Chapter 11. Solutions and Their Properties
Solutions

Solute: material present in least amount
Solvent: material present in most amount

Solution = solvent + solute(s)
**TABLE 11.1** Some Different Kinds of Solutions

<table>
<thead>
<tr>
<th>Kind of Solution</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas in gas</td>
<td>Air (O₂, N₂, Ar, and other gases)</td>
</tr>
<tr>
<td>Gas in liquid</td>
<td>Carbonated water (CO₂ in water)</td>
</tr>
<tr>
<td>Gas in solid</td>
<td>H₂ in palladium metal</td>
</tr>
<tr>
<td>Liquid in liquid</td>
<td>Gasoline (mixture of hydrocarbons)</td>
</tr>
<tr>
<td>Liquid in solid</td>
<td>Dental amalgam (mercury in silver)</td>
</tr>
<tr>
<td>Solid in liquid</td>
<td>Seawater (NaCl and other salts in water)</td>
</tr>
<tr>
<td>Solid in solid</td>
<td>Metal alloys, such as sterling silver (92.5% Ag, 7.5% Cu)</td>
</tr>
</tbody>
</table>

What criteria must be satisfied in order to form a solution?
A. Brass, a substitutional alloy

B. Carbon steel, an interstitial alloy
Solutions form when these three kinds of forces are similar.
An artist’s conception of how a salt dissolves in water
How could we identify the cation and anion?
Dissolving of sugar
Less randomness (less entropy) → More randomness (more entropy)

(a) Solid + Liquid → Solution

(b) Liquid 1 + Liquid 2 → Solution
Solution energy = \( M^+X^- (s) + H_2O \rightarrow M^+(aq) + X^-(aq) \)

Lattice energy = \( M^+(g) + X^-(g) \rightarrow M^+X^- (s) \)

**TABLE 11.2**
Some Enthalpies and Entropies of Solution in Water at 25°C

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_{\text{solv}} ) (kJ/mol)</th>
<th>( \Delta S_{\text{solv}} ) [J/(K\cdot mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>-37.0</td>
<td>10.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.9</td>
<td>43.4</td>
</tr>
<tr>
<td>KCl</td>
<td>17.2</td>
<td>75.0</td>
</tr>
<tr>
<td>LiBr</td>
<td>-48.8</td>
<td>21.5</td>
</tr>
<tr>
<td>NaBr</td>
<td>-0.6</td>
<td>54.6</td>
</tr>
<tr>
<td>KBr</td>
<td>19.9</td>
<td>89.0</td>
</tr>
<tr>
<td>KOH</td>
<td>-57.6</td>
<td>12.9</td>
</tr>
</tbody>
</table>

**Solution energy = \( M^+X^- (s) + H_2O \rightarrow M^+(aq) + X^-(aq) \)**

**Lattice energy = \( M^+(g) + X^-(g) \rightarrow M^+X^- (s) \)**

**TABLE 6.3**
Lattice Energies of Some Ionic Solids (kJ/mol)

<table>
<thead>
<tr>
<th>Cation</th>
<th>( F^- )</th>
<th>( Cl^- )</th>
<th>( Br^- )</th>
<th>( I^- )</th>
<th>( O^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li^+</td>
<td>1036</td>
<td>853</td>
<td>807</td>
<td>757</td>
<td>2925</td>
</tr>
<tr>
<td>Na^+</td>
<td>923</td>
<td>787</td>
<td>747</td>
<td>704</td>
<td>2695</td>
</tr>
<tr>
<td>K^+</td>
<td>821</td>
<td>715</td>
<td>682</td>
<td>649</td>
<td>2360</td>
</tr>
<tr>
<td>Be^{2+}</td>
<td>3505</td>
<td>3020</td>
<td>2914</td>
<td>2800</td>
<td>4444</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>2957</td>
<td>2524</td>
<td>2440</td>
<td>2327</td>
<td>3791</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>2630</td>
<td>2258</td>
<td>2176</td>
<td>2074</td>
<td>3401</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>5215</td>
<td>5492</td>
<td>5361</td>
<td>5218</td>
<td>15,916</td>
</tr>
</tbody>
</table>
A Exothermic solution process

Enthalpy, \( H \)

Solvent aggregated

Solute aggregated

\( H_{\text{initial}} \)
A Exothermic solution process

Enthalpy, $H$

$\Delta H_{\text{soln}} < 0$

$H_{\text{initial}}$

$H_{\text{final}}$
Solvent separated

Solute aggregated

Solution

Δ\(H_{\text{soln}} < 0\)

Enthalpy, \(H\)

\(\Delta H_{\text{solvent}}\)

\(H_{\text{initial}}\)

\(H_{\text{final}}\)

A Exothermic solution process
A Exothermic solution process

\[ \Delta H_{\text{soln}} < 0 \]

\[ H_{\text{initial}} \quad H_{\text{final}} \]
A Exothermic solution process
A Exothermic solution process

\[ \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}} < 0 \]

\[ H_{\text{final}} < H_{\text{initial}} \]
B  Endothermic solution process
Solvent aggregated

Solute aggregated

Solution

\[ \Delta H_{\text{soln}} > 0 \]

\[ H_{\text{final}} \]

\[ H_{\text{initial}} \]

B. Endothermic solution process
B Endothermic solution process
B Endothermic solution process

\[ \Delta H_{\text{soln}} > 0 \]
A Solvent separated
B Solute aggregated
C Solvent aggregated
D Solute separated
E Solution

Enthalpy, $H$

$\Delta H_{\text{solvent}}$

$\Delta H_{\text{solute}}$

$\Delta H_{\text{soln}} > 0$

$H_{\text{final}}$

$H_{\text{initial}}$

$\Delta H_{\text{solute}} + \Delta H_{\text{solvent}}$

**B Endothermic solution process**
**B Endothermic solution process**

The diagram illustrates the enthalpy changes during the solution process. The enthalpy, $H$, is shown vertically, with $H_{\text{initial}}$ at the bottom and $H_{\text{final}}$ at the top. The enthalpy changes are represented as:

- $\Delta H_{\text{solute}}$: Enthalpy change of the solute
- $\Delta H_{\text{solvent}}$: Enthalpy change of the solvent
- $\Delta H_{\text{mix}}$: Enthalpy change during mixing

The diagram shows the separation of solvent and solute, leading to the formation of a solution. The net enthalpy change for the solution process, $\Delta H_{\text{soln}}$, is greater than zero, indicating an endothermic process.

Mathematically, the enthalpy change for the solution process can be expressed as:

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

This equation shows the total enthalpy change during the mixing of the solute and solvent into a solution.
Interactions that must be overcome and those that form

Why do salts with a positive enthalpy of solution form solutions?
Variation of solubility of solids and liquids with temperature
Solubility of gases with temperature

Solvent: H₂O

Solubility (mmol/L) at 1 atm vs. Temperature (°C)
Solubility of gases as a function of pressure

Le Chatelier’s principle

(a) Equilibrium

(b) Pressure increase

(c) Equilibrium restored
Variation of the solubility of gas liquids with pressure

Increasing Pressure

Amount
Le Chatelier’s principle

• If a stress is applied to a system in equilibrium, the system reacts in a way to try to minimize this stress
B is a non-volatile component

Solution of A and B

Vapor pressure of a pure component
Pure solvent A

(a) Equilibrium vapor pressure

(b) Equilibrium vapor pressure
### TABLE 11.3 A Comparison of Various Concentration Units

<table>
<thead>
<tr>
<th>Name</th>
<th>Units</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity (M)</td>
<td>mol solute ( \frac{L}{solution} )</td>
<td>Useful in stoichiometry; measure by volume</td>
<td>Temperature-dependent; must know density to find solvent mass</td>
</tr>
<tr>
<td>Mole fraction ((X))</td>
<td>None</td>
<td>Temperature-independent; useful in special applications</td>
<td>Measure by mass; must know density to convert to molarity</td>
</tr>
<tr>
<td>Mass %</td>
<td>%</td>
<td>Temperature-independent; useful for small amounts</td>
<td>Measure by mass; must know density to convert to molarity</td>
</tr>
<tr>
<td>Molality ((m))</td>
<td>mol solute ( \frac{kg}{solvent} )</td>
<td>Temperature-independent; useful in special applications</td>
<td>Measure by mass; must know density to convert to molarity</td>
</tr>
</tbody>
</table>

Mole fraction of a = \( \frac{n_a}{n_a + n_b + n_c + ...} \)
In comparing the properties of a pure solvent with those of a solution...
in the presence of a non-volatile solute

Colligative properties

- Vapor pressure of solution is lower.
- Boiling point of solution is higher.
- Freezing point of solution is lower.
- Osmosis, the migration of solvent molecules through a semipermeable membrane, occurs when solvent and solution are separated by the membrane.

Colligative property: a physical property that depends on how the amount present
Distillation

- Thermometer
- Water out
- Water in
- Distillation column
- Receiver
- Mixture to be separated
Distillation of two ideal volatile materials

Raoult’s Law:
\[ P_A = x_A P_{Ao} \]
\[ P_B = x_B P_{Bo} \]

\[ P_{T \, obs} = x_A P_{Ao} + x_B P_{Bo} \]
for two volatile components

where \( P_{Ao} \) and \( P_{Bo} \) are the vapor pressures of the pure components

What is the boiling temperature of a 1:1 mixture of toluene/benzene?
Raoult’s Law: $P_A = X_A P_A^o; \quad P_B = X_B P_B^o \quad P_{T \, \text{obs}} = X_A P_A^o + X_B P_B^o$

for two volatile components

\[ 25 \, ^\circ \text{C} \]
Boiling occurs when the total pressure = 760 mm

For a 1:1 mol mixture at 93 °C

\[ P_A = X_A P_{A0}; \quad P_B = X_B P_{B0}; \quad P_{\text{total}} = X_A P_{A0} + X_B P_{B0} \]
Two volatile liquids

For an initial 1:1 mixture of benzene-toluene, the initial composition of the vapor based on its vapor pressure is approximately

\[ P_{\text{toluene}} = 200 \text{ mm} \]

\[ P_{\text{benzene}} = 560 \text{ mm} \]

Treating the vapor as an ideal gas, if we were to condense the vapor:

\[ \frac{P_b V}{P_t V} = \frac{n_b RT}{n_t RT} \]

\[ P_b/P_t = \frac{n_b}{n_t} \]

\[ \frac{n_b}{n_t} = 56/20; \text{ the vapor is enriched in the more volatile component} \]

\[ x_B = \frac{56}{(56+20)} = 0.73 \]
Starting with a 50:50 mixture: (the composition of the first drop)
A Volatile Liquid and Non-volatile Solid

A recipe for making maple syrup requires adding two cups sugar (sucrose, mw 342 g/mol) for every cup of water. Assuming a cup of water contains 300 mL of water and a cup of sugar contains 300 g of sucrose \((C_{12}H_{22}O_{11})\), at what temperature would you expect the syrup to boil given the following vapor pressures of pure water?

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Vapor pressure (mm) pure H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>760</td>
</tr>
<tr>
<td>101</td>
<td>787</td>
</tr>
<tr>
<td>102</td>
<td>815</td>
</tr>
<tr>
<td>103</td>
<td>845</td>
</tr>
<tr>
<td>104</td>
<td>875</td>
</tr>
<tr>
<td>105</td>
<td>906</td>
</tr>
</tbody>
</table>

Raoult’s Law \(P_{\text{obs}} = x_{H_2O}P^0_{H_2O}\)

\(P_{\text{obs}} = 760 \text{ mm for boiling to occur}\)

\(300\text{g}/18\text{ g/mol} = 16.7\text{ mol H}_2\text{O}\)

\(600\text{g}/342\text{ g/mol} = 1.75\text{ mol sugar}\)

\(x_{H_2O} = 16.7/(16.7 + 1.75) = 0.91\)

\(P^0_{H_2O} = P_{\text{obs}}/x_{H_2O}; 760/0.91 = 835 \text{ mm}\)
Boiling Point Elevation for A Volatile Liquid and Non-volatile Solid

\[ \Delta T = K_f m; \quad K_f = \text{boiling point elevation constant} \]

\[ m = \text{molality; moles}/1000\text{g of solvent} \]

\[ K_f (\text{water}) = 0.51 \, ^\circ\text{C}/m \]
Boiling Point Elevation for A Volatile Liquid and Non-volatile Solid

A recipe for making maple syrup requires adding two cups sugar (sucrose, mw 342 g/mol) for every cup of water. Assuming a cup of water contains 300 mL of water and a cup of sugar contains 300 g of sucrose (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}), at what temperature would you expect the syrup to boil given the following vapor pressures of pure water?

sucrose, 600/342 g/mol = 1.75 mol

1.75 mol/300 g H\textsubscript{2}O = x mol/1000gH\textsubscript{2}O

x = 5.83 m molality of sugar

ΔT = K\textsubscript{f} m;  ΔT = 0.51*5.83m;  ΔT = 3 °C

Boiling point of water = 103 °C
Osmosis and osmotic pressure

A simple example of osmosis: evaporation of water from a salt solution

What acts as the semipermeable membrane?
A semipermeable membrane separates a 4% starch solution from a 10% starch solution. Starch cannot pass through the membrane, but water can. What happens?

Osmotic pressure
Osmotic pressure

Solvent molecules on the solution side have a lower concentration and therefore pass through the membrane less frequently.

Solvent molecules on the pure solvent side have a higher concentration and therefore pass through the membrane more frequently.
Osmotic Pressure

\[ \pi = \text{MRT} \]

where \( \pi \) is the osmotic pressure between a pure solvent and a solution containing that solvent; \( M \) is the molarity of the solution (mols/liter), \( R \) is the gas constant, and \( T = \text{temperature} \) (K).

The molarity of the solution refers to the total concentration of all the particles in the solution.
Red blood cells have cell membranes that are semipermeable.

They maintain an osmotic pressure that cannot change without damage occurring.

They must maintain an equal flow of water between the cell and its surrounding environment.

An isotonic solution exerts the same osmotic pressure as red blood cells.

5.0% (m/v) glucose or 0.9% (m/v) NaCl is used medically because each has a solute concentration equal to the osmotic pressure equal to red blood cells.
A hypotonic solution has a lower osmotic pressure than red blood cells (RBCs)
contains fewer dissolved particles than blood serum
causes water to flow into RBCs
causes hemolysis (RBCs swell and may burst)

A hypertonic solution has a higher osmotic pressure than RBCs
contains more dissolved particles than blood serum
causes water to flow out of RBCs
causes crenation (RBCs shrink in size)
The total concentration of dissolved particle in red blood cells is 0.3 M. What would be the osmotic pressure between red cells and pure water if the blood cells were to be placed in pure water at 37 °C?

\[ \pi = 0.3 \text{ moles/liter} \times 0.0821 \text{ liter atm/(mol K)} \times (273.15 + 37) \text{ K} \]

\[ \pi = 0.3 \text{ mol/l} \times 0.0821 \text{ atm/(K mol)} \times 310 \text{ K} \]

\[ \pi = 7.6 \text{ atm} \]

In what direction would the pressure be directed?

1. Normal red blood cell
What is the osmotic pressure developed from a solution of 0.15 M NaCl in contact with a semipermeable membrane of pure water at T = 37 °C?

NaCl + H₂O = Na⁺ + Cl⁻

\[ \pi = nRT \]

\[ \pi = 0.3 \text{ mol/l} \times 0.0821 \frac{\text{atm}}{(\text{K mol})} \times 310.2 \text{ K} \]

\[ \pi = 7.6 \text{ atm} \]
Reverse Osmosis

- Pure solvent
- Solution
- Net movement of solvent
- Semipermeable membrane
- Solute molecules
- Solvent molecules

Osmotic pressure

Applied pressure needed to prevent volume increase
De-salination of sea water

> 30 atm pressure

Osmotic membrane

Pure water out

Seawater in
What happens when polar molecules meet non-polar ones?
Properties of Liquids

Of the three states of matter, only liquids combine the ability to flow with the strength that comes from intermolecular contact, and this combination appears in numerous applications.

Beaded droplets on waxy surfaces
The adhesive (dipole–induced dipole) forces between water and a nonpolar surface are much weaker than the cohesive (H-bond) forces within water. As a result, water pulls away from a nonpolar surface and forms beaded droplets. You have seen this effect when water beads on a flower petal or a freshly waxed car after a rainfall.

Maintaining motor oil viscosity
To protect engine parts during long drives or in hot weather, when an oil would ordinarily become too thin, motor oils contain additives, called **polymeric viscosity index improvers**, that act as thickeners. As the oil heats up, the additive molecules change shape from compact spheres to spaghetti-like strands and become tangled with the hydrocarbon oil molecules. As a result of the greater dispersion forces, there is an increase in viscosity that compensates for the decrease due to heating.

Minimizing a surface
In the low-gravity environment of an orbiting space shuttle, the tendency of a liquid to minimize its surface creates perfectly spherical droplets, unlike the flattened drops we see on Earth. For the same reason, bubbles in a soft drink are spherical because the liquid uses the minimum number of molecules needed to surround the gas. A water strider flies across a pond on widespread legs that do not exert enough pressure to exceed the surface tension.
What happens when there are incompatible interactions are attached to the same molecule?

A typical soap molecule:

\[ \text{CH}_3\text{CH}_{2}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2^- \text{ K}^+ \]

How does soap clear your clothes?
Sodium stearate $\text{C}_{18}\text{H}_{35}\text{COONa}$

- Soap molecules immersed in grease stain
- Nonpolar molecule of grease
Soap in water forms micelles, small spherical objects suspended in water

non-polar

interior

ionic exterior
Other examples of self assembly:
**Figure 13-5** A space-filling model of a typical phospholipid bilayer membrane. The hydrophobic interior is generated by the fatty acyl side chains. Some of these chains have bonds, caused by the double bonds. The different polar head groups all lie on the outer, aqueous surface of the membrane. [See L. Stryer, 1988, Biochemistry, 3rd ed., page 289, W. H. Freeman and Company. Courtesy of L. Stryer.]

**Figure 13-6** Space-filling models and chemical structures of two fatty acids: saturated palmitate and unsaturated oleate. The saturated fatty acid forms a linear molecule; the cis double bond in oleate creates a kink in the hydrocarbon chain. After L. Stryer, 1988, Biochemistry, 3rd ed., W. H. Freeman and Company, p. 285.
Figure 13-1 A phospholipid bilayer constitutes the basic structure of biological membranes. The hydrophobic fatty acyl tails of the phospholipids form the middle of the bilayer; the polar, hydrophilic heads of the phospholipids line both surfaces. Integral proteins have one or more regions embedded in the lipid bilayer. Peripheral proteins are primarily associated with the membrane by specific protein-protein interactions. Oligosaccharides bind mainly to membrane proteins; however, some bind to lipids, forming glycolipids.
Elemental analysis of β-carotene, a dietary source of vitamin A, shows that it contains 10.51 % H and 89.49% C. Dissolving 0.025 g of β-carotene in 1.5 g of camphor gives a freezing point depression of 1.17 °C. What are the molar mass and formula of β-carotene? [K_f for camphor is 37.7 (°C kg/mol)]

\[ \Delta T = K_f m; \quad 1.17 = 37.7 \times m; \quad m = \frac{1.17}{37.7} = 0.031 \text{ mol/1000 g} \]

\[ \text{0.025 g/mw} \beta\text{-carotene/1.5 g camphor} = \frac{x}{1000}; \]

\[ x = 16.67 \text{ g } \beta\text{-carotene/1000 g camphor; } 16.67/\text{mw} = 0.031 \text{ mol} \]

\[ \text{mw} = 537.7 \text{ g/mol} \]

\[ \frac{89.49}{12} = 7.458 \quad \text{C} \quad \frac{7.458}{7.458} = 1 \]

\[ \frac{10.51}{1} = 10.51 \quad \text{H} \quad \frac{10.51}{7.458} = 1.409 \quad \text{C}_1\text{H}_{1.409} \]

\[ n(12 + 1.409) = 537.7 \]

\[ 13.409n = 537.7; \quad n = 40.0 \quad \text{C}_{40}\text{H}_{56} \]
$C_{40}H_{56}$ $\beta$-carotene
Met-enkephalin is one of the so-called endorphins, a class of naturally occurring morphine-like chemicals in the brain. What is the molecular mass of met-enkephalin if 20.0 mL of an aqueous solution containing 15.0 mg of met-enkephalin at 298 K supports a column of water 32.9 cm high? The density of Hg is 13.534 g/mL.

\[
\frac{32.9 \text{ cm H}_2\text{O}}{13.534 \text{ g/mL}} = 2.43 \text{ cm Hg}
\]
Met-enkephalin is one of the so called endorphins, a class of naturally occurring morphine like chemicals in the brain. What is the molecular mass of met-enkephalin if 20.0 mL of an aqueous solution containing 15.0 mg of met-enkephalin at 298 K supports a column of Hg 2.43 cm high?

\[
\pi = \text{MRT} = \frac{2.45}{76 \text{cm/atm}} = M \left( \frac{0.0821 \text{Latm/(K mol)}}{298 \text{K}} \right)
\]

\[
M = \frac{0.03198}{(0.0821 \times 298)}; \quad M = 0.001307 \text{ mole/L}
\]

\[
0.015\text{g/20 mL} = \frac{x}{1000 \text{mL}}; \quad x = 0.75 \text{ g}
\]

\[
0.75/\text{mw} = 0.001307 \text{ mol}; \quad \text{mw} = 573.8
\]
\[ \text{mw} = 573.66; \quad \text{calc} 573.8; \quad C_{27}H_{35}N_{5}O_{7}S \]