Chapter 11. Intermolecular Forces & Properties of Liquids

NOTE – THIS CHAPTER IS ONE OF THE TOP TOPICS ON AP EXAM!!!
NOT ONLY DO YOU NEED TO FOCUS ON THEORY (NO MATH IN THIS TOPIC) BUT YOU MUST READ THE FIGURES TOO!!!

Watch Bozeman Videos & other videos on my website for additional help:
Big Idea 2
“Solids & Liquids”
“London Dispersion Forces”
“Dipole Forces”
“Intermolecular Forces”

Unit 3.3
SAP-6.A Represent the differences between solid, liquid, and gas phases using a particulate-level model.

SAP-6.A.1 Solids can be crystalline, where the particles are arranged in a regular three-dimensional structure, or they can be amorphous, where the particles do not have a regular, orderly arrangement. In both cases, the motion of the individual particles is limited, and the particles do not undergo overall translation with respect to each other. The structure of the solid is influenced by interparticle interactions and the ability of the particles to pack together.

SAP-6.A.2 The constituent particles in liquids are in close contact with each other, and they are continually moving and colliding. The arrangement and movement of particles are influenced by the nature and strength of the forces (e.g., polarity, hydrogen bonding, and temperature) between the particles.

SAP-6.A.3 The solid and liquid phases for a particular substance typically have similar molar volume because, in both phases, the constituent particles are in close contact at all times.

SAP-6.A.4 In the gas phase, the particles are in constant motion. Their frequencies of collision and the average spacing between them are dependent on temperature, pressure, and volume. Because of this constant motion, and minimal effects of forces between particles, a gas has neither a definite volume nor a definite shape.

Ch 10 focused on Gases
Ch 11 & 12 will focus on the Condensed States – Liquids and Solids.
### 11.1 A Molecular Comparison of Gases, Liquids and Solids

**Read p. 444-446**

<table>
<thead>
<tr>
<th></th>
<th>Ch 12</th>
<th>Ch 11</th>
<th>Ch 10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape</strong></td>
<td>Definite</td>
<td>Takes the shape of the container</td>
<td>Not Definite</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>Definite</td>
<td>Definite</td>
<td>Not Definite – will expand to fill the entire container</td>
</tr>
<tr>
<td><strong>Spacing</strong></td>
<td>Particles are VERY close to each other.</td>
<td>Particles are close to each other.</td>
<td>Particles are very far apart from each other.</td>
</tr>
<tr>
<td><strong>Movement of Particles</strong></td>
<td>Only vibration in bonds Diffusion - Does not flow</td>
<td>Constantly moving and sliding past each other. Diffusion - slow</td>
<td>Constantly moving and colliding Diffusion - fast</td>
</tr>
<tr>
<td><strong>Type of mixtures formed</strong></td>
<td>heterogeneous</td>
<td>Homogeneous or heterogeneous (depends on polarity)</td>
<td>Homogeneous</td>
</tr>
<tr>
<td><strong>Compressible</strong></td>
<td>Not compressible</td>
<td>Not compressible</td>
<td>COMPRESSIBLE – large amount of empty space between the particles When pressure is applied to a gas, its volume decreases (Boyle’s Law).</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>Density – usually high densities (sink in water) Density units – g/cm³</td>
<td>Density – usually low densities (sink or float in water) Density units – g/mL</td>
<td>Density – usually low densities Density units – g/L</td>
</tr>
<tr>
<td><strong>Properties/IMFs</strong></td>
<td>Motion of particles is limited to vibration within <strong>crystalline</strong> structure</td>
<td>Properties (BP, VP, viscosity, surface tension) are related to IMFs</td>
<td>Minimal to no IMFs Can be described in terms of amount of gas (moles, pressure, volume, and temperature).</td>
</tr>
</tbody>
</table>
But first you need to understand the BIG difference between **INTRAMOLECULAR vs INTERMOLECULAR** forces.

- We know that molecules of a liquid or solid are composed of atoms held together by “**INTRA**molecular forces” called bonds (Ionic, Covalent, Metallic).
- But individual molecules are aggregated together in a large sample (i.e.: glass of water – millions of water molecules) by attractive forces called “**INTER**molecular forces”.
- So…. **INTRA**molecular forces are the forces that keep the atoms connected in the molecule And **INTER**molecular forces are the forces that hold one molecule attracted to another molecule. See the difference?

**Question:** When a (covalent) molecular substance is heated and undergoes a phase change from a liquid to a gas, what type of attractive forces are broken?

For example, let’s say you have liquid water (left beaker), and you add heat. Do the water molecules break up into hydrogen and oxygen atoms? NOOOOOO!!!!

It’s a **PHASE CHANGE**! Boiling water does NOT break covalent bonds!

Remember Ch 4: A physical change occurs when a substance undergoes a change in properties, but not a change in composition.

You are breaking the water molecules apart from EACH OTHER. **But it’s still water molecules!**

\[
\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}
\]

Converting a gas into a liquid or solid requires the molecules to get closer to each other.

- We can accomplish this by cooling (changing T) or compressing the gas (changing V). Converting a solid into a liquid or gas requires the molecules to move further apart.
- We can accomplish this by heating (changing T) or reducing the pressure on the solid.
So when a (covalent) molecular substance is heated and undergoes a phase change (like how water changes from liquid to gas), what type of attractive forces are broken?

**INTRAmolecular Forces**
the attractive forces that exist **WITHIN** A MOLECULE
[STRONG - particles are relatively close together]

**INTERmolecular (or Interparticle) Forces**
the attractive forces that exist **BETWEEN** MOLECULES (or particles)
[WEAK - particles are relatively far apart]

- Figure 11.3 is a great explanation and visual of intramolecular vs intermolecular forces

**FYI:**
Ch 8 & 9 will deal more with INTRAmolecular forces
Ch 11 deals with INTERmolecular forces (IMFs)
Substances #1 and #2 represent two different elements located in Group 18 (noble gases).

Which substance, #1 or #2, has stronger attractive forces between particles? How can you tell?

What do we know: The elements are changing from a liquid to gas (boiling) and boiling requires energy (heat) to convert the state of matter change.

So...The stronger the attractive forces between the particles, the more energy is requiring to overcome these forces as the substances change from a liquid into a gas!

Substance #2 has stronger attractive forces between the particles. Higher boiling point would be stronger attractive forces.

Substance #1 was Ar and substance #2 was Xe.
- Both noble gases and each substance is composed of individual atoms.
- Both noble gases have different number of electrons...Hint!
- Each substance is classified as nonpolar.
- Since the liquid state does exist for these substances, there must be some attractive forces between the particles that cause the gas to condense into a liquid.
## Unit 3.1

**SAP-5.A** Explain the relationship between the chemical structures of molecules and the relative strength of their intermolecular forces when:

- **a.** The molecules are of the same chemical species.
- **b.** The molecules are of two different chemical species.

<table>
<thead>
<tr>
<th>Learning Objective</th>
<th>Essential Knowledge</th>
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</table>
| **SAP-5.A.1**       | London dispersion forces are a result of the Coulombic interactions between temporary, fluctuating dipoles. London dispersion forces are often the strongest net intermolecular force between large molecules.  
  a. Dispersion forces increase with increasing contact area between molecules and with increasing polarizability of the molecules.  
  b. The polarizability of a molecule increases with an increasing number of electrons in the molecule; and the size of the electron cloud. It is enhanced by the presence of pi bonding.  
  c. The term “London dispersion forces” should not be used synonymously with the term “van der Waals forces.” |
| **SAP-5.A.2**       | The dipole moment of a polar molecule leads to additional interactions with other chemical species.  
  a. Dipole-induced dipole interactions are present between a polar and nonpolar molecule. These forces are always attractive. The strength of these forces increases with the magnitude of the dipole of the polar molecule and with the polarizability of the nonpolar molecule.  
  b. Dipole-dipole interactions are present between polar molecules. The interaction strength depends on the magnitudes of the dipoles and their relative orientation. Interactions between polar molecules are typically greater than those between nonpolar molecules of comparable size because these interactions act in addition to London dispersion forces.  
  c. Ion-dipole forces of attraction are present between ions and polar molecules. These tend to be stronger than dipole- dipole forces. |
| **SAP-5.A.3**       | The relative strength and orientation dependence of dipole-dipole and ion-dipole forces can be understood qualitatively by considering the sign of the partial charges responsible for the molecular dipole moment, and how these partial charges interact with an ion or with an adjacent dipole. |
| **SAP-5.A.4**       | Hydrogen bonding is a strong type of intermolecular interaction that exists when hydrogen atoms covalently bonded to the highly electronegative atoms (N, O, and F) are attracted to the negative end of a dipole formed by the electronegative atom (N, O, and F) in a different molecule, or a different part of the same molecule. |
| **SAP-5.A.5**       | In large biomolecules, noncovalent interactions may occur between different molecules or between different regions of the same large biomolecule. |
Now it is time to consider the forces that condense matter (to form liquids or solids). The forces that hold one molecule to another molecule are referred to as intermolecular forces (IMFs). These forces arise from unequal distribution of the electrons in the molecule and the electrostatic attraction between oppositely charged portions of molecules. We briefly visited the IMFs earlier when discussing the nonideal behavior of gases. These forces cause changes of state by causing changes among the molecules, NOT within them.

Intermolecular forces are much weaker than ionic or covalent bonds (Intramolecular forces).

- For example, boiling H$_2$O causes individual H$_2$O molecules to:
  \[ \text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)} \]
  Heat supplies enough energy to break IMFs holding H$_2$O (l) molecules together, but the bonds (H-O-H….. intramolecular forces) are NOT broken.

- When a substance melts (s→l) or boils (l→g), intermolecular forces are BROKEN.
- When a substances condenses (g→l) or freezes (l→s), intermolecular forces are FORMED.

Van der Waals forces (3 TYPES) are the intermolecular forces that exist between neutral molecules.

1. London-dispersion forces
2. Dipole-dipole forces
3. Hydrogen-bonding forces.

**London-Dispersion Forces (LDF)**

London Dispersion forces - interactions between particles or molecules as a result of temporary or instantaneous dipoles. These are created as a result of the distortion of the electron cloud. They occur because of the continuous motion of electrons.

This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion, at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 10.6.
These are the **WEAKEST** of all intermolecular forces.

**London-dispersion forces exist between ALL MOLECULES!!**

- However, this force is particularly important in interactions of NONPOLAR molecules and NOBLE GAS ATOMS because it is the only attractive force available to them.
- Every C-H molecules have LDF!!!!

**What affects the strength of a dispersion force?**

1. Molecules must be **very close together** for these attractive forces to occur.

- For example in the gas phase, these particles do not experience any attractive forces in between the particles.
- But what happens as the temperature of this sample is decreased?
- The particles begin to experience attractive forces.
2. London-dispersion forces depend on the shape of the molecule.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the ISOMERS (SAME FORMULA, DIFFERENT WAY TO CONNECT ATOMS) $n$-pentane, isopentane, and neopentane (shown in Figure 10.7) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, $C_5H_{12}$, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for $n$-pentane and least for neopentane.

The elongated shape of $n$-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces.

![Diagram](image.png)

**Figure 10.7** The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

SO…..Between two nonpolar molecules of similar mass, the more extended molecule will have the higher boiling point (more extended = more surface area for London dispersion interaction).
3. **Polarizability:** is the ease with which the charge distribution in an electron distribution can be distorted.

**Trend:**
- The larger the molecule, the greater the LDF.
  - **WHY?**...large molecules have a greater number of electrons, making it more polarizable (easier for an uneven electron distribution to occur)
  - **AP Tip for Answering:** Larger the atom/molecule, the larger the electron cloud, thus more polarizable and greater/stronger dispersion forces

**ON THE AP EXAM, DO NOT WRITE THAT A MOLECULE HAS STRONGER LONDON DISPERSION FORCES BECAUSE IT HAS A LARGER MASS!**

**Example of Halogens**
- **Nonpolar molecules have no natural attraction for each other.**
  - To better understand London-Dispersion Forces, let’s examine the halogens. Halogens exist as diatomic molecules at room temperature and atmospheric conditions. **F₂ and Cl₂ are gases, Br₂ is a liquid and I₂ is a solid. Why?**
  - All of these molecules are completely nonpolar and according to theory, not attracted to each other, so one might predict they would all be gases at room temperature.
  - Bromine exists as a liquid at room temperature simply because there is a greater attractive force between its molecules than between those of fluorine or chlorine. Why?
    - Bromine is larger than fluorine or chlorine; it has more electrons and is thus more polarizable. Electrons are in constant motion so it is reasonable that they may occasionally “pile up” on one side of the molecule making a temporary negative pole on that end, leaving a temporary positive pole on the other end.
  - Iodine is a solid since it is larger (than Br, Cl, F), has even more electrons, *is thus* even more polarizable and the attractive forces are thus even greater.
**Dipole-Dipole Forces**

Dipole-Dipole Forces - an attraction between polar molecules in such a way that the partial positive end (δ+) of one molecule is attracted to the partial negative end (δ-) of a nearby molecule.

For example: Hydrochloric acid molecules are held to each other by this type of force.
- HCl—the chlorine pulls the electrons in the bond with greater force than hydrogen so the molecule is polar in terms of electron distribution.
- Two neighboring HCl molecules will align their oppositely charged ends and attract one another.

- **Dipole-dipole forces** exist between neutral POLAR molecules.
- **Dipole-dipole forces have** attraction that enables two polar molecules to attract one another.
- Polar molecules are those which have an UNEVEN charge distribution since their dipole moments do not cancel.
- Compounds exhibiting this type of IMF have higher melting and boiling points than those exhibiting weaker IMFs.
- To determine if a molecule is POLAR, you need to know their ELECTRONEGATIVITY (ability to gain electrons) values (listed in Ch 9).

**a. STUDENT MISCONCEPTION: [THIS IS NOT ALWAYS TRUE] IF YOU ARE GIVEN TWO DIFFERENT CHEMICAL FORMULAS, AND ONE MOLECULE IS POLAR, AND THE OTHER MOLECULE IS NONPOLAR, THE POLAR MOLECULE WILL ALWAYS HAVE A STRONG IMF.**

i. Is it possible that a nonpolar molecule that only experiences London dispersion forces will actually have a higher BP than a polar molecule that experiences both LDFs and dipole-dipole forces?

YES!!!!!!!!!

Keep reading.....
Examples: Suppose you are comparing the relative strength of attractive forces for 2 different substances whose electron clouds are approximately the same size.

\[
\text{N}_2 \quad \text{vs} \quad \text{CO} \\
\text{BP} = 77K \quad \text{BP} = 82K
\]

\[
\begin{array}{ccc}
\text{N} & \equiv & \text{N} \\
\text{C}_3\text{H}_8 & \text{vs} & \text{C}_2\text{H}_3\text{N} \\
\text{BP} = 231K & \text{BP} = 355K \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{C}_4\text{H}_{10} & \text{vs} & \text{C}_3\text{H}_6\text{O} \\
\text{BP} = 261K & \text{BP} = 329K \\
\end{array}
\]

One molecule is nonpolar, and the other molecule is polar. The polar molecule tends to have stronger IMFs.

Example: CCl\(_4\) vs HCl

<table>
<thead>
<tr>
<th>CCl(_4)</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="CCl4" /></td>
<td><img src="image2.png" alt="HCl" /></td>
</tr>
<tr>
<td>Nonpolar molecule (dipoles cancel out)</td>
<td>Polar molecule</td>
</tr>
<tr>
<td>LDFs</td>
<td>LDFs and dipole-dipole forces</td>
</tr>
<tr>
<td>Liquid @ 298K (RT)</td>
<td>Gas @ 298K (RT)</td>
</tr>
<tr>
<td>BP = 350K</td>
<td>BP = 188K</td>
</tr>
</tbody>
</table>
Students assume that HCl has stronger forces because it’s polar with LDFs and dipole-dipole forces, but they don’t take the BP data into account!!

- **But CCl₄ has a higher BP so the LDFs must be stronger— the LDFs must be more significant due to the large electron cloud**

  ii. **Even if one molecule is polar and other is nonpolar... IF YOU ARE GIVEN DATA, YOU HAVE TO CONSIDER THE DATA!**

**EXAMPLE AP QUESTION – 2017**

*(See College board AP Chem YouTube Video 3.1-3.3 ~33min)*

(d) CCl₄(g) can also be produced by reacting CHCl₃(g) with Cl₂(g) at 400°C, as represented by the equation below.

\[
\text{CHCl}_3(g) + \text{Cl}_2(g) \rightarrow \text{CCl}_4(g) + \text{HCl}(g)
\]

At the completion of the reaction a chemist successfully separates the CCl₄(g) from the HCl(g) by cooling the mixture to 70°C, at which temperature the CCl₄(g) condenses while the HCl(g) remains in the gaseous state.

(i) Identify all types of intermolecular forces present in HCl(l).

(ii) What can be inferred about the relative strengths of the intermolecular forces in CCl₄(l) and HCl(l)? Justify your answer in terms of the information above.
TREND:
- For molecules of similar polarity, those with **SMALLER VOLUMES** often have **GREATER** dipole-dipole attractions.
  - WHY??.....Polar molecules need to be close together to form strong dipole-dipole interactions.
- If two molecules have about the same mass and size, then dipole-dipole forces increase with increasing polarity. (See figure below)

Figure 11.8- p.449 Moving left to right, do the dispersion forces get stronger, weaker, or roughly stay the same? (See answer p. A-39 in back of book)
Solubility

- Substances with similar intermolecular interactions tend to be **miscible** (soluble) in one another.

**Intermolecular Forces: Effect on Solubility**

**Main Idea:** The stronger the intermolecular forces between solute molecule and solvent molecule, the greater the solubility of the solute in the solvent.

Think “Like dissolves like.” *(Beware: don’t say these words to AP)*

- **Polar molecules are soluble in polar solvents** (Predominant intermolecular force is dipole-dipole attraction between polar solute molecule and polar solvent molecule).
- **Nonpolar molecules are soluble in nonpolar solvents** (Predominant intermolecular force is London dispersion attraction between nonpolar solute molecule and nonpolar solvent molecule).
- **Polar molecules and nonpolar molecules do not mix.**
  - Do Oil and water mix? Why?

**TREND:**

1. Between two polar molecules, the molecule with the smaller hydrocarbon portion (or the larger polar portion) is more soluble in water.

   - \( \text{CH}_3\text{CH}_2\text{OH} \) Soluble in water
   - \( \text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \) Insoluble in water
   - \( \text{CH}_2\text{(OH)}\text{CH(OH)}\text{CH(OH)}\text{CH(OH)}\text{CH(OH)}\text{CH}_2\text{OH} \) Soluble in water. Large but many OHs that can hydrogen bond with water.

2. If completely nonpolar, insoluble in water (and soluble in nonpolar solvents).

   - \( \text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \) Insoluble in water
Solubility Guided Practice

1. What does this image indicate about the intermolecular interactions of the substances?

2. Which of these pairs of molecules would you expect to mix together?

A.  

B.  

C.  

Examples
Hydrogen Bonding Attractions

**Hydrogen Bonding** - a strong dipole-dipole interaction, which occurs between a H atom (bonded to an N, O, or F) on one molecule and an N, O, or F on another molecule (or another part of a large macromolecule)

Hydrogen bond:

- **Beware:** Hydrogen Bond is NOT a “Bond”!! It’s an IMF!!
- Special type of dipole-dipole force (POLAR molecules)
- **This is the strongest IMF** – stronger than a regular dipole-dipole interaction.
  - **WHY??...**H is small, allowing for dipoles to be in close proximity.
  - N, O, & F all have a small atomic size and are VERY electronegative means that the dipole-dipole interactions are highly polarized.
Experiments show that the boiling points of compounds with \( \text{H–F, H–O, and H–N bonds} \) are abnormally high.

- As a result of these attractions, water has a **high boiling point, high specific heat, and many other unusual properties**.
  - \( \text{H}_2\text{O} \) has a melting point (MP) of 0°C and a boiling point (BP) of 100°C, while \( \text{H}_2\text{S} \) has a melting point of -82°C and a boiling point of -60°C
  - Why the enormous difference?
    - \( \text{H}_2\text{O} \) molecules are held tightly to each other by very strong hydrogen bonding. \( \text{H}_2\text{S} \) molecules are not (just regular dipole-dipole forces).
    - **The stronger the IMF, the more difficult it is to separate the individual molecules from each other.**
    - This results in a higher MP and a higher BP.

**TREND:**
- **BP increases with increasing electron cloud**
  - Why???.....since the more electrons in a molecule, the more polarizable the cloud, the stronger the IMFs, therefore the more Energy needed to overcome those increased attractions and vaporize, thus the higher the boiling point.

Figure 11.10- p.450  To form a Hydrogen - bond
**Ion-Dipole Forces**

**Ion-Dipole Forces** - an attractive force between an ION and a POLAR molecule (interparticle force)

Example: An interaction between an ion (e.g., Na\(^+\)) and the partial charge on the end of a polar molecule/dipole (e.g., water). **DISSOCIATION!!!!**
- Example: NaCl (aq)

Draw Figure 11.13 – p.452
Comparing Intermolecular Forces

Dispersion forces are found in all substances.
- Their strength depends on molecular shapes and molecular weights.

Dipole-dipole forces add to the effect of dispersion forces.
- They are found only in polar molecules.

H-bonding is a special case of dipole-dipole interactions.
- It is the strongest of the intermolecular forces involving neutral species.
- H-bonding is most important for H compounds of N, O, and F.

If ions are involved, ion-dipole (if a dipole is present) and ionic bonding are possible.
- Ion-dipole interactions are stronger than H-bonds.

Keep in mind: IONIC bonds are stronger than van der waals forces (London & Dipole-Dipole)!

![Diagram showing the comparison of intermolecular forces]
11.3 Some Properties of Liquids
Read p.455-457

The Liquid State varies in 3 areas:

1. **Viscosity**
2. **Surface tension**
3. **Capillary Action**

1. **Viscosity** - the resistance of a liquid to flow due to strong IMF.
   - Examples of high viscosity liquids: Maple Syrup or Honey
   - A liquid flow’s by sliding molecules over one another.

   The greater a liquid’s viscosity, the more slowly it flows!
   - Viscosity can be measured by timing how long it takes a certain amount of the liquid to flow.
   - Viscosity is related to the ease with which the molecules of the liquid can move relative to one another.
   - **Viscosity depends on the attractive forces between molecules.**
     - The stronger the intermolecular forces are, the higher the viscosity.
       - **WHY???... molecules are more strongly attracted to each other, preventing them from flowing around each other.**
       - It depends on the attractive forces between molecules and on whether the shapes of the molecules are such that they tend to become entangled (for example, long molecules can become tangled like spaghetti).
   - **Viscosity increases with molecular weight.**
     - The larger the molecule, the higher the viscosity.
   - **Viscosity decreases with increasing temperature.**
     - At higher temperatures the greater average kinetic energy of the molecules overcomes the attractive forces between molecules.
     - Think: cold oil vs hot oil in a pan. Which one flows faster?

2. **Surface Tension** - A measure of the net inward force that must be overcome to expand the surface area of a liquid.

   - The surface of water behaves almost as if it had an elastic skin, as evidenced by the ability of certain insects to “walk” on water.
   - This behavior is due to an imbalance of intermolecular forces at the surface of the liquid.
As shown in FIGURE 11.18, molecules in the interior are attracted equally in all directions, but those at the surface experience a net inward force.

This net force tends to pull surface molecules toward the interior, thereby reducing the surface area and making the molecules at the surface pack closely together.

Because spheres have the smallest surface area for their volume, water droplets assume an almost spherical shape.

This explains the tendency of water to “bead up” when it contacts a surface made of nonpolar molecules, like a leaf or a newly waxed car.

High Surface area indicates strong IMFs.

- WHY??...Molecules are attracted to each OTHER. A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by the molecules below it and on each side.

- Stronger intermolecular forces cause higher surface tension.
  - Water has a high surface tension because of its strong hydrogen bonds.
  - The surface tension of mercury is even higher because of even stronger metallic bonds between the atoms of mercury.
3. **Capillary action** – the spontaneous (happens on its own without outside help) rising of the liquid in a narrow tube.
   - The ability of a liquid to flow against gravity up a narrow tube is due to 2 forces involved: **Cohesive and adhesive forces**:

**COHESIVE forces** are intermolecular forces that bind molecules to one another.

**ADHESIVE forces** are intermolecular forces that bind molecules to a surface of tube. (water bent towards the side of container)

Illustrate this by looking at the **meniscus** in a tube filled with liquid. (See Figure 11.19)
- The meniscus is the shape of the liquid surface.
- Water placed in a glass tube adheres to the glass because the adhesive forces between the water and glass are GREATER than the cohesive forces between water molecules.
  - adhesive forces > cohesive forces, the meniscus is U-shaped (concave like water in glass).
- For mercury, however, the situation is different. Mercury atoms can form bonds with one another but not with the glass.
  - As a result, the cohesive forces are much GREATER than the adhesive forces.
  - cohesive forces > adhesive forces, the meniscus is curved downwards like an INVERTED U-shaped (convex like Hg(l) in glass).
Each state of matter—solid, liquid, gas—can transform into either of the other two states. These transformations are called either PHASE CHANGES or changes of state.

**Every phase change is accompanied by a change in the ENERGY of the system.**
- In a solid, for example, the particles—either molecules, ions, or atoms—are in more or less fixed positions with respect to one another and closely arranged to minimize the energy of the system.
- As the temperature of the solid increases, the particles vibrate about their equilibrium positions with increasingly energetic motion.
- When the solid melts, the particles are freed to move relative to one another, which ordinarily means the average distance between particles increases.

**MELTING** is called **FUSION**.
- The increased freedom of motion of the particles comes at a price, measured by the heat of fusion or enthalpy of fusion, $\Delta H_{\text{fus}}$.

**As the temperature of the liquid increases, the particles move about with increasing energy.**
- One measure of this increasing energy is that the concentration of gas-phase particles above the liquid surface increases with temperature.
- These gas-phase particles exert a pressure called **VAPOR PRESSURE**. (See ch 11.5)
  - Vapor pressure increases with increasing temperature.
- At this point the liquid boils—the particles move into the gaseous state where they are widely separated.
- The energy required to cause this transition is called either the **heat of vaporization** or the **enthalpy of vaporization**, $\Delta H_{\text{vap}}$.

The values of $\Delta H_{\text{vap}}$ tend to be LARGER than the values of $\Delta H_{\text{fus}}$ because in the transition from liquid to gas, particles must essentially sever all their interparticle attractive interactions, whereas in the transition from solid to liquid, many of these attractive interactions remain operative.

- The particles of a solid can move directly into the gaseous state.
- The enthalpy change required for this transition is called the **heat of sublimation**, $\Delta H_{\text{sub}}$.

Phase changes show up in important ways in our everyday experiences.

- When we use ice cubes to cool a drink, for instance, the heat of fusion of the ice cools the liquid.
- We feel cool when we step out of a swimming pool or a warm shower because the liquid water’s heat of vaporization is drawn from our bodies as the water evaporates from our skin.
- Our bodies use this mechanism to regulate body temperature, especially when we exercise vigorously in warm weather.
- A refrigerator also relies on the cooling effects of vaporization.
- Its mechanism contains an enclosed gas that can be liquefied under pressure.
- The liquid absorbs heat as it subsequently evaporates, thereby cooling the interior of the refrigerator.

**Phase changes – 6 transitions**

<table>
<thead>
<tr>
<th>Phase Changes</th>
<th>Energy Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>sublimation: solid $\rightarrow$ gas.</td>
<td>(ENDO)</td>
</tr>
<tr>
<td>melting: solid $\rightarrow$ liquid.</td>
<td>(ENDO)</td>
</tr>
<tr>
<td>vaporization: liquid $\rightarrow$ gas.</td>
<td>(ENDO)</td>
</tr>
<tr>
<td>deposition: gas $\rightarrow$ solid.</td>
<td>(EXO)</td>
</tr>
<tr>
<td>condensation: gas $\rightarrow$ liquid.</td>
<td>(EXO)</td>
</tr>
<tr>
<td>freezing: liquid $\rightarrow$ solid.</td>
<td>(EXO)</td>
</tr>
</tbody>
</table>

***When you can’t remember these, THINK OF HOW WATER CHANGES***

**ENDOTHERMIC** – needing energy
**EXOTHERMIC** – releasing energy

It takes MORE energy to completely separate (break) molecules, than to combining (form) them.
**Heating Curves** – See Figure 11.22 p. 459

Plot of **temperature change versus heat** added over a period of time.

- When we heat an ice cube initially at -25°C and 1 atm pressure, the temperature of the ice increases.
- As long as the temperature is below 0°C, the ice cube remains in the solid state.
- When the temperature reaches 0°C, the ice begins to melt.
- Because melting is an **endothermic process**, the heat we add at 0°C is used to convert ice to liquid water, and the temperature remains constant until all the ice has melted.
- Once all the ice has melted, adding more heat causes the temperature of the liquid water to increase.

![Heating Curves Diagram](image)

- Heating the H$_2$O(s) from -25°C to 0 °C is represented by the line segment AB
- Converting the H$_2$O(s) at 0 °C to H$_2$O(l) at 0 °C is the horizontal segment BC.
- Additional heat increases the temperature of the H$_2$O(l) until the temperature reaches 100 °C (segment CD).
- The heat is then used to convert H$_2$O(l) to H$_2$O(g) at a constant temperature of 100 °C (segment DE).
- Once all the H$_2$O(l) has been converted to H$_2$O(g), the H$_2$O(g) is heated to its final temperature of 125 °C (segment EF)

In segments AB, CD, and EF we are heating a **single phase** from one temperature to another.

- The greater the specific heat (Ch 5.5) of a substance, the more heat we must add to accomplish a certain temperature increase.
- Because the specific heat of water is greater than that of ice, the slope of segment CD is less than that of segment AB.
- This lesser slope means the amount of heat we must add to a given mass of liquid water to achieve a temperature change is greater than the amount we must add to achieve a
temperature change in the same mass of ice.

In segments BC and DE we are converting one phase to another at a constant temperature.

- The temperature remains constant during these phase changes because the added energy is used to overcome the IMF attractive forces between molecules rather than to increase their average kinetic energy.
- During a phase change adding heat causes NO temperature change!

ON the heating curve, you'll notice that applying heat \( (q) \) does one of 2 things:

1. Increases Temperature
2. Causes a change of state

\[
\begin{align*}
\Delta \text{ in Kinetic Energy} & \quad \Delta \text{ in Potential Energy} & \quad \Delta \text{ in Kinetic Energy} & \quad \Delta \text{ in Potential Energy} & \quad \Delta \text{ in Kinetic Energy} \\
\longleftrightarrow \text{ Freezing (exothermic)} & \quad \longleftrightarrow \text{ Condensation (exothermic)} & \quad \longleftrightarrow \text{ Melting (endothermic)} & \quad \text{Vaporization (endothermic)} & \quad \text{Melting (endothermic)}
\end{align*}
\]

\[
\text{Heat (or time that constant amt heat added) in Joules} \rightarrow
\]

**Cooling Curve** – opposite of a heating curve
- Same graph but moving down.
Molecules can escape from the surface of a liquid into the gas phase by evaporation.

- Suppose we place a quantity of ethanol (CH\textsubscript{3}CH\textsubscript{2}OH) in an evacuated, closed container, as in FIGURE 11.23 above.
- The ethanol quickly begins to evaporate.
- As a result, the pressure exerted by the vapor in the space above the liquid increases.
- After a short time the pressure of the vapor attains a constant value, which we call the **VAPOR PRESSURE**.
- At any instant, some of the ethanol molecules at the liquid surface possess sufficient kinetic energy to overcome the attractive forces of their neighbors and, therefore, escape into the gas phase.
- At any particular temperature, the movement of molecules from liquid phase to gas phase goes on continuously.
- As the number of gas-phase molecules increases, however, the probability increases that a molecule in the gas phase will strike the liquid surface and be recaptured by the liquid.
- Eventually, the rate at which molecules return to the liquid equals the rate at which they escape.
- The number of molecules in the gas phase then reaches a steady value, and the pressure exerted by the vapor becomes constant.
- The condition in which two opposing processes occur simultaneously at equal rates is called **DYNAMIC EQUILIBRIUM** (or equilibrium).
  - A liquid and its vapor are in dynamic equilibrium when evaporation and condensation occur at equal rates.
  - It may appear that nothing is occurring at equilibrium because there is no net change in the system.
  - In fact, though, a great deal is happening as molecules continuously pass from liquid state to gas state and from gas state to liquid state.
  - The vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium.
Volatility, Vapor Pressure, and Temperature

When vaporization occurs in an open container, as when water evaporates from a bowl, the vapor spreads away from the liquid.

- Equilibrium never occurs, and the vapor continues to form until the liquid evaporates to dryness.
- Substances with high vapor pressure (such as gasoline) evaporate more quickly than substances with low vapor pressure (such as motor oil).

Liquids that evaporate readily are said to be VOLATILE.
- Hot water evaporates more quickly than cold water because vapor pressure increases with increasing temperature.
- To see why this statement is true, we begin with the fact that the molecules of a liquid move at various speeds (Discussed in Ch 10.7).

FIGURE 11.24 – SEEN ON AP EXAM
- shows the distribution of kinetic energies of the molecules at the surface of a liquid at two temperatures. (The curves are like those shown for gases in Section 10.7.)
As the temperature increases, does the rate of molecules escaping into gas phase increase or decrease?

- **INCREASES!!!** Because the molecules have more KE as the T increases and can escape more easily.
- The molecules move more energetically and more of them can break free from their neighbors and enter the gas phase, increasing the VP!

**Vapor Pressure and Boiling Point**

**FIGURE 11.25** - Summarizes how vapor pressure with temperature for 4 different substances differs greatly in volatility (HINT…what are their IMFs)

- Note that the vapor pressure in all cases increases nonlinearly with increasing temperature.
- The weaker the intermolecular forces in the liquid, the more easily molecules can escape and, therefore, the higher the vapor pressure at a given temperature.

- A liquid boils when its vapor pressure equals the external pressure acting on the liquid surface.
- At this point, bubbles of vapor form within the liquid.
- The temperature at which a given liquid boils increases with increasing external pressure.
- The boiling point of a liquid at 1 atm (760 torr) pressure is called its **NORMAL BOILING POINT**.

- From Figure 11.25 we see that the normal boiling point of water is 100°C.
- The time required to cook food in boiling water depends on the water temperature.
- In an open container, that temperature is 100°C, but it is possible to boil at higher temperatures.
- Pressure cookers work by allowing steam to escape only when it exceeds a predetermined pressure; the pressure above the water can therefore increase above atmospheric pressure.
- The higher pressure causes the water to boil at a higher temperature, thereby allowing the food to get hotter and to cook more rapidly.
- The effect of pressure on boiling point also explains why it takes longer to cook food at high elevations than it does at sea level.
- The atmospheric pressure is lower at higher altitudes, so water boils at a temperature lower than 100 °C, and foods generally take longer to cook.

**Two ways to get a liquid to boil are to:**

- increase temperature or decrease pressure. (Remember: this is the conditions of ideal gases!)
Physical properties such as melting points (MP), boiling points (BP), vapor pressures (VP), etc. can be attributed to the strength of the intermolecular attractions present between molecules.

Using the diagram and information given below, which liquid, C₅H₁₂ or H₂O, has a higher vapor pressure at 300 K? Justify your answer. *(See AP YouTube Video Unit 3.1-3.3 ~40.5min)*

If you increase the temperature of H₂O, the liquid water molecules will start to convert to water VAPOR.

- So there will be less liquid water molecules as the number of water vapor molecules increase.
- **As the temperature increases, the vapor pressure also increases.**
- So C₅H₁₂ has higher vapor pressure and comes to a boil more quickly.

Make sure you understand IMFs and are able to take data to compare VP and BP.

<table>
<thead>
<tr>
<th>Weaker IMFs</th>
<th>Stronger IMFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher VP</td>
<td>Lower VP</td>
</tr>
<tr>
<td>Lower BP</td>
<td>Higher BP</td>
</tr>
</tbody>
</table>
So why is warming a liquid going to increase the vapor pressure?

- **See diagram below – called Maxwell Boltzman diagram**
  - For any sample, there’s a kinetic energy associated to them which is connected to temperature.
  - Each molecule travels at different speeds so they have different kinetic energies.
  - It’s an average of the sample!

This represents what it would take to get out of the liquid phase and into the gas phase.

- Not all the molecules will evaporate at once.
- According to the diagram, only the SHADED blue region are the molecules that have the required kinetic energy to escape the liquid phase.

**What if you raise the temperature? See red curve**

- As you raise the temperature, you increase the average kinetic energy and increases the distribution of energies available in the shaded curve.
Volatile substances - liquid take evaporate easily, changes to a gas easily

- have high VP (vapor pressure), thus weak IMFs!!!
  - WHY??... these liquids evaporate easily from open containers since they have so little attraction for each other.
  - It takes very little energy being absorbed in order for them to escape the surface of the liquid. The heat energy absorbed from a warm room is usually enough to make these substances evaporate quickly. If there is an odor to the substance, these are the liquids you smell almost as soon as you open the bottle! The molecules have been banging against the lid wanting out!
- For example, gasoline (C₈H₁₈ mixture) evaporates much more quickly than water. Therefore, the intermolecular attractive forces that hold one gasoline molecule to another are much weaker than the forces of attraction that hold one water molecule to another water molecule. In fact, water molecules are held together by the strongest of the intermolecular attractive forces, hydrogen bonds.

VP is temperature dependent!!

- As T increases, the VP of a liquid also increases
  - WHY??... because at elevated temperatures, there’s more molecules in the vapor (gas) phase.
  - Heat ‘em up, speed ‘em up, move ‘em out! Increasing the temperature increases the KE (moving energy) which helps them escape AND the increases the speed of the escapees! They bang into the sides of the container with more frequency [more of them escaped]
  - A high boiling point or melting point indicates strong attractive forces.
  - The higher the temperature, the higher the average kinetic energy, the faster the liquid evaporates.
Substances with large molar masses have low VP, mainly due to large LDF.

- As MM ↑ VP ↓
  - WHY??...as molecules increase in size, they also increase in the number of electrons. As the number of electrons increase, the polarizability of the molecule increases so more dispersion forces exist, causing stronger attractions to form between molecules. This decreases the number of molecules that escape and thus lowers the VP.

Separation of Solutions and Mixtures Chromatography

<table>
<thead>
<tr>
<th>Learning Objective</th>
<th>Essential Knowledge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit 3.9</strong></td>
<td><strong>SPQ-3.C.1</strong> The components of a liquid solution cannot be separated by filtration. They can, however, be separated using processes that take advantage of differences in the intermolecular interactions of the components.</td>
</tr>
<tr>
<td><strong>SPQ-3.C</strong> Explain the relationship between the solubility of ionic and molecular compounds in aqueous and nonaqueous solvents, and the intermolecular interactions between particles.</td>
<td>a. Chromatography (paper, thin-layer, and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components of the solution (the mobile phase) and with the surface components of the stationary phase.</td>
</tr>
<tr>
<td></td>
<td>b. Distillation separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components and the effects these interactions have on the vapor pressures of the components in the mixture.</td>
</tr>
</tbody>
</table>

AP CHEMISTRY PRACTICE 3.7-3.10
AP Chemistry: 3.7-3.10 Solutions, Mixtures, and Solubility

WATCH THIS VIDEO BY SEAN BYRNE (Watch ~29 minutes)

The components of a liquid solution cannot be separated by filtration. They can, however, be separated using processes that take advantage of differences in the intermolecular interactions of the components.

- Chromatography (paper, thin-layer, and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components of the solution (the mobile phase) and with the surface components of the stationary phase.
As the mobile phase moves through the stationary phase, it picks up particles from the mixture to be analyzed.

The component parts of the mixture will travel at different rates, based on size and polarity of particle.

- Larger particles will move more slowly
- Particles with a polarity which matches the solvent will move farther. (polar molecules will stick to the polar solvent and move farther)

Important to Remember:
- Paper is usually relatively nonpolar in comparison to the solvent.
- The substance that travels further up the paper is more attracted to the solvent.
- The substance that travels the least is most attracted to the paper.

At t=90sec, what do we see?
- We definitely have mixtures since we see separation.
- Blue dots = same polarity as the solvent since it traveled the farthest.
- Red dots = are probably not the same polarity as solvent

Retention Factor – Answers for Rf values are usually less than 1.
Distillation separates chemical species by taking advantage of the differential strength of intermolecular attractions between and among the components and the effects these interactions have on the vapor pressures of the components in the mixture.

- Distillation separates parts of a mixture based on different boiling points.
- A mixture must have two liquids of different boiling points.
- The mixture is slowly heated to a temperature that is between the boiling points of the liquids.
- The gas particles rise through the still head and meet cooler air.
- The thermometer measures the temperature of the gas.
- Water flows through the condenser, cooling the vapor back into liquid.
- The receiving flask collects the liquid.

Important to Remember:
- Substance collected in the flask at the end is the **distillate** (substance with lower boiling point)
- The substance with the **lower boiling point** has a greater vapor pressure and weaker intermolecular forces.
- The substance with the **higher boiling point** has a lower vapor pressure and stronger intermolecular forces.
- The temperature of the solution will remain constant while a component is boiling off.
- Thermometer should not be touching the bottom of the flask, or the solution will appear hotter than it actually is.
For example:

If you have a mixture of 2 liquids: Sol’n 1 has a BP = 75°C and Sol’n 2 has a BP = 150°C

You would want to boil the solution at a temperature between the 2 solutions so the sol’n 1 with the lower BP will boil first and you will see gas vapor travel up the still head. Then the gas phase will condense through the condenser (surrounded) by cold water and cooled down to be collected as a liquid.

Distillation Guided Practice

A student performed a fractional distillation of a mixture of two straight-chain hydrocarbons, C\textsubscript{7}H\textsubscript{16} and C\textsubscript{8}H\textsubscript{18}.

Using four clean, dry flasks, the student collected the distillate over the volume ranges (A, B, C, and D) shown in the graph to the right.

Over what volume range should the student collect the distillate of the compound with the stronger intermolecular forces?
11.6 Phase Diagrams (Not tested on AP Exam but can be seen on SAT subject test)

PHASE DIAGRAMS—closed systems (exchanges energy only, not matter with surroundings)

- A plot of pressure vs. temperature summarizing all equilibrium between phases.
- Shows us which phase will exist at a given temperature and pressure.

Figure 11.27 – Phase Diagram for a Substance
Features of a phase diagram include:

- **EACH PHASE BOUNDARY (THE LINES) REPRESENTS AN EQUILIBRIUM SET OF TEMPERATURE AND PRESSURE CONDITIONS**
- **vapor-pressure curve**: generally, as temperature increases, vapor pressure increases.
- **“NORMAL” means conditions at 1 atm**
  - **normal melting point**: the temperature at which the VP solid = VP liquid (1 atm)
  - **normal boiling point**: the temperature at which the VP liquid = VP gas (1 atm)
- **TRIPLE POINT**: temperature and pressure at which all three phases are in equilibrium.
- **CRITICAL POINT** for Temperature and Pressure - Gases may be liquefied by increasing the pressure at a suitable temperature.
  - **Critical temperature** is the highest temperature at which a substance can exist as a liquid.
  - **Critical pressure** is the pressure required for liquefaction at this critical temperature.
  - The greater the intermolecular forces, the easier it is to liquefy a substance.
  - Thus, the higher the critical temperature. (check out how high water’s values are…due to strong IMFs)

**Phase Diagrams of H_2O and CO_2**

Figure 11.28p. 465 – Phase Diagram for Water

**Water:**

- In general, an increase in pressure favors the more compact phase of the material.
  - This is usually the solid.
  - Look at the melting curve line…The melting point curve for water slopes to the LEFT.
    - WHY??….Water is a freak! The solid-liquid melting curve line tilts to the LEFT [negative slope] since its solid is LESS dense than its liquid phase—ice floats.
    - (Usually, most solids sink as they are MORE dense than liquids).
- The triple point occurs at 0.0098°C and 4.58 mm Hg.
- The normal melting (freezing) point is 0°C and 1 atm.
- The normal boiling point is 100°C and 1 atm.
- The critical point is \( T_c = 374°C \) and 218 atm.
ex: Consider the phase diagram for water:

**Critical pressure**

Critical point = end point of the liquid-gas line. For H₂O, its (374°C, 218 atm)

**Triple point** = point at which all 3 phases of a substance are present.

**Critical temperature** = above this temperature, vapor can no longer be liquified.

$T_m$ = melting pt.
$T_b$ = boiling pt.

0.0098°C (Triple point temp)

Pressure (atm)

Temperature (°C)
Most substances have a solid-liquid line that has a **POSITIVE SLOPE** since their solid phase is more dense than the liquid. This one is for carbon dioxide.
ANOTHER AP FRQ EXAMPLE WITH STUDENT MISCONCEPTION – AP FRQ2018

(AP YouTube: 3.1-3.3 ~50min)

*Sstudent Misconceptions* RECOGNIZE THESE

- Students failed to identify the IMF’s that are present in BOTH molecules
- Students said that the C – S bonds in CS$_2$ were polar, but did not mention that the two bond dipoles cancel each other out in the linear molecule.
- Students said that the strength of the IMF’s in CS$_2$ are greater than the strength of the IMF’s in COS. But they did not specifically state that the LDF’s in CS$_2$ are greater than the combined LDF’s and dipole-dipole forces in COS.
- Students said that CS$_2$ and COS only have LDF’s
- Students said that both molecules have LDF’s and dipole-dipole forces.
- Students implied or stated that boiling a liquid involves breaking covalent bonds.
- Students used the molar mass as the only reason why CS$_2$ has stronger IMFs
- Students said that dipole-dipole forces are always stronger than LDF’s

4. The table above gives the molecular structures and boiling points for the compounds CS$_2$ and COS.

(a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of CS$_2$(l) is higher than that of COS(l).
1. A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above on the right.

(a) Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

(b) Which dye is present in the unknown sample? Justify your answer.