Chapter 12: Liquids, Solids and Intermolecular Forces

Homework: Read Chapter 12.

Bonus Ch 12: 39, 45, 49, 59, 63, 71, 75, 79, 81, 89, 91, 93, 101

Check MasteringChemistry deadlines

Liquids and solids are quite different from gases due to their attractive forces between the close, lower kinetic energy particles. Interactions between liquid and solid particles are greatly affected by their intermolecular forces (attractions between particles).

- The specific interaction between the molecules in coffee that taste bitter and the taste receptors on the tongue is caused by intermolecular forces—attractive forces that exist between molecules.
- Bitter tastes are usually unpleasant because many of the molecules that cause them are poisons. The sensation of bitterness is probably an evolutionary adaptation that helps us avoid these poisons.
- Living organisms depend on intermolecular forces for many physiological processes.
- The intermolecular forces that exist between all molecules and atoms are responsible for the very existence of liquids and solids.
- The state of a sample of matter—solid, liquid, or gas—depends on the magnitude of intermolecular forces relative to the amount of thermal energy in the sample. The weaker the intermolecular forces relative to thermal energy, the more likely the sample will be gaseous. The stronger the intermolecular forces relative to thermal energy, the more likely the sample will be liquid or solid.

Review Lewis Structures and recall how to determine the polarity of a substance (ionic, ion, polar, and nonpolar).

Review Polar verses Nonpolar particles:

Polar molecules have an overall dipole moment. This dipole moment occurs when polar covalent bonds within a molecule do not cancel. Nonpolar molecules and noble gases have zero dipole moment. In general, like will dissolve in like. Two polar liquids are generally miscible with each other. Two nonpolar liquids are miscible as well. But, when you take a polar liquid (vinegar) and a nonpolar liquid (vegetable oil) the two will be immiscible, and due to different densities one floats on the other.
Properties of Gases:
- low density; (g/l)
- Indefinite shape and volume (takes the shape and volume of its container and can be compressed or expanded).
- Ideal gases have no attraction or repulsion between particles.

Properties of Liquids:
- High density compared to gases; (g/ml)
- Definite volume; not easily compressed
- Indefinite shape, takes the shape of the container
- Lower kinetic energy compared to gas, but higher energy than solid; particles are free to move around each other, as well as vibrate

Properties of Solids:
- High density compared to gases; (g/ml)
- Definite volume; not easily compressed
- Definite shape
- Lowest kinetic energy compared to gas and liquids; particles vibrate about a fixed point
- Strong intermolecular forces relative to thermal energy
- Crystalline (repeating pattern on a molecular scale, ordered) or Amorphous (variable angles and distances between particles-no long range order, disordered)
Attractions:

The very strong **intramolecular forces** include polar and nonpolar covalent bonding as well as ionic bonding. It takes high temperatures to break apart intramolecular attractions. **Intramolecular forces** occur **within molecules/substances** such as H$_2$O- polar covalent bonds between H-O-H within a molecule; within **network solids** such as a diamond that is held by pure covalent bonding between many, many carbons in a macromolecular tetrahedral structure; or **ionic compounds** such as NaCl-electrostatic attractions between Na$^{+1}$ and Cl$^{-1}$.

**Intermolecular forces** are weaker attractions that hold molecules or noble gas particles close together when they are in a liquid or solid form. Gas particles have broken away from the intermolecular forces that hold liquids and solids together. An alternative name for intermolecular forces is the **van der Waals forces**. They include **London Dispersion Forces, dipole-dipole forces**, and **hydrogen bonds**. An additional attraction is the **ion-dipole forces** that occur between polar molecules and ions, as in saltwater.

Strength of Attractions:

The strength of attractions influences the state (solid, liquid, gas) of the substance. Stronger attractions will strongly hold together in a solid form until enough energy/heat/temperature is added to break the attractions and liquefy (high melting points). With more energy (thermal heat-higher temperatures) all the intermolecular attractions will eventually be overcome to form gas particles (boiling point). Particles held by very weak attractions are often gases at fairly low temperatures (low boiling points).

**Types of Intermolecular Forces:** (weakest to stronger)

**London Dispersion Forces:** (also known as Dispersion Force, London force, or van der Waals forces) *The nature of dispersion forces was first recognized by Fritz W. London (1900–1954), a German-American physicist.*

- Attractions are caused by instantaneous dipoles (temporary dipoles) created by the uneven distribution of electrons within the particle at any instant. The temporary dipole in one particle will induce an opposite temporary dipole in a nearby particle. The temporary partial positive and partial negative charges that develop between particles form the attractions.
- These attractions are present in all molecules and atoms
- This is the only attraction force found in nonpolar molecules and noble gases
- Weakest of the attraction forces
- Attractions increase as the molar mass or size of the electron cloud increases
- Attractions increase as the surface area of the particles are more spread out/larger
Dispersion force: An instantaneous dipole on any one helium atom induces instantaneous dipoles on neighboring atoms. The neighboring atoms then attract one another. This attraction is called the dispersion force.

Effect of Differences in Dispersion Forces on Boiling Points of the Noble Gases

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>Molar Mass (g/mol)</th>
<th>Boiling Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.00</td>
<td>4.2 K</td>
</tr>
<tr>
<td>Ne</td>
<td>20.18</td>
<td>27 K</td>
</tr>
<tr>
<td>Ar</td>
<td>39.95</td>
<td>87 K</td>
</tr>
<tr>
<td>Kr</td>
<td>83.80</td>
<td>120 K</td>
</tr>
<tr>
<td>Xe</td>
<td>131.29</td>
<td>165 K</td>
</tr>
</tbody>
</table>
Dipole - Dipole Forces:

- Attractions are caused by permanent dipoles occurring in polar molecules. The molecules line-up so that the partial positive charges on one particle will be attracted to the partial negative charges on a nearby particle.
- These attractions exist between polar molecules that create partial charges $\delta^+$ and $\delta^-$ where the opposites attract.
- A bit stronger attractions compared to dispersion forces. This will cause the same molar mass polar molecule to have a higher melting point than the nonpolar molecule.
- Example: CH$_2$O has a bp = -19.5°C, while C$_2$H$_6$ has a bp = -88°C even though both molar masses are 30 g/mol.
- Attractions increase as the electronegativity difference increases
- Attractions increase as the size of the atoms that attract an opposite charge decreases. The closer the opposite charges can get will make the attraction stronger-similar to a magnet attracting more strongly as the distance between objects is less.

Hydrogen Bonds:

- A special case of the Dipole-Dipole Forces. Hydrogen bonding occurs when H is directly attached to a small highly electronegative atom (F, O, N).
  Due to the electronegativity differences and small size atoms, H will develop a permanent partial positive charge and the F, O, or N atom will develop a permanent partial negative charge. Interactions between two separate particles will strongly attract the opposite charges.
- These attractions are present between two polar molecules that each have H bonded to F, O, or N.
- A bit stronger attractions compared to regular dipole-dipole forces. Water (H$_2$O) has especially strong attractions for its size since each water molecule can be attracted by several hydrogen bonds toward other water molecules.
### Hydrogen Bonding in Water

*Water is a Remarkable Molecule*

- Water has a low molar mass, yet liquid at room temperature.
- It’s relatively high boiling point can be understood by examining its structure.
- The bent geometry of the water molecule and the highly polar nature of the O—H bonds result in a molecule with a significant dipole moment.
- Water’s two O—H bonds allow water molecules to form strong hydrogen bonds with other water molecules, resulting in a relatively high boiling point.
- Water’s high polarity allows it to dissolve many other polar and ionic compounds.
- Water is the main solvent of living organisms, transporting nutrients and other important compounds throughout the body. Life is impossible without water, where liquid water exists, life generally exists. Evidence of water on Mars has fueled hopes of finding life or evidence of life there.
- The way water freezes is unique. Unlike other substances, which contract upon freezing, water expands upon freezing. Because liquid water expands when it freezes, ice is less dense than liquid water. Water reaches its maximum density at 4.0 °C. The frozen layer of ice at the surface of a winter lake insulates the water in the lake from further freezing. If this ice layer were to sink, it could kill bottom-dwelling aquatic life and could allow the lake to freeze solid, eliminating virtually all aquatic life in the lake.
The expansion of water upon freezing is one reason that most organisms do not survive freezing. When the water within a cell freezes, it expands and often ruptures the cell, just as water freezing within a pipe bursts the pipe. Many foods, especially those with high water content, do not survive freezing very well either. Industrial flash-freezing of fruits and vegetables happens so rapidly that the water molecules cannot align into the expanded phase and so the cells are not ruptured.

**Hydrogen Bonding in DNA**

- DNA is composed of thousands of repeating units called nucleotides which contains a base: adenine, thymine, cytosine, or guanine (abbreviated A, T, C, and G).
- The order of these bases along DNA encodes the instructions that specify how proteins are made in each cell of the body.
- DNA consists of two complementary strands wrapped around each other in the now-famous double helix held by hydrogen bonds that occur between the bases on each strand.
- DNA replicates because each base (A, T, C, and G) has a complementary partner with which it hydrogen-bonds. Adenine (A) hydrogen-bonds with thymine (T). Cytosine (C) hydrogen-bonds with guanine (G). The hydrogen bonds are so specific that each base will pair only with its complementary partner.
- When a cell is going to divide, the DNA unzips across the hydrogen bonds that run along its length. New bases, complementary to the bases in each half, add along each of the halves, forming hydrogen bonds with their complement, resulting in two identical copies of the original DNA.
Ion-Dipole Forces:

- Attractions are caused by the charge or an ion attracted to the opposite permanent dipoles charge occurring in polar molecules. The particles order so that the charged ions are surrounded by molecules with the opposite charge permanent dipole.
- These attractions are present in solutions of dissolved ions in a polar solvent.
- Aqueous sodium chloride is a typical example of ion-dipole attraction.

NaCl (aq): Solid sodium chloride dissolves in water when the Na\(^{+1}\) ions are surrounded by the O side of water molecules while the Cl\(^{-1}\) ions are surrounded by the H side of water molecules in “solvent cages”.
Properties of Liquids:

**Surface Tension:** Surface tension is the tendency of liquids to minimize surface area. Molecules on the surface interact with neighbors on only one side resulting in an inward attraction that creates surface tension. Particles with stronger attractions will have more surface tension. Water drops are spherical because water is attracted to itself and wants to minimize is surface area. A paper clip will float on water if it is carefully placed on the surface of the water. It is held up by surface tension.

**Viscosity:** Viscosity is the resistance of liquids to flow. Honey has a greater viscosity compared to water and flows more slowly. Viscosity increases as attractions between particles increase and as the particle size and length increases causing molecular entanglement (spaghetti verses rice)
Phase Changes:

**Evaporation:** *(Also known as Vaporization)* An endothermic physical change when a substance is converted from liquid to gas. The term evaporation is generally used below the normal boiling point while the term vaporization is often used when the phase change occurs at the boiling point. The rate of evaporation increases as

a) temperature increases  
b) strength of attractions decrease  
c) surface area exposed increases.

*Volatile* liquids evaporate readily, while those that do not vaporize easily are *nonvolatile*.

**Condensation:** An exothermic physical change when a substance is converted from a gas to a liquid, the opposite of vaporization.

*At the point where the rates of condensation and evaporation become equal, dynamic equilibrium is reached and the number of gaseous water molecules above the liquid remains constant creating its vapor pressure.*

**Vapor Pressure:** Vapor Pressure is the partial pressure of a gas above a liquid in a closed container in dynamic equilibrium. Vapor pressures increase with higher temperatures but decrease when attractions between the liquid particles are stronger.
**Boiling point:** The temperature for a normal boiling point occurs when the vapor pressure of the liquid to boil reaches 1 atm. It is possible to boil water above 100°F if the pressure above the water exceeds 1 atm. You can boil water below 100°F if the pressure above the liquid is less than 1 atm.

**Enthalpy of Vaporization:** The enthalpy or heat of vaporization ($\Delta H_{vap}$) is the energy required to convert 1 mole of liquid to gas.

For water, $\Delta H_{vap} = +40.7 \, \text{kJ/mol at 100°C}$

The value must change its sign for condensation.

**TABLE 12.2 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Chemical Formula</th>
<th>Normal Boiling Point (°C)</th>
<th>Heat of Vaporization (kJ/mol) at Boiling Point</th>
<th>Heat of Vaporization (kJ/mol) at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>H$_2$O</td>
<td>100.0</td>
<td>40.7</td>
<td>44.0</td>
</tr>
<tr>
<td>isopropyl alcohol (rubbing alcohol)</td>
<td>C$_3$H$_8$O</td>
<td>82.3</td>
<td>39.9</td>
<td>45.4</td>
</tr>
<tr>
<td>acetone</td>
<td>C$_3$H$_6$O</td>
<td>56.1</td>
<td>29.1</td>
<td>31.0</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>C$_4$H$_9$O</td>
<td>34.5</td>
<td>26.5</td>
<td>27.1</td>
</tr>
</tbody>
</table>

**Melting:** An endothermic physical change when a substance is converted from solid to liquid

**Freezing:** An exothermic physical change when a substance is converted from liquid to solid
**Melting Point:** Normal melting point is the temperature a substance will melt at under 1 atm of pressure. This is the same temperature as its **normal freezing point.**

**Enthalpy of Fusion:** The enthalpy or heat of fusion ($\Delta H_{\text{fus}}$) is the energy required to convert 1 mole of solid to liquid.

For water, $\Delta H_{\text{fus}} = +6.02 \text{ kJ/mol at } 0^\circ\text{C}$

The value must change its sign for freezing.

**Sublimation:** An exothermic physical change when a substance is converted directly from solid to gas

**Deposition:** An endothermic physical change when a substance is converted directly from gas to solid

**Specific heat capacity:** The energy (generally in joules) required to change 1 gram of an object by 1°C. No change in phase occurs.

**Heating or Cooling Curves:** calculating the energy involved as it is added or removed from a substance that may be changing its temperature or phases.

\[ Q = mC\Delta T \] for heating or cooling a constant phase.

\[ Q = n\Delta H \] for phase changes

In heating curves, energy is added and all energy values are positive

In cooling curves, energy is removed and all energy values are negative
This diagram shows a heating curve for ice beginning at -25 °C and ending at 125 °C. Label sections i, ii, and iii with the correct processes or states of water.

**Solids**: characteristics, attractions, melting points, solubility, conductivity

*Amorphous versus Crystalline:*

- Solids may be crystalline (a well-ordered array of atoms or molecules) or amorphous (having no long-range order).
- Crystalline solids can be divided into three categories—molecular, ionic, and atomic—based on the individual units that compose the solid.

**Molecular (polar and nonpolar)**

- **Molecular solids** are solids whose composite units are molecules.
- Molecular solids are held together by intermolecular forces; dispersion forces, dipole–dipole forces, and hydrogen bonding.
- Ice (solid H₂O) and dry ice (solid CO₂) are molecular solids. Ice is held together by hydrogen bonds, and dry ice is held together by dispersion forces.
- Molecular solids as a whole tend to have low to moderately low melting points.
- Ice melts at 0 °C and dry ice sublimes at −78 °C.
Ionic

- **Ionic solids** are solids composed of formula units, the smallest electrically neutral collection of cations and anions that compose the compound.
- Ionic solids are held together by electrostatic attractions between cations and anions.
- Table salt (NaCl) and calcium fluoride CaF$_2$ are ionic solids. In NaCl, the attraction between the Na$^+$ cation and the Cl$^-$ anion holds the solid lattice together because the lattice is composed of alternating cations and anions in a three-dimensional array.
- The forces that hold ionic solids together are actual ionic bonds.
- Since ionic bonds are much stronger than any of the intermolecular forces discussed previously, ionic solids tend to have much higher melting points than molecular solids.
- Sodium chloride, an ionic solid, melts at 801 °C, while carbon disulfide, a molecular solid with a higher molar mass, melts at −110 °C.

Atomic

- **Atomic solids** are solids whose composite units are individual atoms.
- Atomic solids can be divided into three categories; covalent atomic solids, nonbonding atomic solids, and metallic atomic solids, each held together by a different kind of force.
- Diamond (C), iron (Fe), and solid xenon (Xe) are atomic solids.

Nonbonding atomic solids, such as solid xenon (Xe), are held together by relatively weak dispersion forces. Xenon atoms have stable electron configurations and therefore do not form covalent bonds with each other. Solid xenon, like other nonbonding atomic solids, has a very low melting point (about −112 °C).
**Metallic atomic solids**, such as iron, silver, and lead have variable melting points.

- Metals are held together by metallic bonds that, in the simplest model, consist of positively charged ions in a sea of electrons.
- Metallic bonds are of varying strengths, with mercury, having its melting point below room temperature (−39 °C), and iron, having a relatively high melting point (1809 °C).
- In the simplest model of a metal, each atom donates one or more electrons to an “electron sea.” The metal consists of the metal cations in a negatively charged electron sea.

**Network atomic solids**

- Covalent atomic solids, such as diamond, are held together by covalent bonds.
- In diamond, each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry. This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule held together by these covalent bonds.
- Since covalent bonds are very strong, covalent atomic solids have high melting points. Diamond is estimated to melt at about 3800 °C.
Atomic solids

Covalent
- Held together by covalent bonds
- High melting points

Nonbonding
- Held together by dispersion forces
- Low melting points

Metallic
- Held together by metallic bonds
- Variable melting points

Silicon
- Covalent solid

Xenon
- Nonbonding solid

Gold
- Metallic solid
Solids and Liquids: Example Problems:

1. Identify the types of intermolecular attractions (London Dispersion, Dipole-dipole, Hydrogen bonding) and/or intramolecular attractions (Covalent or Ionic bonding) that are present in each of the following.
   a) C_2H_6  d) C_8H_{18}  g) N_2  j) MgO
   b) CO_2  e) H_2O  h) KBr  k) BeH_2
   c) OF_2  f) NH_3  i) CH_2O  l) C_{diamond}

2. Arrange the following in order of expected increasing boiling point.
   CH_3CH_2OH  CH_3CH_2CH_3  H_3C–O–CH_3  CH_3CH_2NH_2

3. Why does water boil at a lower temperature on top of a mountain?

4. How much heat does your body lose when 5.00 g of sweat (water) evaporates from your skin at 25°C. At 25°C, ΔH_{vap} = +44.0 kJ/mol

5. How much energy is released as 100 g of steam at 100°C cools to liquid water at 25°C. Given: ΔH_{vap} = +40.7 kJ/mol at 100°C and specific heat capacity of liquid water = 4.184 J/g°C
1. Identify the types of intermolecular attractions (London Dispersion, Dipole-dipole, Hydrogen bonding) and/or intramolecular attractions (Covalent or Ionic bonding) that are present in each of the following.

   a) C₂H₆  \( \text{LDF} \)  
   b) CO₂  \( \text{LDF} \)  
   c) OF₂  \( \text{DD} \)  
   d) C₈H₁₈  \( \text{LDF} \)  
   e) H₂O  \( \text{HB} \)  
   f) NH₃  \( \text{HB} \)  
   g) N₂  \( \text{LDF} \)  
   h) KBr  \( \text{Ionic} \)  
   i) CH₂O  \( \text{DD} \)  
   j) MgO  \( \text{Ionic} \)  
   k) BeH₂  \( \text{LDF} \)  
   l) C\(_{\text{diamond}}\)  \( \text{covalent} \) 

2. Arrange the following in order of expected increasing boiling point.

CH₃CH₂OH  CH₃CH₂CH₃  H₃C–O–CH₃  CH₃CH₂NH₂

Weakest attraction, lowest Boiling point  CH₃CH₂CH₃

H₃C–O–CH₃

CH₃CH₂NH₂

Strongest attraction, highest Boiling point  CH₃CH₂OH

3. Why does water boil at a lower temperature on top of a mountain?

   The atmosphere pressure is lower on the mountain so it takes a lower temperature for the vapor pressure of water to equal the atmosphere pressure and boil.

4. How much heat does your body lose when 5.00 g of sweat (water) evaporates from your skin at 25°C. At 25°C, \( \Delta H_{\text{vap}} = +44.0 \, \text{kJ/mol} \)

\[
Q = n \Delta H_{\text{vap}} = 12.2 \, \text{kJ}
\]

5. How much energy is released as 100 g of steam at 100°C cools to liquid water at 25°C. Given: \( \Delta H_{\text{vap}} = +40.7 \, \text{kJ/mol} \) at 100°C and specific heat capacity of liquid water = 4.184 J/g°C

\[
Q₁ = -n \Delta H_{\text{vap}} = -226.1 \, \text{kJ}
\]

\[
Q₂ = mCΔT = -31.4 \, \text{kJ}
\]

\[
Q_{\text{total}} = -257.5 \, \text{kJ} = -258 \, \text{kJ}
\]