

Chem 116 POGIL Worksheet - Week 3

Intermolecular Forces, Liquids, and Solids

Why?

Most substances can exist in either gas, liquid, or solid phase under appropriate conditions of temperature and pressure. The phase that we see under ordinary conditions (room temperature and normal atmospheric pressure) is a result of the forces of attraction between molecules or ions comprising the substance. The strength of these attractions also determines what changes in temperature and pressure are needed to effect a phase transition.

Learning Objectives

- Know the kinds and relative strengths of intermolecular attractive interactions
- Understand the concept of polarizability
- Understand the effects of strengths of intermolecular forces on phase changes and substance properties such as viscosity and surface tension
- Understand the concepts of critical pressure, critical temperature, vapor pressure, normal boiling point, normal melting point, critical point, and triple point

Success Criteria

- Be able to judge relative strengths of intermolecular forces of attraction and their effects on properties for a series of compounds
- Be able to interpret heating curves and calculate quantities related to temperature and enthalpies of phase changes
- Be able to interpret and sketch phase diagrams

Prerequisite

Have read Chapter 11

Information (Intermolecular Forces)

The tendency of a substance to be found in one state or the other under certain conditions is largely a result of the kinds forces of attraction that exist between the particles comprising it. We will concentrate on the forces between molecules in molecular substances, which are called **intermolecular forces**. (Forces that exist within molecules, such as chemical bonds, are called *intramolecular forces*.) The greater the strength of the intermolecular forces, the more likely the substance is to be found in a **condensed state**; i.e., either a liquid or solid. As we have seen, the model of an ideal gas assumes that the gas particles (molecules or atoms) have virtually no forces of attraction between them, are widely separated, and are constantly moving with high velocity and kinetic energy. In truth, there are forces of attraction between the particles, but in a gas the kinetic energy is so high that these cannot effectively bring the particles together. With stronger intermolecular forces or lower kinetic energy, those forces may draw molecules closer together, resulting in a condensed phase. Going from gas to liquid to solid, molecular velocities and particle separations diminish progressively as structural order increases. In the case of liquids, molecular attractions give rise to **viscosity**, a resistance to flow. Also, the absence of intermolecular forces above the surface of a liquid results in **surface tension**, the development of a “skin” on the surface, which causes beading of liquid droplets and also allows light objects to

rest on a liquid surface without sinking (e.g., water bugs). Solids have stronger intermolecular forces, making them rigid, with essentially no tendency to flow. Although the mix of types and strengths of intermolecular forces determines the state of a substance under certain conditions, in general most substances can be found in any of the three states under appropriate conditions of temperature and pressure. Changing those conditions can induce a change in the state of the substance, called a **phase transition**.

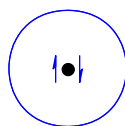
Key Questions

1. Is the average kinetic energy of molecules greater or lesser than the energy of intermolecular forces of attraction in (a) solids, (b) liquids, and (c) gases?
2. Why does increasing the temperature cause a substance to change in succession from a solid to a liquid to a gas?
3. Why do substances with high surface tension also tend to have high viscosities?
4. Why do surface tension and viscosity decrease with increasing temperature?

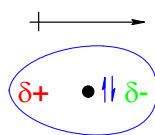
Information (Kinds of Intermolecular Forces)

We will consider the following types of intermolecular forces: **London dispersion**, **dipole-dipole**, and **hydrogen bonding**. London dispersion forces and dipole-dipole forces are collectively known as **van der Waals forces**. Molecules can have any mix of these three kinds of intermolecular forces, but all substances at least have London dispersion forces.

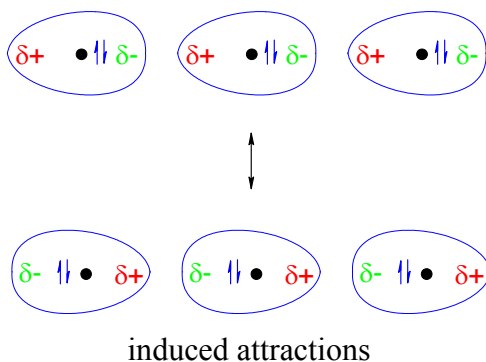
London dispersion forces exist for all substances, whether composed of polar or nonpolar molecules. They arise from the formation of temporary, instantaneous polarities across a molecule from circulations of electrons. An instantaneous polarity in one molecule may induce an opposing polarity in an adjacent molecule, resulting in a series of attractive forces among neighboring molecules.



average electron distribution



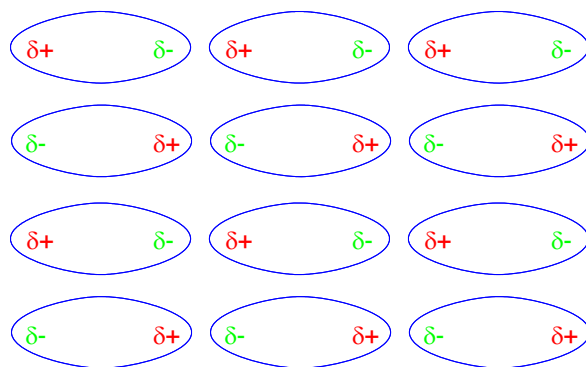
momentary distribution (polar)



London dispersion forces arise from changing electron distributions. Because all molecules have electrons, all molecular substances have London dispersion forces, regardless of whether they are polar or non-polar. Molecules with higher molecular weights have more electrons, which are generally more loosely held. This makes their electron clouds more deformable from nearby charges, a characteristic called **polarizability**. As a result, substances with higher molecular weights have higher London dispersion forces and consequently tend to have higher melting points, boiling points, and enthalpies of vaporization. The following data for the diatomic halogens nicely illustrate these trends.

Element	F ₂	Cl ₂	Br ₂	I ₂
m.p. (°C)	-220	-101	-7.3	114
b.p. (°C)	-188	-34	58.8	184
At 25 °C	gas	gas	liquid	solid

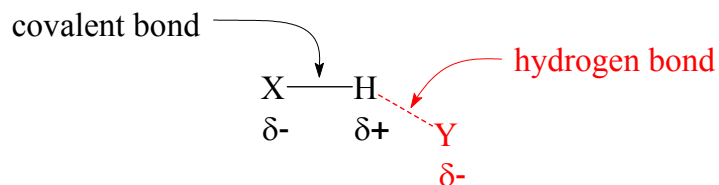
Dipole-dipole forces of attraction exist between molecules that are polar – those that have a permanent dipole moment. The polarities of individual molecules tend to align by opposites, drawing the molecules together and thereby favoring a condensed phase.



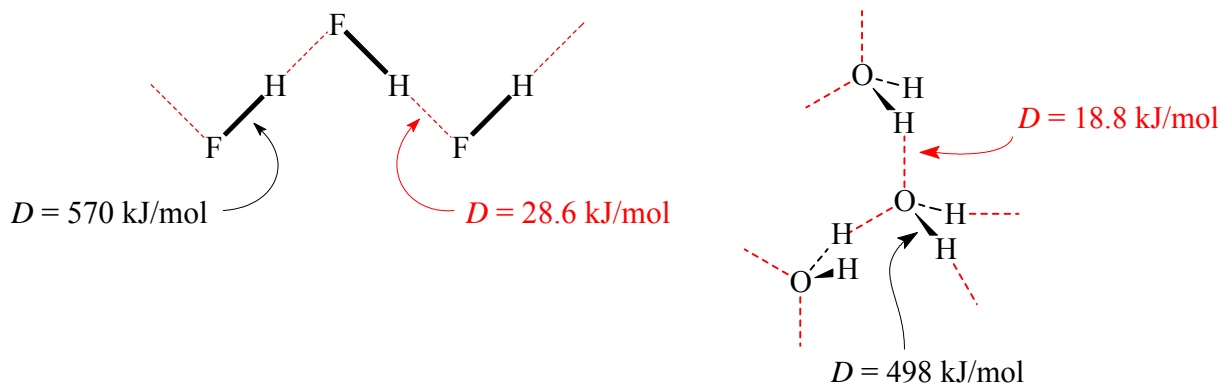
These additional forces of attraction must be overcome in a transition to a less-ordered phase (e.g., solid to liquid, liquid to gas), so substances with dipole-dipole attractions between their

molecules tend to have higher melting points and boiling points than comparable compounds composed of nonpolar molecules, which only have London dispersion intermolecular forces.

A hydrogen bond is a non-covalent attraction between a hydrogen that is covalently bonded to a very electronegative atom (X) and another very electronegative atom (Y), most often on an adjacent molecule. (X and Y may be the same or different elements.)



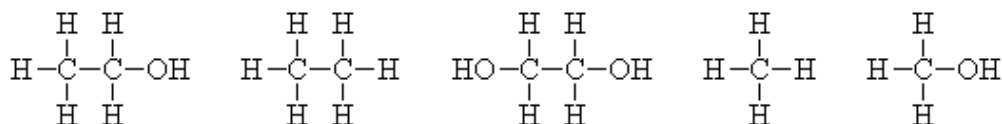
For the most part, only compounds in which hydrogen is covalently bonded to O, N, or F are candidates for hydrogen bonding. Covalent bonds with these elements are very polar, resulting in a partial negative charge (δ^-) on the O, N, or F. This partial negative charge can be attracted to the partial positive charge (δ^+) of the hydrogen in an X–H bond on an adjacent molecule. Thus, the H \cdots Y hydrogen bond, unlike the covalent X–H bond, results mainly from electrostatic attraction. Hydrogen bond strengths typically are in the range 4 - 46 kJ/mol, much less than the strengths of typical covalent bonds. Nonetheless, hydrogen bond strength is significantly greater than either London dispersion forces or dipole-dipole forces. Hydrogen bonds in HF(s) and H₂O(s) are intermediate in strength within this range.



Nonpolar molecules only have London dispersion forces, which tend to be the weakest of the three kinds of intermolecular forces. Polar molecules add another kind of force, beyond their London forces, and so have stronger overall intermolecular forces of attraction. If a molecule is capable of hydrogen bonding, then it has all three kinds of intermolecular forces and has the strongest overall mix. As the kinds of intermolecular forces increase, substances have a greater tendency to exist in a condensed phase, have higher melting points and boiling points, and as liquids have lower vapor pressure and lower viscosity.

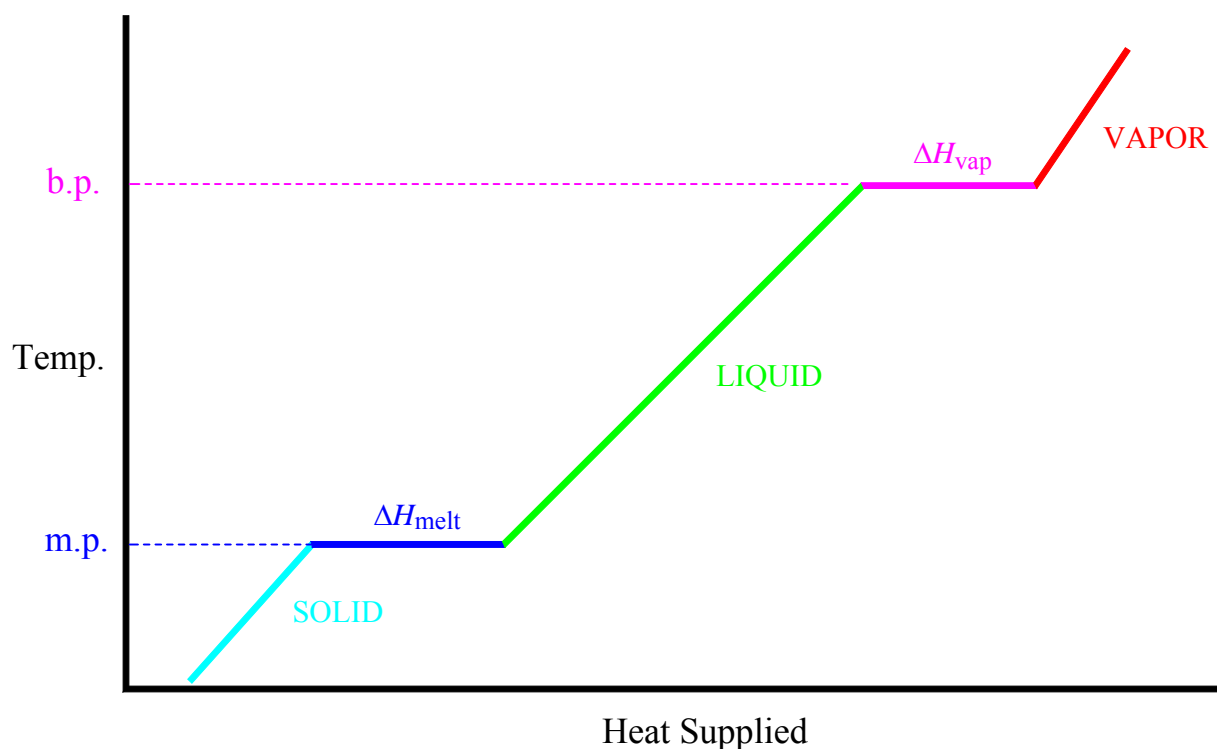
Key Questions

- Name the kind or kinds of intermolecular forces that must be overcome to convert the following from liquid or solid to gas: (a) Br_2 , (c) CH_3OH , (d) CO_2 , (e) HCN , (f) NH_3
- Normal alkanes are hydrocarbons with unbranched carbon chains, having a general formula $\text{C}_n\text{H}_{2n+2}$. At room temperature, ethane, C_2H_6 , is a gas; hexane, C_6H_{14} , is a liquid; and octadecane, $\text{C}_{18}\text{H}_{38}$, is a solid. Describe the intermolecular forces present in each substance and explain the differences in their room-temperature phases.
- Arrange the following in order of increasing boiling point:



Information (Heating Curves)

As we continuously heat a solid substance, such as ice, over time it can pass through all phases, giving a behavior represented by the following **heating curve**.



For a given input of heat, q , the temperature rises by different amounts in the solid, liquid, and vapor phases due to the different heat capacities for each phase. In a single phase, $\Delta T = q/C$, where C is the heat capacity for the phase in the range of the temperature change. Put another

way, in a single phase the amount of heat that must be added to raise the temperature a certain amount, ΔT , is given by $q = C \Delta T$. At both the melting point and boiling point, the temperature remains constant with heat input so long as both phases involved with the transition exist. At these points, all the heat is used to effect the conversion of one phase into another (from solid to liquid at the melting point or from liquid to vapor at the boiling point). Once conversion is complete, the temperature of the substance will rise with addition of heat. At the melting point, the amount of heat required to convert one mole of substance from solid to liquid defines the **molar heat of fusion**, ΔH_{fus} , also called the molar heat of melting, ΔH_{melt} . At the boiling point, the amount of heat required to convert one mole of substance from liquid to vapor is called the **molar heat of vaporization**, ΔH_{vap} .

Key Question

8. How much heat is required to heat 10.0 g of ice at $-5.00\text{ }^{\circ}\text{C}$ to become liquid water at $+7.00\text{ }^{\circ}\text{C}$? In this temperature range, the heat capacity of $\text{H}_2\text{O}(s)$ is $37.7\text{ J/mol}\cdot\text{K}$, and the heat capacity of $\text{H}_2\text{O}(l)$ is $75.8\text{ J/mol}\cdot\text{K}$. The molar heat of fusion of ice is 6.01 kJ/mol .

Information (Vapor Pressure)

If a liquid is placed in a closed container, both evaporation and condensation will occur simultaneously. Initially, evaporation predominates, because there are so few molecules in the vapor phase above the liquid. As more and more molecules build up in the vapor, some will strike the liquid surface, be attracted to liquid molecules, and rejoin the liquid phase. At some point the rate of molecules escaping the liquid will equal the rate of molecules rejoining it from the vapor. This marks the onset of a state of **dynamic equilibrium** at which the rates of evaporation and condensation are equal. At this point, the number of vapor molecules in the volume above the liquid remains constant over time. The resulting partial pressure of the vapor in equilibrium with the liquid is the **vapor pressure**. The vapor pressure depends upon the nature of the liquid (ΔH_{vap}), the kinetic energy of the molecules (increasing with temperature), and the resulting vapor concentration.

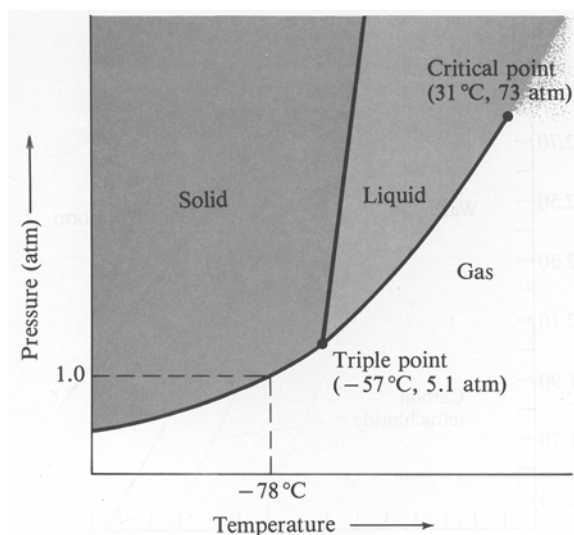
Although different substances may have different vapor pressures at the same temperature (higher for more volatile substances), all vapor pressures increase with increasing temperature. When the temperature is high enough that a liquid's vapor pressure equals the ambient pressure, boiling will commence. At temperatures where the vapor pressure is lower than the ambient pressure, no bubbles of vapor can form in the liquid, because the greater air pressure would cause them to collapse. The higher the ambient pressure, the higher the boiling point will be. For this reason, we define the normal boiling point at 1 atm. Conversely, boiling occurs at a lower temperature when the ambient pressure is lower. For example, Mt. Washington (elevation 6288 ft) has a typical air pressure of 610 torr. At $94\text{ }^{\circ}\text{C}$, the vapor pressure of water is 610.90 torr, so this is approximately the boiling point of water atop Mt. Washington. Consequently, foods tend to require longer cooking times at high altitudes.

Key Questions

9. Explain how each of the following affects the vapor pressure of a liquid: (a) the volume of the liquid, (b) the volume of the container, (c) the surface area of the liquid, (d) the temperature, (e) intermolecular forces of attraction, (f) the density of the liquid.

Information (Phase Diagrams)

The relationships between temperature and pressure and the phase transitions of a substance can be summarized in a **phase diagram**. The phase diagram for carbon dioxide is shown below.



For any combination of temperature and pressure that falls entirely within a phase region, only that one phase will exist. Lines on the diagram represent combinations of temperature and pressure under which two phases coexist (e.g., gas-liquid, liquid-solid, solid-gas). The **triple point** is the combination of temperature and pressure at which all three phases are simultaneously in equilibrium. The **critical point** marks the limit on the ability to condense a vapor with applied pressure at high temperature. Above this point it is not possible to condense the gas regardless of increasing pressure. The **critical temperature**, T_c , is the point above which a gas cannot be liquified, regardless of the pressure. The **critical pressure**, P_c , is the minimum pressure needed to cause condensation at the critical temperature. Above the critical point the substance exists as a **supercritical fluid**.

Key Questions

10. Describe the phases and/or phase transitions experienced by CO_2 under the following conditions:
- Heating from $-100\text{ }^\circ\text{C}$ to $30\text{ }^\circ\text{C}$ at 1.0 atm
 - Heating from $-100\text{ }^\circ\text{C}$ to $50\text{ }^\circ\text{C}$ at 70 atm
 - A sample at $35\text{ }^\circ\text{C}$ and 100 atm
 - A sample at $-50\text{ }^\circ\text{C}$ and 6.0 atm
11. Does carbon dioxide have a normal boiling point? Explain.

12. Describe the conditions under which liquid carbon dioxide boils.