Liquids

Intermolecular Interactions

Real gases vs. ideal gases:

1. High pressure $\rightarrow$ high density $\rightarrow$ stronger interactions.

2. Low temperature $\rightarrow$ slower speeds $\rightarrow$ weak interactions become more important.

Dipole-Dipole Interactions

An ideal dipole is a matched, separated pair of positive and negative charges.

The overall interaction can be attractive or repulsive.
Dipole-dipole interactions are *weak* and *short-range*, relative to ion-ion interactions. This is because

While charge-charge interactions go as

\[ E_{c-c} \propto -\frac{1}{R} \]

dipole-dipole interactions in disordered systems go as

\[ E_{d-d} \propto -\frac{1}{R^6} \]

**London Dispersion Forces**

Molecules without dipole moments also have attractive interactions due to *instantaneous dipoles*.

The ease of inducing a dipole *also* scales with the polarizability of the atom or molecule. This dipole-dipole interaction is the London
dispersion force, and also goes as

\[ E_{\text{London}} \propto \frac{1}{R^6} \]

An alternate way to think about the London force is to say that when we bring two non-polar molecules close together, the electrons on each find a way to rearrange slightly to lower the energy of the system.

**Boiling Points**

Predict trends in boiling points by gauging the strength of intermolecular interactions.

1. Estimate magnitude of molecular dipoles (from electronegativity.)

2. Estimate polarizability (from size.)

**Hydrogen Bonds**

Molecules with H atoms bound to electronegative atoms—O, F, and N, and sometimes S and Cl—can interact via *hydrogen bonding*. This is most important in water.
Hydrogen bonding is short-range (like covalent bonds) and is typically on the order of 10–50 times weaker than a covalent bond; this is still substantially stronger than a dipole-dipole interaction. Hydrogen bonding leads to big excursions from periodic trends for H$_2$O, HF, and NH$_3$:

**Equilibrium Vapor Pressure**

In a *closed* container with no partial pressure of the compound:

Evaporation will occur with no condensation to balance it. This will increase the partial pressure, which, in turn, increases the condensation rate. Eventually, the partial pressure increases to the point where the evaporation and condensation rates are the same, and an equilibrium—the *equilibrium vapor pressure*—is reached.
Because the evaporation rate depends so strongly on temperature, so does the equilibrium vapor pressure.

At the point where the equilibrium vapor pressure meets the atmospheric pressure, we get the normal boiling point for the liquid.

The vapor pressure rises exponentially with temperature; that is,

\[ P \propto e^{-C/T} \]

It’s more common to deal with this as a logarithmic expression, where it is called the Clausius-Clapeyron equation:

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

Here,

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

is the heat of vaporization: the energy required for a molecule (or mole) to break the intermolecular attractions and escape into the gas phase. It is common to use the Clausius-Clapeyron equation in ratio form:

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

The normal boiling point of water is 100 °C, or 373.15 K, and

\( \Delta H_{\text{vap}} = 40.7 \text{ kJ mol}^{-1} \)

At the normal boiling point, the partial pressure equals the atmospheric pressure, so we have

\[ T_1 = 373.14 \text{ K} \]

\[ P_1 = 1 \text{ atm} \]

\[ \Delta H_{\text{vap}} = 40.7 \text{ kJ mol}^{-1} \]
We can now calculate the partial pressure at $T_2 = 298.15$ K (25 °C or 77 °F).

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

\[
\ln \frac{P_2}{1 \text{ atm}} = -\frac{40.7 \text{ kJ mole}^{-1}}{8.314 \text{ J mole}^{-1} \text{ K}^{-1}} \left( \frac{1}{298.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right)
\]

\[
= -3.300
\]

\[
\frac{P_2}{1 \text{ atm}} = 0.03688
\]

\[
\frac{P_2}{P_2} = 0.03688 \text{ atm}
\]

That is, at 100% relative humidity, the air holds 3.7% water. Note a few things about units:

1. You will never take the log or exponent (or sine or cosine) of something with units; $e^{298K}$ is simply not meaningful.

2. All units must and do cancel in the argument of the natural log in the C-C equation—note that you can use any pressure units you wish, as long as you are consistent.

3. All units must and do cancel on the right-hand side of the equation.
Changes of State

Commonly used names:

<table>
<thead>
<tr>
<th>State</th>
<th>Process</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>vaporization</td>
<td>gas</td>
</tr>
<tr>
<td>solid</td>
<td>fusion</td>
<td>liquid</td>
</tr>
<tr>
<td>solid</td>
<td>sublimation</td>
<td>gas</td>
</tr>
</tbody>
</table>

and for the reverse processes:

<table>
<thead>
<tr>
<th>State</th>
<th>Process</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>condensation</td>
<td>gas</td>
</tr>
<tr>
<td>solid</td>
<td>freezing</td>
<td>liquid</td>
</tr>
<tr>
<td>solid</td>
<td>deposition</td>
<td>gas</td>
</tr>
</tbody>
</table>

Phase Diagrams

For any given material, we can draw a phase diagram that shows us how the state of the material depends on the temperature and pressure.
You can reason out the placement of your phases like so:

**solids** form at low temperatures and at high pressures,

**gases** form at high temperatures and low pressures, and

**liquids** form at low temperatures and high pressures.

At constant pressure, the solid is present at low temperature, followed by melting to form the liquid and evaporation to form the gas.
A typical phase diagram will include:

- Solid, liquid, and gas phases.
- The normal melting and boiling points.
- The triple point.
- The critical point.
- The sublimation line.
- The fusion line.
- The evaporation line.
- The critical point.