

Chapter 11 HW pp. 494 - 501: Set 1- 8, 10, 12, 16, 19, 20; Set 2- 36, 40, 48, 52, 54, 56;  
Set 3- 74, 75, 78, 82, 85, 93, 96; Set 4- 110, 118, 125, 126, 133, 137, 140.

## Intermolecular Attractive Forces and Liquids and Solids

### A. Intermolecular Attractive Forces

1. Johannes van der Waals
  - a. Tried to explain why something condenses. As the molecules slow down in a gas being cooled something must pull these molecules together to change phase. Intermolecular forces. The higher the temperature at which the gas condenses the stronger the intermolecular forces. There are two basic types
  - b. London dispersion forces (Dispersion interaction or momentary dipole forces) {Named for Fritz London}
    - (1) This type exists between all molecules. The larger the molecule ( number of electrons) the greater the attraction. This is the weakest van der Waals force. This can also be viewed as a momentary dipole. Since the electrons are constantly moving about the molecule, it is logical to assume at a particular time most of the electrons will be clustered about one end of a molecule thus creating a momentary unequal distribution of charge or a dipole. This creates attractive forces between two molecules, momentarily.
  - c. Dipole - Dipole attractive force.
    - (1) This only exists between dipoles (polar molecules with two distinct regions of opposite charge). This is a stronger force than dispersion. The slightly positive end of a molecule is attracted to the slightly negative end of another.
    - (2) A special type of Dipole - Dipole attraction is a hydrogen bond. This is the strongest type of dipole - dipole attraction since the hydrogen only has one valence electron and its proton is easily exposed. This exposed proton attracts other negatively charged regions of other dipoles. This has 5% of the strength of a covalent bond. It is not a true chemical bond but is important in determining properties.

### B. Liquids - Least common phase of matter in universe because liquid phase of any substance can exist only within a narrow range of temperature and pressure.

1. General description - no definite shape, definite volume
2. KMT description
  - a. consists of particles ( ions, atoms, molecules )
  - b. substance is a liquid because of the arrangement and behavior of particles not the nature of particles
  - c. particles are in constant motion

- d. particles are closer together and lower in energy and entropy than gas particles thus the attractive forces must be stronger than gas and limits motion
- e. kinetic energy is high enough so the particles are not bound together as in solids.

3. Properties

- a. Fluidity - ability to flow since particles are not bound about a fixed position, the  $E_K$  overcomes attractive forces.
- b. One Free Surface - attractive forces are strong enough to hold particles together on one surface
- c. Relatively high density - 1000 times greater than corresponding gas; particles are more closely packed due to attractive forces.
- d. Relative incompressibility - particles are closely packed and can evenly distribute pressure in all directions
- e. Dissolving ability - Definition - when one substance is added to another so that, after mixing, only one phase is observed, the substance has been dissolved. Liquid is the most common dissolving agent. Why? Motion of particles and attractive forces they exert on solute.
- f. Ability to diffuse - any liquid will gradually diffuse throughout any other liquid in which it can be dissolved. Due to constant random motion of particles. Occurs slower than gases since forward moving particles of closely packed liquid will soon strike another particle, changing its path and attractive forces impede movement. Increases with temperature since avg.  $E_K$  increases thus the particles are moving faster.
- g. Surface tension - common to all liquids to different degrees; attractive forces tend to pull adjacent parts of liquid's surface together, thus making the surface less penetrable by solid bodies; acts to minimize free surface area - as a result, liquid droplets tend to be spherical shape which is the least possible surface area.
- h. Capillary action - tendency for liquid to rise up a narrow tube resulting from the attractive forces between particles and glass
- i. Evaporation - process by which a liquid or solid changes to a gas is vaporization; process by which particles escape from the surface of a non-boiling liquid and enter into gaseous phase is evaporation. Some particles are moving faster than other particles and can escape spontaneously into gaseous phase. This lowers the liquid's  $E_K$  and allows it to absorb energy from the surroundings thus giving more particles enough energy to escape. This is a continuous

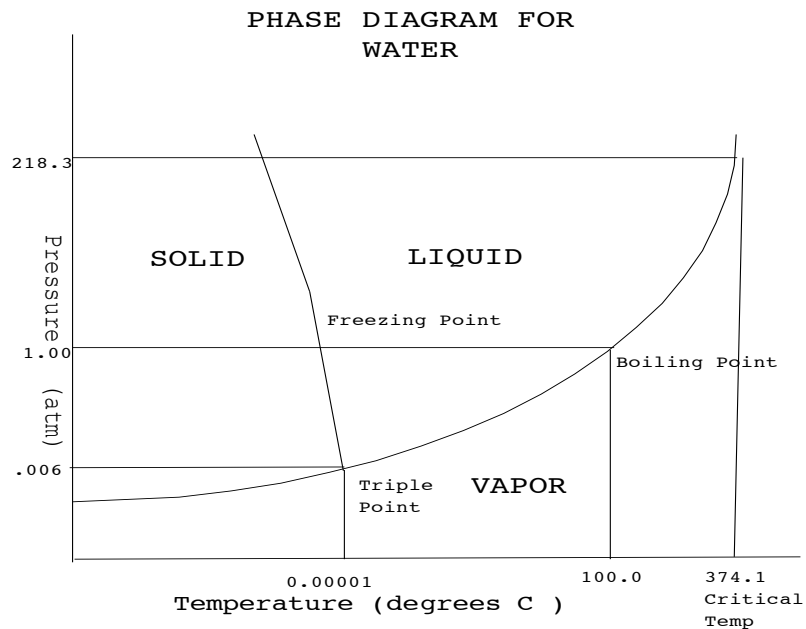
process until all liquid is evaporated. No noticeable temperature change.

-This also causes vapor pressure in a closed system. Equilibrium is reached when as many particles are going to vapor as are returning to liquid. This is continuous thus dynamic. Rates are equal not particles. When equilibrium is reached the vapor pressure is called the equilibrium vapor pressure. Vapor pressure is directly related to intermolecular attractive forces. Substances with strong IM forces have low vapor pressures; weak IM forces have high vapor pressures.

- j. Boiling - When bubbles appear throughout liquid ; this occurs when the equilibrium vapor pressure equals the atmospheric pressure. The temp at which this occurs is called the boiling point. The temperature at which the vapor pressure of a solid equals the vapor pressure of the corresponding liquid is melting point. Depends on IM forces - weak IM forces (non polar, low molar mass) - low boiling point and melting point ; strong IM forces (polar) - high boiling and melting points. If a solid has a high enough vapor pressure the solid will sublime - turn to gas without passing through the liquid phase (iodine). How does boiling differ from evaporation ? Evaporation occurs at surface while boiling occurs throughout liquid. A liquid with a very low boiling point and evaporates readily at room temp is said to be volatile, high vapor pressures.
- k. Condensation & Liquefaction - Condensation is vapor to liquid while liquefaction is gas to liquid. Cooling gas / vapor slows the particles until the IM forces can take hold. Compression helps since van der Waals forces are effective for short distances. Associated terms - critical temperature ( $T_c$ ) - temp above which no amount of pressure can liquefy gas. Indication of strength of IM forces. ( Table ) critical pressure ( $P_c$ ) - minimum pressure needed to liquefy gas at  $T_c$  .
- l. Freezing - As liquid is cooled  $E_k$  is small enough for IM forces to hold particle about a fixed point with an orderly arrangement (solid). All liquids freeze. Wax freezes at room temp
- m. Liquid - Vapor equilibrium - In a closed system we have  
liquid + energy  $\rightleftharpoons$  vapor and then  
vapor  $\rightleftharpoons$  liquid + energy  
once equilibrium is reached ( rates are equal ) we have  
liquid + energy  $\rightleftharpoons$  vapor

If this equilibrium is disturbed by a stress, the equilibrium will shift to relieve that stress and form a new equilibrium at a new rate – Le-Chatelier's Principle .

- n. Phase Diagram - A diagram used to show the relationships between solids, liquids and gases. It is a graph of temperature vs. pressure that indicates the conditions under which gaseous, liquid or solid phase of a substance exists. The negative slope of solid - liquid line means if pressure drops ice melts at a higher temperature. As temp drops below triple point, the temp of sublimation decreases with decreasing pressure. This is how food is freeze - dried..



vaporize ice and lower press after freezing.

- o. Most common liquid - Water.  
 Why does ice float? Less Dense ? Why ? Water's bond angle is  $105^{\circ}$ , this creates openings in crystal. Water has strong hydrogen bonds - strong IM forces - high boiling point - low vapor pressure and high critical temp. Water is most dense at  $4^{\circ}\text{C}$ ; as ice melts particles are closest at  $4^{\circ}\text{C}$  then move apart and break hydrogen bonds

C. Solids

1. General definition - definite shape, definite volume
2. KMT description
  - a. Consists of particles ( ions, atoms, molecules )
  - b. Avg. kinetic energy is lower than gas and liquid particles thus less motion; particles move back and forth about fixed position.

- c. More closely packed than gases or liquids thus IM forces are more important ; dipole-dipole, dispersion interaction, hydrogen bonds; hold solid particles in place.
  - d. Much more orderly since held in place and therefore very low entropy.
3. Particle model of a solid
- a. description in terms of the arrangement and motion of the solid particles and the attractive forces between them.
  - b. two types of solids
    - 1) crystalline solid - most common - consists of crystal, particles are arranged in an orderly geometric repeating pattern.
    - 2) amorphous solids - super cooled liquids; from Greek a(without) + Morphe(form); particles arranged randomly
4. Properties
- a. Definite shape - crystalline solids are geometrically regular; amorphous solids do maintain a definite shape (temporary), but no geometry and can have any shape.
  - b. Definite volume - since particles are very closely packed, strong IM forces; all surfaces are free
  - c. Non fluidity - particles are held in fixed position; some amorph do flow very slowly - very viscous
  - d. Definite melting point - temp where a solid becomes a liquid;  $E_k$  of particles overcome IM forces; amorphous solids have no definite m.p.( this is why they are called super cooled liquids - retain certain liquid properties at temperatures which appear to be solid
  - e. High Density - particles are tightly packed
  - f. Incompressibility - particles are as close as they are going to get at normal conditions ( FYI- Discover article - Element Smith pounds elements closer together than normal.)
  - g. Slow rate of diffusion - particles are still in motion - at surface some can migrate to other solids; rate is a million times slower than in liquids.
5. Closer look at crystalline solids
- a. classified by arrangement and shape -Done by X-ray crystallography , as X-ray passes through crystal it gives a distinct pattern similar to light passing through a prism as in spectroscopy lab.
  - b. crystalline structure is the total 3-D arrangement of particles
  - c. Unit cell is the smallest portion of a crystal lattice that shows the pattern ( simplest repeating pattern ).
  - e. seven basic shapes

NAME	Axes	Angles between axes
isometric or cubic	all equal axes	all 90°
tetragonal	2 equal	all 90°
rhombohedral	all equal	all not 90°
orthorhombic	all unequal	all 90°
monoclinic	all unequal	2 = 90°, 1 not
triclinic	all unequal	no 90°
hexagonal	3 equal	1 = 90°, 3 = 60°

- f. central shapes may contain different type of unit cells for example : simple cubic - each particle has 6 immediate neighbors and contains 1 atom; face-centered - each particle has 12 immediate neighbors and contains 4 atoms; body centered - each particle has 8 immediate neighbors and contains 2 atoms.
- g. Forces that keep crystals together (4 basic types of crystals)
- 1) Ionic Crystal -contains ions, Group1 or 2 w/Group16 or 17, strong binding (+) (-) attraction results in hard & brittle, high melting points and good insulators.
  - 2) Covalent Network Crystals - contains single atoms giant or macromolecules; hard & brittle, high melting points, nonconductors or semiconductors.
  - 3) Metallic Crystals - positive ions of metal surrounded by a cloud of valence electrons donated by metal atoms and belonging to the crystal as a whole, binding force is between (+) ions and electrons; electrons are free to migrate through crystal lattice thus high electrical conductivity; m.p. vary
  - 4) Covalent Molecular Crystals - covalently bonded molecules held together by IM forces between molecules; non polar molec.= dispersion interaction; polar molec. = dipole-dipole and dispersion; low melting points, easily vaporized, soft and good insulators
6. More about Morphs
- a. amorphous forms of metal alloys prepared by rapid cooling of thin films of metals- atoms do not have time to arrange themselves - resulting in “metallic glass”, strong flexible more resistant to corrosion than crystals of same composition.
  - b. isomorphism - crystals of different solids with same structural shape
  - c. polymorphism - crystals of same substance with 2 or more shapes

7. Nothing's Perfect
- Defects or dislocations either within unit cell structure (ions missing others in place) or extra layer.
  - Some defects are on purpose and helpful
    - man made defects - crystals are "doped" ; used to make semiconductors...Si & Ge can be made to conduct electricity, if As is added - extra electron available to move across crystal. If Ga is added - short an electron and electrons fill "hole."
  - Other impurities
    - If water is in crystal that is if ions are chemically bonded to water ( hydrated ions ) & then crystallize - hydrated crystal or hydrates. To remove water - heat , lower pressure , then they become anhydrous.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
    - some substances absorb water from air - hygroscopic
    - some absorb enough to dissolve - deliquescent
8. What the heck is a liquid crystal ?
- crystalline solid very orderly, liquid very unorderedly - random in all three dimensions; solid loses crystalline order in only one or two dimensions at melting point form liquid crystals. ( smectic - retain 2 orders ; nematic - retains 1 order )

D. Energy involved in Phase Changes

- Substances boil and melt at constant temps. This is due to energy needed for phase change to occur. IM forces are overcome.
- Energy required to melt one gram of a substance at its melting point is called the heat of fusion ( $\Delta H_f$ ) (  $\text{H}_2\text{O} = 334 \text{ J / g}$  )
- Energy required to vaporize 1 g of a substance at its boiling point is called the heat of vaporization ( $\Delta H_v$ ) (  $\text{H}_2\text{O} = 2260 \text{ J / g}$  )
- Also involved is the specific heat ( amount of heat needed to raise 1 g of a substance  $1 \text{ C}^0$  .) since substance needs to reach its m.p. or b.p. (  $C_p$  )
 
$$\text{H}_2\text{O}_{(l)} = 4.18 \text{ J / g C}^0 \qquad \text{H}_2\text{O}_{(s)} = 2.06 \text{ J / g C}^0$$

$$\text{H}_2\text{O}_{(v)} = 2.02 \text{ J / g C}^0$$
- Formula  $q = m(\Delta T)C_p$  not needed just catch the fever !
 

$q = \text{Heat (J)}$      $m = \text{mass (g)}$      $\Delta T = \text{change in temp ( C}^0 \text{ )}$   
 $C_p = \text{specific heat}$