Intermolecular Forces
IMF’s

Unit J
Chapter 11
Intermolecular Forces

Forces that exist *between* molecules.

1. London Dispersion Forces (aka LDFs)
   » Between all molecules
     (but it’s the only force between nonpolar molecules.)

2. Dipole-dipole forces
   » Between polar molecules

3. Hydrogen “bonding”
   » Between “special” polar molecules

4. Ion-dipole forces
   » Between ions and polar molecules
   » Particularly between ions and water in a solution
   » We have already been talking about this, and will continue to do so
London Dispersion Forces

- **Temporary dipoles** that occur in one molecule can *induce* temporary dipoles in the next molecule.

- ALL molecules exhibit dispersion forces.
  - But, these are the ONLY forces that occur between nonpolar molecules.

- The ease with which an electron cloud can be distorted by another molecule is called its *polarizability* (aka “swishability”)

- **Factors that affect polarizability**
  - Larger size, electron cloud
  - Longer straighter chain
Dispersion forces increase with increasing size of electron cloud

- We will look at boiling temperatures to give us insight to strength of IMF’s
- BP increases as the size of the molecule increases.
- The larger molar mass indicates larger size which makes its electron cloud more polarizable (“squishable”) and easier to induce instantaneous dipoles.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>-187.9°C</td>
</tr>
<tr>
<td>Cl₂</td>
<td>-34.4°C</td>
</tr>
<tr>
<td>Br₂</td>
<td>59°C</td>
</tr>
<tr>
<td>I₂</td>
<td>184.6°C</td>
</tr>
</tbody>
</table>
Dipole-Dipole Forces

- Positive and negative attractive and repulsive forces that occur between polar molecules.
Hydrogen “bonding”

- Interactions between a hydrogen (attached to O, N, F) on one molecule and the electronegative atom (O, N or F) on the other molecule.

- “A hydrogen bond is something that a molecule does, not something that a molecule has.”
  ✓ Fred Vital
Hydrogen “Bonding” breaks the trend

- Group IV hydrides
  » As expected, BP decreases as size of molecule decreases.

- Group VI hydrides
  » As expected, BP decreases as size of molecule decreases.
  » But the H$_2$O BP is much higher due to the strong IMF’s of hydrogen “bonding”
Predicting IMF Strengths

• First we should consider hydrogen bonding… (that’s APs trump card) but if H-bonding is not present…
  » But don’t forget, even non-polar oil boils at much higher temp than H-bonding water!!

• When asked to compare the strength of IMF’s between molecules, you may feel conflicted and need to prioritize.

• When molecules are of comparable size and comparable shape, look to differences in polarities to decide.

• When molecules differ in their size, the size of the electron cloud (molecule-do not use mass) will be the deciding factor, regardless of any differences in polarities (unless hydrogen bonding is in effect).
What type of intermolecular forces exist in dimethyl ether, CH$_3$OCH$_3$?

Chose all that apply?

1. dipole-dipole forces
2. hydrogen bonding
3. London dispersion forces
What type of intermolecular forces exist in dimethyl ether, CH$_3$OCH$_3$?

Chose all that apply:

1. dipole-dipole forces
2. hydrogen bonding
   - None of the hydrogens are attached to oxygen, so there cannot be hydrogen bonding.
3. London dispersion forces
Same chemical formula and size just different shapes.

- Propyl alcohol (a) boils at 97.2
- Isopropyl alcohol (b) boils at 82.5
- Both exhibit hydrogen “bonding” and dispersion forces, so why are their BP’s different? Two Reasons.
  1. The longer straight chain of (a) allows for greater surface area contact which makes the molecule have more effective dispersion forces than (b).
  2. The central position of the -OH in (b) is shielded and is prevented from hydrogen bonding as effectively as in (a)
Just how strong?

- Intermolecular forces are much weaker than ionic or covalent bonds. Yet strong enough to have an impact on the physical properties of substances.

<table>
<thead>
<tr>
<th>Force Type</th>
<th>Energy Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole-dipole</td>
<td>87 kJ/g and not usually much higher</td>
</tr>
<tr>
<td>London Dispersion forces</td>
<td>Can be as low as 43 kJ/g but ranges much higher with larger electron cloud</td>
</tr>
<tr>
<td>Hydrogen “bonding”</td>
<td>2,260 kJ/g</td>
</tr>
<tr>
<td>Covalent (H–O) bond</td>
<td>51,890 kJ/g</td>
</tr>
</tbody>
</table>
What properties are affected by intermolecular forces?

- Boiling point
- Vapor pressure
- Melting point
- The density of ice – next slide
- Viscosity – Corn syrup viscosity at various temps demo
- Surface tension – Let’s take a look at the lizard video
- Energy required to make phase changes: $\Delta H_{vaporization}$ and $\Delta H_{fusion}$
- Energy require to make temperature changes: Specific heat capacity
Density of Ice

• Break out the water molecule kits to understand why ice in its hexagonal crystals is less dense than water, and why snow flakes are nearly always six-sided or six-pronged.

• Observe the ethan crystal in contact with the water. What to you notice?

• Mix in the NaCl crystals. What evidence indicates which ion is blue, which is green. Two reasons.
Heating a Substance from Solid to Gas

- Observe the slope of the vertical sections
- Observe the length of the plateau
Heating a Substance from Solid to Gas

- Calculate the energy required to completely evaporate 15 g of ice at −25°C
  - $\Delta H_f^\circ \text{H}_2\text{O}_(L) \text{ -285 kJ/mol}$
  - $\Delta H_f^\circ \text{H}_2\text{O}_(g) \text{ -242 kJ/mol}$
  - $\Delta H_f^\circ \text{H}_2\text{O}_(s) \text{ -291 kJ/mol}$
  - $c$ of $\text{H}_2\text{O}_(L) \text{ 4.18 J/g°C}$
  - $c$ of $\text{H}_2\text{O}_(g) \text{ 1.79 J/g°C}$
  - $c$ of $\text{H}_2\text{O}_(s) \text{ 2.1 J/g°C}$
Calculation Energy for Temperature Changes and Phase Changes

• Temperature changes
  » Heat = SHC * Mass * ΔT

• Phase changes
  » Heat = ΔH\text{phase change} * mass
    » ΔH\text{fusion}
      ✓ Solid → Liquid or Liquid → solid
    » ΔH\text{vaporization}
      ✓ Liquid → Gas or Gas → Liquid
Vaporization or Evaporation

• Remember that temperature is an average.
• At a particular temp some molecules go fast some go slow.
• A certain amount of molecules will have enough energy to sever all attractions to the liquid and fly into the air.
• Remember that the shape of the curve changes as temperature increases.
• Thus at a higher temperature, a larger number of molecules, meet the requirement of that amount of energy required to fly off as a gas.
Vapor (Dynamic) Equilibrium

- When first put into an enclosed space, molecules will vaporize.
- Vapor Equilibrium
  - Eventually the amount vaporizing will equal the amount condensing.
  - This causes a particular vapor pressure based completely on temperature of the liquid.
  - The size of the container or the presence of other gases play no role.
  - This is a dynamic equilibrium.
Measuring Vapor Pressure

- A closed-end gas bulb manometer set up to measure vapor pressure.
Different liquids will cause different vapor pressures at a given temperature.
Vapor Pressure Curves

- IMF’s will effect the shape and location of the vapor pressure curve
- Lower IMF liquids are more volatile.
- A liquid is said to be *boiling* when its vapor pressure reaches atmospheric pressure.
Vapor Pressure Problems

![Graph showing the relationship between vapor pressure and temperature.](https://via.placeholder.com/720x540.png)
Vapor Pressure Problems

• This particular volatile liquid has a molar mass of 78 g/mole.
• At 25°C if you sealed 0.5 g of this liquid into a 650 ml flask, will equilibrium vapor pressure be reached?
• If yes, how much liquid is left on the bottom?
• If no, what is the vapor pressure?
• If no, what mass more should be added to reach equilibrium vapor pressure?
Vapor Pressure Problems

- Let’s assume 300 mm at 25º
- This particular volatile liquid has a molar mass of 78 g/mole.
- At 25ºC if you sealed 0.5 g of this liquid into a 650 ml flask, will equilibrium vapor pressure be reached?
- If yes, how much liquid is left on the bottom?
- If no, what is the vapor pressure?
- If no, what mass more should be added to reach equilibrium vapor pressure?

\[
P = \frac{nRT}{V} \quad \frac{(0.5/78)(62.36)(298)}{0.65} = 183\text{mm}
\]

\[
n = \frac{PV}{RT} \quad \frac{(325)(0.65)}{(62.36)(298)} = 0.0105\text{mol} \times 78\text{g/mol} = 0.88\text{g}
\]
Vapor Pressure Problems

• Let’s assume 300 mm at 25º
• This particular volatile liquid has a molar mass of 78 g/mole.
• At 25ºC if you sealed 0.5 g of this liquid into a 650 ml flask, will equilibrium vapor pressure be reached?
• If yes, how much liquid is left on the bottom?
• If no, what is the vapor pressure?
• If no, what mass more should be added to reach equilibrium vapor pressure?

\[
P = \frac{nRT}{V} \quad \frac{(0.5 \text{ g}) \times (298 \text{ K}) \times (62.4 \text{ atm L/mol K})}{0.65 \text{ L}} = 183 \text{ mm Hg}
\]

\[
n = \frac{PV}{RT} \quad \frac{(300 \text{ mm Hg}) \times (0.65 \text{ atm})}{(62.36 \text{ atm L/mol K}) \times (298 \text{ K})} = 0.0105 \text{ mol} \times 78 \text{ g/mol} = 0.82 \text{ g}
\]
Vapor Pressure Equilibrium Curve

- This diagram only tells part of the story.
- It shows us the relationship between liquid and gas at various temperatures.
- Any point on the line are conditions in which the gas and liquid are in equilibrium.
- Shifting the pressure or temperature will upset the equilibrium and push the substance to liquid or gas.
Bonding in Solids

Chapter 11
Part III
Crystalline vs Amorphous

• Crystalline solid (aka crystal lattice)
  » Highly ordered, regular, repeating pattern
  » Resulting in flat surfaces or faces
  » With definite angles allowing for gemstone cuts
  » e.g. ionic solids and some network covalent solids

• Amorphous solid (“without form”)
  » No orderly structure
  » No defined faces
  » Varying IMF’s throughout resulting in melting temperature over a temperature range thus softening before melting
  » e.g. rubber or glass
Metallic Solids – A model to explain metallic properties

- Metal atoms are aligned in a regular and repeating pattern.
- Outermost electrons can wander freely throughout - essentially “delocalized”
- Electrons move easily in response to electrical field making metals good conductors of electricity.
- Free electrons can transmit kinetic energy easily making metals good conductors of heat.
- Low ionization energies
- Easily oxidized
- Malleable and ductile
- Shiny luster
Ionic Solids

• Ionic compounds pack themselves to minimize their $(-/\ -$ and $+/\ +$) repulsions and maximize their $(+/\ -$) attractions.
Network Covalent Solids

- **Diamonds**
  - Atoms are covalently bonded 4 times.
  - Very strong and hard.
  - High MP = 4400°C

- **Graphite**
  - Atoms are covalently bonded 3 times within the layer.
  - Layers are loosely bonded by overlapping, unhybridized p orbitals.
  - Slides off easily for pencils & lubricant.
  - Delocalized electrons
  - Conducts electricity
  - High MP = 4492°C
SiO$_2$ Network Covalent Solid

Network Solid
quartz

Amorphous Solid
glass
Network Covalent Solids

• Carbon, C
  » Diamonds
  » Graphite

• Silicon dioxide, SiO$_2$
  » Quartz
  » Glass

• Carborundum
  » SiC

• Silicon
  » Si
Molecular Solids

• Molecules held together by IMF’s
  » Dipole-dipole forces
  » London dispersion forces
  » Hydrogen “bonding”

• These forces are weaker than the previous three types of solids discussed.
  » Lower MP usually less than 200ºC
  » Often gases or liquids at room temp and often need to be cooled to become solid.
  » Heavier molecules can be solid at room temp.

• Properties depend on strength of IMF’s and ability to pack efficiently.
### Types of Crystalline Solids

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Form of Unit Particles</th>
<th>Forces Between Particles</th>
<th>Properties</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Atoms or molecules</td>
<td>London dispersion forces, dipole-dipole forces, hydrogen bonds</td>
<td>Fairly soft, low to moderately high melting point, poor thermal and electrical conduction</td>
<td>Argon, Ar; methane, CH₄; sucrose, C₁₂H₂₂O₁₁; Dry Ice™, CO₂</td>
</tr>
<tr>
<td>Covalent-network</td>
<td>Atoms connected in a network of covalent bonds</td>
<td>Covalent bonds</td>
<td>Very hard, very high melting point, often poor thermal and electrical conduction</td>
<td>Diamond, C; quartz, SiO₂ (aka silicon carbide, Carborundum)</td>
</tr>
<tr>
<td>Ionic</td>
<td>Positive and negative ions</td>
<td>Electrostatic attractions</td>
<td>Hard and brittle, high melting point, poor thermal and electrical conduction</td>
<td>Typical salts—for example, NaCl, Ca(NO₃)₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Atoms</td>
<td>Metallic bonds</td>
<td>Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile</td>
<td>All metallic elements—for example, Cu, Fe, Al, Pt</td>
</tr>
</tbody>
</table>

- Spend some time in your text, absorbing the information and examples on this table.
List the molecules in order of lowest to highest boiling temp?

1. \( A < B < C \)
2. \( C < B < A \)
3. \( B < C < A \)
4. \( A < C < B \)
5. \( B < A < C \)
6. \( C < A < B \)
List the molecules in order of lowest to highest boiling temp?

1. A < B < C
2. C < B < A
3. B < C < A
4. A < C < B
5. B < A < C
6. C < A < B
List the molecules in order of lowest to highest *melting* temp?

1. $A < B < C$
2. $C < B < A$
3. $B < C < A$
4. $A < C < B$
5. $B < A < C$
6. $C < A < B$
List the molecules in order of lowest to highest *melting* temp?

1. \( A < B < C \)
2. \( C < B < A \)
3. \( B < C < A \)
4. \( A < C < B \)
5. \( B < A < C \)
6. \( C < A < B \)
Molecular Solid Examples

- BP is affected by the IMF’s between molecules in the liquid phase.
- MP is affected by the IMF’s AND the efficiency of the packing ability.
- The H bonding in phenol trumps all and makes it hard to boil and hard to melt.
- Toluene’s dispersion forces are greater than benzene making it’s boiling point higher, but it’s “dangling” methyl group makes it awkward to pack, and thus easier to melt.
- Benzene’s dispersion forces are weakest making it have the lowest boiling point, but its very efficient packing makes it have a higher melting point than toluene.

<table>
<thead>
<tr>
<th></th>
<th>BP °C</th>
<th>MP °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>Toluene</td>
<td>111</td>
<td>-95</td>
</tr>
<tr>
<td>Phenol</td>
<td>182</td>
<td>43</td>
</tr>
</tbody>
</table>
Alloys

Mixtures of Metals
What’s so Ideal about the Ideal Gas Law?

\[ PV = nRT \]
The “Ideal” Gas Law

• Kinetic Molecular Theory is dependent upon a gas behaving as if the gas particles have NO IMFs.

• KMT also considers gases to be “point masses.” That is to say, the size of each atom is insignificant.

• The two statements above are true, the gases behave “ideally.”

• However, we know these two statements aren’t always perfectly true.
Graphing PV/RT at various pressures

• PV=nRT, thus for 1 mole of any gas, » PV/RT = 1
• The graph of PV/RT vs P for one mole of an ideal gas would be the dashed line.

![Graph showing PV/RT at ~300K](image-url)
Real Gases Deviate from the Ideal

• For one mole of the gases shown, the graph of $PV/nT$ vs $P$ actually looks like this.

![Graph showing real gases deviating from ideal gas behavior at ~300K](image)

- **N$_2$**
- **CH$_4$**
- **H$_2$**
- **CO$_2$**

At ~300K
The not so ideal “Ideal” Gas Law

• If $n$ is larger than 1, at a particular $P$, then $V$ must be bigger than it “should” be.

$$n = \frac{PV}{RT}$$

• If $n$ is smaller than 1, at a particular $P$, then $V$ must be smaller than it “should” be.

at $\sim 300K$
What would make V smaller?

- IMFs
- If below the line
- The V is smaller because the IMFs are playing a role.
- The darker molecule is “feeling the love” and thus not pushing as hard as it “ideally should” and causing less volume (if in a flexible container).
Some gases do exhibit IMFs

• Order the IMFs from weakest to strongest for:
  » N₂, CH₄, CO₂, H₂
  » All of these gases are nonpolar, thus which would have the weakest to strongest dispersion forces?
  » H₂ < N₂ < CH₄ < CO₂
Larger IMFs = Less Ideal

- Weaker < stronger IMFs
- $\text{H}_2 < \text{N}_2 < \text{CH}_4 < \text{CO}_2$
- The molecule with the smallest IMFs deviates least below the line.
- The deviation increases with increasing IMFs

at $\sim 300\text{K}$
What would make V larger?

• Usually molecules are far apart and their personal molecule size is irrelevant, however when “cramped” together, their personal size begins to matter.

• If above the line

• The volume of each individual molecule begins to matter and actually take up some space.
What would make V larger?

- At high pressures, PV/RT begins to deviate above the line because V is larger than the ideal, because the size of each individual molecule is taking up some space creating a larger than ideal volume.

![Diagram showing the deviation of PV/RT at high pressures](image.png)

At ~300K

Graph showing the deviation of PV/RT for different gases at high pressures.
Variations from the Ideal as a function of Temperature

- Why is the deviation below the line less of a factor at higher temps?
Variations from the Ideal as a function of Temperature

- At higher temperature, the IMFs play less of a role, because the faster moving molecules do not allow IMFs to occur.

![Graph showing variations in ideal gas behavior with temperature change for N₂.](image)
The van der Waals Equation
Predicting Real Gas Pressures

- \[ P = \frac{nRT}{V} \]

- \[ \left( P + \frac{n^2a}{V^2} \right)(V - nb) = nRT \]

*correction for volume of molecules*

*correction for IMFs*

• written this way in your text: \[ P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \]
correction for IMFs  
correction for volume of molecules

\[
\left( P + \frac{n^2 a}{V^2} \right)(V - nb) = nRT
\]

**TABLE 10.3 van der Waals Constants for Gas Molecules**

<table>
<thead>
<tr>
<th>Substance</th>
<th>( a ) (L(^2)-atm/mol(^2))</th>
<th>( b ) (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0341</td>
<td>0.02370</td>
</tr>
<tr>
<td>Ne</td>
<td>0.211</td>
<td>0.0171</td>
</tr>
<tr>
<td>Ar</td>
<td>1.34</td>
<td>0.0322</td>
</tr>
<tr>
<td>Kr</td>
<td>2.32</td>
<td>0.0398</td>
</tr>
<tr>
<td>Xe</td>
<td>4.19</td>
<td>0.0510</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.244</td>
<td>0.0266</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.39</td>
<td>0.0391</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.36</td>
<td>0.0318</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>6.49</td>
<td>0.0562</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>5.46</td>
<td>0.0305</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>2.25</td>
<td>0.0428</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>3.59</td>
<td>0.0427</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>20.4</td>
<td>0.1383</td>
</tr>
</tbody>
</table>
Surface Tension

- Adhesion
- Cohesion
- creates a meniscus

- only cohesion
- no adhesion
- reverse meniscus
Do you remember these terms? Ortho, Meta, Para

The End