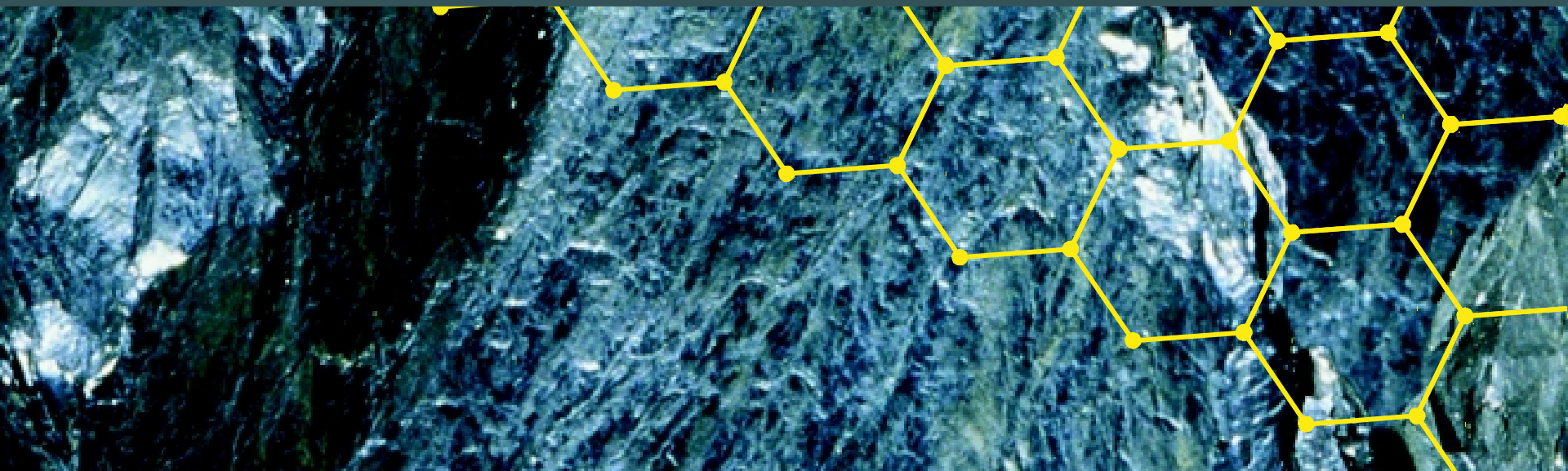


# CHEMISTRY

an atoms-focused approach

**Gilbert  
Kirss  
Foster**



## Chapter 11

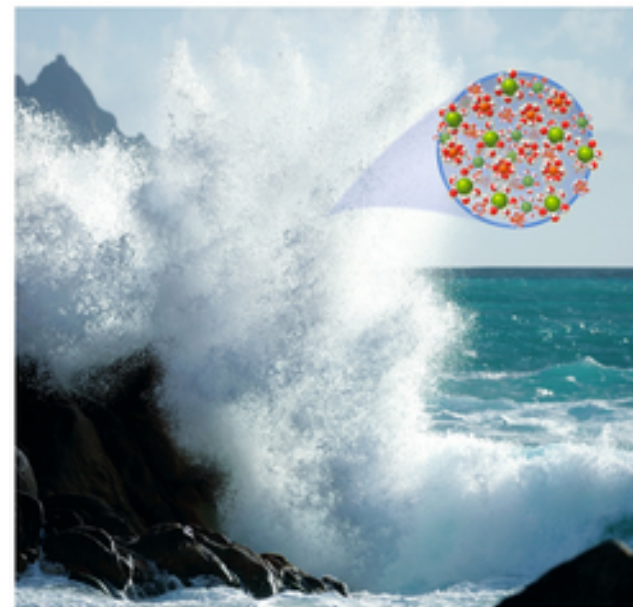
Properties of Solutions

Their Concentrations and Colligative Properties

# Chapter Outline



- 11.1 Energy Changes when Substances Dissolve
- 11.2 Vapor Pressure
- 11.3 Mixtures of Volatile Substances
- 11.4 Colligative Properties of Solutions
- 11.5 Osmosis and Osmotic Pressure
- 11.6 Using Colligative Properties to Determine Molar Mass

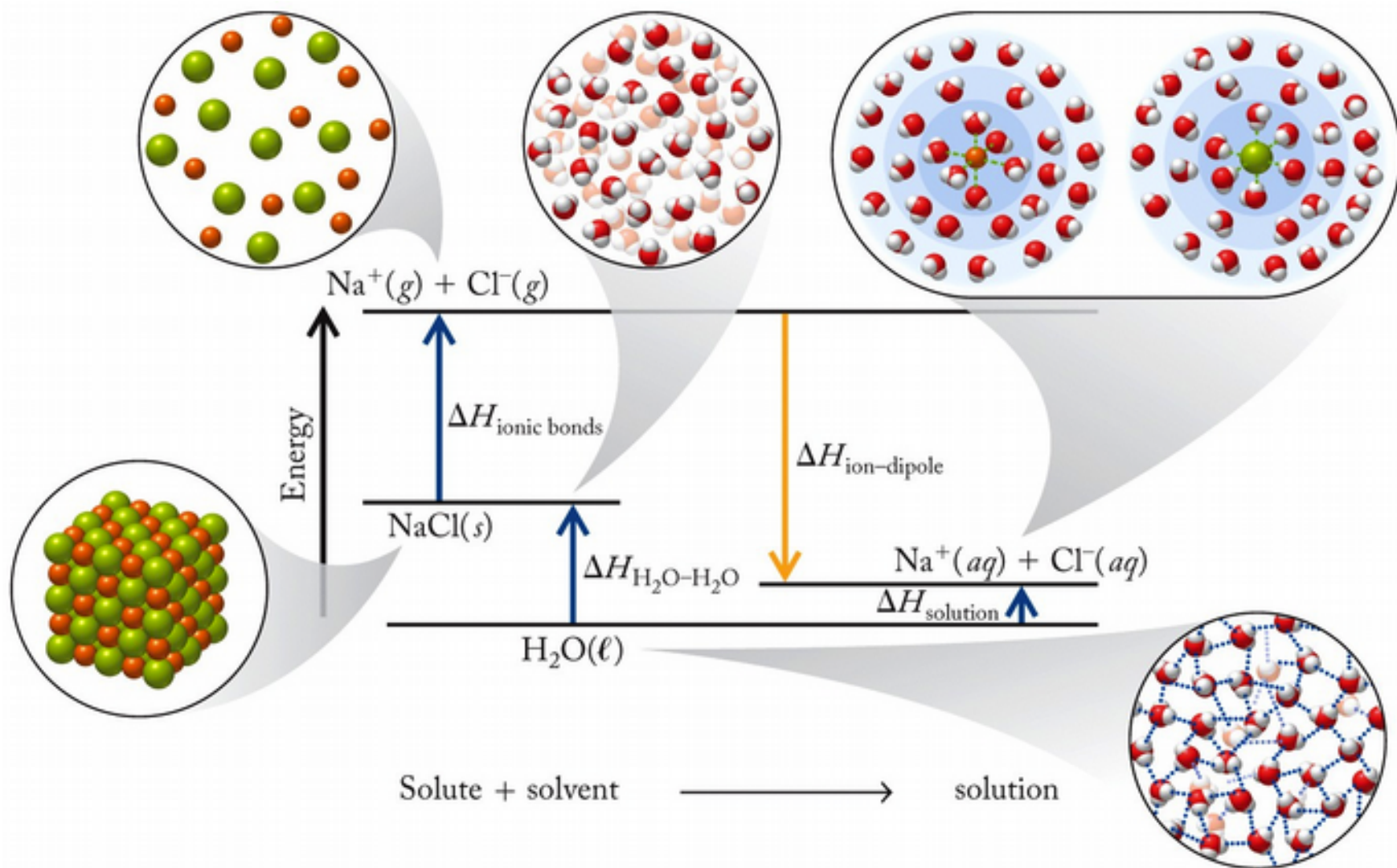


# Enthalpy of Solution



- Dissolution of Ionic Solids:
  - **Enthalpy of solution** ( $\Delta H_{\text{soln}}$ ) depends on:
    - Energies holding solute ions in crystal lattice
    - Attractive force holding solvent molecules together
    - Interactions between solute ions and solvent molecules
  - $\Delta H_{\text{soln}} = \Delta H_{\text{ion-ion}} + \Delta H_{\text{dipole-dipole}} + \Delta H_{\text{ion-dipole}}$
  - When solvent is water:
    - $\Delta H_{\text{soln}} = \Delta H_{\text{ion-ion}} + \Delta H_{\text{hydration}}$

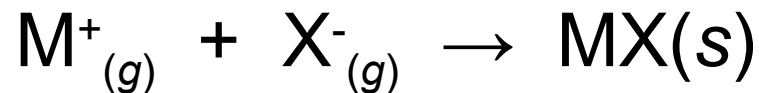
# Dissolution of Ionic Compound



# Lattice Energy



- **Lattice Energy ( $U$ ):**
  - Energy released when 1 mol of an ionic compound forms from its free ions in the gas phase



$$U = \frac{k(Q_1 Q_2)}{d}$$

where  $k$  is proportionality constant and depends on lattice structure



- Lattice Energy ( $U$ ): Energy released when crystal lattice is formed
- $\Delta H_{\text{ion-ion}} =$  Energy required to remove ions from crystal lattice

$$\Delta H_{\text{ion-ion}} = -U$$

$$\text{And: } \Delta H_{\text{soln}} = \Delta H_{\text{hydration}} - U$$

# Born–Haber Cycle and Lattice Energy

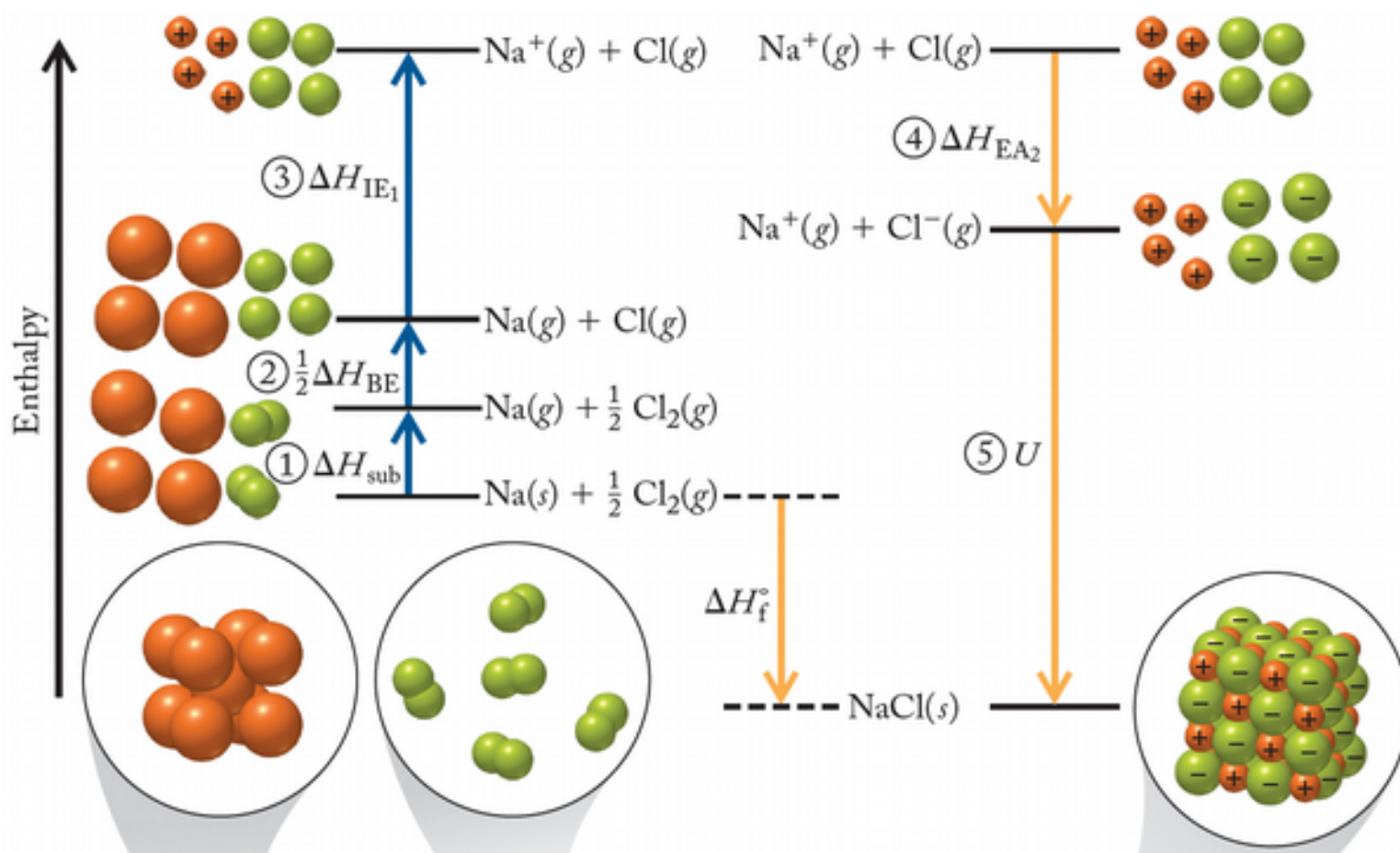


- **Born–Haber Cycle:**
  - Series of steps with corresponding  $\Delta H$ s that describe the formation of an ionic solid from its elements
  - e.g.,  $\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)} \quad \Delta H_f^\circ = -411.2 \text{ kJ}$
- **Steps:**
  - 1. Sublimation of 1 mol  $\text{Na(s)} \rightarrow \text{Na(g)} = \Delta H_{\text{sub}}$
  - 2. Breaking bonds of  $\frac{1}{2}$  mol of  $\text{Cl}_2(\text{g}) = \frac{1}{2} \Delta H_{\text{BE}}$
  - 3. Ionization of 1 mol  $\text{Na(g)}$  atoms  $= \text{IE}_1$
  - 4. Ionization of 1 mol  $\text{Cl(g)}$  atoms  $= \text{EA}_1$
  - 5. Formation of 1 mol  $\text{NaCl(s)}$  from ions(g)  $= U$

# Born–Haber Cycle

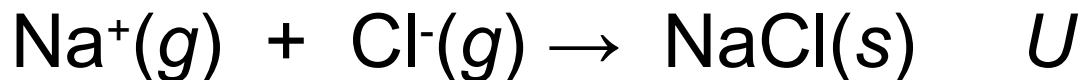
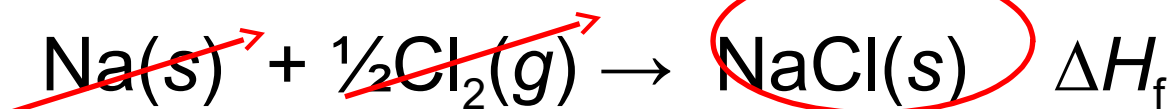
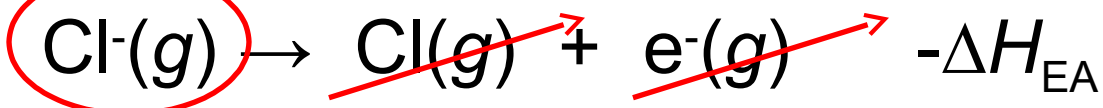
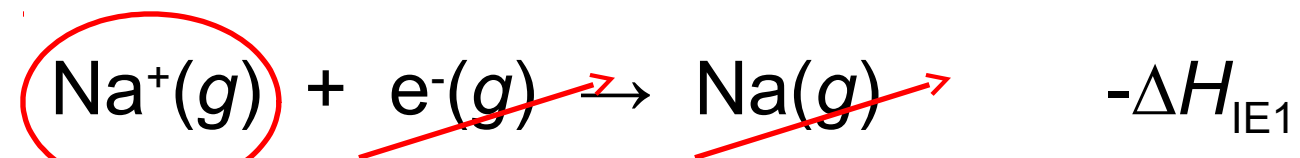


- $$\Delta H_f^\circ = \Delta H_{\text{sub}} + \frac{1}{2} \Delta H_{\text{BE}} + \text{IE}_1 + \text{EA}_1 + U$$





# Calculating $U$



$$U = \Delta H_{\text{f}} - \frac{1}{2} \Delta H_{\text{BE}} - \Delta H_{\text{EA}} - \Delta H_{\text{sub}} - \Delta H_{\text{IE1}}$$



**TABLE 11.3**    **Enthalpies of Solution of Some Common Molecular Compounds in Water**

<b>Compound</b>	<b><math>\Delta H_{\text{solution}}</math> (kJ/mol)</b>
HCl	-74.8
NH <sub>3</sub>	-30.5
CH <sub>3</sub> CH <sub>2</sub> OH	-10.6
CH <sub>3</sub> OH	-3.0
CH <sub>3</sub> COOH	-1.5

# Chapter Outline

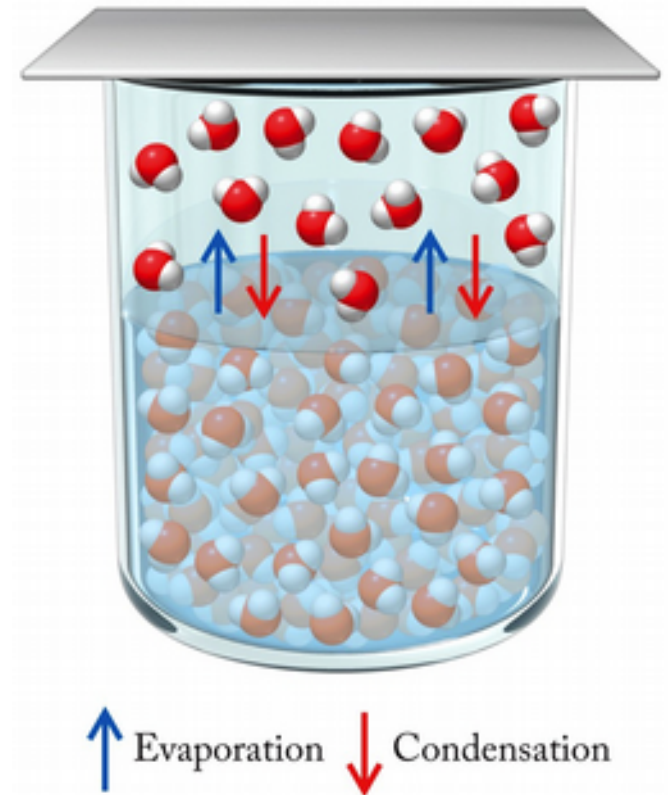


- 11.1 Energy Changes when Substances Dissolve
- 11.2 Vapor Pressure
- 11.3 Mixtures of Volatile Substances
- 11.4 Colligative Properties of Solutions
- 11.5 Osmosis and Osmotic Pressure
- 11.6 Using Colligative Properties to Determine Molar Mass

# Vapor Pressure of Solutions



- **Vapor Pressure:**
  - Pressure exerted by a gas in equilibrium with liquid
  - Rates of evaporation/condensation are equal
- **Normal Boiling Point:**
  - Boiling point when ambient pressure is standard pressure



# Factors Affecting Vapor Pressure



- Temperature/Surface Area/Intermolecular forces (Discussed in Chapter 6):
  - Stronger forces = Higher  $E_k$  needed to enter gas phase.
- Presence of Nonvolatile Solute:
  - Affects rate of evaporation, decreases vapor pressure of solution compared to pure solvent

# Clausius–Clapeyron Equation



- **Clausius–Clapeyron Equation:**  
Relates vapor pressure of a substance to different temperatures to its heat of vaporization

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

# Chapter Outline



- 11.1 Energy Changes when Substances Dissolve
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# Fractional Distillation



- Method of separating a mixture of compounds based on their different boiling points
- Vapor phase enriched in more volatile component





# Solutions of Volatile Components



- Raoult's Law:

- Total vapor pressure of an ideal solution depends on how much the partial pressure of each volatile component contributes to total vapor pressure of solution

- $$P_{\text{total}} = \chi_1 P_1^\circ + \chi_2 P_2^\circ + \chi_3 P_3^\circ + \dots$$

where  $\chi_i$  = mole fraction of component  $i$ , and

$P_i^\circ$  = equilibrium vapor pressure of pure volatile component at a given temperature

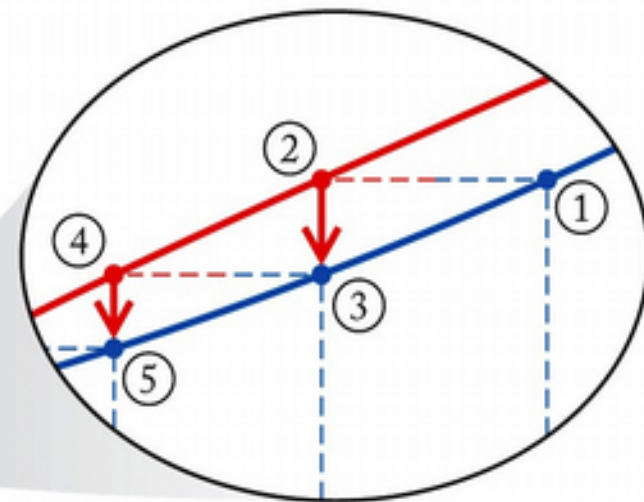
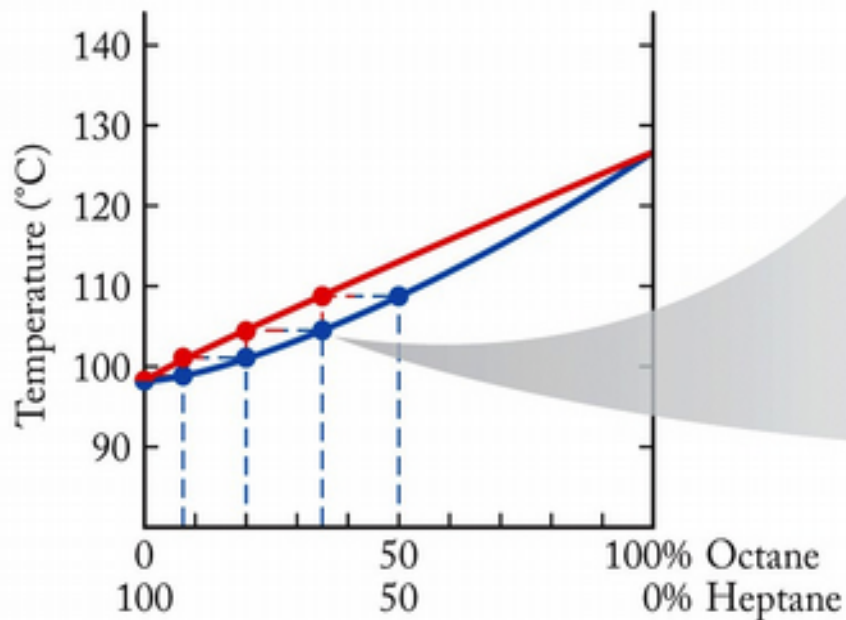
# Fractional Distillation



Boiling Points:

heptane = 98°C

octane = 126°C



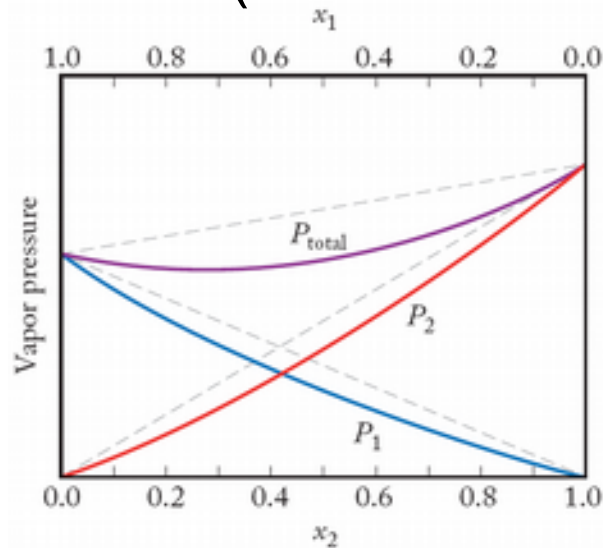
- ① Solution boils at this temperature
- ② Vapor has this composition
- ③ Vapor condenses, then boils
- ④ Vapor has this composition
- ⑤ Vapor condenses, then boils

# Real vs. Ideal Solutions

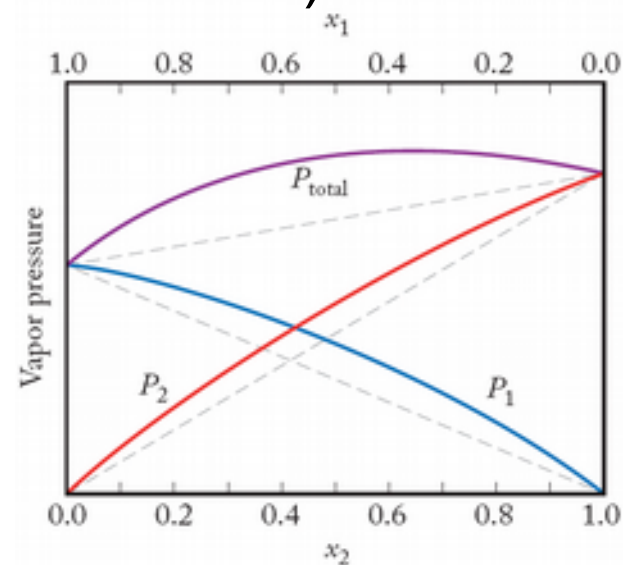


- Deviations from Raoult's Law:  
Due to differences in solute–solvent and solvent–solvent interactions

(dashed lines = ideal behavior)



Negative deviations



Positive deviations

# Practice: Vapor Pressure of Solution



A solution contains 100.0 g of water (MW = 18.0 g/mol) and 25.00 g of ethanol (MW = 44.0 g/mol). What are the mole fractions of water and ethanol, and the vapor pressure of the solution at 25°C?

( $P^{\circ}_{\text{water}} = 23.8 \text{ torr}$ ;  $P^{\circ}_{\text{ethanol}} = 58.7 \text{ torr}$ )

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

# Chapter Outline



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# Colligative Properties of Solutions



- **Colligative Properties:**
  - Set of properties of a solution relative to the pure solvent
  - Due to solute–solvent interactions
  - Depend on concentration of solute particles, not the identity of particles
  - Include lowering of vapor pressure, boiling point elevation, freezing point depression, osmosis and osmotic pressure

# Vapor Pressure of Solutions



- **Raoult's Law:**
  - Vapor pressure of solution is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of solvent in the solution
  - $P_{\text{solution}} = \chi_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$
- Vapor pressure lowering:
  - A *colligative property* of solutions (Section 11.5)
- **Ideal Solution:**
  - One that obeys Raoult's law

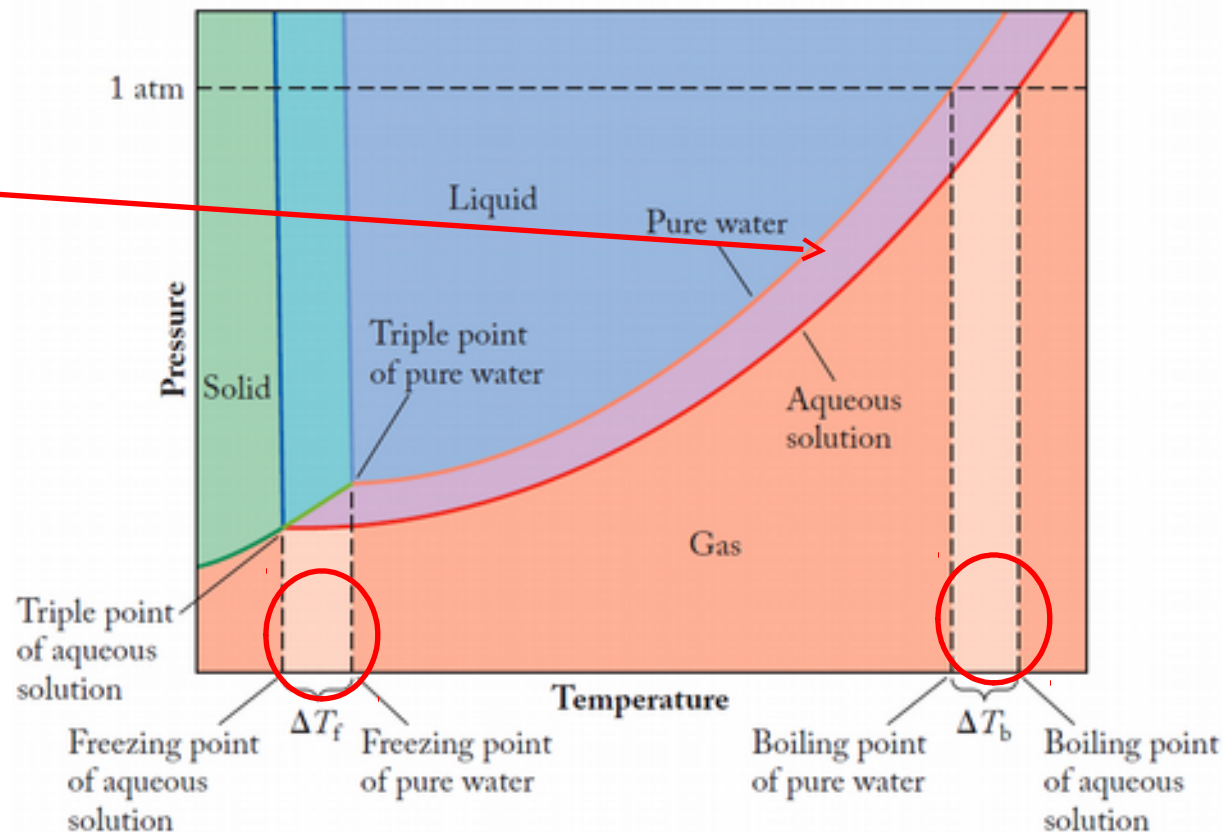
# Colligative Properties of Solutions



- Colligative Properties:

Vapor pressure lowering

Consequences:  
 $\Delta$  in b.p. and f.p. of solution relative to pure solvent





# Solute Concentration: Molality

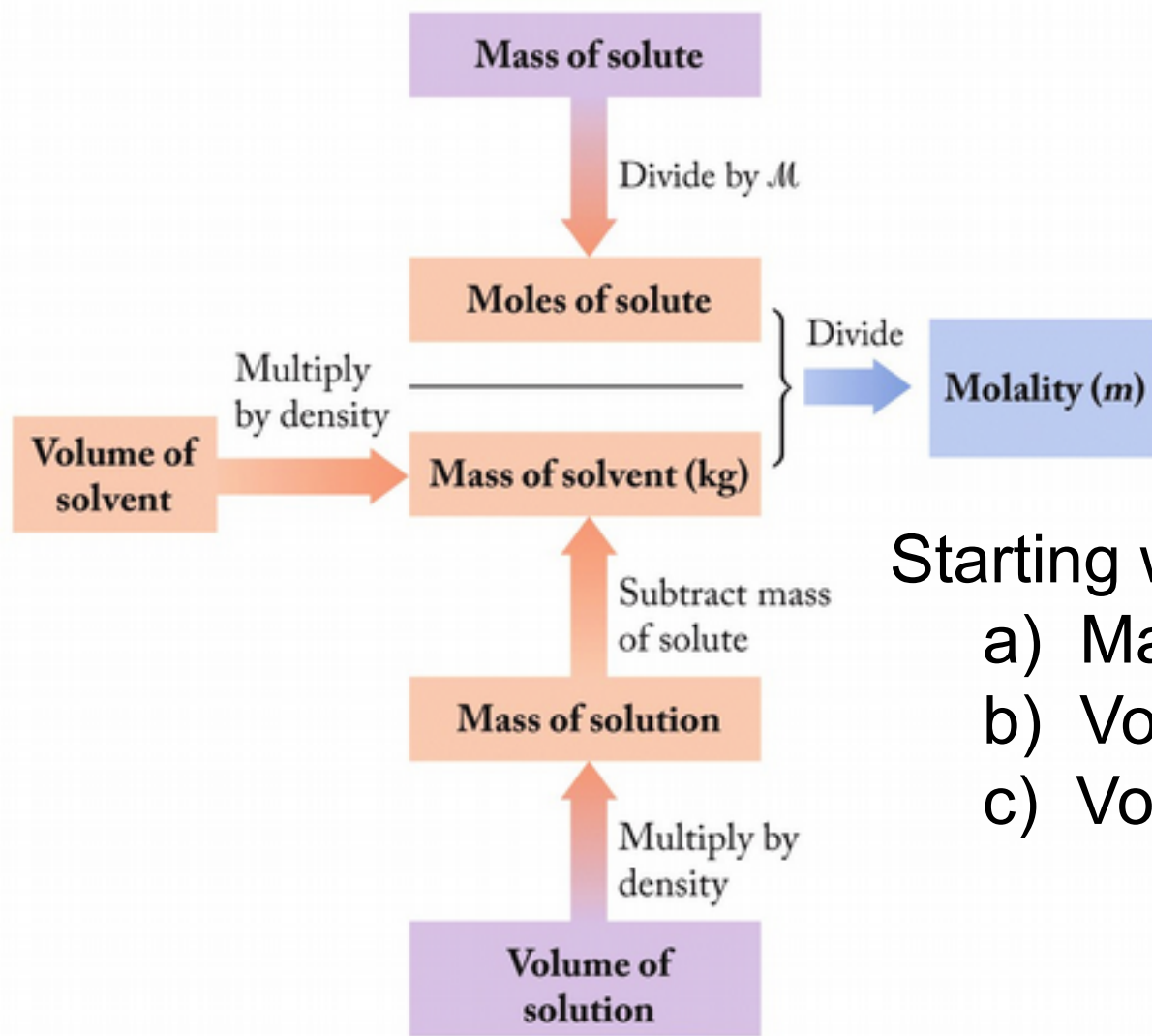


- Changes in boiling point/freezing point of solutions depends on **molality**:

$$m = \frac{n_{\text{solute}}}{\text{kg of solvent}}$$

- Preferred concentration unit for properties involving temperature changes because it is independent of temperature
- For typical solutions: molality > molarity

# Calculating Molality



Starting with:

- Mass of solute
- Volume of solvent, or
- Volume of solution

# Practice: Molality #1



Calculate the molality of a solution containing 0.875 mol of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 1.5 kg of water.

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

# Practice: Molality #2



Seawater contains  $0.558\text{ M Cl}^-$  at the surface at  $25^\circ\text{C}$ . If the density of seawater is  $1.022\text{ g/mL}$ , what is the molality of  $\text{Cl}^-$  in seawater?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

# Boiling Point Elevation and Freezing Point Depression



- Boiling Point Elevation ( $\Delta T_b$ ):
  - $\Delta T_b = K_b \cdot m$
  - $K_b$  = boiling point elevation constant of solvent;  $m$  = molality
- Freezing Point Depression ( $\Delta T_f$ ):
  - $\Delta T_f = K_f \cdot m$
  - $K_f$  = freezing point depression constant;  $m$  = molality

# Practice: Boiling Point Elevation



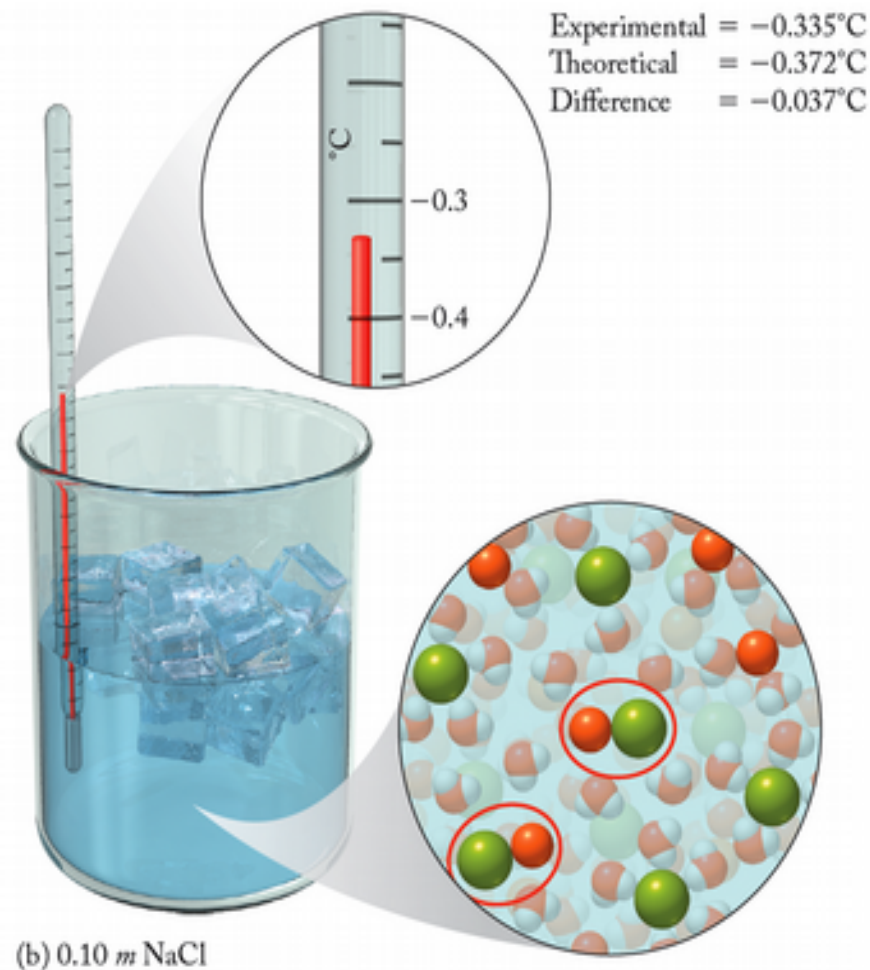
Cinnamon owes its flavor and odor to cinnamaldehyde ( $C_9H_8O$ ). Determine the boiling point elevation of a solution of 100 mg of cinnamaldehyde dissolved in 1.00 g of carbon tetrachloride ( $K_b = 2.34^\circ\text{C}/m$ ).

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

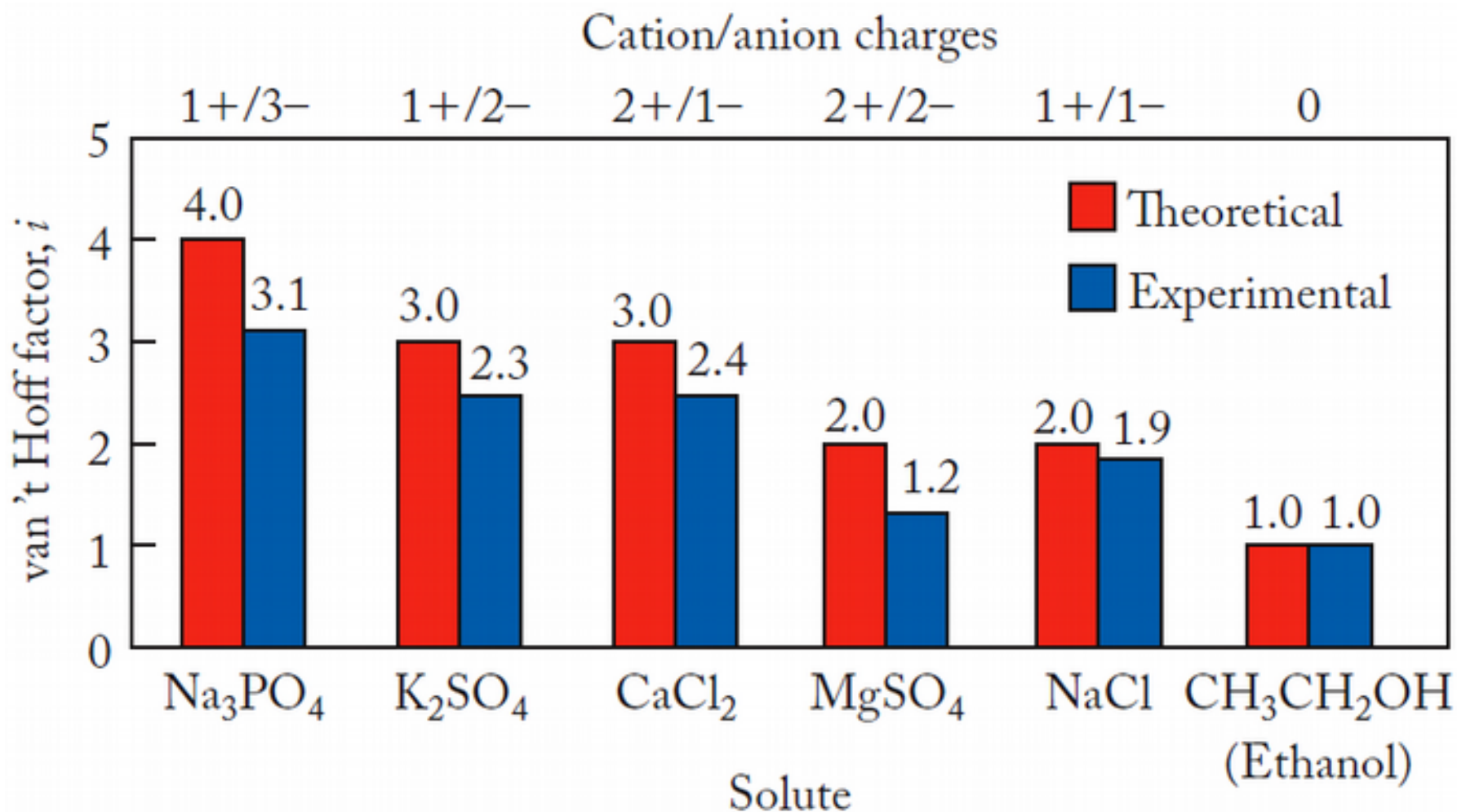
# The van't Hoff Factor



- Solutions of Electrolytes:
  - Need to correct for # of particles formed when ionic substance dissolves
- **van't Hoff Factor ( $i$ ):**
  - # ions in formula unit.
  - e.g., NaCl,  $i = 2$
  - $\Delta T_b = i \cdot K_b \cdot m$        $\Delta T_f = i \cdot K_f \cdot m$
  - (Deviations  $\rightarrow$  ion pair formation.)



# Values of van't Hoff Factors





# Practice: Freezing Point Depression



$\text{CaCl}_2$  is widely used to melt frozen precipitation on sidewalks after a winter storm. Could  $\text{CaCl}_2$  melt ice at  $-20^\circ\text{C}$ ? Assume that the solubility of  $\text{CaCl}_2$  at this temperature is 70.0 g/100.0 g of  $\text{H}_2\text{O}$  and that the van't Hoff factor for a saturated solution of  $\text{CaCl}_2$  is 2.5 ( $K_f$  for water is  $1.86^\circ\text{C}/m$ ).

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:

# Chapter Outline



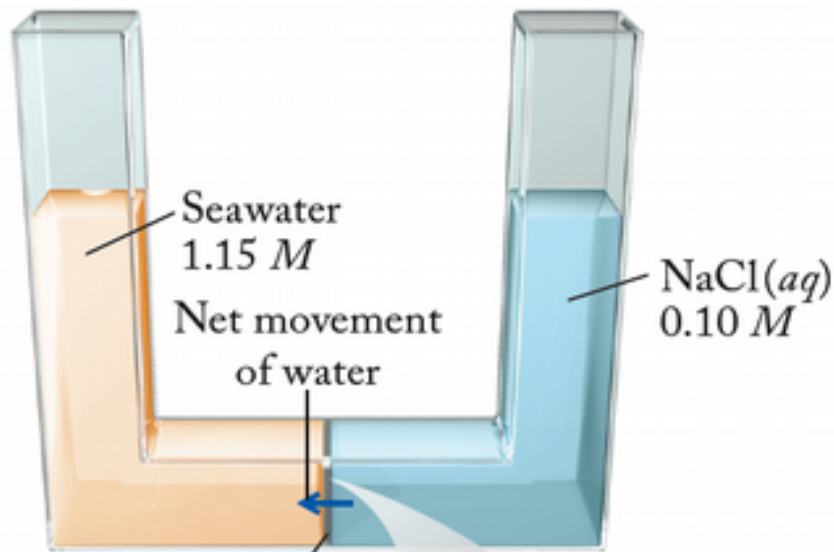
- 11.1 Energy Changes when Substances Dissolve
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# Osmosis

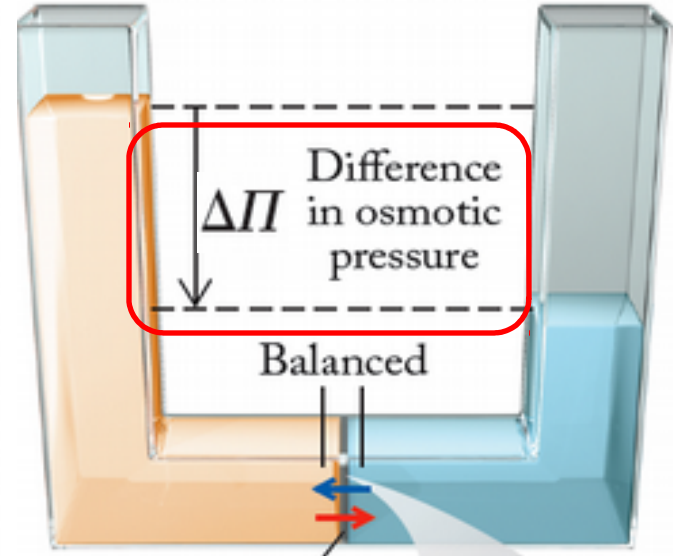
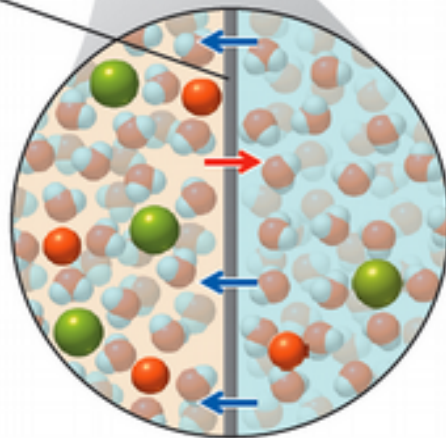


- **Osmosis:**
  - Flow of fluid through a semipermeable membrane to balance the concentration of solutes in solutions on the two sides of the membrane
- **Osmotic Pressure ( $\Pi$ ):**
  - Pressure applied across a membrane to stop the flow of solvent through membrane
  - $\Pi = i MRT$  ( $M$  = molarity of solution)

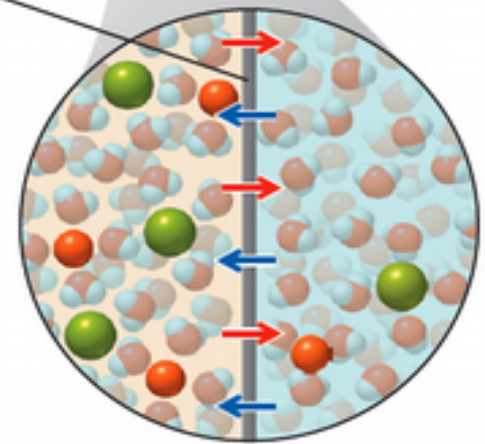
# Osmosis at the Molecular Level



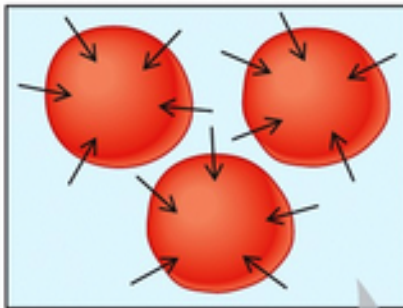
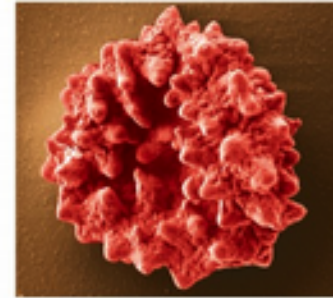
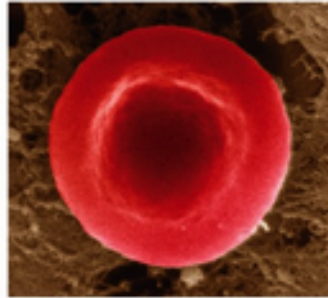
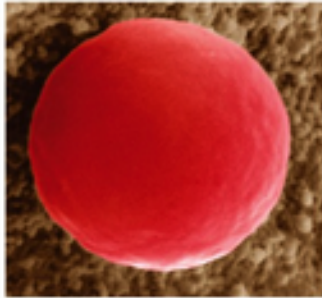
(a) Semipermeable membrane



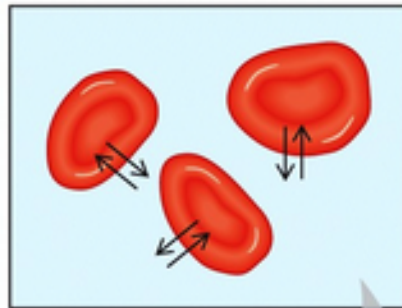
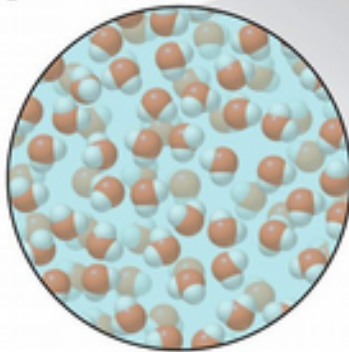
(b) Semipermeable membrane



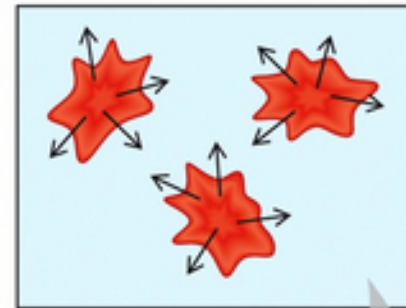
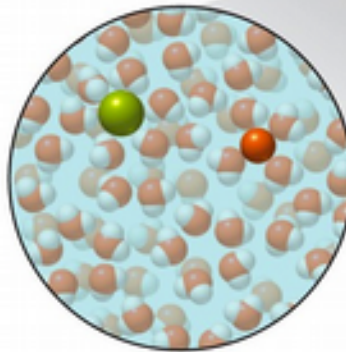
# Osmosis: Medical Application



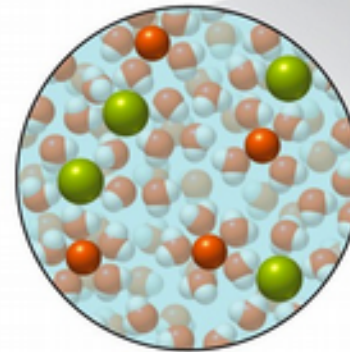
(a) Hypotonic solution  
(pure water)



(b) Isotonic solution



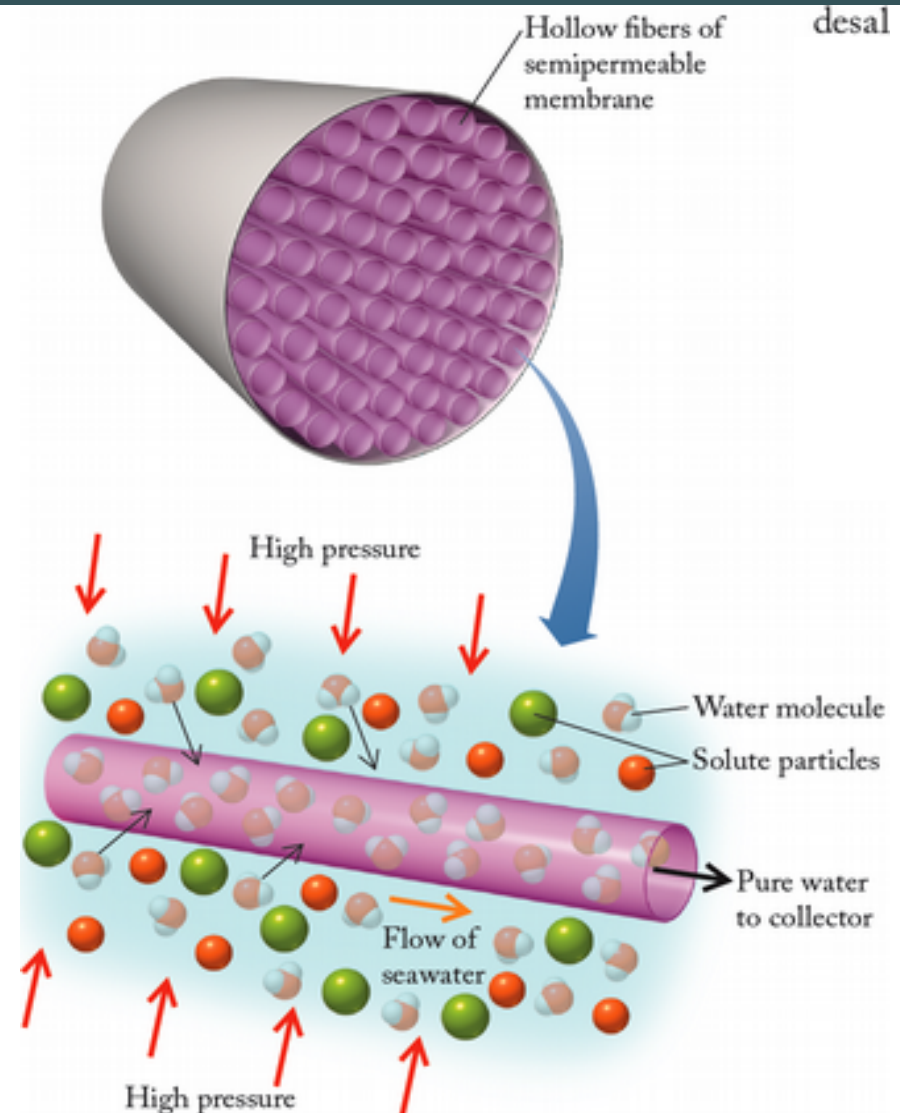
(c) Hypertonic solution



# Reverse Osmosis



- Process in which solvent is forced through a semipermeable membrane, leaving a more concentrated solution behind
- Application: Desalination / water purification



# Chapter Outline



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# Molar Mass from Colligative Properties



- Rearrange colligative property relationships:

- $\Delta T_f, \Delta T_b$ :

$$\Pi = M R T = \frac{\left(\frac{g}{M}\right)}{V} R T \Rightarrow M = \left(\frac{g \times R T}{V \Pi}\right)$$

- Osmotic Pressure:  $\Pi = M R T = \frac{\left(\frac{g}{M}\right)}{V} R T \Rightarrow M = \left(\frac{g \times R T}{V \Pi}\right)$

- Typically used only for nonelectrolyte solutes  
(Osmotic pressure most common application)



# Practice: Molar Mass from Colligative Properties






The freezing point of a solution prepared by dissolving  $1.50 \times 10^2$  mg of caffeine in 10.0 g of camphor is  $3.07^\circ\text{C}$  lower than that of pure camphor ( $K_f = 39.7^\circ\text{C}/m$ ). What is the molar mass of caffeine?

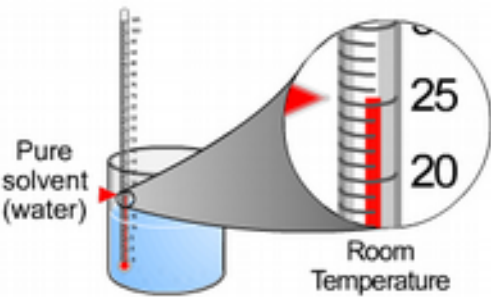
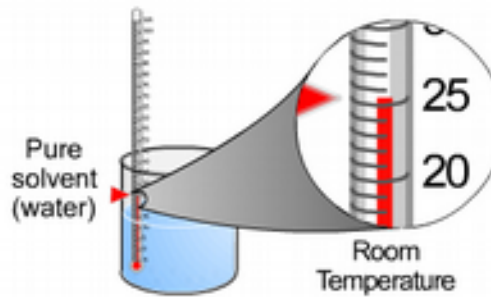
- Collect and Organize:
- Analyze:
- Solve:
- Think about It:





# ChemTours: Chapter 11



Chapter 11 **BOILING AND FREEZING POINTS**   

Boiling-point elevation and freezing-point depression

Boiling-point elevation	Freezing-point depression
<p>A solution exhibits a higher boiling temperature than that of pure solvent.</p> <p><math>T_b = K_b m</math></p>  <p>Pure solvent (water) Room Temperature</p>	<p>A solution exhibits a lower freezing temperature than that of pure solvent.</p> <p><math>T_f = K_f m</math></p>  <p>Pure solvent (water) Room Temperature</p>

Section 2 of 11    

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This concludes the  
Lecture PowerPoint  
presentation for  
Chapter 11

# CHEMISTRY

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