Chapter 13
Properties of Solutions

Learning goals and key skills:

- Describe how enthalpy and entropy changes affect solution formation.
- Describe the relationship between intermolecular forces and solubility, “like dissolves like”.
- Describe the role of equilibrium in the solution process and relationship to the solubility of a solute.
- Describe the effect of temperature on solubility of solids and gases in liquids.
- Describe the relationship between partial pressure of a gas and solubility.
- Calculate the concentration of a solution in terms of molarity, molality, mole fraction, percent composition, and ppm and be able to interconvert between them.
- Describe what a colligative property is and explain the van’t Hoff factor.
- Calculate the vapor pressure of a solvent over a solution.
- Calculate the boiling point elevation and freezing point depression of a solution.
- Calculate the osmotic pressure of a solution.
- Use colligative properties of solutions to calculate molar masses of solutes.
- Explain the difference between a solution and a colloid.
- Explain how hydrophilic and hydrophobic colloids can be stabilized in water.
Mixtures

**Mixture** – Have variable composition and can be separated into component parts by physical methods. Mixtures contain more than one kind of molecule, and their properties depend on the relative amount of each component present in the mixture.

**Homogeneous Mixture (solution)** – Uniform composition.

<table>
<thead>
<tr>
<th>Gaseous solution</th>
<th>air (N₂, O₂, CO₂, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid solution</td>
<td>seawater (H₂O, salts, etc.)</td>
</tr>
<tr>
<td>Solid solution</td>
<td>brass (Cu and Zn)</td>
</tr>
</tbody>
</table>

Solutions

- Solutions are homogeneous mixtures consisting of a **solvent** and one or more **solute**s.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

<table>
<thead>
<tr>
<th>State of Solution</th>
<th>State of Solvent</th>
<th>State of Solute</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Gas</td>
<td>Air</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Gas</td>
<td>Oxygen in water</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Alcohol in water</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Gas</td>
<td>Salt in water</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Liquid</td>
<td>Hydrogen in palladium</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>Mercury in silver</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Silver in gold</td>
</tr>
</tbody>
</table>

Formation of solutions is favored by the increase in entropy that accompanies mixing.
Intermolecular interactions

Extent of solution formation depends on:
1. Solute-solute interactions
2. Solvent-solvent interactions
3. Solvent-solute interactions

Solutions

As a solution forms, the solvent pulls solute particles apart and surrounds, or solvates, them.
Solvation and Hydration

For aqueous solutions, solute (H₂O)-solvent interactions are referred to as *hydration*.

The general term for interaction between solvent and solute is called *solvation*.

**Energetics of solutions**

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

Solutions form spontaneously, generally, if the \( \Delta H_{\text{soln}} \) is negative (i.e. exothermic).
Entropy

Increasing the entropy (i.e., disorder or randomness) of a system lowers the energy of the system.

Physical dissolution vs chemical reaction

Here is a single displacement/redox reaction:

\[ \text{Ni (s)} + 2 \text{HCl (aq)} \rightarrow \text{NiCl}_2 (aq) + \text{H}_2 (g) \]

We can’t get back the original Ni (or HCl) by physical methods, so this is NOT physical dissolution – it is a chemical reaction.
Saturated vs unsaturated solutions

**Saturated**
- Solvent holds as much solute as is possible at that temperature.
- Dissolved solute is in dynamic equilibrium with solid solute particles.

**Unsaturated**
- Less than the maximum amount of solute is dissolved in the solvent at that temperature.

Supersaturated solutions

- Solvent holds more solute than is normally possible at that temperature. The concentration is higher than the solubility.
- These solutions are unstable; crystallization can usually be stimulated by adding a “seed crystal” or scratching the side of the flask.
Gases in solution

- In general, the solubility of gases in water increases with increasing mass.
- The stronger the solute–solvent interaction, the greater the solubility of a solute in that solvent.
- Larger molecules have stronger London dispersion forces.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molar Mass (g/mol)</th>
<th>Solubility (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>28.0</td>
<td>$0.69 \times 10^{-3}$</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>32.0</td>
<td>$1.38 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ar</td>
<td>39.9</td>
<td>$1.50 \times 10^{-3}$</td>
</tr>
<tr>
<td>Kr</td>
<td>83.8</td>
<td>$2.79 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

"Like dissolves like"

- Polar substances tend to dissolve in polar solvents.
- Nonpolar substances tend to dissolve in nonpolar solvents.

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Solubility in H\textsubscript{2}O</th>
<th>Solubility in C\textsubscript{6}H\textsubscript{14}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}OH (methanol)</td>
<td>∞</td>
<td>0.12</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}OH (ethanol)</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}OH (propanol)</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH (butanol)</td>
<td>0.11</td>
<td>∞</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH (pentanol)</td>
<td>0.030</td>
<td>∞</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OH (hexanol)</td>
<td>0.0058</td>
<td>∞</td>
</tr>
</tbody>
</table>

*Expressed in mol alcohol/100 g solvent at 20°C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.
Effect of pressure on gases in solution

- The solubility of liquids and solids does not change appreciably with pressure.
- The solubility of a gas in a liquid is directly proportional to its pressure.
Pressure and solubility: Henry’s Law

- The solubility of a gas is proportional to the partial pressure of the gas above the solution.

\[ S_g = kP_g \]

- \( S_g \) is the solubility of the gas
- \( k \) is the Henry’s law constant for that gas in that solvent
- \( P_g \) is the partial pressure of the gas above the liquid.

Temperature and solubility

Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.
Temperature and solubility

The opposite is true of gases:
- Carbonated soft drinks are more “bubbly” if stored in the refrigerator.
- Warm lakes have less $O_2$ dissolved in them than cool lakes.

Colligative properties

- Colligative properties depend only on the number of solute particles present, not on the identity of the solute particles.

- Four important colligative properties are
  - Vapor pressure lowering
  - Boiling point elevation
  - Melting point depression
  - Osmotic pressure forms/increases
**Expressing concentrations**

Mass % of A = \( \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 100 \)

**Parts per Million (ppm)**

\[ \text{ppm} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^6 \]

**Parts per Billion (ppb)**

\[ \text{ppb} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^9 \]

Mole Fraction \( X_A \) = \( \frac{\text{moles of A}}{\text{total moles in solution}} \)

Molarity \( M \) = \( \frac{\text{mol of solute}}{\text{L of solution}} \)

Molality \( m \) = \( \frac{\text{mol of solute}}{\text{kg of solvent}} \)
Changing Molarity to Molality

If we know the density of the solution, we can calculate the molality from the molarity, and vice versa.

Example 1

Dissolve 62.1 g (1.00 mol) of ethylene glycol, C_2H_6O_2, in 250. g H_2O. Calculate the mass percentage of ethylene glycol, mole fraction of ethylene glycol, and molality.
Example 2

A saturated solution of manganese (II) chloride (MM 125.84 g/mol) in H$_2$O (MW = 18.02 g/mol) is 43.6% MnCl$_2$ by mass. Calculate the molality.

Example 3

A solution is made from dissolving lithium bromide (FW = 86.845 g/mol) in acetonitrile (CH$_3$CN, 41.05 g/mol). Calculate the molality if the 1.80 molar solution has a density of 0.826 g/mL.
Vapor Pressure

- Because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.
- Therefore, the vapor pressure of a solution is lower than that of the pure solvent.

Vapor pressure: Raoult’s Law

The extent to which a nonvolatile solute lowers the vapor pressure is proportional to its concentration.

$$P_{\text{solution}} = X_{\text{solvent}}P^o_{\text{solvent}}$$

- $X$ is the mole fraction of the SOLVENT
- $P^o$ is the normal vapor pressure of SOLVENT at that temperature

Vapor pressure lowering, $\Delta P$

$$\Delta P = X_{\text{solute}}P^o_{\text{solvent}}$$
Example

At 20 °C the vapor pressure of water is 17.5 torr. If we add enough glucose, \( \text{C}_6\text{H}_{12}\text{O}_6 \), to obtain

\[
X_{\text{H}_2\text{O}} = 0.800 \\
X_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.200
\]

What is the vapor pressure?
Freezing Point Depression

Colligative Properties of Electrolytes and the van’t Hoff factor

Properties depend on the number of particles dissolved, solutions of electrolytes show greater changes than those of nonelectrolytes.

\[ \Delta T_b = iK_b m \]
\[ \Delta T_f = -iK_f m \]

for dilute solutions, \( i \approx \) whole number

Note: The van’t Hoff factor can also be used in other colligative properties.
Boiling point elevation

\[ \Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m \]

\( K_b \) is the molal boiling point elevation constant, a solvent dependent property.

Freezing point depression

\[ \Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m \]

\( K_f \) is the molal freezing point depression constant of the solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normal Boiling Point (°C)</th>
<th>( K_b ) (°C/m)</th>
<th>Normal Freezing Point (°C)</th>
<th>( K_f ) (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, H₂O</td>
<td>100.0</td>
<td>0.51</td>
<td>0.0</td>
<td>1.86</td>
</tr>
<tr>
<td>Benzene, C₆H₆</td>
<td>80.1</td>
<td>2.53</td>
<td>5.5</td>
<td>5.12</td>
</tr>
<tr>
<td>Ethanol, C₂H₅OH</td>
<td>78.4</td>
<td>1.22</td>
<td>-114.6</td>
<td>1.99</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl₄</td>
<td>76.8</td>
<td>5.02</td>
<td>-22.3</td>
<td>29.8</td>
</tr>
<tr>
<td>Chloroform, CHCl₃</td>
<td>61.2</td>
<td>3.63</td>
<td>-63.5</td>
<td>4.68</td>
</tr>
</tbody>
</table>

\( \Delta T_b \) is added to the normal boiling point of the solvent.

\( \Delta T_f \) is subtracted from the normal freezing point of the solvent.
**Example**

Antifreeze consists of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0% (weight) aqueous solution. $K_{b,\text{H}_2\text{O}} = 0.51\, ^\circ\text{C}/\text{m}$, $K_{f,\text{H}_2\text{O}} = 1.86\, ^\circ\text{C}/\text{m}$

**Example**

Arrange the following aqueous solutions in order of decreasing freezing point.

(a) 0.20 m ethylene glycol
(b) 0.12 m potassium sulfate
(c) 0.10 m magnesium chloride
(d) 0.12 m potassium bromide
In osmosis, there is net movement of solvent from the area of higher solvent concentration (lower solute concentration) to the area of lower solvent concentration (higher solute concentration).

Osmosis in cells

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are isotonic.
Osmotic pressure

The pressure required to stop osmosis, known as osmotic pressure, \( \Pi \), is

\[
\Pi = i \left( \frac{n}{V} \right) RT = iMRT
\]

where \( M \) is the molarity of the solution

Example

3.50 mg of a protein is dissolved in water to form a 5.00 mL solution. The osmotic pressure was found to be 1.54 torr at 25 °C. Calculate the molar mass of the protein.
Colloidal dispersions or colloids

Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity. You can think of them as somewhere in between homogeneous and heterogeneous mixtures.

<table>
<thead>
<tr>
<th>Phase of Colloid</th>
<th>Dispersing (solvent-like) Substance</th>
<th>Dispersed (solute-like) Substance</th>
<th>Colloid Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Gas</td>
<td>—</td>
<td>None (all are solutions)</td>
</tr>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Liquid</td>
<td>Aerosol</td>
<td>Fog</td>
</tr>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>Solid</td>
<td>Aerosol</td>
<td>Smoke</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Gas</td>
<td>Foam</td>
<td>Whipped cream</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsion</td>
<td>Milk</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Solid</td>
<td>Sol</td>
<td>Paint</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Gas</td>
<td>Solid foam</td>
<td>Marshmallow</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Liquid</td>
<td>Solid emulsion</td>
<td>Butter</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>Solid sol</td>
<td>Ruby glass</td>
</tr>
</tbody>
</table>

Tyndall effect

- Colloid particles are large enough to scatter light.
- Most colloids appear cloudy or opaque.
Motion of colloids due to numerous collisions with the much smaller solvent molecules.

<table>
<thead>
<tr>
<th>Radius of sphere, nm</th>
<th>Mean Free Path, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.23</td>
</tr>
<tr>
<td>10</td>
<td>0.390</td>
</tr>
<tr>
<td>100</td>
<td>0.123</td>
</tr>
<tr>
<td>1000</td>
<td>0.039</td>
</tr>
</tbody>
</table>