Chapter 12
Solutions and Their Behavior

Types of Solutions

- **Unsaturated** – holds less than maximum capacity at a given T
- **Supersaturated** – contains more than the saturation limit (very unstable)
- **Saturated** – maximum amount of solute dissolved at a given T
Concentration Units

Molarity \((M)\) = \(\frac{\text{moles of solute}}{\text{liter of solvent}}\)  
Temperature dependent

Molality \((m)\) = \(\frac{\text{moles of solute}}{\text{kilogram of solvent}}\)  
Temperature independent

Mole fraction \((\chi_A)\) = \(\frac{\text{moles of solute A}}{\text{total moles}}\)
Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.

e.g.

Vapor-Pressure Lowering – Raoult’s Law

Adding an inert, nonvolatile solute to a solvent lowers the equilibrium vapor pressure of the solvent. The partial pressure of the solvent depends on its mole fraction ($\chi$)
Problem 12.51. A solution is prepared by dissolving 393 g of sucrose (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) in 624 g of water. What is the vapor pressure of this solution at 30 °C? (The vapor pressure of water is 31.8 mmHg at 30 °C.)
Solutions with Two Volatile Solutes

Ideal Solution

\[ P_T = P_{\text{benzene}} + P_{\text{toluene}} \]

\[ P_A = X_A P_A^0 \]
\[ P_B = X_B P_B^0 \]
\[ P_T = P_A + P_B \]
\[ P_T = X_A P_A^0 + X_B P_B^0 \]

\( P_T \) is greater than predicted by Raoult’s law

\( P_T \) is less than predicted by Raoult’s law

Force A-B < Force A-A \& Force B-B

Force A-B > Force A-A \& Force B-B
Boiling-Point Elevation

\[ \Delta T_b = T_b - T_b^0 \]

\( T_b^0 \) is the boiling point of the pure solvent

\( T_b \) is the boiling point of the solution

\[ T_b > T_b^0 \quad \Delta T_b > 0 \]

\[ \Delta T_b = K_b \cdot m \]

\( m \) is the molality of the solution

\( K_b \) is the molal boiling-point elevation constant (\(^\circ C/m\))
**Freezing-Point Depression**

\[ \Delta T_f = T_f^0 - T_f \]

- \( T_f^0 \) is the freezing point of the pure solvent
- \( T_f \) is the freezing point of the solution

\( T_f^0 > T_f \quad \Delta T_f > 0 \)

\[ \Delta T_f = K_f m \]

- \( m \) is the molality of the solution
- \( K_f \) is the molal freezing-point depression constant (°C/m)

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**TABLE 12.2**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normal Freezing Point (°C)*</th>
<th>( K_f ) (°C/m)</th>
<th>Normal Boiling Point (°C)*</th>
<th>( K_b ) (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>1.86</td>
<td>100</td>
<td>0.52</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.5</td>
<td>5.12</td>
<td>80.1</td>
<td>2.53</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-117.3</td>
<td>1.99</td>
<td>78.4</td>
<td>1.22</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>16.6</td>
<td>3.90</td>
<td>117.9</td>
<td>2.93</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.6</td>
<td>20.0</td>
<td>80.7</td>
<td>2.79</td>
</tr>
</tbody>
</table>

* Measured at 1 atm.
Using Colligative Properties to Determine Molar Mass

Can be accomplished using freezing point depression or boiling point elevation

Example 12.8

Ethylene glycol (EG), CH₃(OH)CH₂(OH), is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C). Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water. Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g.

**Strategy** This question asks for the depression in freezing point of the solution.

\[ \Delta T_f = K_f m \]

The information given enables us to calculate the molality of the solution and we refer to Table 12.2 for the \( K_f \) of water.
Colligative Properties of Electrolyte Solutions

Colligative properties depend on the number of particles, so if an ionic compound is dissolved, it's dissociation increases the total number of particles delivered to solution. This increases $\Delta T_f$ and $\Delta T_b$.

$\Delta T_f =$

$\Delta T_b =$

$i =$ van't Hoff factor, a scaling factor that approximately equals the number of particles produced after dissociation of the ionic compound.

e.g. NaCl

$\text{MgCl}_2$
Chapter problem 12.77(a). What are the boiling and freezing points for a solution containing 21.2 g of NaCl in 135 mL of water? $K_f = 1.86 \, ^\circ\text{C/m}$ and $K_b = 0.52 \, ^\circ\text{C/m}$

**A Molecular View of the Solution Process**

**Liquids Dissolving in Liquids**

Two liquids that mix completely together are said to be MISCIBLE - otherwise they are IMMISCIBLE.

- CuSO$_4$(aq)
- Nonpolar CCl$_4$
- Nonpolar octane (C$_8$H$_{18}$)
Mixing of Polar Liquids

Polar molecules can break up groups of other polar molecules through dipole-dipole interactions, resulting in a thorough mixing.

Mixing of Polar and Nonpolar Liquids

The weak London forces present in the CH₃CH₂CH₃ molecules are not strong enough to break the hydrogen bonds, so the two liquids are immiscible.
Mixing Nonpolar Liquids

London forces are the only interactions, but the strength of these forces between CCl₄ molecules is comparable to those between C₆H₁₄ molecules, so the two liquids are miscible with each other.

General Observation:

Solids Dissolving in Liquids – Like Dissolves Like Again

The solvent molecules must be able to overcome the attractive forces holding the solute molecules/atoms/ions together.
Temperature and Solubility

Solid solubility and temperature – most solids exhibit increased solubility with temperature, but exceptions do exist

![Graph showing solubility vs. temperature for various substances]

- Solubility increases with increasing temperature
- Solubility decreases with increasing temperature

Fractional crystallization is the separation of a mixture of substances into pure components on the basis of their differing solubilities.

Suppose you have 90 g KNO₃ contaminated with 10 g NaCl.

**Fractional crystallization:**

1. Dissolve sample in 100 mL of water at 60°C
2. Cool solution to 0°C
3. All NaCl will stay in solution (s = 34.2g/100g)
4. 78 g of PURE KNO₃ will precipitate (s = 12 g/100g).

90 g – 12 g = 78 g
Temperature and Solubility

Gas solubility and temperature

solubility usually decreases with increasing temperature – Why?

Pressure and Solubility of Gases

The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (Henry’s law).

\[ c = kP \]

- \( c \) is the concentration (M) of the dissolved gas
- \( P \) is the pressure of the gas over the solution
- \( k \) is a constant (mol/L•atm) that depends only on temperature
Chemistry In Action: The Killer Lake

8/21/86
CO₂ Cloud Released
1700 Casualties

Trigger?
• earthquake
• landslide
• strong Winds

Lake Nyos, West Africa