Chapter 11
Solutions, Part I
Solutions

Homogeneous mixtures are called solutions.

The component of the solution that changes state is called the solute.

The component that keeps its state is called the solvent.

If both components start in the same state, the major component is the solvent.
# Kinds of Solutions

<table>
<thead>
<tr>
<th>Gas in gas</th>
<th>Air (O₂ in N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas in liquid</strong></td>
<td>Carbonated water (CO₂ in H₂O)</td>
</tr>
<tr>
<td><strong>Gas in solid</strong></td>
<td>H₂ in palladium metal</td>
</tr>
<tr>
<td><strong>Liquid in liquid</strong></td>
<td>Gasoline, tequila</td>
</tr>
<tr>
<td><strong>Liquid in solid</strong></td>
<td>Dental amalgam (Hg in Ag)</td>
</tr>
<tr>
<td><strong>Solid in liquid</strong></td>
<td>Salt water (NaCl in H₂O)</td>
</tr>
<tr>
<td><strong>Solid in solid</strong></td>
<td>Sterling silver (Cu in Ag)</td>
</tr>
</tbody>
</table>
What Happens When a Solute Dissolves?

There are attractive forces between the solute particles holding them together. There are also attractive forces between the solvent molecules.

When we mix the solute with the solvent, there are attractive forces between the solute particles and the solvent molecules.

If the attractions between solute and solvent are strong enough, the solute will dissolve.
Salt vs. Sugar Dissolved in Water

Ionic compounds **dissociate** into ions when they dissolve.

Molecular compounds **do not dissociate** into ions when they dissolve.
Dissociation vs Ionization

When ionic compounds dissolve in water, the anions and cations are separated from each other. This is called **dissociation**.

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

When compounds containing polyatomic ions dissociate, the polyatomic group stays together as one ion.

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

When strong acids dissolve in water, the molecule **ionizes** into H+ and anions.

\[ \text{H}_2\text{SO}_4(aq) \rightarrow 2 \text{H}^+(aq) + \text{SO}_4^{2-}(aq) \]
Solution Concentrations
**Solution Concentration Qualitative Description**

*Concentrated solutions* have a large amount of solute compared to solvent.

*Dilute solutions* have a small amount of solute compared to solvent.
Quantitative Descriptions of Solutions

One method for describing a solution is to quantify the amount of solute in a given amount of solution.
Solution Concentration - Molarity

Moles of solute per 1 liter of solution

Used because it describes how many molecules of solute in each liter of solution

Molarity = \frac{\text{moles of solute}}{\text{Liters of solution}}
Using Molarity in Calculations

Molarity shows the relationship between the moles of solute and liters of solution.

If a sugar solution concentration is 2.0 M, then 1.0 liter of solution contains 2.0 moles of sugar.

2.0 mol sugar
1.0 L soln

Questions one might ask:
What is the molarity of....?
How many liters contain....?
How many moles....?
How many grams of....?
How would I prepare....?
The Big Picture of Stoichiometry

Moles of A \rightleftharpoons \text{Molar Mass}\leftleftharpoons \text{Moles of B}

Liters of a Solution of A \rightleftharpoons \text{Mole to Mole Ratio*}\leftleftharpoons \text{Liters of a Solution of B}

Grams of A \rightleftharpoons \text{Molar Mass}\leftleftharpoons \text{Grams of B}

Particles of A \rightleftharpoons \text{Avogadro’s Number}\leftleftharpoons \text{Particles of B}

*from balanced equation
11.1

Vapor Pressure of Solutions
Vapor Pressure of a Liquid

The vapor pressure of a liquid is the pressure exerted by a gas in equilibrium with its liquid phase in a sealed container.

The rates of evaporation and condensation are equal.
Factors Affecting Vapor Pressure

**Temperature:**

as T increases, KE increases, V.P. increases

**Intermolecular forces** (Chapter 10):

Stronger forces, higher KE needed to enter gas phase, V.P. decreases

**Presence of nonvolatile solute:**

Affects rate of evaporation, decreases V.P. of solution compared to pure solvent


Vapor Pressure of Solutions

Vapor pressure lowering:

The vapor pressure of solution of a nonvolatile solute is decreased because some of the surface area of the solution is occupied by solute molecules

A *colligative property* of solutions

Raoult’s Law:

The vapor pressure of solution is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solvent in the solution.

\[ P_{\text{solution}} = \chi_{\text{solvent}} \cdot P_{\text{solvent}} \]

Ideal solution:

One that obeys Raoult’s law
A Demonstration

(a) Pure water  Seawater
(b) Nearly empty chamber  Diluted seawater
11.2
Solubility of Gases in Water
Solubility of Gases in Water

Solubility generally given in moles/L (M)

Generally lower solubility than ionic or polar covalent solids

Solubility decreases as temperature increases
Temperature Dependence of Gas Solubility

The graph illustrates the solubility of different gases in water as a function of temperature. The x-axis represents the temperature in °C, while the y-axis shows the solubility in mg gas per 100 g of water. The graph includes lines for total air, nitrogen in air, and oxygen in air, each showing a decreasing solubility with increasing temperature.
Henry’s Law:

The concentration of a sparingly soluble, chemically unreactive gas in a liquid is proportional to the partial pressure of the gas.

\[ C_{\text{gas}} = k_H P_{\text{gas}} \]

- \( C = \) concentration of the gas in solution
- \( k_H = \) Henry’s law constant
- \( P_{\text{gas}} = \) partial pressure of gas
Henry's Law:

\[ C_{\text{gas}} = k_H P_{\text{gas}} \]
### Henry’s Law Constants for Gas Solubility in Water at 20°C:

<table>
<thead>
<tr>
<th>Gas</th>
<th>$k_H$ [mol/(L · atm)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$3.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>O₂</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>N₂</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>CO₂</td>
<td>$3.5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Pressure Dependence of Gas Solubility

![Graph showing the pressure dependence of gas solubility. The graph plots solubility (mg gas/100 g water) against gas pressure (atm) for various gases: NO, Ar, O₂, CH₄, N₂, and H₂. Each gas has a different straight line with a positive slope, indicating an increase in solubility with increasing pressure.]
Pressure Dependence of Gas Solubility

- CO₂ under pressure
- CO₂ dissolved in solution
- CO₂ pressure released
- CO₂ bubbles out of solution
11.3 Energy Changes During Dissolution of Ionic Solids
Dissolution of Ionic Compounds

(a) ion–ion lattice energy + (b) dipole–dipole hydration + (c) ion–dipole hydration = (d) solution
Temperature Dependence of Solubility of Ionic Compounds
Lewis Theory Predictions for Ionic Bonding

Lewis theory predicts the number of electrons a metal atom should lose or a nonmetal atom should gain.

This allows us to predict the formulas of ionic compounds that result.

It also allows us to predict the relative strengths of the resulting ionic bonds from Coulomb’s Law.

\[ F = \frac{kq_1q_2}{r^2} \]
Energetics of Ionic Bond Formation

The ionization energy of the metal is endothermic:

\[ \text{Na}(s) \rightarrow \text{Na}^+(g) + 1 \text{ e}^- \quad \Delta H^\circ = +496 \text{ kJ/mol} \]

The electron affinity of the nonmetal is exothermic:

\[ \frac{1}{2}\text{Cl}_2(g) + 1 \text{ e}^- \rightarrow \text{Cl}^- (g) \quad \Delta H^\circ = -244 \text{ kJ/mol} \]

Therefore the formation of the ionic compound should be endothermic.

But the heat of formation of most ionic compounds is exothermic and generally large.

\[ \text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s) \Delta H^\circ_f = -411 \text{ kJ/mol} \]

Why?
Ionic Bonding & the Crystal Lattice

The *extra energy* that is *released* comes from the formation of a structure in which every cation is surrounded by anions.

This structure is called a *crystal lattice*.

The *crystal lattice* is held together by electrostatic attractions.

The *crystal lattice maximizes* these *attractions* between cations and anions, leading to the most stable arrangement.
Lattice Energy

\[ \text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s) \rightarrow \Delta H^\circ = \text{lattice energy} \]

Gaseous ions coalesce. Heat is emitted.
Lattice Energy

The extra stability that accompanies the formation of the crystal lattice is measured as the **lattice energy**.

The **lattice energy** is the energy released when the solid crystal forms from separate ions in the gas state

1) always exothermic
2) Can be calculated from knowledge of other processes

*Lattice energy depends directly on size of charges and inversely on distance between ions.*

\[ F = \frac{kq_1q_2}{r^2} \]
Born-Haber Cycle

1. $\Delta H_{\text{sub}}$
   - $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Na}(g) + \frac{1}{2} \text{Cl}_2(g)$

2. $\frac{1}{2} \Delta H_{\text{BE}}$
   - $\text{Na}(g) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Na}(g) + \text{Cl}(g)$

3. $\Delta H_{\text{IE}_1}$
   - $\text{Na}^+(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}(g)$

4. $\Delta H_{\text{EA}_2}$
   - $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s)$

5. $U$
   - $\text{NaCl}(s)$

$\Delta H_f^*$
Born-Haber Cycle

- Sublimation
- Bond breaking
- Ionization
- Electron affinity
- Lattice energy
**Born-Haber Cycle**

1) \( \text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Na}(g) + \frac{1}{2}\text{Cl}_2(g) \) (sublimation) \(+ H_{\text{sub}}\)

2) \( \text{Na}(g) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Na}(g) + \text{Cl}(g) \) (bond energy) \(+ \frac{1}{2}H_{\text{BE}}\)

3) \( \text{Na}(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}(g) \) (ionization) \(+H_{\text{IE1}}\)

4) \( \text{Na}^+(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \) (electron affinity) \(-H_{\text{EA}}\)

5) \( \text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s) \) (lattice energy) \(-U\)

\[ \Delta H_f = U \]

\[ U = H_f - \frac{1}{2}H_{\text{BE}} - H_{\text{EA}} - H_{\text{sub}} - H_{\text{IE1}} \]
The force of attraction between charged particles is inversely proportional to the distance between them.

Larger ions mean the center of positive charge (nucleus of the cation) is farther away from the negative charge (electrons of the anion).

- Larger ion $\rightarrow$ weaker attraction
- Weaker attraction $\rightarrow$ smaller lattice energy
## Lattice Energies of Some Ionic Solids (kJ/mole)

\[
(M_a^+ + X_b^- \rightarrow M_aX_b) \quad (a \text{ and } b \text{ vary})
\]

<table>
<thead>
<tr>
<th>Cations</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>2,925</td>
</tr>
<tr>
<td>Na+</td>
<td>923</td>
<td>787</td>
<td>747</td>
<td>704</td>
<td>2,695</td>
</tr>
<tr>
<td>K+</td>
<td>821</td>
<td>715</td>
<td>682</td>
<td>649</td>
<td>2,360</td>
</tr>
<tr>
<td>Be^{2+}</td>
<td>3,505</td>
<td>3,020</td>
<td>2,914</td>
<td>2,800</td>
<td>4,443</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>2,957</td>
<td>2,524</td>
<td>2,440</td>
<td>2,327</td>
<td>3,791</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>2,630</td>
<td>2,258</td>
<td>2,176</td>
<td>2,074</td>
<td>3,401</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>5,215</td>
<td>5,492</td>
<td>5,361</td>
<td>5,218</td>
<td>15,916</td>
</tr>
</tbody>
</table>
Lattice Energy and Heat of Hydration

\[ \Delta H_{\text{solution, NaCl}} = \Delta H_{\text{hydration, NaCl(aq)}} - U_{\text{NaCl}} \]

\[ \Delta H_{\text{hydration, NaCl(aq)}} = \Delta H_{\text{hydration, Na}^+(g)} + \Delta H_{\text{hydration, Cl}^-(g)} \]
### Enthalpies of Hydration of Selected Cations and Anions

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\Delta H_{\text{hydration}}$ (kJ/mol)</th>
<th>Anion</th>
<th>$\Delta H_{\text{hydration}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>$-536$</td>
<td>F$^-$</td>
<td>$-502$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>$-418$</td>
<td>Cl$^-$</td>
<td>$-368$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>$-335$</td>
<td>Br$^-$</td>
<td>$-335$</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>$-305$</td>
<td>I$^-$</td>
<td>$-293$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>$-289$</td>
<td>ClO$_4^-$</td>
<td>$-238$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$-1903$</td>
<td>NO$_3^-$</td>
<td>$-301$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$-1591$</td>
<td>SO$_4^{2-}$</td>
<td>$-1017$</td>
</tr>
</tbody>
</table>

*aBased on enthalpy of hydration of H$^+$ as $-1105$ kJ/mol.*
Dissolving ionic compounds in water.

\[ \Delta H_{\text{soln}} = 3.9 \text{kJ/mol} \]

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

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

\( \Delta H_{\text{solute}} = -\Delta H_{\text{lattice}} \)

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

NaCl
Dissolving ionic compounds in water.

\[
\text{NaCl} \quad \text{NaOH} \quad \text{NH}_4\text{NO}_3
\]
Dissolving ionic compounds in water.

\[ \text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \]

Enthalpy, \( H \)

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

\( \Delta H_{\text{soln}} = 25.7 \text{ kJ/mol} \)
11.4
Mixing of Volatile Solutes
Fractional Distillation

Method of separating a mixture of compounds on the basis of their different boiling points.

Vapor phase enriched in more volatile component.
Fractional Distillation

Boiling points:
- Heptane = 98°C
- Octane = 126°C

(a) Ideal situation. Fractional distillation of a mixture of heptane and octane produces two plateaus at the boiling points of the two components.

(b) Distillation of a mixture of heptane and octane
(1) Solution begins to distill
(2) Solution finishes distilling
Fractional Distillation

Boiling points:
- Heptane = 98°C
- Octane = 126°C

(c) Boiling points of octane/heptane mixtures (blue curve) and the composition of the vapors produced at those boiling points (red curve)

1. Solution boils at this temperature
2. Vapor has this composition
3. Vapor condenses, then boils
4. Vapor has this composition
5. Vapor condenses, then boils
Solutions of Volatile Components

For mixtures containing more than one volatile component:

Partial pressure of each volatile component contributes to total vapor pressure of solution.

\[ P_{\text{total}} = \chi_1 P_1^\circ + \chi_2 P_2^\circ + \chi_3 P_3^\circ + \ldots \]

Where \( \chi_i = \text{mole fraction of component } i \), and

\( P_i^\circ = \text{equilibrium vapor pressure of pure volatile component at a given temperature} \)
In ideal solutions, the resulting solute-solvent interactions are equal to the sum of the broken dilute-solute and solvent-solvent interactions.
Real (Nonideal) Solutions

Deviations from Raoult’s Law:

Due to differences in solute–solvent and solvent–solvent interactions (dashed lines = ideal behavior)

Negative deviations

Positive deviations
**Practice Problem: Vapor Pressure of Solution**

1) A solution contains 100.0 g of water (MW = 18.0 g/mol) and 25.00 g of ethanol (MW = 44.0 g/mol). What are the mole fractions of water and ethanol, and the vapor pressure of the solution at 25°C? \((P_{\text{water}} = 23.8 \text{ torr}; P_{\text{ethanol}} = 58.7 \text{ torr})\)

\[
\begin{align*}
100.0 \text{ g H}_2\text{O} \times \frac{1.00 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} &= 5.549 \text{ mol H}_2\text{O} \\
25.00 \text{ g C}_2\text{H}_6\text{O} \times \frac{1.00 \text{ mol C}_2\text{H}_6\text{O}}{46.07 \text{ g C}_2\text{H}_6\text{O}} &= 0.5426 \text{ mol C}_2\text{H}_6\text{O} \\
&\text{6.092 total moles}
\end{align*}
\]

\[
\begin{align*}
P_{\text{water}} &= (\chi_{\text{water}})(23.8 \text{ torr}) = (\frac{5.549}{6.092})(23.8 \text{ torr}) = 21.7 \text{ torr} \\
P_{\text{ethanol}} &= (\chi_{\text{water}})(58.7 \text{ torr}) = (\frac{0.5426}{6.092})(58.7 \text{ torr}) = 5.23 \text{ torr}
\end{align*}
\]