CHAPTER 10.1
INTERMOLECULAR FORCES

https://www.youtube.com/watch?v=08kGgrqZXA
<table>
<thead>
<tr>
<th>Force</th>
<th>Model</th>
<th>Basis of Attraction</th>
<th>Energy (kJ/mol)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td><img src="image" alt="Ionic Model" /></td>
<td>Cation–anion</td>
<td>400–4000</td>
<td>NaCl</td>
</tr>
<tr>
<td>Covalent</td>
<td><img src="image" alt="Covalent Model" /></td>
<td>Nuclei–shared e− pair</td>
<td>150–1100</td>
<td>H–H</td>
</tr>
<tr>
<td>Metallic</td>
<td><img src="image" alt="Metallic Model" /></td>
<td>Cations–delocalized electrons</td>
<td>75–1000</td>
<td>Fe</td>
</tr>
</tbody>
</table>
## Variations in Covalent Intermolecular Bonds

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Value</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonbonding (Intermolecular)</td>
<td>Ion-dipole</td>
<td>40–600</td>
<td>Na⁺⋯⋯O⁻⁻⁻</td>
</tr>
<tr>
<td></td>
<td>Polar bond to H–dipole charge (high EN of N, O, F)</td>
<td>10–40</td>
<td>O⁻⁻⁻⋯⋯H⋯⋯O⁻⁻⁻</td>
</tr>
<tr>
<td></td>
<td>Dipole-dipole</td>
<td>5–25</td>
<td>I–Cl⋯⋯I–Cl</td>
</tr>
<tr>
<td></td>
<td>Ion–induced dipole</td>
<td>3–15</td>
<td>Fe²⁺⋯⋯O₂</td>
</tr>
<tr>
<td></td>
<td>Dipole–induced dipole</td>
<td>2–10</td>
<td>H–Cl⋯⋯Cl⋯⋯Cl–Cl</td>
</tr>
<tr>
<td></td>
<td>Dispersion (London)</td>
<td>0.05–40</td>
<td>F–F⋯⋯F–F</td>
</tr>
</tbody>
</table>
ION-DIPOLE INTERACTIONS

• The attraction between the ions and the dipole of the water is greater than the attraction between oppositely charged ions.
• This allows ionic substances to be dissolved in polar solvents.
THE HYDROGEN BOND

• Hydrogen bonds are a dipole-dipole intermolecular force.

• Hydrogen bonds can occur when a H atom in a molecule is bound to a small, highly electronegative atom, with lone pairs of electrons.

• The H from one of these molecules is attracted to the lone pairs of the electronegative atom on another molecule.

• Typically formed with H bond to N, O or F.
HYDROGEN BONDS IN WATER

- Hydrogen bond donor
- Hydrogen bond acceptor
QUESTION

Which of the following compounds forms intermolecular hydrogen bonds?

Answer:

CH₄  A
CH₃CH₂SH  B
CH₃CH₂OH  C
PH₃  D
HYDROGEN BONDING & BOILING POINT

• Boiling points increase with the mass of the substance.
• Without hydrogen bonding water would boil at about -80°C.
• Strong H bonding necessitates more energy to separate the molecules in order to form a gas.
POLAR MOLECULES & DIPOLE-DIPOLE FORCES

Molecules that are polar, but do not necessarily form hydrogen bonds (e.g. CH$_2$Cl$_2$), are able to influence each other when in liquid or solid form.
POLARIZABILITY & CHARGE-INDUCED DIPOLE FORCES

- Polarizability increases down a group.
  - The larger electron clouds, further from the nucleus are easier to polarize.

- Polarizability decreases left to right across a period.
  - Increased Zeff results in smaller electron clouds.

- Cations are less polarizable than their parent atom.

- Anions are more polarizable than their parent atom.
DISPERSION FORCES AMONG NONPOLAR MOLECULES

- Nonpolar compounds can gain temporary polarity as their electrons move.

- This polarity can influence the polarity of other compounds when they are close to each other.

- Dispersion (London) forces are important in the attraction of all substances.
The structure of a molecule will influence the forces that act upon it. Two different forms of $\text{C}_5\text{H}_{12}$ have different extents of dispersion forces, thus different boiling points.
MOLECULAR MASS & BOILING POINT

- Increased molecular mass correlates with an increase in the number of electrons.

- A larger number of electrons allows for greater polarizability.

- Heavier atoms, or molecules with more atoms, have greater dispersion forces and higher boiling points.
Based off the principles of intermolecular forces, which of the following will have a higher boiling point?

(a) He  (b) Ne  (c) Ar  (d) Kr  (e) Xe

Answer: E
SUMMARY OF INTERMOLECULAR FORCES

INTERACTING PARTICLES
(atoms, molecules, ions)

Ions present:
- Ions only: IONIC BONDING (Section 9.2)
- Ions + polar molecules: ION-DIPOLE FORCES

Ions not present:
- Polar molecules only: DIPOLE-DIPOLE FORCES
- H bonded to N, O, or F
- Polar + nonpolar molecules: DIPOLE-INDUCED DIPOLE FORCES
- Nonpolar molecules only: DISPERSION FORCES only

DISPERSION FORCES ALSO PRESENT
NON-COVALENT INTERACTIONS IN PROTEINS

Ionic bonding
Hydrogen bonding
Dispersion forces

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QUESTION

Rank the compounds below in order of increasing melting points (1=highest). Also determine the dominant intermolecular force for each compound in a pure solution.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rank (1=highest)</th>
<th>Intermolecular force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1</td>
<td>Ionic</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>4</td>
<td>Dispersion</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>3</td>
<td>Hydrogen bonding</td>
</tr>
<tr>
<td>NaI</td>
<td>2</td>
<td>Ionic</td>
</tr>
</tbody>
</table>
QUESTION

In which series below are the compounds listed in order of increasing melting point?

Answer:

A

Na$_2$O < NaI < C$_2$H$_5$OH < C$_3$H$_8$

B

C$_3$H$_8$ < C$_2$H$_5$OH < NaI < Na$_2$O

C

NaI < Na$_2$O < C$_3$H$_8$ < C$_2$H$_5$OH

D

C$_2$H$_5$OH < C$_3$H$_8$ < Na$_2$O < NaI
LECTURE OBJECTIVES

• Chapter 10.2
  - Distinguish between adhesive and cohesive forces.
  - Define viscosity, surface tension, and capillary rise.
  - Describe the roles of intermolecular forces in the above properties/phenomena.

• Chapter 10.3
  - Define phase transitions and phase transition temperatures.
  - Explain the relation between phase transition temperatures and intermolecular attractive forces.
  - Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes.
PROPERTIES OF THE LIQUID STATE

- Surface tension
- Capillarity
- Viscosity
THE MOLECULAR BASIS OF SURFACE TENSION

• For a liquid, the surface molecules interact with fewer molecules than those “inside” the liquid.

• Surface molecules have net a downward attraction due to the intermolecular forces.

• Pushing into the liquid increases the total surface area, requiring energy to disrupt more of the attractive forces.
## SURFACE TENSION & INTERMOLECULAR FORCES

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Surface tension (J/m²) at 20°C</th>
<th>Major force(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl ether</td>
<td>(CH₃CH₂)₂O</td>
<td>$1.7 \times 10^{-2}$</td>
<td>dipole-dipole: dispersion</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>$2.3 \times 10^{-2}$</td>
<td>H bonding</td>
</tr>
<tr>
<td>Butanol</td>
<td>CH₃(CH₂)₃OH</td>
<td>$2.5 \times 10^{-2}$</td>
<td>H bonding; dispersion</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>$7.3 \times 10^{-2}$</td>
<td>H bonding</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>$48 \times 10^{-2}$</td>
<td>Metallic bonding</td>
</tr>
</tbody>
</table>
Based off the principles of intermolecular forces, which of the following liquids will have a higher surface tension?

(a) Hg
(b) H₂O
(c) CH₃CH₂OCH₂CH₃
(d) CH₃CH₂OH
(e) CH₃CH₂CH₂OH
CAPILLARY ACTION

• The meniscus (top layer) of water in a thin tube is curved downward, whereas the meniscus for mercury is curved upwards.

• Water can hydrogen bond (adhesive force) with the glass (SiO₂) and forming these bonds pulls some water up the glass walls.

• Hg forms metallic bonds which are much stronger than any dispersive forces with SiO₂. The Hg pulls away from the glass surface and tries to form as many metallic bonds (cohesive force) as possible.
VISCOSITY

• The viscosity of a solution is related to how easily the molecules in the liquid can move past each other.

• Higher temperatures increase molecular velocity, making it easier to overcome the attractive forces.

• The shape of the molecules also influence the viscosity: small spherical molecules do not interact strongly with each other (e.g. CCl\textsubscript{4}), larger molecules interact more strongly with each other, restricting their movement.
QUESTION

Which of the following liquids would you expect to have the lowest surface tension?

Answer:

A  Pb
B  CH₃OCH₃
C  HOCH₂CH₂OH
D  H₂O
E  CH₃CH₂OH
VAPORIZATION & CONDENSATION

• A liquid in a sealed container can vaporize - with some of the liquid becoming a gas.

• The gas molecules moving around in the container may occasionally collide with the liquid - returning to the liquid phase (condensation).

• When vaporization and condensation are in equilibrium (at a given temperature) the pressure of the gas is termed the vapor pressure for the substance.

Example 10.5 Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:

Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although the size of this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid - returning to the liquid phase - with some of the liquid becoming a gas.

When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue. When vaporization and condensation are in equilibrium (at a given temperature) the pressure of the gas is termed the vapor pressure for the substance.
VAPOR PRESSURE

- **Vapor pressures vary** from substance to substance, based on the **intermolecular forces** of the substance.

- The stronger the intermolecular forces, the **harder it is to get a molecule into the gas phase** at a given temperature.

- At the same temperature, different substances will have different boiling points.
In order to for molecules of a liquid to enter the gas phase they must overcome the intermolecular forces of the liquid.

- The intermolecular forces stick individual molecules to each other.
- Increasing temperature gives the molecules more kinetic energy and more molecules can overcome the intermolecular forces.

Vaporization of a liquid is faster at higher temperatures.
• The **boiling point** of a liquid occurs when the **vapor pressure** of the liquid is equal to the external pressure (atmospheric) around it.

• Changing the pressure around the liquid changes the boiling point (i.e. mountain top versus sea level)

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**Figure 10.24**

The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

**Example 10.6**

**A Boiling Point at Reduced Pressure**

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure 10.24 to determine the boiling point of water at this elevation.

**Solution**

The graph of the vapor pressure of water versus temperature in Figure 10.24 indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

**Check Your Learning**

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure 10.24 to determine the approximate atmospheric pressure at the camp.

**Answer:** Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the **Clausius-Clapeyron equation**:

\[
\frac{1}{T} = \frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_0} + \frac{1}{T_0} \ln \left( \frac{p}{p_0} \right)
\]

where \( \Delta H_{\text{vap}} \) is the enthalpy of vaporization for the liquid, \( R \) is the gas constant, and \( \ln A \) is a constant whose value depends on the chemical identity of the substance. This equation is often rearranged into logarithmic form to yield the linear equation:

\[
\ln \left( \frac{p}{p_0} \right) = \ln A - \frac{\Delta H_{\text{vap}}}{RT}
\]
CLAUSIUS-CLAPEYRON EQUATION

• There is a direct relationship between the a substance's vapor pressure and the temperature, described by the Clausius-Clapeyron equation.

• By measuring the pressure of substance at two different temperatures we can determine the enthalpy of vaporization ($\Delta H_{vap}$) of the substance.

• $\Delta H_{vap}$ is the amount of energy needed to convert a mole of the liquid to a gas.