Chapter 12 Solutions and Their Properties

The Solution Process

Solvated ions (or solute molecules) are surrounded and stabilized by a shell of solvent molecules.

Heats of Solution

exothermic ex. NaOH
endothermic ex. NH₄NO₃

energy of solvation interactions vs. lattice energy (forces holding solid together)

- Processes in which the energy content of the system decreases tend to occur spontaneously.
- Processes in which the disorder of the system increases tend to occur spontaneously.
- Formation of solutions is favored by the increase in disorder that accompanies mixing.

Variations in heats of solution due to interplay of three kinds of interactions.

- Solvent-solvent: positive $\Delta H_1$
- Solute-solute: positive $\Delta H_2$
- Solvent-solute: negative $\Delta H_3$

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

**saturation** - solution in equilibrium with undissolved solid.

NaCl (s) in equilibrium with Na⁺(aq) and Cl⁻(aq)

\[
\text{Solute} + \text{Solvent} \xrightarrow{\text{dissolve}} \overset{\text{crystallize}}{\text{Solution}}
\]

**Supersaturated solutions** - contains a greater than equilibrium amount of solute.

**Liquids in liquids**
The stronger the attractions between solute and solvent molecules, the greater the solubility.

miscible vs. immiscible

**miscible** completely soluble in all proportions
- polar-polar (water-ethanol)
- nonpolar-nonpolar

**immiscible** polar-nonpolar (water-oil)

**Solids in liquids**

yes: in water - salts, sugar
- in benzene - (nonpolar) naphthalene

no: naphthalene will not dissolve in water
- sugar will not dissolve in benzene

Substances with similar intermolecular attractive forces tend to be soluble in one another; "like dissolves like"
Solution Composition

*mole fraction*, moles of species A divided by the total number moles

\[ X_A = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + n_C + \ldots} \]

*molarity* moles of A per liter of solution

\[ M_A = \frac{n_A}{V} \]

*molality*, m, of species B equals the number of moles of B divided by the mass of solvent, A, (kilograms of solvent)

\[ m_B = \frac{n_B}{w_A (kg)} \]

*weight percentage* of species B,

\[ \left( \frac{w_B}{w} \right) \times 100\% \]

Use density as a conversion factor between molality and molarity.

- find total mass of solution from molality.
- use density to find total volume of solution.
- divide number of moles (from molality) by volume of solution.
Example:
A sulfuric acid solution containing 571.6 g of H₂SO₄ per liter of solution has a density of 1.329 g/cm³.
Calculate (a) the mass percentage; (b) the mole fraction; (c) the molality; (d) the molarity of H₂SO₄ in this solution.
Pressure Effects

*Henry's Law*, the solubility of the gas increases in direct proportion to its partial pressure above the solution.

\[ C_g = kP_g \]

- \( C_g \) is solubility of gas
- \( k \) is Henry’s law constant
- \( P_g \) is partial pressure of gas

**Example**: Determine the solubility of H\(_2\)S (g) at 0°C and a partial pressure of 18.9 mm Hg. \( k = 0.195 \text{ mol/L\cdot atm} \)

Temperature Effects

Most substances are more soluble at higher temperatures.

The solubility of gases in water decreases with increasing temperature.

Thermal pollution of lakes and streams.
**Colligative Properties** (dependent on the number of solute particles, not the identity)

**Raoult's law**

\[ P_A = X_A P_A^\circ \quad \text{solvent, A} \]

“involatile solute” in a solvent, solid solutes, have a vapor pressure that is negligible. This will not hold for liquid or gas solutes.

For solutions of two volatile liquids, calculate the pressure of each liquid using Raoult's law.

\[ P_T = P_A + P_B \]

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

**Example:** Assume you dissolve 10.0 g of sugar \((C_{12}H_{22}O_{11})\) in 225 mL of water and warm the solution to 60°C. What is the vapor pressure of the water over this solution? The vapor pressure of water at 60° is 149.4 mm Hg.
Example 2: The vapor pressure of ethanol (C$_2$H$_5$OH, M = 46.07) at 20°C is 44 mm Hg, and the vapor pressure of methanol (CH$_3$OH, M = 32.04) at the same temperature is 94 mm Hg. A mixture of 30.0 g of methanol and 45.0 g of ethanol is prepared (and can be assumed to behave ideally). (a) Calculate the vapor pressure of above this solution at 20°C. (b) Calculate the mole fraction of each component in the vapor above this solution at 20°C.
Boiling-Point Elevation

\[ \Delta T_{bp} = K_{bp}m_{solute} \]
\[ \Delta T = T_b - T_b^\circ \]

Freezing Point Depression

\[ \Delta T_f = K_{fp}m_{solute} \]
\[ \Delta T = T_f^\circ - T_f \]

Molal boiling point elevation constant: K·kg/mol (°C/m)
Molal freezing point depression constant: K·kg/mol (°C/m)

Example: What will be the freezing point and boiling point of an aqueous solution containing 55.0 g of glycerol, \( \text{C}_3\text{H}_5(\text{OH})_3 \), and 250 g of water. For water, \( K_{bp} = 0.51 \) °C/m and \( K_f = 1.86 \) °C/m.
Osmotic Pressure

There is a natural tendency for the solvent to pass from the pure solvent chamber through the membrane into the solution chamber.

The excess pressure that must be applied to the solution to produce equilibrium is known as osmotic pressure, $\Pi$.

$$\pi = MRT = \left( \frac{n}{V} \right)RT$$

$\pi$ - osmotic pressure  
$M$ - molar concentration of solute  
$R$ - gas constant (0.082057 L atm/mol K)  
$T$ - temperature in Kelvins

Isotonic - identical osmotic pressure.

Hypotonic - solution of lower osmotic pressure.

Hyertonic - solution of higher osmotic pressure.

Cucumbers and water retention.

Example: The average osmotic pressure of blood is 7.7 atm at 25°C. What concentration of glucose, $C_6H_{12}O_6$, will be isotonic with blood?
Colligative Properties of Electrolyte Solutions

van't Hoff factor, \( i \), (number of ions in salt)

\[
i = \frac{\text{actual number of particles in soln after dissolution}}{\text{number of formula units initially dissolved in soln}}
\]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( i ) (calculated)</th>
<th>( i ) (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.0</td>
<td>1.9</td>
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<tr>
<td>MgCl(_2)</td>
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<tr>
<td>FeCl(_3)</td>
<td>4.0</td>
<td>3.4</td>
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</tbody>
</table>

Ion Pairing

dilution

charge on ions

\[
\Delta T_b = iK_b m
\]
\[
\Delta T_f = iK_f m
\]
\[
\pi = iMRT
\]
Using change in \( bp \) or \( fp \) to find molar mass

- Divide the change in temperature by the freezing point depression constant or boiling point elevation constant. This should give the molality.

\[
\frac{\Delta T_{bp}}{K_{bp}} = m_{solute} \quad \frac{\Delta T_{fp}}{K_{fp}} = m_{solute}
\]

Use mass of solvent to determine the number of moles of solute

Divide mass of solute by moles of solute to find molar mass

**Example:** Crystals of azulene, 0.640 g, which has an empirical formula of \( C_5H_4 \), are dissolved in 99.0 g of benzene. The boiling point of the solution is 80.23°C. What is the molecular formula of azulene? The boiling point of benzene is 80.10°C. \( K_{bp} \) of benzene is +2.53 °C/m.
**Using osmotic pressure**

Divide osmotic pressure by RT to find concentration

\[
\frac{\Pi}{RT} = C_B
\]

**Example:** A 1.40 g sample of polyethylene is dissolved in enough benzene to give exactly 100 mL of solution. The measured osmotic pressure of the solution is 1.86 mm Hg at 25°C. Calculate the average molecular mass of the polymer.

**Using vapor pressure**

Divide lowered pressure by pressure of pure solvent to determine mole fraction of solvent, \(X_A\). Find mole fraction of solute by \(1-X_A=X_B\).
**Colloids**

Particles that are large on the molecular scales but are still small enough to remain suspended indefinitely in a solvent system.

- scatter light
- high molecular weight
- high surface area

<table>
<thead>
<tr>
<th>Dispersing Medium</th>
<th>Dispersed Phase</th>
<th>Name</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas</td>
<td>Liquid</td>
<td>aerosol</td>
<td>fog, mist</td>
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<tr>
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<td>aerosol</td>
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<td>solid sol</td>
<td>certain alloys (steel),</td>
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<td>gemstones (glass with</td>
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<td></td>
<td></td>
<td></td>
<td>dispersed metal)</td>
</tr>
</tbody>
</table>

**Hydrophilic and Hydrophobic Colloids**

![Hydrophobic tail](image1)

![Hydrophilic head](image2)