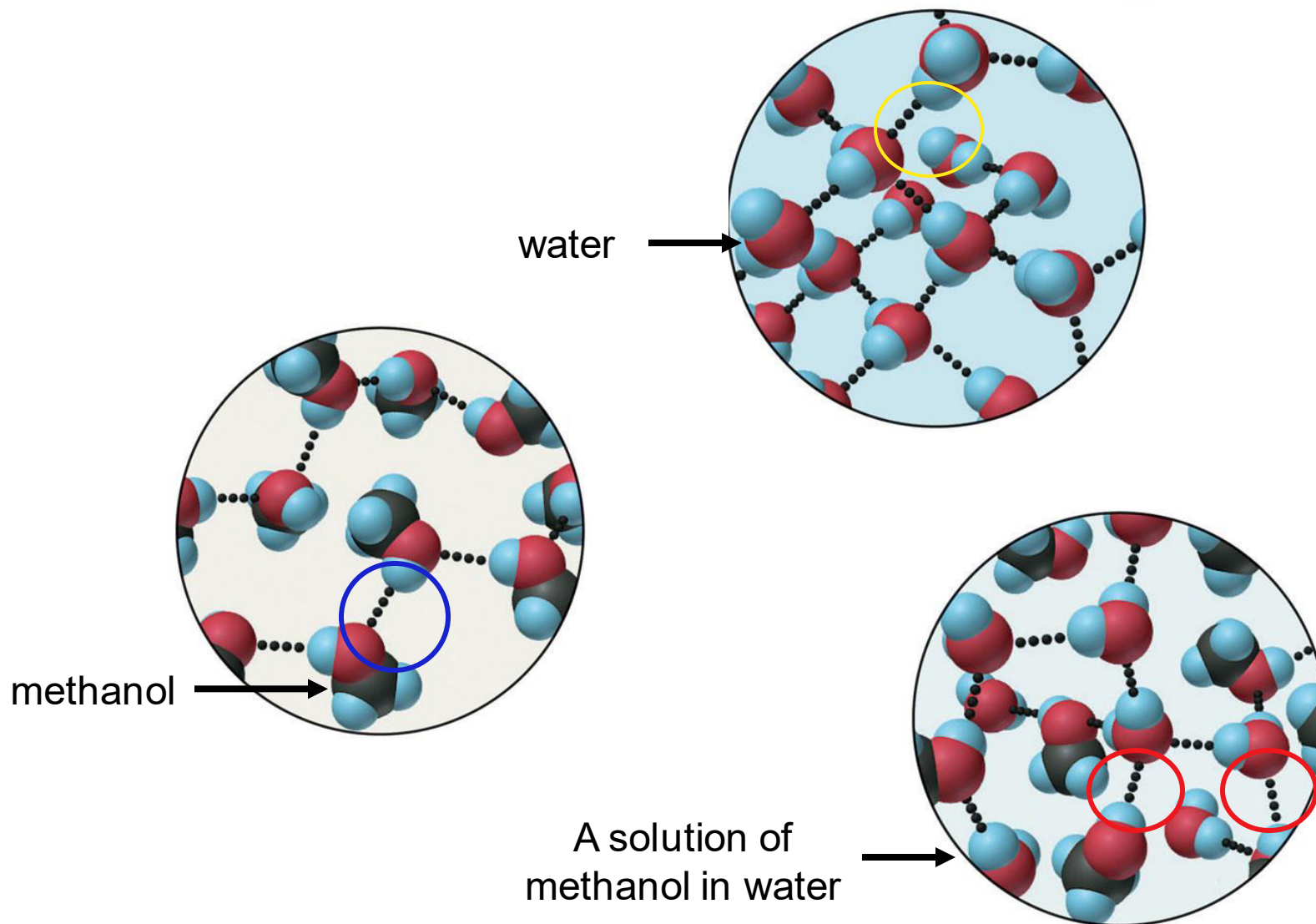
Table 13.2 Solubility* of a Series of Alcohols in Water and Hexane

Alcohol	Model	Solubility in Water	Solubility in Hexane
CH ₃ OH (methanol)		∞	1.2
CH ₃ CH ₂ OH (ethanol)		∞	∞
CH ₃ (CH ₂) ₂ OH (propanol)		∞	∞
CH ₃ (CH ₂) ₃ OH (butanol)		1.1	∞
CH ₃ (CH ₂) ₄ OH (pentanol)		0.30	∞
CH ₃ (CH ₂) ₅ OH (hexanol)		0.058	∞

*Expressed in mol alcohol/1000 g solvent at 20°C.

Figure 13.3

Like dissolves like: solubility of methanol in water.



SAMPLE PROBLEM 13.1 Predicting Relative Solubilities of Substances

PROBLEM: Predict which solvent will dissolve more of the given solute:

- (a) Sodium chloride in methanol (CH_3OH) or in propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)
- (b) Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) in hexane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) or in water.
- (c) Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) in water or in ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)

PLAN: Consider the intermolecular forces which can exist between solute molecules and consider whether the solvent can provide such interactions and thereby substitute.

SOLUTION:

- (a) Methanol - NaCl is ionic and will form ion-dipoles with the -OH groups of both methanol and propanol. However, propanol is subject to the dispersion forces to a greater extent.
- (b) Water - Hexane has no dipoles to interact with the -OH groups in ethylene glycol. Water can H bond to the ethylene glycol.
- (c) Ethanol - Diethyl ether can interact through a dipole and dispersion forces. Ethanol can provide both while water would like to H bond.

Table 13.3

Correlation Between Boiling Point and Solubility in Water

Gas	Solubility (M)*	bp (K)
He	4.2×10^{-4}	4.2
Ne	6.6×10^{-4}	27.1
N ₂	10.4×10^{-4}	77.4
CO	15.6×10^{-4}	81.6
O ₂	21.8×10^{-4}	90.2
NO	32.7×10^{-4}	121.4

* At 273K and 1 atm



Heats of solution and solution cycles

1. *Solute particles separate from each other* - endothermic

solute (aggregated) + heat $\longrightarrow$ solute (separated) $\Delta H_{\text{solute}} > 0$

2. *Solvent particles separate from each other* - endothermic

solvent (aggregated) + heat $\longrightarrow$ solvent (separated) $\Delta H_{\text{solvent}} > 0$

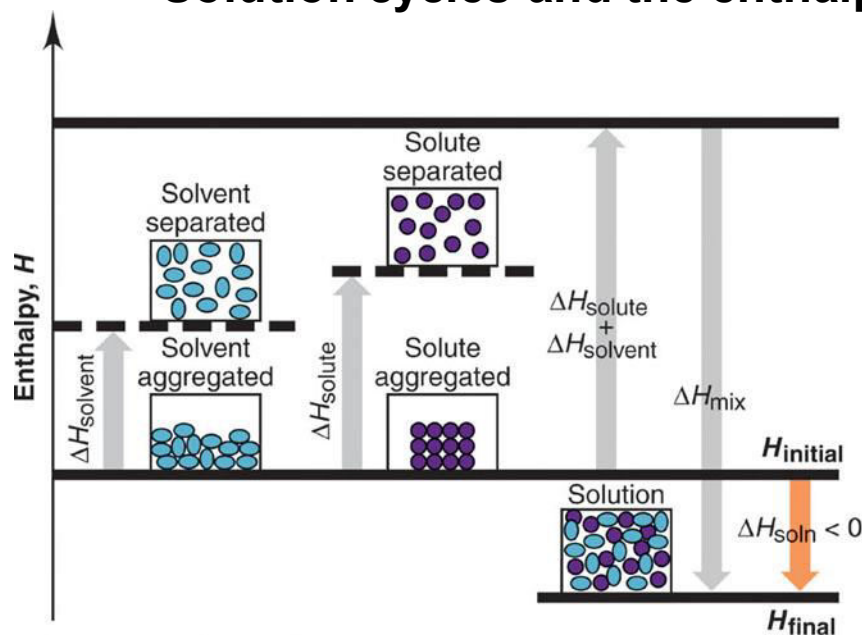
3. *Solute and solvent particles mix* - exothermic

solute (separated) + solvent (separated) $\longrightarrow$ solution + heat $\Delta H_{\text{mix}} < 0$

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

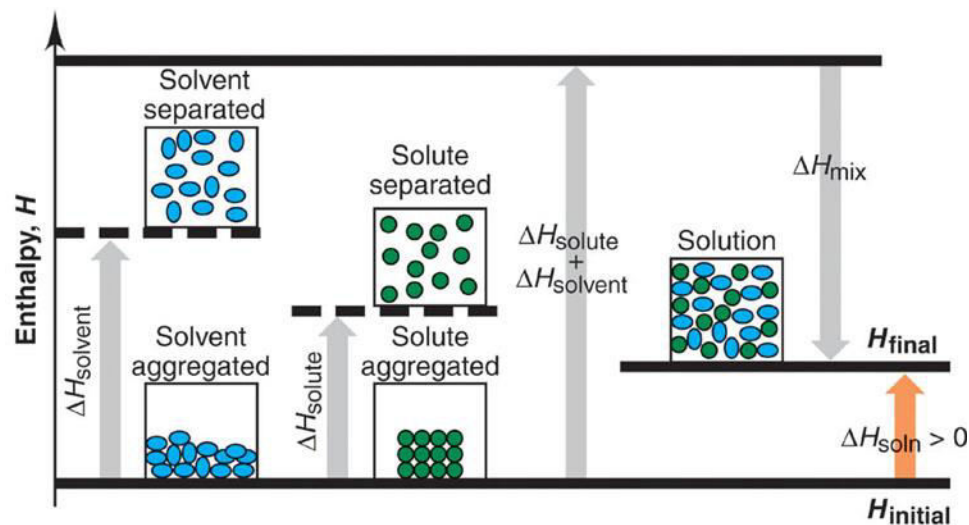
Figure 13.4

Solution cycles and the enthalpy components of the heat of solution.



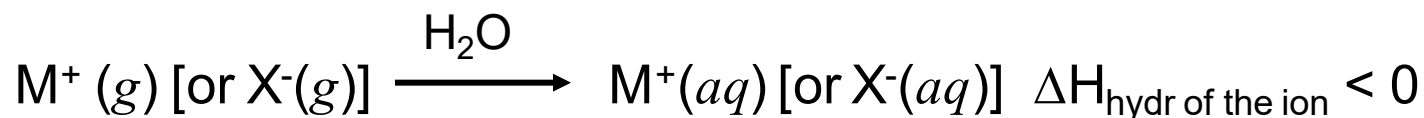
Exothermic solution process

Endothermic solution process



Heats of Hydration

solvation of ions by water - always exothermic



ΔH_{hydr} is related to the charge density of the ion, that is, coulombic charge and size matter.

Lattice energy is the ΔH involved in the formation of an ionic solid from its gaseous ions.

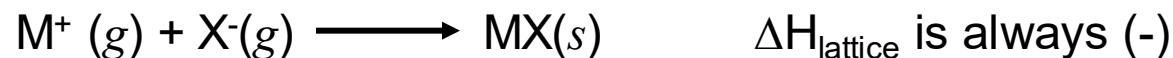


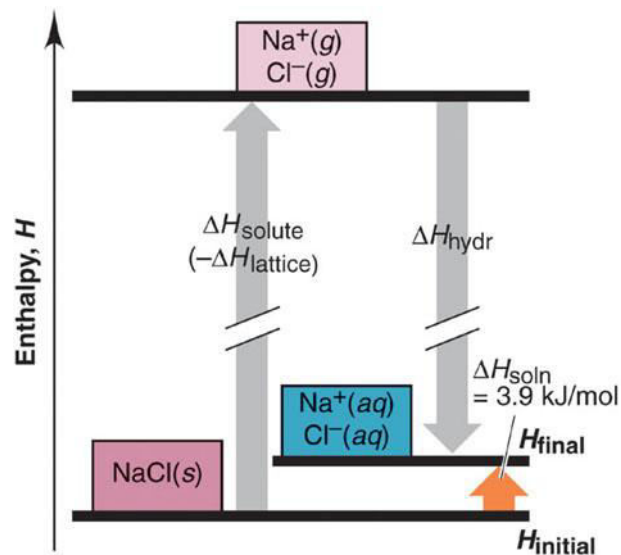
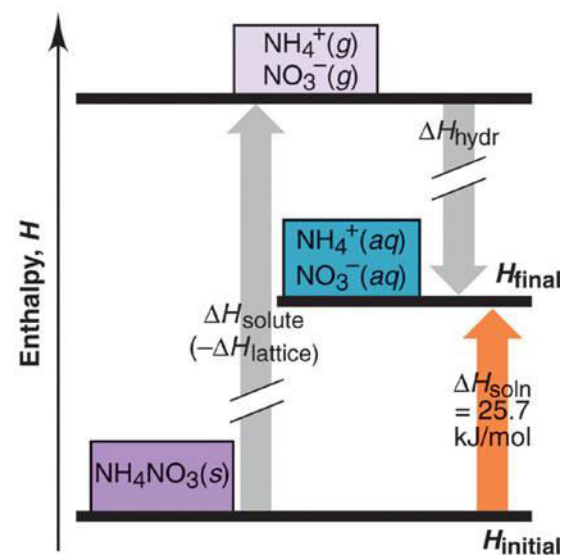
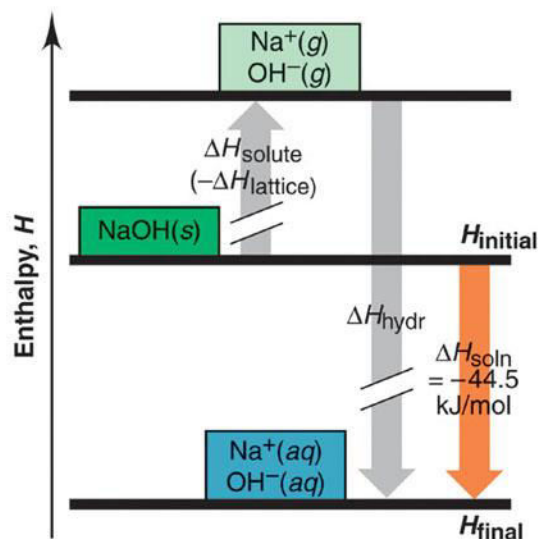
Figure 13.5 Dissolving ionic compounds in water.**NaCl** **NH_4NO_3** **NaOH**

Figure 13.6

Enthalpy diagrams for dissolving **NaCl** and **octane** in hexane.

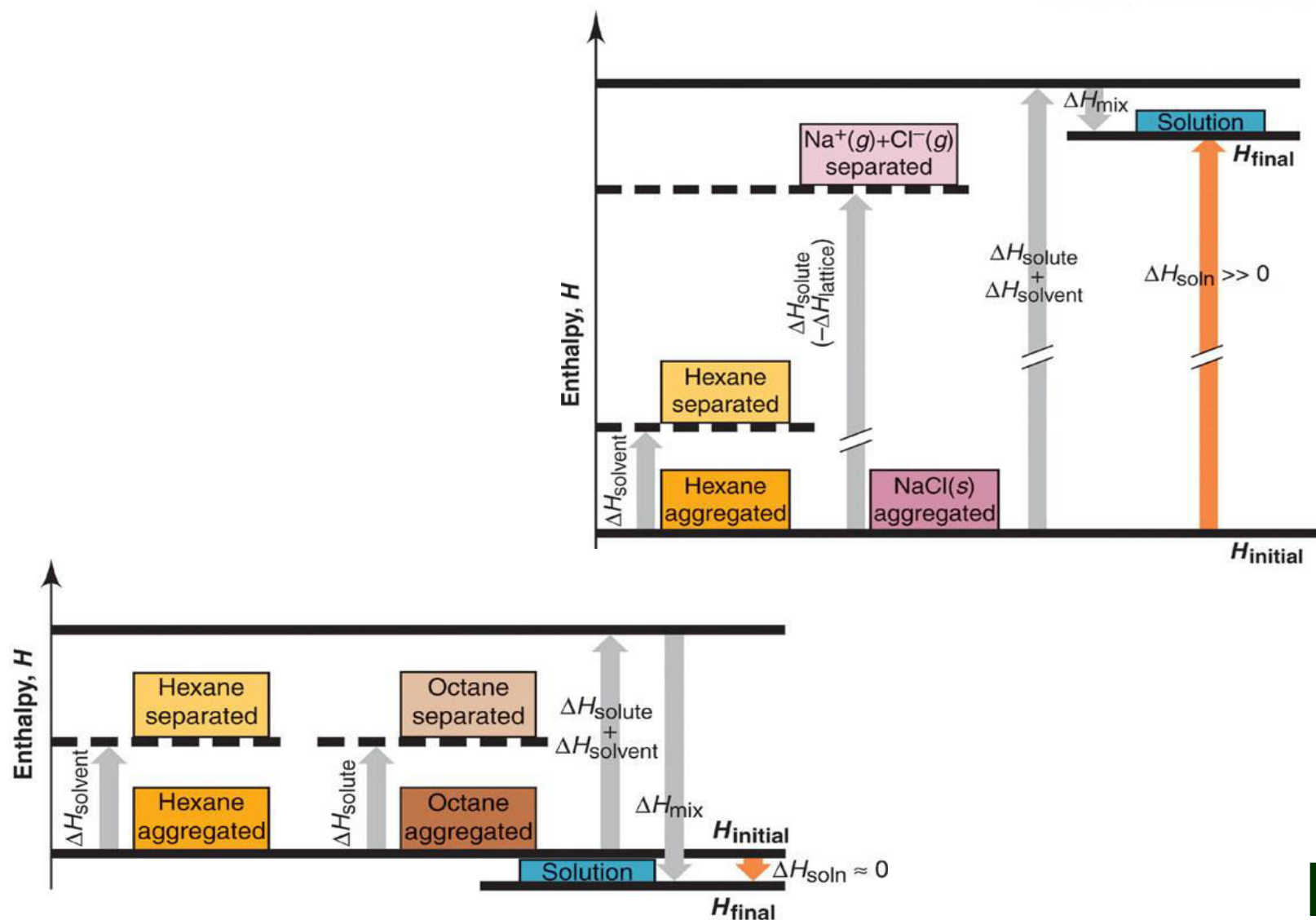
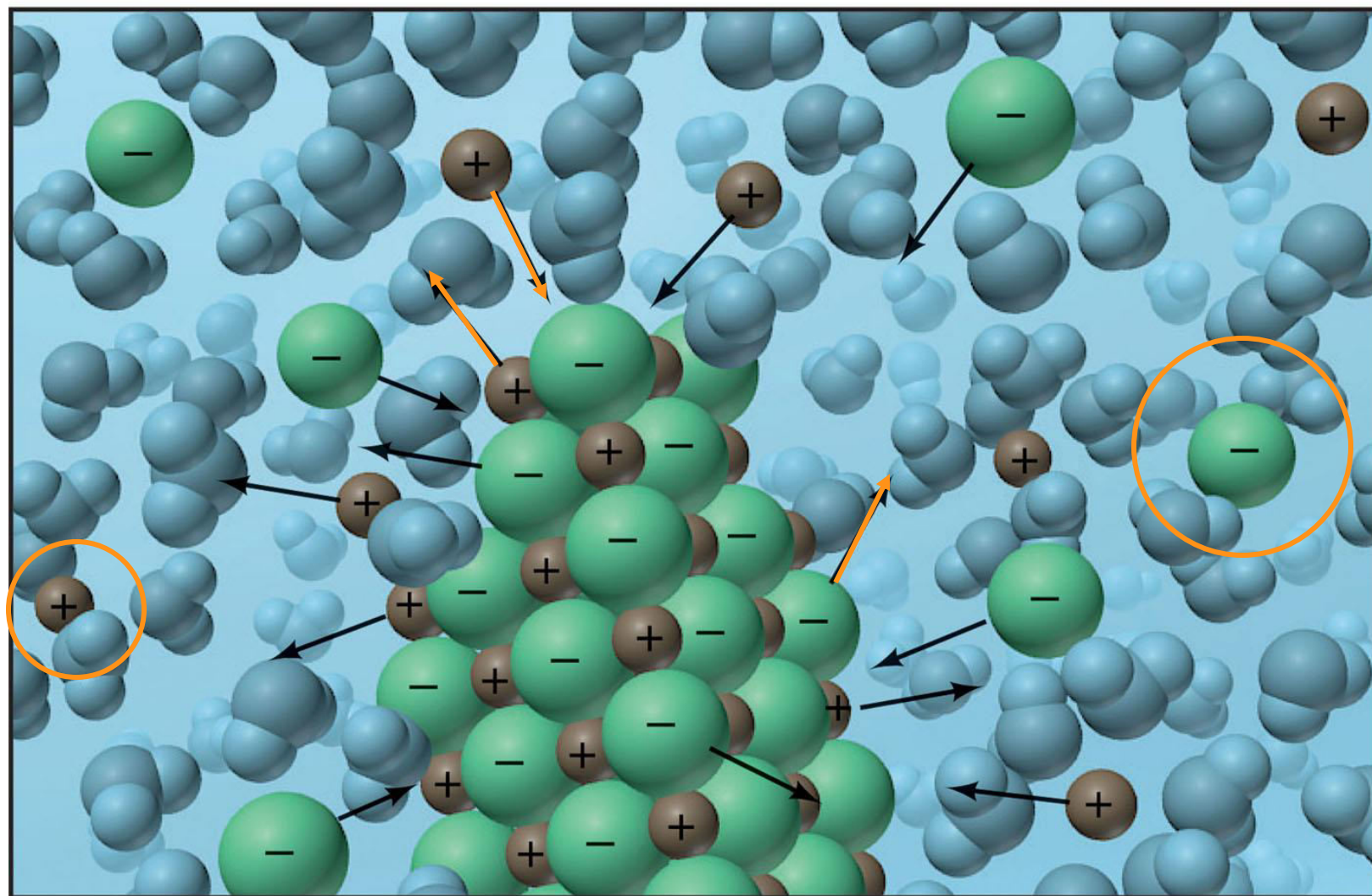


Figure 13.7 **Equilibrium in a saturated solution.**



solute (undissolved) $\rightleftharpoons$ solute (dissolved)

Figure 13.8

Sodium acetate crystallizing from a supersaturated solution.



Figure 13.9

The relation between solubility and temperature for several ionic compounds.

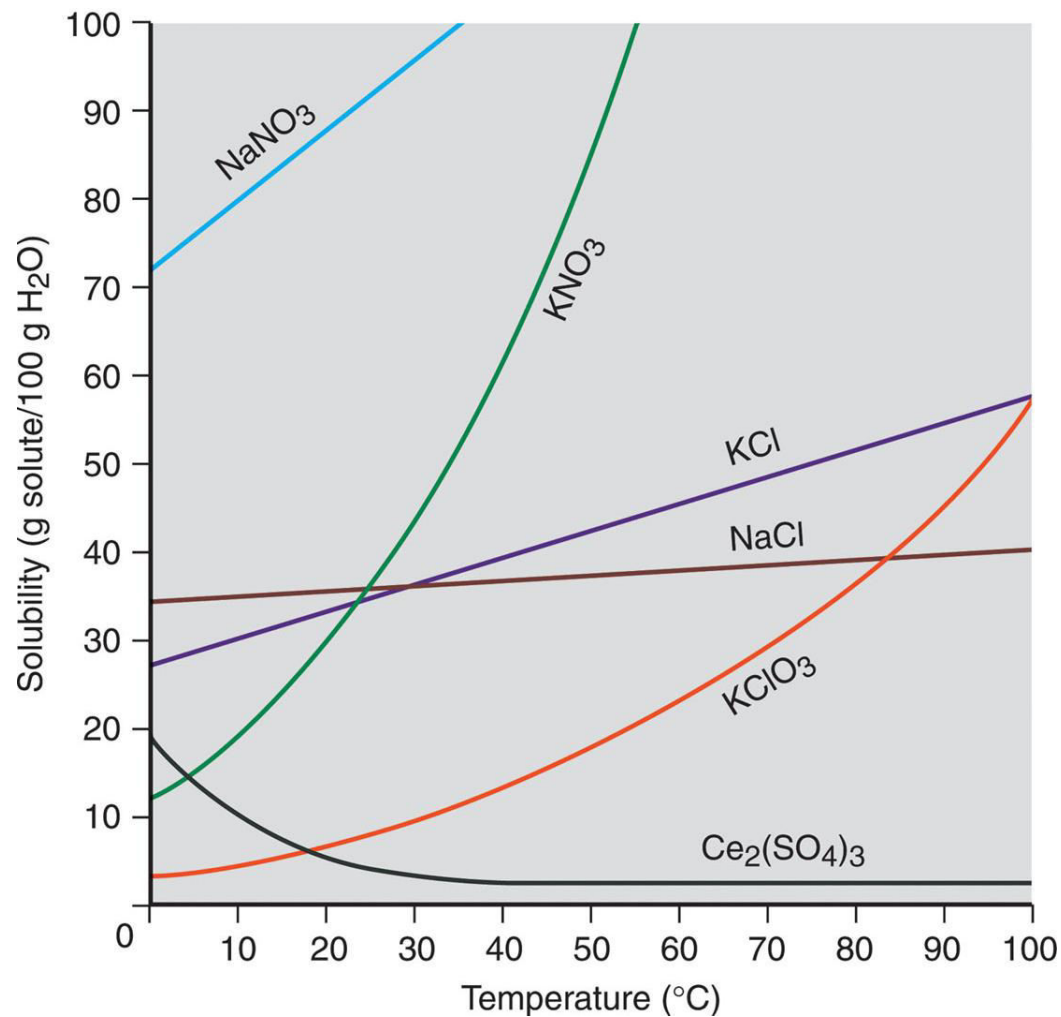
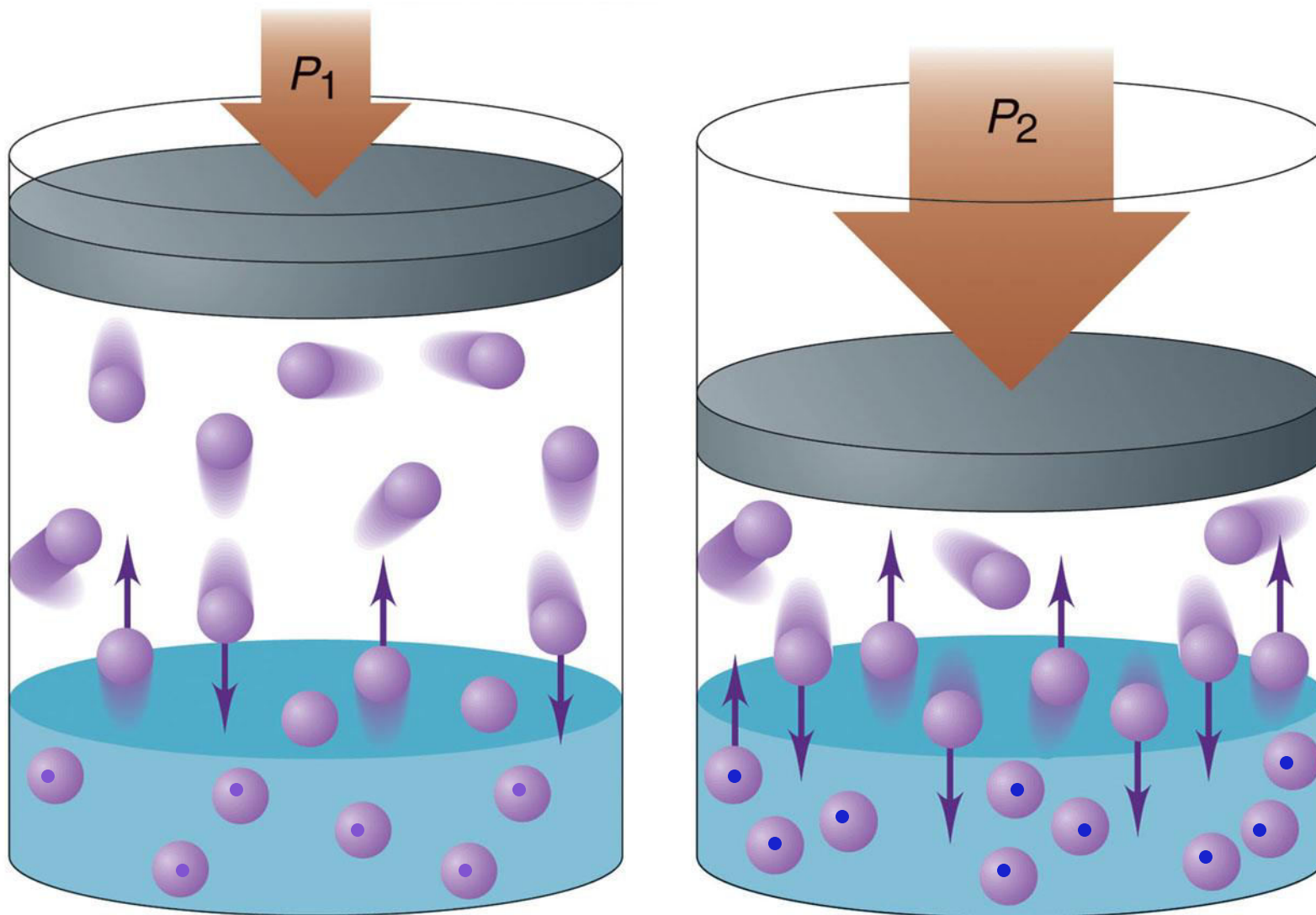


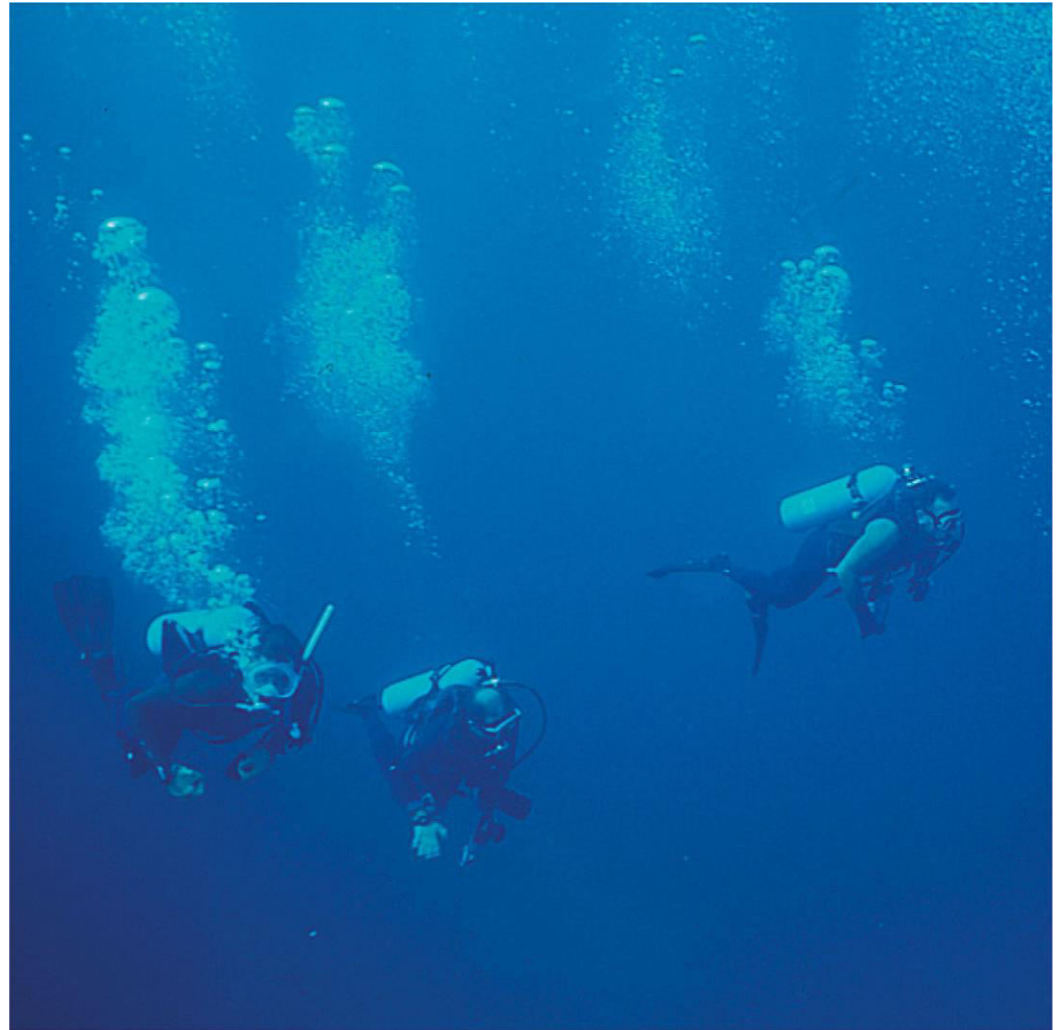
Figure 13.10 The effect of pressure on gas solubility.



Henry's Law

$$S_{gas} = k_H \times P_{gas}$$

The solubility of a gas (S_{gas}) is directly proportional to the partial pressure of the gas (P_{gas}) above the solution.



SAMPLE PROBLEM 13.2 Using Henry's Law to Calculate Gas Solubility

PROBLEM: The partial pressure of carbon dioxide gas inside a bottle of cola is 4 atm at 25°C. What is the solubility of CO₂? The Henry's law constant for CO₂ dissolved in water is 3.3 x10⁻² mol/L*atm at 25°C.

PLAN: Knowing k_H and P_{gas}, we can substitute into the Henry's law equation.

SOLUTION:
$$S_{\text{CO}_2} = (3.3 \times 10^{-2} \text{ mol/L} \cdot \text{atm})(4 \text{ atm}) = 0.1 \text{ mol/L}$$

Table 13.4 Concentration Definitions

Concentration Term	Ratio
Molarity (M)	$\frac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (m)	$\frac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\frac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\frac{\text{volume of solute}}{\text{volume of solution}}$
Mole fraction (χ)	$\frac{\text{amount (mol) of solute}}{\text{amount (mol) of solute} + \text{amount (mol) of solvent}}$

SAMPLE PROBLEM 13.3 Calculating Molality

PROBLEM: What is the molality of a solution prepared by dissolving 32.0 g of CaCl_2 in 271 g of water?

PLAN: We have to convert the grams of CaCl_2 to moles and the grams of water to kg. Then substitute into the equation for molality.

SOLUTION:

$$32.0 \text{ g CaCl}_2 \times \frac{\text{mole CaCl}_2}{110.98 \text{ g CaCl}_2} = 0.288 \text{ mole CaCl}_2$$

$$\text{molality} = \frac{0.288 \text{ mole CaCl}_2}{271 \text{ g H}_2\text{O} \times \frac{\text{kg}}{10^3 \text{ g}}} = 1.06 \text{ } m \text{ CaCl}_2$$

SAMPLE PROBLEM 13.4 Expressing Concentration in Parts by Mass, Parts by Volume, and Mole Fraction

PROBLEM: (a) Find the concentration of calcium (in ppm) in a 3.50-g pill that contains 40.5 mg of Ca.

(b) The label on a 0.750-L bottle of Italian chianti indicates “11.5% alcohol by volume”. How many liters of alcohol does the wine contain?

(c) A sample of rubbing alcohol contains 142 g of isopropyl alcohol ($\text{C}_3\text{H}_7\text{OH}$) and 58.0 g of water. What are the mole fractions of alcohol and water?

PLAN: (a) Convert mg to g of Ca, find the ratio of g Ca to g pill and multiply by 10^6 .

(b) Knowing the % alcohol and total volume, we can find volume of alcohol.

(c) Convert g of solute and solvent to moles; find the ratios of parts to the total.



SAMPLE PROBLEM 13.4 Expressing Concentrations in Parts by Mass, Parts by Volume, and Mole Fraction

continued

SOLUTION: (a)
$$\frac{40.5 \text{ mg Ca} \times \frac{\text{g}}{10^3 \text{ mg}}}{3.5 \text{ g}} \times 10^6 = 1.16 \times 10^4 \text{ ppm Ca}$$

(b)
$$0.750 \text{ L chianti} \times \frac{11.5 \text{ L alcohol}}{100 \text{ L chianti}} = 0.0862 \text{ L alcohol}$$

(c)
$$\text{moles ethylene glycol} = 142 \text{ g} \times \frac{\text{mole}}{60.09 \text{ g}} = 2.36 \text{ mol C}_2\text{H}_6\text{O}_2$$

$$\text{moles water} = 38.0 \text{ g} \times \frac{\text{mole}}{18.02 \text{ g}} = 3.22 \text{ mol H}_2\text{O}$$

$$\frac{2.39 \text{ mol C}_2\text{H}_8\text{O}_2}{2.39 \text{ mol C}_2\text{H}_8\text{O}_2 + 3.22 \text{ mol H}_2\text{O}}$$

= 0.423

$\chi \text{ C}_2\text{H}_6\text{O}_2$

$$\frac{3.22 \text{ mol H}_2\text{O}}{2.39 \text{ mol C}_2\text{H}_8\text{O}_2 + 3.22 \text{ mol H}_2\text{O}}$$

= 0.577

$\chi \text{ H}_2\text{O}$

Interconverting Concentration Terms

- To convert a term based on amount (mol) to one based on mass, you need the molar mass. These conversions are similar to mass-mole conversions.
- To convert a term based on mass to one based on volume, you need the solution *density*. Working with the mass of a solution and the density (mass/volume), you can obtain volume from mass and mass from volume.
- Molality involves quantity of *solvent*, whereas the other concentration terms involve quantity of *solution*.



SAMPLE PROBLEM 13.5 Converting Concentration Terms

PROBLEM: Hydrogen peroxide is a powerful oxidizing agent used in concentrated solution in rocket fuels and in dilute solution as a hair bleach. An aqueous solution H_2O_2 is 30.0% by mass and has a density of 1.11 g/mL. Calculate its

- (a) Molality (b) Mole fraction of H_2O_2 (c) Molarity

PLAN: (a) To find the mass of solvent we assume the % is per 100 g of solution. Take the difference in the mass of the solute and solution for the mass of peroxide.

(b) Convert g of solute and solvent to moles before finding χ .

(c) Use the density to find the volume of the solution.

SOLUTION: (a) g of H_2O = 100. g solution - 30.0 g H_2O_2 = 70.0 g H_2O

$$\text{molality} = \frac{\frac{30.0 \text{ g H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \times 0.882 \text{ mol H}_2\text{O}_2}{\frac{70.0 \text{ g H}_2\text{O}}{10^3 \text{ g}}} = 12.6 \text{ } m \text{ H}_2\text{O}_2$$

SAMPLE PROBLEM 13.5 Converting Concentration Terms

continued

$$(b) \quad 70.0 \text{ g H}_2\text{O} \quad \frac{\text{mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 3.88 \text{ mol H}_2\text{O}$$

$$\frac{0.882 \text{ mol H}_2\text{O}_2}{0.882 \text{ mol H}_2\text{O}_2 + 3.88 \text{ mol H}_2\text{O}} = 0.185 \chi \text{ of H}_2\text{O}_2$$

$$(c) \quad 100.0 \text{ g solution} \quad \frac{\text{mL}}{1.11 \text{ g}} = 90.1 \text{ mL solution}$$

$$\frac{0.882 \text{ mol H}_2\text{O}_2}{90.1 \text{ mL solution} \quad \frac{\text{L}}{10^3 \text{ mL}}} = 9.79 \text{ M H}_2\text{O}_2$$

Colligative Properties

Raoult's Law (vapor pressure of a solvent above a solution, P_{solvent})

$$P_{\text{solvent}} = \chi_{\text{solvent}} \times P_{\text{solvent}}^0$$

where P_{solvent}^0 is the vapor pressure of the pure solvent

$$P_{\text{solvent}}^0 - P_{\text{solvent}} = \Delta P = \chi_{\text{solute}} \times P_{\text{solvent}}^0$$

Boiling Point Elevation and Freezing Point Depression

$$\Delta T_b = K_b m$$

$$\Delta T_f = K_f m$$

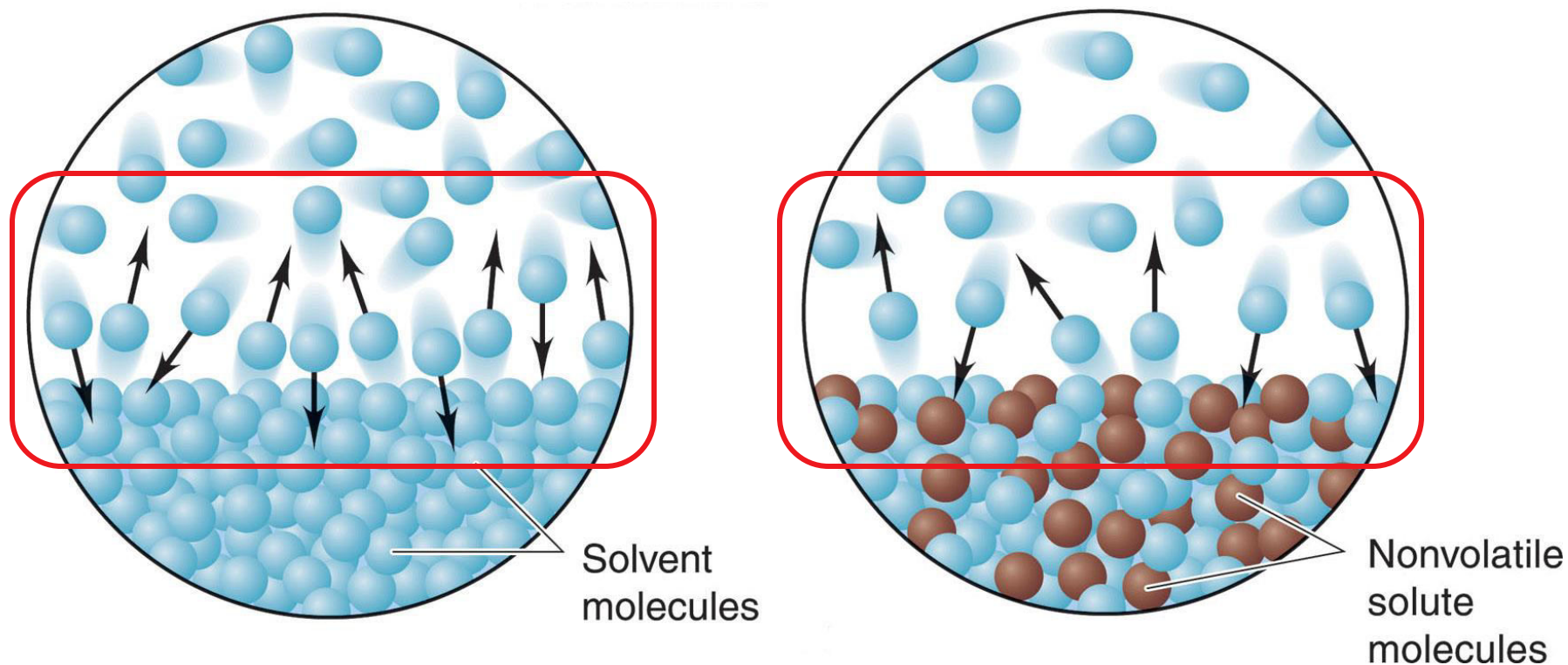
Osmotic Pressure

$\pi = M R T$ where M is the molarity, R is the ideal gas law constant and T is the Kelvin temperature



Figure 13.11

The effect of a solute on the vapor pressure of a solution.



SAMPLE PROBLEM 13.6 Using Raoult's Law to Find the Vapor Pressure Lowering

PROBLEM: Calculate the vapor pressure lowering, ΔP , when 10.0 mL of glycerol ($\text{C}_3\text{H}_8\text{O}_3$) is added to 500. mL of water at $50.^\circ\text{C}$. At this temperature, the vapor pressure of pure water is 92.5 torr and its density is 0.988 g/mL. The density of glycerol is 1.26 g/mL.

PLAN: Find the mol fraction, χ , of glycerol in solution and multiply by the vapor pressure of water.

SOLUTION:

$$10.0 \text{ mL C}_3\text{H}_8\text{O}_3 \times \frac{1.26 \text{ g C}_3\text{H}_8\text{O}_3}{\text{mL C}_3\text{H}_8\text{O}_3} \times \frac{\text{mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3} = 0.137 \text{ mol C}_3\text{H}_8\text{O}_3$$

$$500.0 \text{ mL H}_2\text{O} \times \frac{0.988 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{\text{mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 27.4 \text{ mol H}_2\text{O}$$

$$\Delta P = \left(\frac{0.137 \text{ mol C}_3\text{H}_8\text{O}_3}{0.137 \text{ mol C}_3\text{H}_8\text{O}_3 + 27.4 \text{ mol H}_2\text{O}} \right) \times 92.5 \text{ torr} = 0.461 \text{ torr}$$

$\chi = 0.00498$

Figure 13.12

Phase diagrams of solvent and solution.

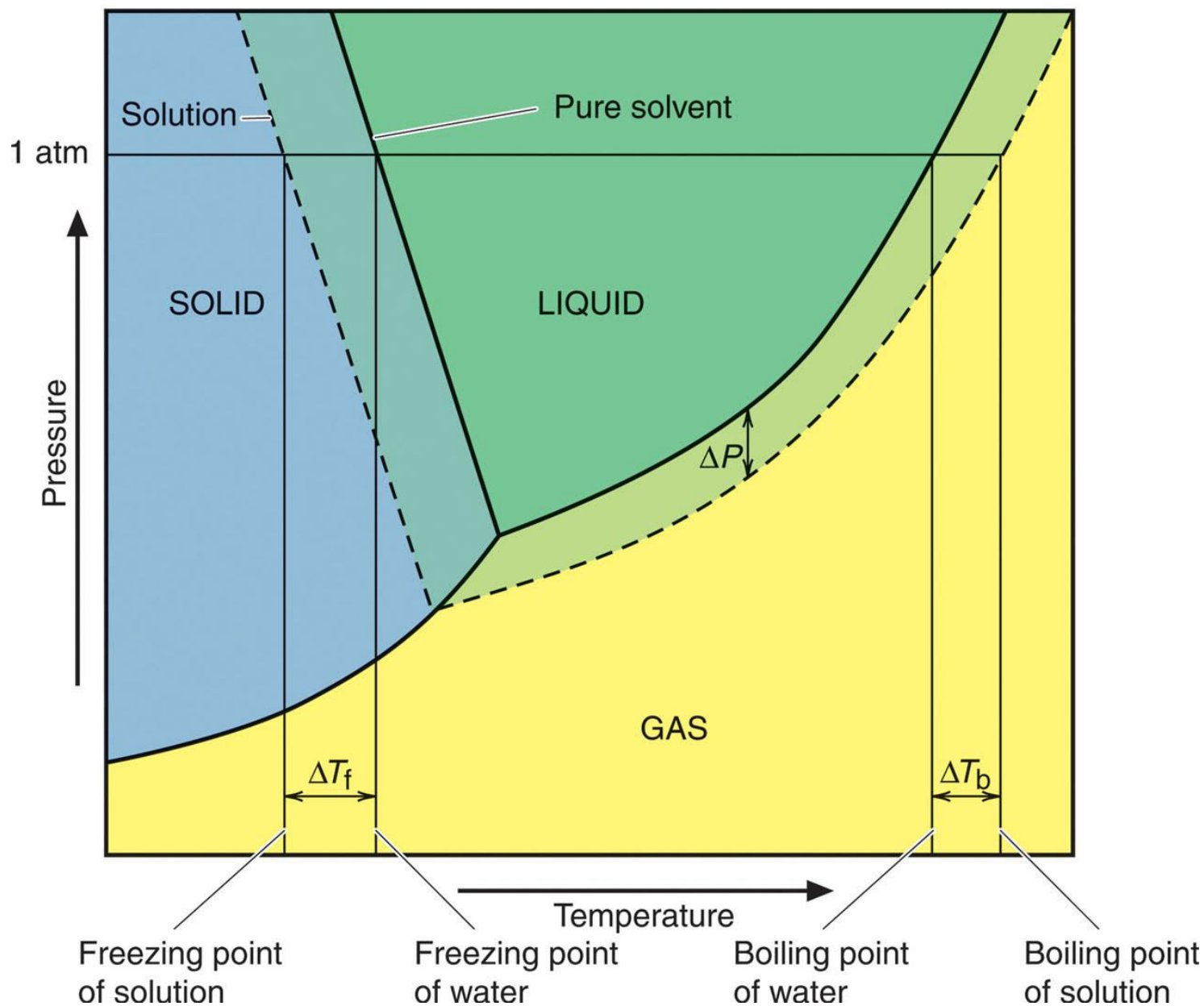


Table 13.5 Molal Boiling Point Elevation and Freezing Point Depression Constants of Several Solvents

Solvent	Boiling Point (°C)*	K_b (°C/m)	Melting Point (°C)	K_b (°C/m)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	-111.5	3.83
Carbon tetrachloride	76.5	5.03	-23	30.
Chloroform	61.7	3.63	-63.5	4.70
Diethyl ether	34.5	2.02	-116.2	1.79
Ethanol	78.5	1.22	-117.3	1.99
Water	100.0	0.512	0.0	1.86

*at 1 atm.

SAMPLE PROBLEM 13.7 Determining the Boiling Point Elevation and Freezing Point Depression of a Solution

PROBLEM: You add 1.00 kg of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) antifreeze to your car radiator, which contains 4450 g of water. What are the boiling and freezing points of the solution?

PLAN: Find the # mols of ethylene glycol; m of the solution; multiply by the boiling or freezing point constant; add or subtract, respectively, the changes from the boiling point and freezing point of water.

SOLUTION:

$$1.00 \times 10^3 \text{ g C}_2\text{H}_6\text{O}_2 \times \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.07 \text{ g C}_2\text{H}_6\text{O}_2} = 16.1 \text{ mol C}_2\text{H}_6\text{O}_2$$

$$\frac{16.1 \text{ mol C}_2\text{H}_6\text{O}_2}{4.450 \text{ kg H}_2\text{O}} = 3.62 \text{ } m \text{ C}_2\text{H}_6\text{O}_2$$

$$\Delta T_{\text{bp}} = 0.512 \text{ } ^\circ\text{C}/m \times 3.62m = 1.85^\circ\text{C} \quad \Delta T_{\text{fp}} = 1.86 \text{ } ^\circ\text{C}/m \times 3.62m$$

$$\text{BP} = 101.85 \text{ } ^\circ\text{C}$$

$$\text{FP} = -6.73 \text{ } ^\circ\text{C}$$

Osmotic Pressure

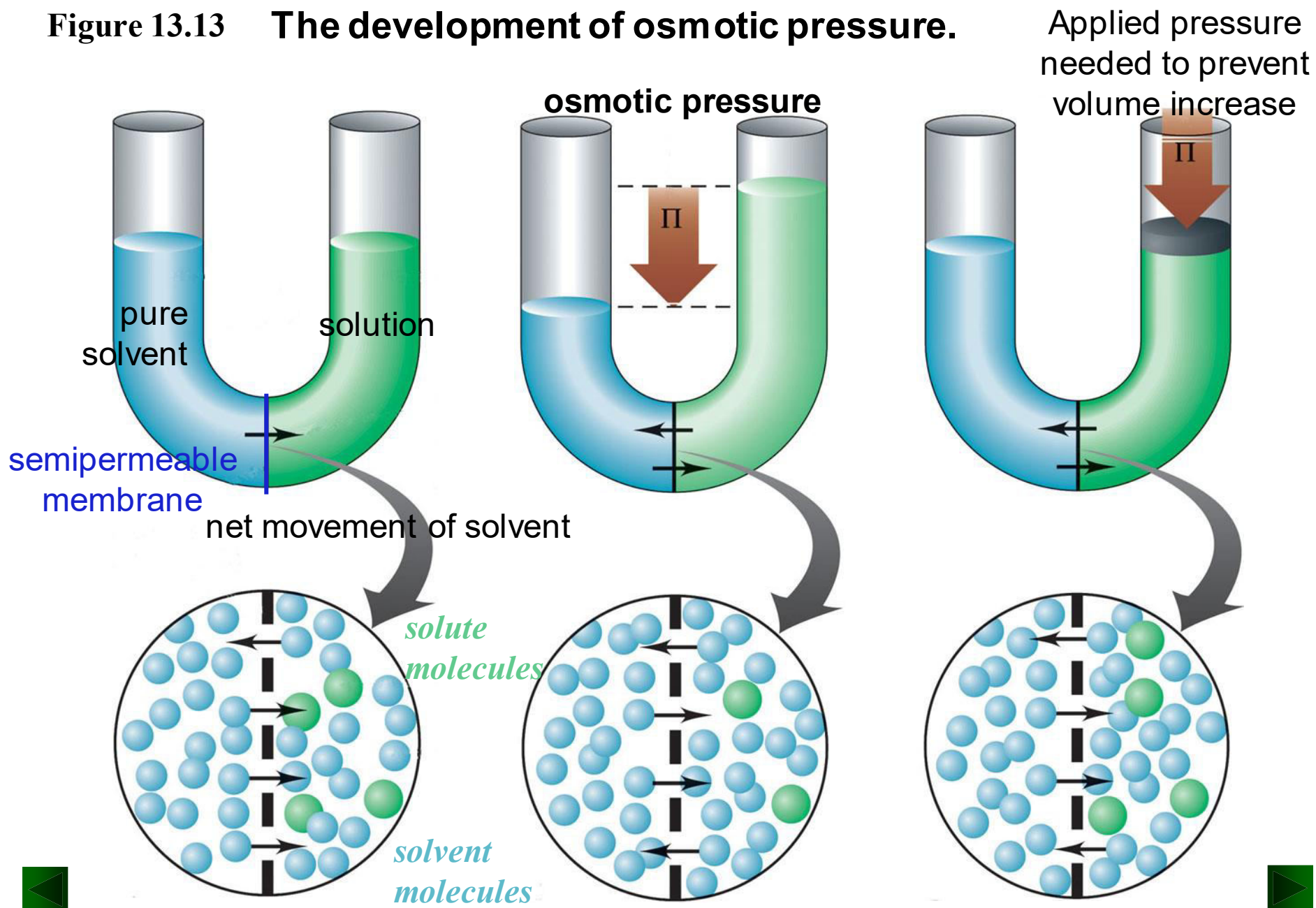
The symbol for osmotic pressure is π .

$$\pi \propto \frac{n_{\text{solute}}}{V_{\text{solution}}} \quad \text{or} \quad \pi \propto M$$

$$\pi = \frac{n_{\text{solute}}}{V_{\text{solution}}} RT = MRT$$



Figure 13.13 The development of osmotic pressure.



SAMPLE PROBLEM 13.8 Determining Molar Mass from Osmotic Pressure

PROBLEM: Biochemists have discovered more than 400 mutant varieties of hemoglobin, the blood protein that carries oxygen throughout the body. A physician studying a variety associated with a fatal disease first finds its molar mass (M). She dissolves 21.5 mg of the protein in water at 5.0°C to make 1.50 mL of solution and measures an osmotic pressure of 3.61 torr. What is the molar mass of this variety of hemoglobin?

PLAN: We know π as well as R and T . Convert π to atm and T to degrees K. Use the π equation to find M and then the amount and volume of the sample to get to M .

SOLUTION:

$$M = \frac{\pi}{RT} = \frac{3.61 \text{ torr} \frac{\text{atm}}{760 \text{ torr}}}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(278.1 \text{ K})} = 2.08 \times 10^{-4} \text{ M}$$

$$\frac{2.08 \times 10^{-4} \text{ mol}}{\text{L}} (1.50 \text{ mL}) \frac{\text{L}}{10^3 \text{ mL}} = 3.12 \times 10^{-8} \text{ mol}$$

$$21.5 \text{ mg} \frac{\text{g}}{10^3 \text{ mg}} \frac{1}{3.12 \times 10^{-8} \text{ mol}} = 6.89 \times 10^4 \text{ g/mol}$$

Colligative Properties of Electrolyte Solutions

For electrolyte solutions, the compound formula tells us how many particles are in the solution.

The van't Hoff factor, i , tells us what the “effective” number of ions are in the solution.

van't Hoff factor (i)

$$i = \frac{\text{measured value for electrolyte solution}}{\text{expected value for nonelectrolyte solution}}$$

For vapor pressure lowering: $\Delta P = i(\chi_{\text{solute}} \times P^0_{\text{solvent}})$

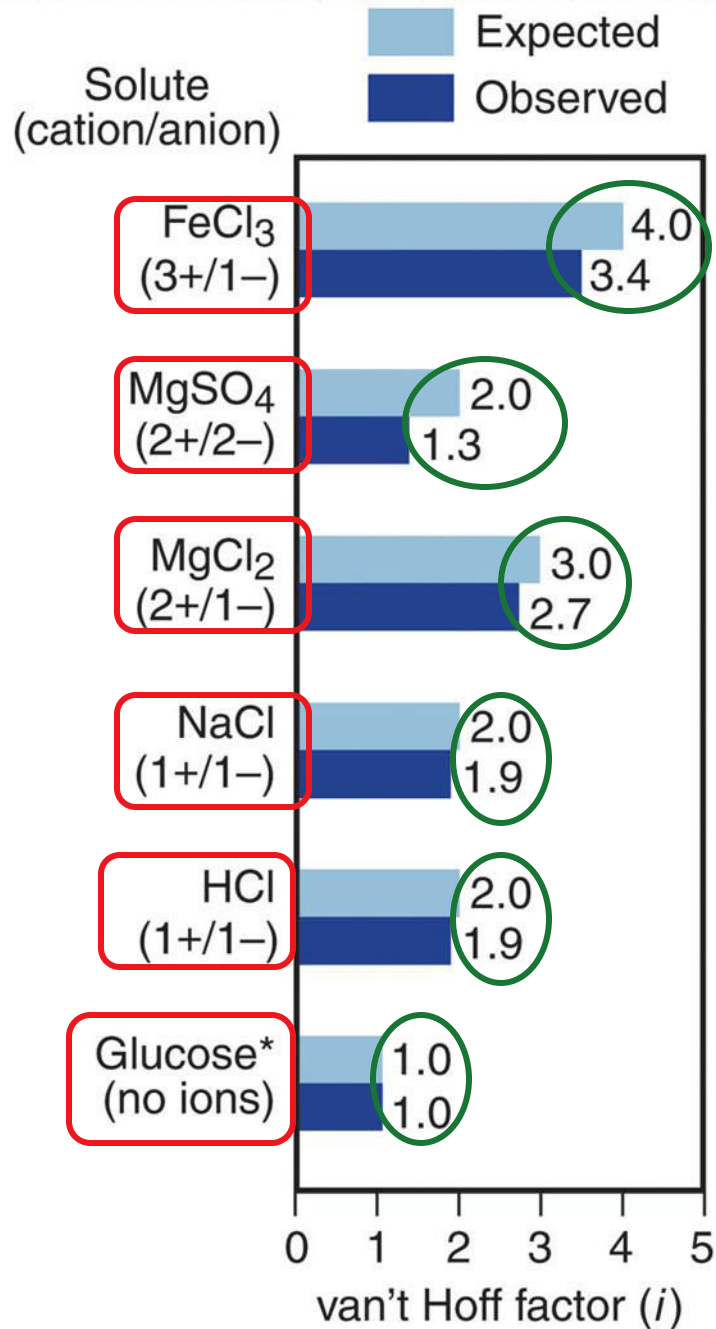
For boiling point elevation: $\Delta T_b = i(K_b m)$

For freezing point depression: $\Delta T_f = i(K_f m)$

For osmotic pressure : $\pi = i(MRT)$

Figure 13.14

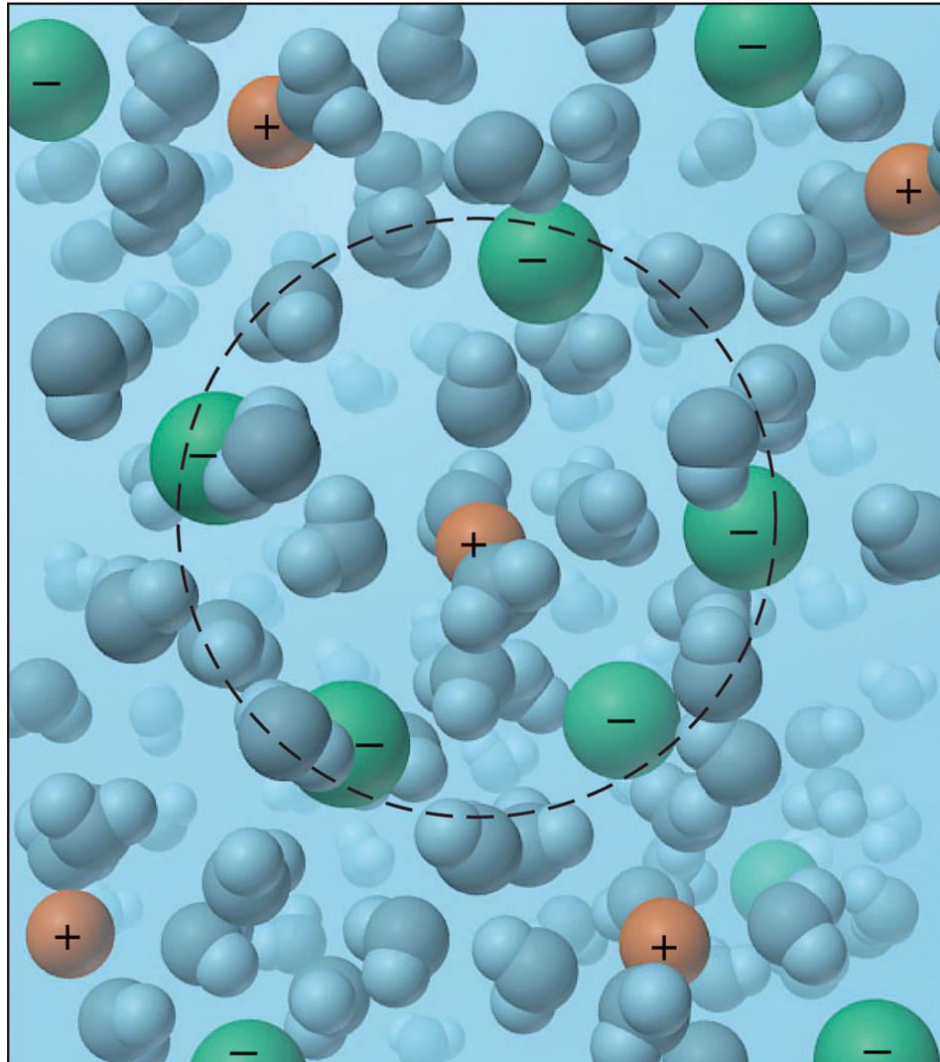
Nonideal behavior of electrolyte solutions.



*Nonelectrolyte shown for comparison

Figure 13.15

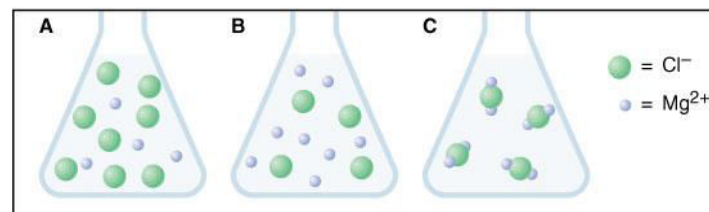
An ionic atmosphere model for nonideal behavior of electrolyte solutions.



SAMPLE PROBLEM 13.9 Depicting a Solution to Find Its Colligative Properties

PROBLEM: A 0.952-g sample of magnesium chloride is dissolved in 100. g of water in a flask.

- (a) Which scene depicts the solution best?
- (b) What is the amount (mol) represented by each green sphere?



- (c) Assuming the solution is ideal, what is its freezing point (at 1 atm)?

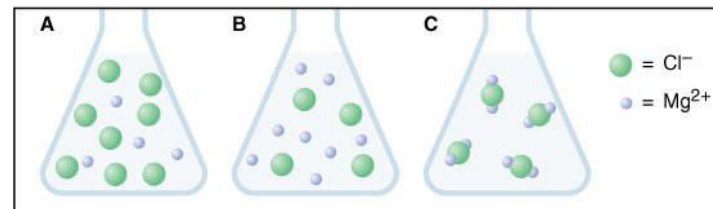
PLAN:

- (a) Consider the formula for magnesium chloride, an ionic compound.
- (b) Use the answer to part (a), the mass given, and the mol mass.
- (c) The total number of mols of cations and anions, mass of solvent, and equation for freezing point depression can be used to find the new freezing point of the solution.

SAMPLE PROBLEM 13.9 Depicting a Solution to Find Its Colligative Properties

continued

(a) The formula for magnesium chloride is MgCl_2 ; therefore the correct depiction must be A with a ratio of 2 Cl^- / 1 Mg^{2+} .



$$(b) \quad \text{mols } \text{MgCl}_2 = \frac{0.952 \text{ g } \text{MgCl}_2}{95.21 \text{ g } \text{MgCl}_2 / \text{mol } \text{MgCl}_2} = 0.0100 \text{ mol } \text{MgCl}_2$$

$$\text{mols } \text{Cl}^- = 0.0100 \text{ mol } \text{MgCl}_2 \times \frac{2 \text{ mols } \text{Cl}^-}{1 \text{ mol } \text{MgCl}_2} = 0.0200 \text{ mols } \text{Cl}^-$$

$$\text{mols/sphere} = \frac{0.0200 \text{ mols } \text{Cl}^-}{8 \text{ spheres}} = 2.50 \times 10^{-3} \text{ mols/sphere}$$

SAMPLE PROBLEM 13.9 Depicting a Solution to Find Its Colligative Properties

continued

$$(c) \quad \text{molality (m)} = \frac{0.0100 \text{ mol MgCl}_2}{100. \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}}} = 0.100 \text{ m MgCl}_2$$

Assuming this is an IDEAL solution, the van't Hoff factor, *i*, should be 3.

$$\Delta T_f = i (K_f m) = 3(1.86 ^\circ\text{C/m} \times 0.100 \text{ m}) = 0.558 ^\circ\text{C}$$

$$T_f = 0.000 ^\circ\text{C} - 0.558 ^\circ\text{C} = - 0.558 ^\circ\text{C}$$

