Properties of Solutions

Figure 17.1: The formation of a liquid solution can be divided into three steps.

Figure 17.2: (a) Enthalpy of solution $\Delta H_{\text{soln}}$ has a negative sign (the process is exothermic) if Step 3 releases more energy than is required by Steps 1 and 2. (b) $\Delta H_{\text{soln}}$ has a positive sign (the process is endothermic) if Steps 1 and 2 require more energy than is released in Step 3.

Entropy Usually Favors Making Solutions Because There Are More Possible Arrangements of the Atoms or Molecules.

Table 17.1 Various Types of Solutions

<table>
<thead>
<tr>
<th>Example</th>
<th>State of Solution</th>
<th>State of Solute</th>
<th>State of Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air, natural gas</td>
<td>Gas</td>
<td>Gas</td>
<td>Gas</td>
</tr>
<tr>
<td>Vodka in water</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Brass, steel</td>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
</tr>
<tr>
<td>Carbonated water (soda)</td>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>Snow, sugar solution</td>
<td>Liquid</td>
<td>Solid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Hydrogen in platinum</td>
<td>Solid</td>
<td>Gas</td>
<td>Solid</td>
</tr>
</tbody>
</table>

Entropy Usually Favors Making Solutions Because There Are More Possible Arrangements of the Atoms or Molecules.

Concentration

Molarity = Moles of solute/Liters of Solution (M)

Molality = Moles of solute/Kg of Solvent (m)

Mole Fraction = Moles solute/total number of moles

Mass % = Mass solute/total mass x 100
A sample of NaNO₃ weighing 8.5 grams is placed in a 500 ml volumetric flask and distilled water was added to the mark on the neck of the flask. Calculate the Molarity of the resulting solution.

Convert the given grams of solute to moles of solute:

\[ \frac{8.5 \text{ g NaNO}_3}{85 \text{ g NaNO}_3} = 0.1 \text{ mole NaNO}_3 \]

Convert given ml of solution to liters:

\[ \frac{500 \text{ ml}}{1000 \text{ ml}} = 0.5 \text{ liter} \]

Apply the definition for Molarity: Molarity = moles NaNO₃ / volume of the solution in liters

\[ M = \frac{0.1 \text{ mole}}{0.5 \text{ liter}} = 0.200 \text{ Molar NaNO}_3 \]

Determine the mole fraction of KCl in 3000 grams of aqueous solution containing 37.3 grams of Potassium Chloride KCl.

1. Convert grams KCl to moles KCl using the molecular weight of KCl

\[ \frac{37.3 \text{ g KCl}}{74.6 \text{ g KCl}} = 0.5 \text{ mole KCl} \]

2. Determine the grams of pure solvent water from the given grams of solution and solute

Total grams = 3000 grams = Mass of solute + Mass of water
Mass of pure solvent = (3000 - 37.3) gram = 2962.7 gram
Determine the mole fraction of KCl in 3000 grams of aqueous solution containing 37.3 grams of Potassium Chloride KCl.

3. Convert grams of solvent H₂O to mols
   
   \[
   \frac{1 \text{ mol}}{18.0 \text{ grams}} = 164.6 \text{ mols H₂O}
   \]

4. Apply the definition for mole fraction mole fraction = moles of KCl / Total mols of KCl and water = 0.5 / (0.5 + 164.6) = 0.5 / 165.1 = 0.00303

Assuming the density of water to be 1 g/mL we approximate the density of a dilute aqueous solution to be 1 g/mL.

\[
1 \text{ ppm} = \frac{1 \mu g}{1 \text{ g}} = \frac{1 \mu g}{1 \text{ g}} \times \frac{1 \text{ g}}{1 \text{ ml}} = \frac{1 \mu g}{1 \text{ ml}}
\]

\[
1 \text{ ppb} = \frac{1 \text{ ng}}{1 \text{ mL}} = \frac{1 \mu g}{1 \text{ L}}
\]
Factors Affecting Solubility

Solute-Solvent Interactions

- Polar liquids tend to dissolve in polar solvents.
- Miscible liquids: mix in any proportions.
- Immiscible liquids: do not mix.
- Intermolecular forces are important: water and ethanol are miscible because the broken hydrogen bonds in both pure liquids are re-established in the mixture.
- The number of carbon atoms in a chain affect solubility: the more C atoms the less soluble in water.

Factors Affecting Solubility

Solute-Solvent Interactions

- The number of -OH groups within a molecule increases solubility in water.

Factors Affecting Solubility

Gas – solvent: Pressure Effects

- Solubility of a gas in a liquid is a function of the pressure of the gas.
- The higher the pressure, the more molecules of gas are close to the solvent and the greater the chance of a gas molecule striking the surface and entering the solution.
  - Therefore, the higher the pressure, the greater the solubility.
  - The lower the pressure, the fewer molecules of gas are close to the solvent and the lower the solubility.
Factors Affecting Solubility

Gas – solvent: Pressure Effects

Henry’s Law: \[ C_g = kP_g \]

- \( C_g \) is the solubility of gas, \( P_g \) the partial pressure, \( k \) = Henry’s law constant.
- Carbonated beverages are bottled under > 1 atm. As the bottle is opened, \( P_g \) decreases and the solubility of \( CO_2 \) decreases. Therefore, bubbles of \( CO_2 \) escape from solution.

Gas – solvent: Pressure Effects

dissolution of \( SO_2 \) and \( NO_x \) → ACID RAIN

\[ \text{dissolution of } SO_2 \] and \( NO_x \) → ACID RAIN

\[ \text{CaCO}_3(s) + H^+ \rightarrow CO_2(g) + H_2O + Ca^{2+} \]

Factors Affecting Solubility

Temperature Effects

- Experience tells us that sugar dissolves better in warm water than cold, but Coca Cola goes flat when warm.
- As temperature increases, solubility of solids generally increases.
- As temperature increases, solubility of gases generally decreases.
Factors Affecting Solubility
Temperature Effects: solids

Factors Affecting Solubility
Temperature Effects: gasses

Lake Nyos in Cameroon

Thermodynamics of Solubility

\[ \Delta G = \Delta H - T \Delta S \]
Solubility increases if \( \Delta G \) becomes more negative.

When \( \Delta S \) is positive, \( \Delta G \) becomes more negative when \( T \) increases. Solubility will increase when \( T \) increases.

When \( \Delta S \) is negative, \( \Delta G \) becomes more positive when \( T \) increases. Solubility will decrease when \( T \) increases.

Compare

- \( \text{KCl(s)} \rightarrow \text{K}^+ (aq) + \text{Cl}^- (aq) \)
  \( \Delta S \) positive - \( \Delta G \) ↓
- gas → liquid
  \( \Delta S \) negative - \( \Delta G \) ↑

Thermodynamics of Solubility

Temperature Dependence of Gas Solubility

- \( \Delta G = \Delta H - T \Delta S \)
- gas → solution
- \( \Delta S \) is negative
- \( \Delta H \) is negative
- \( -T\Delta S \) is positive
- \( \Delta G \) becomes more positive when \( T \) increases
- Therefore, solubility decreases

Henry’s Law Constant Depends on \( T \)
Factors Affecting Solubility
Temperature Effects

- Gases are less soluble at higher temperatures.
- Thermal pollution: if lakes get too warm, CO₂ and O₂ become less soluble and are not available for plants or animals.
- In global warming modeling, CO₂ may be released from the oceans.

Thermodynamics of Phase Changes

Why does a liquid at A form a solid when the temperature is lowered to B?

Why does a liquid at A form a solid when the temperature is lowered to B?

Colligative Properties

- Colligative properties depend on quantity of solute molecules.
- (E.g. freezing point depression and boiling point elevation.)

Thermodynamics for Phase Change

\[ \Delta G = \Delta H - T \Delta S \]

- Liquid → solid
- \( \Delta H \) is negative (stronger intramolecular forces)
- \( \Delta S \) is negative (more order)
- \(-T\Delta S\) is positive
- As \( T \) decreases, \(-T\Delta S\) becomes smaller
- \( \Delta G \) goes to zero when \( \Delta H = T \Delta S \) (at \( T = T_{\text{fusion}} \))
- For \( T \) less than \( T_{\text{fusion}} \) \( \Delta G \) is negative, solid is stable.
**Colligative Properties**

**Lowering the Vapor Pressure**

- Non-volatile solvents reduce the ability of the surface solvent molecules to escape the liquid.
- Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends on the amount of solute.

*(mass, number, volume, what?)*

---

**Question of the Day**

What happens?

---

The vapor pressure of pure water is greater than the vapor pressure of the solution.

---

Water condenses in the solution because the vapor pressure in the chamber is greater than the equilibrium vapor pressure of the solution.

---

An Interesting Phenomenon

Vapor pressures for A and B are unequal.

Vapor pressure is a colligative property: It depends on the amount of solute.

Which has the lower vapor pressure?

---

After a time, the levels are unequal.

*What conditions exist when the equilibrium point is reached and no further change in the volumes occurs?*
Raoult’s Law

- Raoult’s Law:
  - \( P_A \) is the vapor pressure of A with solute
  - \( P_A^o \) is the vapor pressure of A alone
  - \( X_A \) is the mole fraction of A

\[
P_A = X_A P_A^o
\]

For a solution that obeys Raoult’s law, a plot of \( P_{\text{soln}} \) versus \( x_{\text{solvent}} \) yields a straight line.

\[
y = mx + b; \ b = 0
\]

\[
y = P_{\text{soln}} \\
x = x_{\text{solvent}} \\
m = P_{\text{soln}}^o
\]

Raoult’s Law for two liquids

\[
P_{\text{Total}} = X_A P_A^o + X_B P_B^o
\]

Example of a Near-Ideal Solution

Benzene, \( \text{C}_6\text{H}_6 \)

Toluene, \( \text{C}_7\text{H}_8\text{CH}_3 \)

Benzene and Toluene

Benzene and Toluene
Calculation of Vapor Composition
(50/50 mix of boiling benzene and toluene)

- $P^o_{toluene} = 38$ Torr; $P^o_{benzene} = 92$ Torr
- Take $X_b = X_t = 0.50$
- $P_A = X_A P^o_A$ Raoult’s Law
- $P_b = (92$ Torr$)(0.5) = 46$ Torr;
- $P_t = (38$ Torr$)(0.5) = 19$ Torr
- $P_{total} = 46 + 19 = 65$ Torr

- What is the composition above the solution?

- $P^o_{toluene} = 38$ Torr; $P^o_{benzene} = 92$ Torr
- Take $X_b = X_t = 0.50$
- $P_A = X_A P^o_A$ Raoult’s Law
- $P_b = (92$ Torr$)(0.5) = 46$ Torr;
- $P_t = (38$ Torr$)(0.5) = 19$ Torr
- $P_{total} = 46 + 19 = 65$ Torr

- $X_A^{vap} = P_A / P_{total}$
- $X_b^{vap} = 46$ Torr/65 Torr = 0.71
- $X_t^{vap} = 1.00 - 0.71 = 0.29$

Raoult’s Law

- Ideal solution: one that obeys Raoult’s law.
- Raoult’s law breaks down when the solvent-solvent and solute-solute intermolecular forces differ from solute-solvent intermolecular forces.

Example of a non-ideal solution

95 ml solution
50 ml ethanol
50 ml water
Volumes are not additive
A Distillation Apparatus

A Problem

• 20 g of an unknown solid is dissolved in 125 g of water at 25°C. What is the molecular weight of the solid if the observed vapor pressure was 21.72 torr and pure water usually has a vapor pressure of 23.76 torr at this temperature?

The Solution

\[ P_{\text{tot}} = \chi_{H_2O} P_{H_2O} \]

\[ \chi_{H_2O} = \frac{P_{\text{soln}}}{P_{H_2O}} = \frac{21.72}{23.76} = 0.9141 \]

\[ \chi_{H_2O} = \frac{\text{mol } H_2O}{(\text{mol } H_2O + \text{mol unknown})} \]

\[ 0.9141 = \frac{125 \text{ g }/(18 \text{ g/mol } H_2O)}{125 \text{ g }/(18 \text{ g/mol } H_2O) + 20 \text{ g }/(X \text{ g/mol})} \]

\[ X = 30.87 \text{ g/mol} \]
Colligative Properties

Boiling-Point Elevation

Molal boiling-point-elevation constant, $K_b$, expresses how much $\Delta T_b$ changes with molality, $m$:

$$\Delta T_b = K_b m$$

Colligative Properties

Freezing-Point Depression

- Decrease in freezing point ($\Delta T_f$) is directly proportional to molality ($K_f$ is the molal freezing-point-depression constant):

$$\Delta T_f = K_f m$$

Problem:

- A 0.0182-g sample of an unknown substance is dissolved in 2.135 g of benzene.
- The solution freezes at 5.14 °C instead of at 5.50 °C for pure benzene.
- $K_f$ (benzene) = 5.12 °C kg/mol
- What is the molecular weight of the unknown substance?

Solution:

Freezing point depression $\rightarrow$ molality

$$\Delta T_f = (5.50-5.14) = 0.36 \, ^\circ C$$

- $\Delta T_f = K_f m$
- $M = 0.36 \, ^\circ C / (5.12 \, ^\circ C \, kg/mol) = 0.070 \, m$

Solution:

- Find the moles of unknown solute from the definition of molality:
  - $\text{Mol}_{\text{solute}} = m \times \text{kg solvent}$
  - $\text{Mol}_{\text{solute}} = 0.070 \, \text{mol} \times 0.002135 \, \text{kg solvent} = 1.5 \times 10^{-4} \, \text{mol}$

Solution:

- Molar mass $= \frac{0.0182 \, \text{g}}{1.5 \times 10^{-4} \, \text{mol}} = 1.2 \times 10^2 \, \text{g/mol}$
  - (molecular weight = $1.2 \times 10^2 \, \text{g/mol}$)
Colligative Properties of Ionic Solutions

- For solutes that are electrolytes, we must rewrite the formulas for boiling-point elevation and freezing-point depression.

\[ \Delta T_b = i \cdot K_{b} \]
\[ \Delta T_f = i \cdot K_{f} \]

Here \( i \) is the number of ions resulting from each formula unit of the solute.

### Table 12.2

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Normal Freezing Point, °C</th>
<th>( K_f ), °C m(^{-1} )</th>
<th>Normal Boiling Point, °C</th>
<th>( K_b ), °C m(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>16.63</td>
<td>3.90</td>
<td>117.90</td>
<td>3.07</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.53</td>
<td>5.12</td>
<td>80.10</td>
<td>2.53</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.55</td>
<td>20.0</td>
<td>80.74</td>
<td>2.79</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>5.6</td>
<td>8.1</td>
<td>210.8</td>
<td>5.24</td>
</tr>
<tr>
<td>Water</td>
<td>0.00</td>
<td>1.86</td>
<td>100.00</td>
<td>0.512</td>
</tr>
</tbody>
</table>

NB: PROPERTY OF THE SOLVENT (NOT OF THE SOLUTE)

**Figure 17.21:** In a aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.

Osmosis


- Osmosis: the movement of a solvent from low solute concentration to high solute concentration.

- There is movement in both directions across a semipermeable membrane.

- As solvent moves across the membrane, the fluid levels in the arms becomes uneven - their concentrations even.

**Van't Hoff factor (i)**

Factor which accounts for deviation of colligative property due to electrolytic nature of solute.

Van’t Hoff Factor (i)

Can be measured by

\[ i = \frac{\text{measured colligative property (from Expt)}}{\text{Expected value if solute were nonelectrolyte}} \]

- a) Typical non-electrolyte i.e., urea, sucrose, glucose van’t Hoff, \( i = 1 \).

- b) For electrolytic solute:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ideal (i)</th>
<th>Measured (i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>H2SO4</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>MgCl2</td>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>AICl4</td>
<td>4</td>
<td>3.2</td>
</tr>
</tbody>
</table>
**Colligative Properties**

**Osmosis**

- Eventually the pressure difference between the arms stops osmosis.

![Diagram of osmosis](image)

A semipermeable membrane separating water and an aqueous solution of glucose.

---

**An experiment in osmosis**

![Diagram of experiment](image)

---

**Osmosis**

- Osmotic pressure, \( \pi \), is the pressure required to stop osmosis:

\[
\pi = MRT
\]

- \( \Pi \) = osmotic pressure
- \( M \) = Molarity (mol/L)
- \( R \) = Ideal Gas Constant
- \( T \) = Temperature (K)
Osmotic Pressure is a VERY sensitive measure of Molarity

Seawater contains 3.4 g NaCl per liter
M = \(\frac{3.4 \text{ g}}{58.5 \text{ g/L}}\) = 0.0582 M

\(\Pi = (0.0582 \text{ mol/L})(0.0821 \text{L atm/mol K })(298\text{K}) = 0.142 \text{ atm}\)

1 atm supports column of water 10.34 m length
\((0.42 \text{ atm})(10.34 \text{ m/atm}) = 4.34 \text{ m}\)
\((4.34 \text{ m})(3.28 \text{ ft/m}) \sim 14.2 \text{ feet}\)

Tonicity is a relative term

- **Hypotonic Solution** - One solution has a lower concentration of solute than another.
- **Hypertonic Solution** - One solution has a higher concentration of solute than another.
- **Isotonic Solution** - Both solutions have the same concentrations of solute.

Osmosis

- **Crenation:**
  - Red blood cells placed in hypotonic solution (relative to intracellular solution);
  - There is a higher solute concentration in the surrounding tissue than in the cell;
  - Osmosis occurs and water passes through the membrane out of the cell.
  - The cell shrivels up.

- **Hemolysis:**
  - Red blood cells placed in a hypotonic solution;
  - There is a lower solute concentration outside the cell;
  - Osmosis occurs and water moves into the cell.
  - The cell bursts.
- To prevent crenation or hemolysis, IV (intravenous) solutions must be isotonic.
Osmosis

Crenation  Hemolysis:

<table>
<thead>
<tr>
<th>Hypertonic solution</th>
<th>Hypotonic Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larger II</td>
<td>Smaller II</td>
</tr>
</tbody>
</table>

Plant and Animal Cells put into various solutions

Osmosis

- Examples of osmosis:
  - Cucumber placed in NaCl solution loses water to shrivel up and become a pickle.
  - Limp carrot placed in water becomes firm because water enters via osmosis.
  - Salty food causes retention of water and swelling of tissues (edema).
  - Water moves into plants through osmosis.
  - Salt added to meat or sugar to fruit prevents bacterial infection (a bacterium placed on the salt will lose water through osmosis and die).

Drinking Seawater will Cause Dehydration of Body Tissues
Colligative properties

- Vapor pressure – Mole fraction
- Freezing point depression – molality
- Boiling point elevation – molality
- Osmosis – Molarity

Figure 17.22: The Tyndall effect
Figure 17.23: Representation of two colloidal particles