Unit 12
Properties of Solutions
Unit 12 Topics

- Expressing Concentrations of Solutions

- Compounds in Aqueous Solution
  - Electrolytes: strong, weak, non

- Solubility
  - Net ionic equations
  - Factors affecting solubility

- Types of Solutions
  - Saturated, non-saturated, super saturated

- Colligative Properties
Ways of Expressing Concentrations of Solutions
Mass Percentage

Mass % of A = \( \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 100 \)
Parts per Million and Parts per Billion

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 ($X$)

$$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$$

- In some applications, one needs the mole fraction of *solvent*, not solute—make sure you find the quantity you need!
Molarity ($M$)

$$M = \frac{\text{mol of solute}}{\text{L of solution}}$$

- Because volume is temperature dependent, molarity can change with temperature.
Molality \((m)\)

\[
m = \frac{\text{mol of solute}}{\text{kg of solvent}}
\]

Because both moles and mass do not change with temperature, molality (unlike molarity) is *not* temperature dependent.
Changing Molarity to Molality

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

Example: Commercial hydrobromic acid, HBr, is 40.0% by weight. The density of this solution is 1.38 g/mL. Calculate the molality, molarity, and mole fraction of this HBr solution.

- 40.0% HBr means that 100 g of solution contains:
  40.0 g HBr and 60.0 g H₂O

Moles HBr = 40.0 g x (1 mole/80.9 g) = 0.494 mol
Moles H₂O = 60.0 g x (1 mole/18.0 g) = 3.333 mol

\[
X_{\text{HBr}} = \frac{0.494}{0.494 + 3.333} = 0.129 \text{ (or 12.9 mole %)}
\]

\[
m = \frac{\text{moles HBr}}{\text{kg H₂O}} = \frac{0.494 \text{ mole}}{0.0600 \text{ kg}} = 8.23 \text{ m}
\]

- To find molarity, need volume of solution (from density):
  Volume of 100 g of solution = 100 g x (1 mL/1.38 g) = 72.5 mL

\[
M = \frac{\text{mole HBr}}{\text{L soln}} = \frac{0.494 \text{ mol}}{0.0725 \text{ L}} = 6.82 \text{ M}
\]
Solutions
Compounds in Aqueous Solution

HCl(aq) + NaOH(aq) → H₂O(l) + NaCl(aq)

This is a reaction in which reactants are in solution.

Solution – homogeneous mixture composed of two parts:

solute – the medium which is dissolved
solvent – the medium which dissolves the solute.
Compounds in Aqueous Solution

Compounds in Water

Some compounds conduct electricity when dissolved in water – *electrolytes*

Those compounds which do not conduct electricity when dissolved in water are called – *nonelectrolytes*
Compounds in Aqueous Solution

Ionic Compounds in Water (Electrolytes)

The conductivity of the solution is due to the formation of ions when the compound dissolves in water

$$\text{NaCl}(s) \xrightarrow{H_2O} \text{Na}^+(aq) + \text{Cl}^-(aq)$$

These ions are not the result of a chemical reaction, they are the result of a dissociation of the molecule into ions that compose the solid.
Compounds in Aqueous Solution

Molecular Compounds in Water (Nonelectrolytes)

In this case no ions are formed, the molecules just disperse throughout the solvent.

\[ \text{sugar}(s) \xrightarrow{\text{H}_2\text{O}} \text{sugar}(aq) \]
There are exceptions to this, some molecules are strongly attracted to water and will react with it.

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]
Compounds in Aqueous Solution

Strong and Weak Electrolytes

**Strong electrolytes** – A substance which completely ionizes in water.

For example:

\[ HCl + H_2O \rightarrow H_3O^+ + Cl^- \]
Strong and Weak Electrolytes

*Weak electrolyte*: A substance which partially ionizes when dissolved in water.

For example:

\[ CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+ \]
Compounds in Aqueous Solution

Strong and Weak Electrolytes

\[
CH_3CO_2H + H_2O \Leftrightarrow CH_3CO_2^- + H_3O^+
\]

Notice that the arrow in this reaction has two heads, this indicates that two opposing reactions are occurring simultaneously.
Precipitation Reaction

Aqueous KI, Aqueous Pb(NO₃)₂ → Solid PbI₂ with K⁺ and NO₃⁻
**Solubility**: amount of solute that will dissolve in a given volume of solvent at equilibrium.

**Soluble**: a substance which dissolves in a solvent.

**Insoluble**: a substance which does not dissolve in a solvent

**Miscible**: when two liquids dissolve in each other in any proportion

**Immiscible**: liquids will not dissolve in each other
Precipitation Reaction

- A reaction which forms a solid (precipitate)

\[ \text{AgNO}_3(aq) + \text{NaCl(aq)} \rightarrow \text{AgCl(s)} + \text{NaNO}_3(aq) \]

- AgCl is classified as an insoluble substance
Compounds in Aqueous Solution

Solubility Guidelines for Ionic Compounds

1. Most nitrates (NO$_3^-$) and acetates (CH$_3$CO$_2^-$) are soluble in water.

2. All chlorides are soluble except: Hg$^+$, Ag$^+$, Pb$^{2+}$, Cu$^+$

3. All sulfates are soluble except: Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$

4. Carbonates (CO$_3^{2-}$), Phosphates (PO$_4^{3-}$), Borates (BO$_3^{3-}$), Arsenates (AsO$_4^{3-}$), and Arsenites (AsO$_3^{3-}$) are insoluble.

5. Hydroxides (OH$^-$) of group Ia and Ba$^{2+}$ and Sr$^{2+}$ are soluble.

6. Most sulfides (S$^{2-}$) are insoluble.
Precipitation Reaction

Net Ionic Equation

\[
\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})
\]

- AgNO\(_3\) and NaNO\(_3\) are electrolytes in solution so they actually occur as free ions.

\[
\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow
\]

\[
\text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})
\]
Precipitation Reaction

Net Ionic Equation

\[ \text{Ag}^+(\text{aq}) + \text{NO}_3^-\text{(aq)} + \text{Na}^+(\text{aq}) + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)} + \text{Na}^+(\text{aq}) + \text{NO}_3^-\text{(aq)} \]

- Notice that \( \text{NO}_3^-\text{(aq)} \) and \( \text{Na}^+(\text{aq}) \) occur in both the left and right side of the equation.

- These are called *spectator ions*. 
Precipitation Reaction

Net Ionic Equation

\[ \text{Ag}^+(\text{aq}) + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)} \]

- With the spectator ions removed, the resulting equation shows only the ions involved in the reaction remain.

- This is a *net ionic equation*. 
How Does a Solution Form?

As a solution forms, the solvent pulls solute particles apart and surrounds, or solvates, them.
How Does a Solution Form

If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.
Types of Solutions

• Saturated
  ➢ Solvent holds as much solute as is possible at that temperature.
  ➢ Dissolved solute is in dynamic equilibrium with solid solute particles.
Types of Solutions

• Unsaturated
  ➢ Less than the maximum amount of solute for that temperature is dissolved in the solvent.
Types of Solutions

• Supersaturated
  ➢ Solvent holds more solute than is normally possible at that temperature.
  ➢ These solutions are unstable; crystallization can usually be stimulated by adding a “seed crystal” or scratching the side of the flask.
Factors Affecting Solubility

- Chemists use the axiom “like dissolves like”:
  - Polar substances tend to dissolve in polar solvents.
  - Nonpolar substances tend to dissolve in nonpolar solvents.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Solubility in H₂O</th>
<th>Solubility in C₆H₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH (methanol)</td>
<td>∞</td>
<td>0.12</td>
</tr>
<tr>
<td>CH₃CH₂OH (ethanol)</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃CH₂CH₂OH (propanol)</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₃OH (butanol)</td>
<td>0.11</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CH₃OH (pentanol)</td>
<td>0.030</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CH₂CH₂OH (hexanol)</td>
<td>0.0058</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CH₂CH₂CH₂OH (heptanol)</td>
<td>0.0008</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.
Factors Affecting Solubility

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

• In general, the solubility of gases in water increases with increasing mass.
• Larger molecules have stronger dispersion forces.

**TABLE 13.2  Solubilities of Gases in Water at 20°C, with 1 atm Gas Pressure**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solubility (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>$0.69 \times 10^{-3}$</td>
</tr>
<tr>
<td>CO</td>
<td>$1.04 \times 10^{-3}$</td>
</tr>
<tr>
<td>O₂</td>
<td>$1.38 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ar</td>
<td>$1.50 \times 10^{-3}$</td>
</tr>
<tr>
<td>Kr</td>
<td>$2.79 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
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.
Henry’s Law

\[ S_g = kP_g \]

where

- \( S_g \) 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.
Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.
• 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

• Changes in colligative properties depend only on the number of solute particles present, not on the identity of the solute particles.

• Among colligative properties are
  - Vapor pressure lowering
  - Boiling point elevation
  - Melting point depression
  - Osmotic pressure
Vapor Pressure

Because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.
Vapor Pressure

Therefore, the vapor pressure of a solution is lower than that of the pure solvent.
Raoult’s Law

\[ P_A = X_A P^\circ_A \]

where

- \( X_A \) is the mole fraction of compound A
- \( P^\circ_A \) is the normal vapor pressure of A at that temperature

**NOTE:** This is one of those times when you want to make sure you have the vapor pressure of the *solvent.*
Boiling Point Elevation and Freezing Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent.
Boiling Point Elevation

The change in boiling point is proportional to the molality of the solution:

$$\Delta T_b = K_b \cdot m$$

where $K_b$ is the molal boiling point elevation constant, a property of the solvent.

$\Delta T_b$ is added to the normal boiling point of the solvent.
Freezing Point Depression

- The change in freezing point can be found similarly:
  \[ \Delta T_f = K_f \cdot m \]

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

\( \Delta T_f \) is subtracted from the normal freezing point 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, ( \text{H}_2\text{O} )</td>
<td>100.0</td>
<td>0.51</td>
<td>0.0</td>
<td>1.86</td>
</tr>
<tr>
<td>Benzene, ( \text{C}_6\text{H}_6 )</td>
<td>80.1</td>
<td>2.53</td>
<td>5.5</td>
<td>5.12</td>
</tr>
<tr>
<td>Ethanol, ( \text{C}_2\text{H}_5\text{OH} )</td>
<td>78.4</td>
<td>1.2</td>
<td>-114.6</td>
<td>.99</td>
</tr>
<tr>
<td>Carbon tetrachloride, ( \text{CCl}_4 )</td>
<td>76.8</td>
<td>5.02</td>
<td>-22.3</td>
<td>29.8</td>
</tr>
<tr>
<td>Chloroform, ( \text{CHCl}_3 )</td>
<td>61.2</td>
<td>3.6</td>
<td>-63.5</td>
<td>.68</td>
</tr>
</tbody>
</table>
Boiling Point Elevation and Freezing Point Depression

Note that in both equations, $\Delta T$ does not depend on what the solute is, but only on how many particles are dissolved.

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

\[
\Delta T_f = K_f \cdot m
\]
Example Problem

- A solution of 6.400 g of an unknown compound in 100.0 g of benzene (C₆H₆) boils at 81.7 °C. Determine the molecular mass of the unknown.

Data for benzene:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_f</td>
<td>5.07 °C/m</td>
</tr>
<tr>
<td>T_f</td>
<td>5.07 °C</td>
</tr>
<tr>
<td>K_b</td>
<td>2.53 °C/m</td>
</tr>
<tr>
<td>T_b</td>
<td>80.2 °C</td>
</tr>
</tbody>
</table>

\[
\Delta T_b = K_b m
\]

\[
\Delta T_b = 81.7 - 80.2 = 1.5 \text{ °C}
\]

\[
m = \frac{\Delta T_b}{K_b} = \frac{1.5 \text{ °C}}{2.53 \text{ °C/m}} = 0.593 \text{ m}
\]

\[
= \frac{0.593 \text{ mol cmpd}}{\text{kg benzene}}
\]

\[
0.1000 \text{ kg benzene} \times \frac{0.593 \text{ mol cmpd}}{\text{kg benzene}} = 0.0593 \text{ moles cmpd}
\]

Molecular mass = g/mole = \[
\frac{6.400 \text{ g cmpd}}{0.0593 \text{ mol cmpd}} = 1.1 \times 10^2 \text{ g/mol}
\]
Colligative Properties of Electrolytes

Since these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.
Colligative Properties of Electrolytes

However, a 1 \textit{M} solution of NaCl does not show twice the change in freezing point that a 1 \textit{M} solution of methanol does.
van’t Hoff Factor

One mole of NaCl in water does not really give rise to two moles of ions.
van’t Hoff Factor

Some Na\(^+\) and Cl\(^-\) reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of NaCl.
The van’t Hoff Factor

• Reassociation is more likely at higher concentration.
• Therefore, the number of particles present is concentration dependent.
The van’t Hoff Factor

We modify the previous equations by multiplying by the van’t Hoff factor, \( i \)

\[ \Delta T_f = K_f \cdot m \cdot i \]
IV. Colligative Properties

E. Colligative Properties of Solutions Containing Ions

Predicting van’t Hoff factors

\[
\text{NaCl(s)} \rightarrow \text{Na}^+ (aq) + \text{Cl}^- (aq)
\]

1 particle + 1 particle = 2 particles

\[i_{predicted} = 2\]

\[
\text{Na}_2\text{SO}_4(s) \rightarrow 2 \text{Na}^+ (aq) + \text{SO}_4^{2-}(aq)
\]

2 particles + 1 particle = 3 particles

\[i_{predicted} = 3\]
Incorporating the van’t Hoff factor

- Boiling point elevation:
  \[ \Delta T_{bp} = m \cdot i \cdot k_b \]

- Freezing point depression:
  \[ \Delta T_{fp} = m \cdot i \cdot k_f \]
Osmosis

- Some substances form semipermeable membranes, allowing some smaller particles to pass through, but blocking other larger particles.
- In biological systems, most semipermeable membranes allow water to pass through, but solutes are not free to do so.
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).
Osmotic Pressure

- The pressure required to stop osmosis, known as osmotic pressure, $\pi$, is

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

where $M$ is the molarity of the solution.

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are isotonic.
Molar Mass from Colligative Properties

We can use the effects of a colligative property such as osmotic pressure to determine the molar mass of a compound.

125 mg of an alkaline earth metal chloride (XCl₂) dissolved in enough water to make 50.0 mL of solution at 298°C has an osmotic pressure of 1.16 atm. Identify the alkaline earth metal.

- Use the measured osmotic pressure to determine the molar concentration of dissolved particles.
- Use the molarity of dissolved particles, and knowledge of the compound formula, to determine the molarity of the compound.
- Use the molarity of the compound and the volume of solution to determine the number of moles of compound in solution.
- Use the number of moles of compound and the number of grams of compound in solution to determine molar mass.
- Knowing molar mass, determine the identity of the alkaline earth chloride.