Chapter 11 Intermolecular Forces, Liquids, and Solids

Intermolecular forces explain boiling points, melting points, vapor pressure

### Characteristic Properties of Gases, Liquids, and Solids

<table>
<thead>
<tr>
<th>State of Matter</th>
<th>Volume/Shape</th>
<th>Density</th>
<th>Compressibility</th>
<th>Motion of Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Assumes the volume and shape of the container</td>
<td>Low</td>
<td>Very Compressible</td>
<td>Very free motion</td>
</tr>
<tr>
<td>Liquid</td>
<td>Has a definite volume but assumes the shape of the container</td>
<td>High</td>
<td>Only slightly compressible</td>
<td>Slide past one another freely</td>
</tr>
<tr>
<td>Solid</td>
<td>Has a definite volume and shape</td>
<td>High</td>
<td>Virtually incompressible</td>
<td>Vibrate about fixed positions</td>
</tr>
</tbody>
</table>
**Bonding Polarity and Electronegativity - a review**

nonpolar covalent bond - electrons are shared equally between atoms.

**polar covalent bond** – one atom attracts electrons more strongly than the other.

**electronegativity** – the ability of an atom in a molecule to attract electrons to itself.

Pauling scale, F 4.0  Cs 0.7

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>2.2</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN</td>
<td>1.0</td>
<td>1.6</td>
<td>1.8</td>
<td>2.5</td>
<td>3.0</td>
<td>3.4</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>1.3</td>
<td>1.6</td>
<td>1.9</td>
<td>2.2</td>
<td>2.6</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notice: EN increases left to right, and down to up.

**Bond polarity**

<table>
<thead>
<tr>
<th>Compound</th>
<th>F₂</th>
<th>HF</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN difference</td>
<td>4.0 – 4.0 = 0</td>
<td>4.0 – 2.1 = 1.9</td>
<td>4.0 – 1.0 = 3.0</td>
</tr>
<tr>
<td>Type of Bond</td>
<td>Nonpolar covalent</td>
<td>Polar Covalent</td>
<td>Ionic</td>
</tr>
</tbody>
</table>

In general:  
EN difference < 0.5  Nonpolar

0.5 < EN difference < 2.0  Polar

EN difference > 2.0  Ionic
Dipole moments

\[
\begin{align*}
\text{H—F—H—F—H—F} \\
\text{H—F} & \quad \text{Na}^+ \quad \text{F—H} \quad \text{F—H} \quad \text{Cl}^- \quad \text{H—F}
\end{align*}
\]

\[
\begin{array}{c}
\delta^+ \\
\delta^-
\end{array}
\]

\[\text{H} \quad \text{F} \quad \text{H} \quad \text{F} \]

Polar Molecules

Molecular Dipoles: Center of mass of positive charge (nuclei) doesn’t coincide with the center of mass of all negative charges (electrons).

Examples:

\[
\begin{align*}
\text{H—H} & \quad \text{Br—Br} & \quad \text{H—Br} & \quad \text{Br—I}
\end{align*}
\]
**Ion-Dipole Forces** - Attraction between a polar molecule and ions.

Anions are attracted to the positive end of the polar molecule.

\[
\begin{align*}
\text{Anion} & \quad \text{Polar Molecule} \\
\delta^- & \quad \delta^+ \\
\text{Na}^+ & \quad \text{H}_2\text{O} \\
\text{Cl}^- & \quad \text{H}_2\text{O} \\
\end{align*}
\]

**Dipole-Dipole Forces**

Molecules with permanent dipoles resulting from atoms with very different electronegativities.

\[
\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]
**London Dispersion Forces** (in all atoms!)

polarizability ("swishy bathtub")

Electrons swish back and forth to form instantaneous dipoles with nuclei.

**Induced dipoles**

\[
\begin{array}{c}
2^+ \\
\downarrow \quad \downarrow
\end{array}
\begin{array}{c}
2^+ \\
\delta^- \quad \delta^+
\end{array}
\quad \text{10}^{-15} \text{ sec later}
\begin{array}{c}
2^+ \\
\downarrow \quad \downarrow
\end{array}
\begin{array}{c}
2^+ \\
\delta^- \quad \delta^+
\end{array}
\]

- Force \(\propto\) number of electrons

Ex: I > Br > Cl > F

larger molecules tend to be more polarizable -they have more electrons

- Force \(\propto\) number of contact points

More branching means more surface area- more contact
Hydrogen Bonding

\[ \text{X–H–} \hat{\text{Y}} \]

X, Y must be N, O, F only!

London < Dipole-Dipole < Hydrogen Bonding < Ion-Dipole < Ionic

Size Factors

1) Neutral, nonpolar molecules have only London forces

2) The charge or dipole in ions or polar molecules is spread out over the ion or molecule. So, the larger the molecule (ion), the weaker the effect of the charge.
Large \leftarrow \text{strong} \rightarrow \text{Large} \quad \text{(uncharged)}

Small \leftarrow \text{strong} \rightarrow \text{Small} \quad \text{(charged)} \quad \text{(Lattice energy)}

Large \leftarrow \text{weaker} \rightarrow \text{Small} \quad \text{(any)}

\textbf{Properties of Liquids}

Adhesive forces – between molecules in a liquid and those of container

Cohesive forces – from intermolecular forces of liquid

Surface tension – higher with higher adhesive forces

Capillary action – spontaneous rising of liquid in a narrow tube

Viscosity – resistance to flow

\propto \text{to cohesive forces}

Surface Tension
Phase Changes

\[ X(s) \rightarrow X(l) \quad \Delta H_{fus} = 10 \text{kJ/mol} \]
\[ X(l) \rightarrow X(g) \quad \Delta H_{vap} = 50 \text{kJ/mol} \]
\[ X(s) \rightarrow X(g) \quad \Delta H_{sub} = 60 \text{kJ/mol} \]

fusion (–melting)  vaporization (–condensation)  sublimation

Calculate the amount of energy evolved when water cools from 130°C (steam) to ice at -40°C. The specific heat of steam is 1.99 J/g °C., the specific heat of water is 4.184 J/g°C, the specific heat of ice is 2.03 J/g°C. The molar heat of vaporization of water is 40.79 kJ/mol and the molar heat of fusion is 6.01 kJ/mol.
**Vapor Pressure** - the partial pressure of the vapor when it is in dynamic equilibrium with the liquid.

Evaporation is the escape of molecules from the surface of liquid.

\[
\text{X(l)} \quad \rightarrow \quad \text{X(g)} \quad \Delta H_{\text{vap}} \quad \text{Molar enthalpy of vaporization}
\]

\[
\text{X(g)} \quad \rightarrow \quad \text{X(l)} \quad -\Delta H_{\text{vap}}
\]

\[
\text{X(l)} \quad \leftrightarrow \quad \text{X(g)} \quad \text{When allowed to come to Equilibrium}
\]

Equilibrium when: rate of vaporization equals rate of condensation

**Using Kinetic-Molecular Theory to Explain.**

Value of Vapor Pressure related to IM forces and temperature.
**Clausius-Clapeyron Equation** - relates the vapor pressure of a liquid to the inverse of its temperature.

\[
\ln P = -\frac{\Delta H_{vap}}{RT} + C
\]

\(C\) is a constant characteristic of each substance.

\[
\ln \frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right)
\]

\[
\Delta H_{vap} = \frac{(\ln P_1 - \ln P_2)R}{\frac{1}{T_2} - \frac{1}{T_1}} = \left( \frac{P_1}{P_2} \right)^R \left( \frac{T_1 - T_2}{T_1 T_2} \right)
\]

boiling point \(\equiv T\) where \(P_{vap} = P_{external}\)

melting point \(\equiv T\) where \(P_{vap(sol)} = P_{vap(liq)}\)

normal boiling point \(\equiv T\) where \(P_{vap} = 1 \text{ atm}\)

normal m.p. \(\equiv T\) where \(P_{vap} = 1 \text{ atm and } P_{vap(sol)} = P_{vap(liq)}\)

**Example:** Propanoic acid has a \(\Delta H_{vap} = 32.14 \text{ kJ/mol}\) at a temperature of 25°C. Calculate the vapor pressure for proanoic acid at this temperature. \((C = 7.76)\)
Structures of Solids

amorphous solids - disordered structure

crystalline solids - highly arranged (periodic) structure

Lattice  

unit cell: smallest repeating unit

Diffraction

Bragg Equation:  

\[ d = \frac{n\lambda}{2\sin \theta} \quad n\lambda = 2d\sin \theta \]

\[ \lambda \quad n \]

\[ d \quad \theta \]

Assume atoms are uniform, hard spheres arranged with "closest packing" in layers.

"hexagonal closest packed" (hcp)  
ababab

"cubic close packed" (face centered cubic)  
abcabcabc

Coordination number - number of particles immediately surrounding the particle in the crystal.

The CN is twelve (12) in each close-packed structures.

Other packing arrangements:

Simple cubic:  
...a-a-a-a-  
CN = 6

Body-centered cubic:  
...a-b-a-b-a-b-  
CN = 8
<table>
<thead>
<tr>
<th>position</th>
<th>fraction inside</th>
<th>number on a cube</th>
<th>total number</th>
</tr>
</thead>
<tbody>
<tr>
<td>center</td>
<td>1</td>
<td>1</td>
<td>1 x 1 = 1</td>
</tr>
<tr>
<td>face</td>
<td>1/2</td>
<td>6 (dice)</td>
<td>1/2 x 6 = 3</td>
</tr>
<tr>
<td>edge</td>
<td>1/4</td>
<td>12</td>
<td>1/4 x 12 = 3</td>
</tr>
<tr>
<td>corner</td>
<td>1/8</td>
<td>8</td>
<td>1/8 x 8 = 1</td>
</tr>
</tbody>
</table>

Example:

**Bonding in Solids**

**Metal Alloys**

- **Substitutional**: one metal present in a large percentage forms the lattice. Other metal(s) also form points in lattice.

- **Interstitial**: one metal forms lattice, non-metal atoms in interstices.

**Molecular solids** - covalent bonding within molecules, but relatively weak forces between molecules (intermolecular forces of attraction.) Also in some elements: $\text{P}_4$, $\text{S}_8$, $\text{I}_2$. 
**Covalent-Network** - large networks (2D or 3D) or chains are held together by covalent bonds between atoms.

Insulators, conductors, semiconductors

Ex: diamond, graphite, GaN, silicon dioxide (quartz, glass)

**Carbon:**

**Allotropes** - different structural forms of the same element which differ in physical and chemical properties.

Diamond - all carbons are sp³ hybridized and covalently bonded with tetrahedral geometries.

Graphite - 2-dimensional sheets of fused six-membered rings; each carbon is sp² hybridized.

Fullerene - a spherical C₆₀ molecule with the shape of a soccer ball.

Other examples of allotropes: O₂ (oxygen) and O₃ (ozone); red phosphorus and white phosphorus.

**Silica** (SiO₂) four single bonds between silicon and oxygens in a covalent network structure.

Quartz - crystalline (see page 404).

Quartz glass - result of heating silica above 1600°C and then cooling the viscous liquid.

Si-O bonds re-form in a random arrangement amorphous solid.

If mix in additives - prepare a wide variety of glass.

- window glass - add CaCO₃ and Na₂CO₃.
- colored glass - add transition metal ions.
- borosilicate glass (Pyrex) - add B₂O₃; resistant to thermal shock because it doesn't expand much on heating.

**Ionic** - ions held together by ionic bonds (electrostatic interaction between oppositely charged ions)
Ex: LiF, CsCl, CaF₂

**Metallic** - bonding is due to valence electrons that are delocalized throughout the entire solid "positive ions immersed in a sea of delocalized valence electrons"

**Phase Diagrams**

**Boundary line** - points on this line represent pressure/temperature combinations at which the two phases are in equilibrium

**Triple point** - temperature and pressure where solid, liquid, and gas are in equilibrium.

**Critical Temperature** – the highest temperature at which a substance can exist as a liquid.

**Critical Pressure** - the pressure required to liquefy a gas at its critical point.

**Critical Point** - a point defined by the critical temperature and critical pressure.

**Supercritical fluid** - a substance that is neither a liquid nor a gas.