## Chapter 11. Solutions

A solution is a homogeneous mixture of substances. Solvent is the majority component, solute is the minority component.

### Conversion Problem

Find the molarity of an aqueous solution of NaCl given that the density of the solution is 1.025 g/mL at 20°C and the NaCl concentration is 3.50 weight %.

- Mass of 1 L solution = (1.025 g/mL) (1000 mL) = 1025 g
- Mass NaCl in 1 L solution = (1025 g)(0.0350) = 35.875 g
- Mol NaCl in 1 L solution = (35.875 g)/(58.45 g/mol) = 0.614 M

### Energetics of Dissolution

\[ A + B \xrightarrow{\Delta H_{\text{diss}}} \text{A/B (solution)} \]

- \( \Delta H_{\text{diss}} < 0 \): exothermic; mixing is energetically favorable
- \( \Delta H_{\text{diss}} > 0 \): endothermic; mixing is energetically unfavorable

How to determine \( \Delta H_{\text{diss}} \)?

Compare molecular interactions in starting materials to those in solution.

Dissolution is favored by entropy so long as \( \Delta H_{\text{diss}} \) is not strongly endothermic.

## Units of Concentration

<table>
<thead>
<tr>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>molarity (M)</td>
<td>moles A / liters of solution</td>
</tr>
<tr>
<td>molality (m)</td>
<td>moles A / kg of solvent</td>
</tr>
<tr>
<td>mole fraction</td>
<td>( X_A = \frac{\text{moles } A}{\text{total moles}} )</td>
</tr>
<tr>
<td>weight percent</td>
<td>( \frac{\text{grams } A}{\text{total grams}} \times 100 )</td>
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## Solubility - How much can dissolve?

Saturated solution = concentration in equilibrium w/ excess solute

"Solubility" of a solute = concentration of saturated solution

Dynamic equilibrium:

\[ \text{dissolution rate} = \text{precipitation rate} \]

Unsaturated solution: concentration < solubility

Supersaturated solution: concentration > solubility

Unstable situation: precipitation can be slow

What determines solubility? Salt dissolves in H₂O but sand doesn't. Alcohol mixes with H₂O but oil doesn't.

## Enthalpy of Dissolution

\[ \text{NaCl/H}_2\text{O} \xrightarrow{\Delta H_{\text{diss}}} \text{Na}^{+}{}^\text{ion (strong)} + \text{Cl}^{-}{}^\text{ion (strong)} + \text{H}_2\text{O} \xrightarrow{\Delta H_{\text{diss}}} \text{H-bonding (moderate)} \]

Break apart:

\[ \Delta H_{\text{diss}} \]

Solution ion-dipole/hydration (strong)

Form:

- Octane/H₂O
- Octane (oil) dispersion forces (weak)
- H₂O H-bonding (moderate)
- Solution dispersion forces (weak)

\[ \Delta H_{\text{diss}} \]

Not favorable to break H-bonds to produce dispersion interactions:

- Octane/CCl₄
- Octane dispersion forces (weak)
- CCl₄ dispersion forces (weak)
- Solution dispersion forces (weak)

\[ \Delta H_{\text{diss}} \]

Small; not strongly favorable or unfavorable
### Qualitative Solubility Trend

Ionic and polar solutes soluble in polar solvent

Non-polar solutes soluble in non-polar solvent

“like dissolves like”

### ConcepTest

Which is more soluble in water, KBr or toluene (C\(_7\)H\(_8\))

**BLUE:** KBr

**PINK:** toluene

### Le Chatelier’s Principle

A change in the conditions of equilibrium results in an adjustment that tends to counteract the change.

Consider a gas in equilibrium with a saturated solution of the gas in a liquid solvent:

- Gas is compressed, increasing the partial pressure
- Solubility increases to remove solute molecules from the gas phase, thereby decreasing the partial pressure

### Henry’s Law

Partial pressure affects gas solubility in liquid solvent

**Henry’s Law:** \[ \text{solubility} = kP \]

**Henry’s law constant**

**Typical units:**
- Solubility (mol/L)
- \(k\) (mol/L⋅atm)
- \(P\) (atm)

### Temperature Effects

Very predictable for gaseous solutes: solubility decreases with increasing \(T\)

Another consequence of Le Chatelier’s principle, dissolution of gases is generally exothermic.

Saturated gas solution at \(T_1\)

Change

Add heat

Adjustment

Gas leaves solution

Solution at \(T_1 > T_2\)

Endothermic reverse rxn

Cools solution

Less predictable for solid solutes: commonly increases with increasing \(T\)

### Colligative Properties

Depend only on the amount of solute present, not the identity

Compared to the behavior of the pure solvent, a solution has:
- Lower vapor pressure of solvent molecules
- Higher boiling point
- Lower freezing point
- Osmotic pressure

Due to increased entropy in a solution compared to the pure solvent.
**Raoult’s Law - Nonvolatile Solute**

Vapor pressure in equilibrium with a solution.

Non-volatile solute case assumes solute has zero vapor pressure.

\[ P_{\text{total}} = P_A + P_B = X_A P_A^0 + X_B P_B^0 \]

This is an approximation, valid for ideal solutions, where the solution is dilute and solvent-solute intermolecular forces are similar to solvent-solvent forces.

since entropy of solution is higher than in pure solvent, \( \Delta S_{\text{solv}} \) is not as large and vaporization is not as favored

**Raoult’s Law Example**

What is the vapor pressure of water above a sucrose (MW=342.3 g/mol) solution prepared by dissolving 158.0 g of sucrose in 641.6 g of water at 25 °C?

The vapor pressure of pure water at 25 °C is 23.76 mmHg.

\[ \text{mol sucrose} = \frac{(158.0 \, \text{g})/(342.3 \, \text{g/mol})}{\text{mol sucrose}} = 0.462 \, \text{mol} \]
\[ \text{mol water} = \frac{(641.6 \, \text{g})/(18 \, \text{g/mol})}{\text{mol sucrose}} = \frac{35.6}{35.6 + 0.462} = 0.987 \]
\[ P = X_{\text{water}} P_{\text{water}} = (0.987)(23.76 \, \text{mm Hg}) = 23.46 \, \text{mm Hg} \]

**Raoult’s Law - Volatile Solute**

Liquid liquid mixtures often have two volatile components.

Consider individual Raoult’s law for each liquid.

\[ P_A = X_A P_A^0 \]
\[ P_B = X_B P_B^0 \]

\[ P_{\text{total}} = P_A + P_B = X_A P_A^0 + X_B P_B^0 \]

**BP Elevation/FP Depression**

Boiling and freezing points (temperatures) are modified by a solute.

Boiling point elevation can be considered a consequence of vapor pressure reduction.

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

\[ [\Delta T_c] = K_c m \]

where \( m \) is total solute molality

**Thermodynamics of BP Elevation**

in general, at the boiling point \( [\Delta G_{\text{vap}}] = [\Delta H_{\text{vap}}] = T_b \, [\Delta S_{\text{vap}}] = 0 \)

so \( T_b = [\Delta H_{\text{vap}}] / [\Delta S_{\text{vap}}] \)

for an ideal solution, \( [\Delta H_{\text{vap}}] = [\Delta H_{\text{vap}}^0] \)

however, because the solution has higher entropy than pure solvent \( [\Delta S_{\text{vap}}] < [\Delta S_{\text{vap}}^0] \)

so \( T_b = [\Delta H_{\text{vap}}] / [\Delta S_{\text{vap}}] > T_{b}^0 = [\Delta H_{\text{vap}}^0] / [\Delta S_{\text{vap}}^0] \)

**BP Elevation Example**

What is the boiling point of a solution prepared by dissolving 39.1 g of NaCl in 100 g of water? \( K_b (\text{H}_2\text{O}) = 0.51 \degree \text{C/m} \)

\[ m = \frac{\text{mol Na}^+ + \text{mol Cl}^-}{\text{kg H}_2\text{O}} = \frac{2(\text{mol NaCl})}{\text{kg H}_2\text{O}} = \frac{(2)(39.1 \, \text{g})}{0.100 \, \text{kg}} = 13.4 \, \text{m} \]

\[ [\Delta T_b] = K_b m = (0.51 \degree \text{C/m})(13.4 \, \text{m}) = 6.8 \degree \text{C} \]

b.p. = 100.0 + 6.8 = 106.8 °C
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Osmotic Pressure

- Start with only solvent
- Add solute to right side
- Solvent moves to right in an attempt to dilute and equalize concentrations
- Pressure difference is called osmotic pressure, $\Pi$
- $\Pi = MRT$
  - Total solute molarity

Osmotic Pressure v. Ideal Gas Law

- Osmotic pressure "looks" like ideal gas law:
  - $\Pi = MRT$ vs. $P = \frac{\mu}{V}$
  - $\mu$ replaces $P$
  - $M$ (mol/L) replaces $n/V$ (mol/L)
- Units are exactly the same as ideal gas law: atm, K, L, etc.

Osmotic Pressure Example

7.68 mg of an unknown substance is dissolved in enough chloroform to make 10.0 mL of solution.

What is the molar mass of the substance if the osmotic pressure at 25 °C is 26.57 mm Hg?

$\Pi = \frac{(26.57 \text{ mm Hg})}{(760 \text{ mm Hg/atm})} = 0.0350 \text{ atm}$

$T = 298 \text{ K}$

$\Pi = 0.0350 \text{ atm} = MRT = \left[\frac{0.00768 \text{ g}}{0.010 \text{ L}} \frac{(0.0821 \text{ atm‧L/mol‧K})}{298 \text{ K}}\right]$

$MM = \left[\frac{0.00768 \times 0.0821 \times 298}{0.0350 \times 0.010}\right] = 537 \text{ g/mol}$