Chapter 11: Intermolecular Attractions and Liquids

• Intermolecular Forces
• Properties of Liquids
The 3 States

A Gas: Molecules are far apart and fill the available space

B Liquid: Molecules are close together but move relative to each other

C Solid: Molecules are close together, packed in a regular array, and move very little relative to each other.
Water & it’s Phases

What are the effects of adding heat to ice?

- Ice (solid)
- Water (liquid)
- Steam (gas)

6.02 kJ/mol
40.7 kJ/mol
Intermolecular and Intramolecular Forces

**Intramolecular Forces** - are the forces that hold atoms together in a molecule/compound.

**Intermolecular Forces** are the forces between various molecules.
Types of Intermolecular Forces

1. Ion - Dipole
2. Dipole-Dipole Forces
3. Dipole - Induced Dipole
4. Instantaneous Dipole-Induced Dipole
Review: Dipole Moment

(a) No net dipole moment
(b) Net dipole moment
Ion - Dipole Interactions

NaCl crystal structure

NaCl in water

sodium (Na)
chlorine (Cl)
What are the Forces of Ion-Dipole Attractions?

Coulombic: \[ F = \frac{kq\mu}{r^2} \]

where:
\( q \) = charge of ion
\( \mu = \text{“charge” of dipole} \)
\( \mu = qd \)
\( q = \text{charge} \)
\( d = \text{separation of charge in polar molecule} \)

Factors That Influence Ion-Dipole Attractions

- Distance Between Ion & Dipole
- Charge of Ion
- Magnitude of Dipole
What are the Forces of Ion-Dipole Attractions?

**Coulombic:** \[ F = k \frac{q \mu}{r^2} \]

where:
- \( q \) = charge of ion
- \( \mu \) = “charge” of dipole
  - \( \mu = qd \)
  - \( q = \) charge
  - \( d = \) separation of charge in polar molecule

**Factors That Influence Ion-Dipole Attractions**

Explains why Polar Solvents Dissolve Ionic Compounds
What are the Forces of Ion-Dipole Attractions?

Coulombic: $ F = \frac{kq \mu}{r^2}$

where:
- $q$ = charge of ion
- $\mu$ = “charge” of dipole
  - $\mu = qd$
    - $q$ = charge
    - $d$ = separation of charge in polar molecule

- Smaller the ion radii the closer the interaction
  - the stronger the force
- Greater the ion charge the stronger the force
- Greater the dipole moment the stronger the force

See table 11.1 of text
Dipole-Dipole Forces

Intermolecular Forces between dipoles
Which Statements are True of a Molecule that exhibits Dipole-Dipole attractions?

i. It is polar

ii. It is asymmetrical

iii. It must contain H attached to F, O, or N

i & ii only

ii & iii only

i only

ii only

iii only
Dipole Moments and Boiling Pts

2 Compounds Have Similar Dipole Moments and Different Molar Masses. Which Would Have the Higher Boiling Point?

<table>
<thead>
<tr>
<th>Molecule</th>
<th>FW (g/mol)</th>
<th>BP (°C)</th>
<th>ΔH°_vap (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>32</td>
<td>-112</td>
<td>12.10</td>
</tr>
<tr>
<td>GeH₄</td>
<td>77</td>
<td>-90</td>
<td>14.06</td>
</tr>
</tbody>
</table>
2 Compounds Have Similar Molar Masses and Different Dipole Moments. Which Would Have the Higher Boiling Point?

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<th>ΔH°_vap (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>28</td>
<td>-196</td>
<td>5.57</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>-192</td>
<td>6.04</td>
</tr>
</tbody>
</table>
Hydrogen Bonding

Very strong dipole-dipole interactions
H-Bonding

Occurs when Hydrogen is attached to a highly electronegative atom.

\[
\begin{array}{ccc}
\text{N-H} & \cdot & \text{N-} \\
\text{N-H} & \cdot & \text{O-} \\
\text{N-H} & \cdot & \text{F-} \\
\text{O-H} & \cdot & \text{N-} \\
\text{O-H} & \cdot & \text{O-} \\
\text{O-H} & \cdot & \text{F-} \\
\end{array}
\]

Requires Unshared Electron Pairs of Highly Electronegative Elements
Structure of Ice

Observe the orientation of the Hydrogen Bonds
Which Statements are True of a Molecule that Exhibits Hydrogen Bonding?

i. It is polar
ii. It is asymmetrical
iii. It must contain H attached to F, O, or N

i & ii only
ii & iii only
i only
ii only
iii only
Dipole Induced Dipole

Polar Molecule Induces Dipole in a Non-Polar Molecule

Allows Water to Dissolve Diatomic Gasses Like Oxygen
London Dispersion Forces

- Instantaneous Induced Dipole-Dipole interactions
- Very Weak always present in the condensed phase

Electrons temporarily shifted to one side of the atom. This side develops a partial negative charge. Neighboring atoms respond with partial charges of their own.
Polarization

-The Process of Inducing a Dipole

**Polarizability** - Ease with which a molecule can be polarized

-Polarizable molecules have loosely bound valence electrons.

-For a given group, the larger the radii, the more polarizable
Properties of Liquids

• Vaporization and Condensation
• Vapor Pressure
• Clausius-Clapeyron Eq
• Boiling Point
• Critical Temperature and Pressure
• Surface Tension, Capillary Action and Viscosity
What is the **Vapor Pressure** \((P_v)\) of a Liquid?

The *equilibrium* pressure exerted by molecules of a volatile liquid which have escaped the surface and entered the gas phase.

The partial pressure due to the vapor
What factors influence the vapor pressure?

1. Temperature
2. $\Delta H_v$  Enthalpy of Vaporization
3. Surface Area

Would this be an “open” or “closed” container?
Vapor Pressure

- CH₃CH₂OCH₂CH₃
- CH₃CH₂OH
- H₂O
- CH₂OH
- CH₂OH

Graph shows vapor pressure vs. temperature for various compounds:
- Diethyl ether
- Ethyl alcohol (ethanol)
- Water
- Ethylene glycol

Normal boiling point:
- 34.6°C
- 78.3°C
- 100°C
How does the temperature effect the vapor pressure?

\[ P_v = ke \frac{-\Delta H_{vap}}{RT} \]
Clausius-Clapeyron Equation

Relates the vapor pressure of a liquid to it’s enthalpy of vaporization and the absolute temperature

\[ \ln P_v = \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T} \right) + C \]  \hspace{1cm} \text{(eq. 12.1)}

or

\[ P_v = e^{\frac{-\Delta H_{vap}}{RT} + C} = e^{-\frac{\Delta H_{vap}}{RT}} e^C = k e^{\frac{-\Delta H_{vap}}{RT}} \]
11.6 What is Boiling?

A liquid boils when it’s vapor pressure equals the ambient pressure.

Notice there are two ways to boil.
What is Boiling?

What Does Normal Boiling Point and Normal Freezing Point Mean?
What is Boiling?

How does a Pressure cooker work?

Why does it take longer to cook an egg on top of a mountain than down at the sea shore?
Which of the following will affect the boiling point of a substance?

A. Molecular mass of the material
B. Intermolecular attractions
C. The external pressure on the material
D. All of these
E. None of these
Intermolecular Forces and Phase Transitions

- **Sublimation**: $\Delta H > 0$, $\Delta S > 0$
- **Deposition**: $\Delta H < 0$, $\Delta S < 0$
- **Vaporization**: $\Delta H > 0$, $\Delta S > 0$
- **Condensation**: $\Delta H < 0$, $\Delta S < 0$
- **Fusion (melting)**: $\Delta H > 0$, $\Delta S > 0$
- **Freezing**: $\Delta H < 0$, $\Delta S < 0$
The stable phase of matter is determined by the interplay of intermolecular forces and kinetic energy.

- The higher the temperature, the greater the kinetic energy, the more fluid the state
- The greater the cohesive (intermolecular) forces, the less fluid the state
- The heavier the mass, the less fluid the state
Dispersion Forces

Give Two Reasons Why Iodine Is a Solid While Fluorine Is a Gas at STP

<table>
<thead>
<tr>
<th>Halogen</th>
<th>mp (K)</th>
<th>bp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>53.5</td>
<td>85.0</td>
</tr>
<tr>
<td>Cl₂</td>
<td>172.2</td>
<td>238.6</td>
</tr>
<tr>
<td>Br₂</td>
<td>265.9</td>
<td>331.9</td>
</tr>
<tr>
<td>I₂</td>
<td>386.7</td>
<td>457.5</td>
</tr>
</tbody>
</table>

TABLE 10.3  Melting Points and Boiling Points of the Halogens
Boiling Pts of Simple Hydrocarbons

Boiling points of simple hydrocarbons in degrees Kelvin

Simple hydrocarbons have only London dispersion forces as intermolecular forces
Intermolecular Forces and Phase Transitions of Covalent Binary Hydrides
Class Quiz

Which have the higher boiling point and Why?

a. HCl or HI?

b. HF or HCl?

c. H₂O or H₂S?

d. CH₄ or SiH₄?
Critical Temperature & Pressure

At High Temperature & Pressure the Vapor/Fluid Boundary Disappears

- High T means high KE, which overcomes intermolecular forces (like gas)
- High P means molecules are forced next to each other (like liquid)

Critical Point - the highest pt where both phases can coexist
- **Surface Tension**: Energy required to disrupt a liquid surface

- **Viscosity**: Resistance to Flow

- Ethanol: \( \text{H-H} \text{-C-C-O-H} \text{-H-H} \)

- Glycerol: \( \text{H-H-H} \text{-C-C-C-H} \text{-O-O-O} \text{-H-H-H} \)
Surface Tension & Viscosity

-Cohesive Forces: forces holding liquid together

What are the Cohesive Forces for Mercury & Water?
Meniscus & Capillary Action

Adhesive Forces - between different substance (wall & fluid)

Adhesive > Cohesive
Adhesive < Cohesive