READING

- We will discuss some of Chapter 5 that we skipped earlier (Van der Waals equation, pp. 145-8), but this is just a segue into intermolecular forces: Sections 8.4 and 8.5.
- We will probably skip all of sections 8.1 – 8.3 & 8.6.
- Next Week: THERMODYNAMICS (Chapter 9).
Evidence for Intermolecular Forces in Gases

- Deviations from ideal gas behavior in real gases:
  - effects of the volume of gas molecules
  - Effects of forces acting between the molecules.
- Still based on Coulomb forces (but cancelation effects lead to other labels for this)
- Much weaker than ionic or covalent chemical bonds
- Types we will consider:
  - dipole forces
  - dispersion forces
  - hydrogen bonding

Ideal Gases vs. Real Gases

- Most gases obey the ideal gas law under normal conditions ...
- but most substances are not gases under normal conditions
- Limitations on use of ideal gas model?
  - check assumptions of model
Assumptions in Ideal Gas Model

- Of various assumptions, the two most questionable are:
  - The molecules themselves occupy zero volume (i.e., point masses)
  - The molecules do not exert any attractive or repulsive forces upon each other

- When are these assumptions unreasonable?
  - High pressures and/or low temperatures

\[ PV = nRT \] — breaks down at high P.

\[ \text{Cl}_2 \text{ at } 298K \]  
\( (T_b = 239 \text{ K}) \)
Comparison of gases at 298K

\[
\frac{PV}{nRT} \text{ vs. } P \text{ at 200, 300, 600K.}
\]

(for F\(_2\))

\(T_b = 85 \text{ K}\)
Van der Waals Equation of State
(Don’t memorize; Do understand what the parameters mean)

First let’s write the ideal gas law in terms of molar volume

\[ PV_m = RT \quad \text{where} \quad \frac{V}{n} = V_m = \text{molar volume} \]

It’s helpful to use \( V_m \) if we want to focus on the behavior of the gas, without regard for how much gas there is. The Van der Waals equation of state in terms of molar volumes is

\[
\left( P + \frac{a}{V_m^2}\right) (V_m - b) = RT
\]

Rearranging, \[ P = \left( \frac{RT}{V_m - b}\right) - \frac{a}{V_m^2} \]
Van der Waals Equation of State
(Don’t memorize the derivation!)

\[ P = \left( \frac{RT}{V_m - b} \right) - \frac{a}{V_m^2} \]

Multiplying both sides by \( \frac{V_m}{RT} \) \( \Rightarrow \)

\[ \frac{PV_m}{RT} = 1 - \frac{b}{V_m} \left( \frac{a}{RT} \right) \]

We can use a power series in \( \frac{b}{V_m} \):

\[ 1 + \frac{b}{V_m} + \left( \frac{b}{V_m} \right)^2 + \cdots \]

Very small (neglect)

\[ \frac{PV_m}{RT} = 1 + \left( b - \frac{a}{RT} \right) \frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \cdots \]

Slope in plot of \( \frac{PV_m}{RT} \) vs \( \frac{1}{V_m} \)

see p. 146 in text
Molecule-scale info from non-ideality of gases

\[ \text{slope} = b - \frac{a}{RT} \]

Some Van der Waals Constants

<table>
<thead>
<tr>
<th>Gas</th>
<th>( a ) (atm L(^2) mol(^{-2}))</th>
<th>( b ) (L mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia, NH(_3)</td>
<td>4.170</td>
<td>0.03707</td>
</tr>
<tr>
<td>Argon, Ar</td>
<td>1.345</td>
<td>0.03219</td>
</tr>
<tr>
<td>Carbon dioxide, CO(_2)</td>
<td>3.592</td>
<td>0.04267</td>
</tr>
<tr>
<td>Helium, He</td>
<td>0.034</td>
<td>0.0237</td>
</tr>
<tr>
<td>Hydrogen, H(_2)</td>
<td>0.2444</td>
<td>0.02261</td>
</tr>
<tr>
<td>Hydrogen fluoride, HF</td>
<td>9.433</td>
<td>0.0739</td>
</tr>
<tr>
<td>Methane, CH(_4)</td>
<td>2.253</td>
<td>0.04278</td>
</tr>
<tr>
<td>Nitrogen, N(_2)</td>
<td>1.390</td>
<td>0.03913</td>
</tr>
<tr>
<td>Oxygen, O(_2)</td>
<td>1.360</td>
<td>0.03183</td>
</tr>
<tr>
<td>Sulfur dioxide, SO(_2)</td>
<td>6.714</td>
<td>0.05636</td>
</tr>
<tr>
<td>Water, H(_2)(_2)</td>
<td>5.464</td>
<td>0.03049</td>
</tr>
</tbody>
</table>

Scale with magnitude of intermolecular forces

Scale with size of molecules
Ion-Ion Forces

- The potential energy, $E_{\text{ion-ion}}$, of ion-ion interactions (giving rise to Coulomb forces), has the longest range of forces that affect chemistry.

$$E_{\text{ion-ion}} \propto \frac{q_1 q_2}{r_{12}}$$

- These strong, long-range forces are responsible for ionic bonds.

Ion-Dipole Forces

- Because “both ends” of a dipole interact with a nearby ion, there is a lot of cancellation of the net Coulomb $E_{\text{ion-ion}}$ of ion-ion interactions.

$$E_{\text{ion-dipole}} \propto \frac{|q_{\text{ion}}|\mu_{\text{dipole}}}{r^2}$$

- These are weaker, but still one of the strongest of intermolecular forces.
Dipole-Dipole Forces

Here, “both ends” of both dipoles interact with each other via Coulomb interactions.

\[ E_{\text{dipole-dipole}} \propto -\frac{(\mu_{\text{dipole}})^2}{r^3} \]

Weaker still, but still stronger than the case when molecules have no dipole moment.

\[ E_{\text{dip-dip (ave, gas)}} \propto -\frac{\mu_1^2 \mu_2^2}{r^6} \]

In a collection of dipoles, oppositely charged ends of the dipoles will attract each other. Similarly charged ends will repel.

These forces will cause dipoles to line up with one another and “stick together.”

\[ + \quad - \]
\[ \text{or} \]
\[ + \quad - \quad + \quad - \]
Dispersion Forces

- Non-polar molecules also form condensed phases. H₂ is a liquid below 20 K, and He is a liquid below 4.2 K (at 1 atm pressure)
- Forces?
- "Dispersion forces" due to induced dipoles
- Arise because electrons are not static
- Present in all molecules

Transient Dipoles - H₂ example

- H₂ molecule: average e⁻ density is symmetric
- But at any given instant, the 2 e⁻’s may both be on the same “end” of the molecule, creating a transient dipole.
- The transient dipole in one molecule will influence other molecules, so that the induced dipoles will “line up” just like “real” or permanent dipoles.
Transient Dipoles - H₂ example

H₂, one e⁻ on each end  H₂, both e⁻’s on same end, producing temporary dipole

Transient dipole sets up similar dipoles in nearby molecules, and molecules line up to maximize attractive forces.

Strength of Intermolecular Forces

- Strength of forces between molecules determines physical state (solid, liq., gas)
- Strength of dispersion forces increases as molecules become larger; **scale with the “surface area” of each molecule involved**
  - more e⁻’s in larger, more “deformable” orbitals
    → more “polarizable”
- Stronger intermolecular forces lead to higher melting & boiling points.
Distance dependence of Intermolecular Potential energies

\[ \begin{align*}
V_{\text{Coulomb}}(r) & \sim \frac{1}{r} \quad \text{Ionic bonds} \\
V_{\text{ion-dipole}}(r) & \sim \frac{1}{r^2} \quad \text{Solvation of ions in solution} \\
V_{\text{dipole-dipole}}(r) & \sim \frac{1}{r^3} \quad \text{Intermolecular forces in polar compounds} \\
V_{\text{dispersion}}(r) & \sim \frac{1}{r^6} \quad \text{Intermolecular forces in non-polar compounds}
\end{align*} \]

Comparison of alkane b.p.s

<table>
<thead>
<tr>
<th>(n)-alkane</th>
<th>boiling points</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>-161.6 °C</td>
</tr>
<tr>
<td>CH(_3)CH(_3)</td>
<td>-89 °C</td>
</tr>
<tr>
<td>CH(_3)CH(_2)CH(_3)</td>
<td>-42.1 °C</td>
</tr>
<tr>
<td>CH(_3)(CH(_2))(_2)CH(_3)</td>
<td>-0.5 °C</td>
</tr>
<tr>
<td>CH(_3)(CH(_2))(_3)CH(_3)</td>
<td>36.1 °C</td>
</tr>
<tr>
<td>CH(_3)(CH(_2))(_4)CH(_3)</td>
<td>69 °C</td>
</tr>
</tbody>
</table>
F₂ vs. I₂: Polarizability Differences

Intermolecular forces & physical state

V-d-W constants

F₂: \( a = 1.154 \text{ atm-L}^2\text{-mol}^{-2}, \ b = 0.02896 \text{ L-mol}^{-1} \)

Br₂: \( a = 9.61 \text{ atm-L}^2\text{-mol}^{-2}, \ b = 0.0591 \text{ L-mol}^{-1} \)
Comparison of Halogen b.p.s

<table>
<thead>
<tr>
<th></th>
<th>boiling points</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>-188 °C</td>
<td>greenish gas</td>
</tr>
<tr>
<td>Cl₂</td>
<td>-34 °C</td>
<td>yellow-green gas</td>
</tr>
<tr>
<td>Br₂</td>
<td>59 °C</td>
<td>blood-red liquid</td>
</tr>
<tr>
<td>I₂</td>
<td>185 °C</td>
<td>purple solid</td>
</tr>
</tbody>
</table>

Iodine Sublimation
Strength of Intermolecular Forces

- Big, polarizable molecules tend to have high boiling points.
- Polar molecules tend to have higher boiling points than non-polar molecules with similar size & shape.

Polar Molecules

- Many molecules have a dipole moment due to polarity of bonds & shape of molecule
- The strength of intermolecular forces between polar molecules will be influenced by dipolar forces.
- Examples for dipole moments: 
  HF vs. BeF_2 vs. BF_3 vs. CH_2F_2 vs. CF_4
Dipole Moments (see Sec. 8.4)

- Both polarity of bonds and molecular shape (symmetry) are important
- Polar molecules tend to have higher boiling points than non-polar molecules with similar size & shape:

- Dipole-dipole interactions hold polar molecules together more strongly than non-polar molecules with similar size & shape:
Effect of Molecular Shape & Symmetry

Which compound has the highest boiling point?

\[
\text{CH}_3-\text{C≡N}: \quad \overset{\cdot}{\text{O}}=\text{C}=\overset{\cdot}{\text{O}}
\]

acetonitrile \hspace{1cm} 

\[
\text{carbon dioxide}
\]

b.p. 82 °C \hspace{1cm} \text{sublimes @ -78 °C}

(no liquid at 1 atm.)
Hydrogen Bonding

- Special case of dipole-dipole interaction
- Occurs only in molecules containing H bound to a very electronegative atom (F, O, or N)
- Stronger than usual due to small size of H-atom (more concentrated positive charge)
- H “end” of one molecule is attracted to the electronegative “end” of another molecule

Examples of Hydrogen Bonds

- Hydrogen fluoride
- Ammonia-water
- Water-ethanol
- Formic acid
1-propanol; H-bonding

H-bonded “base pair” in DNA

Thymine

Adenine
Another DNA “base pair”

Cytosine  Guanine

definition

Schematic DNA Construction
Hydrogen bonds and water

- H-bonds give water some special properties:
  - high melting & boiling points, essential for our existence
  - structure of ice is very “open” and very stable
  - density of water increases slightly on melting, so ice floats

- H-bonds also important in structure of biomolecules like proteins, DNA, ...

Hydrogen bonding in Ice

Ice has a very “open” diamond-like structure. In liquid H₂O collapse occurs when a few H-bonds break. Liquid H₂O is therefore denser than ice.
Boiling Points of Simple Hydrogen-Containing Compounds

\( \text{H}_2\text{O}, \text{HF and NH}_3 \text{ have unusually high b.p.s despite their “top-row” status...} \)

This is a result of hydrogen bonding!