

AMSAT Chemistry

Intermolecular Forces (IMFs) Topic#12 Abridged Notes

- A. Kinetic molecular theory (KMT) (particles of matter are always in motion)
- Gases (no definite shape or volume)
 - Ideal gas (hypothetical gas that meets assumption of KMT)
 - Tiny particles that are very far apart, collisions are elastic (no loss of energy), continuous motion, no attractive forces, T directly proportional to KE
 - Liquids (no definite shape but definite volume)
 - Particles are closely packed, attracted to each other and container.
 - Have a vapor pressure (some particles have enough KE to escape the surface of the liquid)
 - More ordered than gases
 - Fluids (substances that flow; $\text{He}(l)$ flows uphill!)
 - Relatively high density (1000 times $>$ than (g))
 - Relatively incompressible (water is only compressed 4% under 1000 atm pressure, pressure is transferred throughout the liquid (hydraulics; car brakes))
 - Exhibit diffusion, but slower than gases.
 - Surface tension – force that pulls surface particles towards center of liquid, seeks smallest surface area possible (sphere)
 - Capillary action – the attraction between a liquid and a solid
 - Adhesive forces – attraction between (l) and (s)
 - Cohesive forces – attraction between liquid particles.
 - Ethanol vs. $\text{H}_2\text{O}(l)$ vs. $\text{Hg}(l)$
 - Vaporization – process of a (l) becoming a (g)
 - Evaporation – (l) to (g) at T between melting point (mp) and boiling point (bp).
 - Boiling point (bp) – T at which a (l) spontaneously forms gaseous bubbles dependent on atmospheric pressure.
 - Can make a liquid boil at any temperature as long as the VP above is equal to the ambient P (surrounding P)
 - Normal bp – bp where the atmospheric P is 1 atm.
 - Higher P – higher bp
 - Lower P – lower bp
 - Solids (definite shape and definite volume)
 - Particles are very close together and held firmly in place (fixed) with only rotational and vibrational movement.
 - Can be ordered (crystals) or disordered (amorphous).
 - Crystalline solids – very ordered, smallest part called a unit cell (metals, ionic solids).
 - Crystal structure (crystal lattice) is made up of repeating unit cells (think of a brick wall)
 - Definite m.p.
 - Types
 - Metallic – solid pure metals ($\text{Fe}(s)$, $\text{Mg}(s)$, $\text{Hg}(l)$, etc.)
 - Ionic – matrix of cations and anions (NaCl , MgO , Fe_2O_3 , etc.)
 - Molecular – polar (H_2S , H_2O , HCl , etc.), nonpolar molecules (H_2 , Cl_2 , CO_2 , etc.) and atoms (noble gases: He, Xe etc.)
 - Network covalent – covalent bonding between particles ($\text{C}(\text{dia})$, graphite, etc.)
 - Amorphous solids
 - Disordered arrangement of the particles (glass, wax, plastics)
 - Considered a “supercooled liquid”. These solids will flow over time.
 - Older buildings with original glass must have the panes flipped every so many years; bottom of glass becomes thicker with time.
 - Melts over a range of temperatures
 - Densest form of matter (except water where liquid form is densest).
 - Have a coefficient of expansion unique to the solid. (engineers use the coefficient of expansion when designing a project; bridges have an expansion joint on both sides of the bridge)
 - Very little diffusion, only at surface.

- i. Coulombic Forces (electrostatic – attractions between negative & positive particles)
 1. Ion-ion
 - a. Ionic compounds – attraction between cations and anions
 - i. Crystal lattice energy is the energy released when gaseous cations and anions come together to form the ionic solid.
 1. The coulombic force of attraction within the ionic compound is high. The stronger the force, the larger the crystal lattice energy.
 - a. In the equation for coulombic force, k is a constant, q_1 and q_2 are the charges on the ions involved, and d is the distance between particles. When the particles are oppositely charged, the force is negative and positive when they are the same charge.

$$F = k \frac{q_1 \times q_2}{d^2}$$
 2. Two things to know about the strength of the ionic interaction (force)
 - a. Distance – small atoms are closer, which results in a strong attraction and a higher lattice E where larger atoms result in a weaker attraction and lower lattice energy.
 - i. $\text{NaF} > \text{CsF}$
 - b. Charge – higher positive and negative charges result in a stronger coulombic force of attraction resulting in higher lattice energy.
 - i. $\text{NaF} < \text{MgF}_2$
 2. Ion-dipole
 - a. Forces of attraction between an ionic compound dissolved in a polar solvent (H_2O).
 - b. When NaCl dissolves in water, the Na^+ is attracted and surrounded by the oxygens in water, and the Cl^- are attracted and surrounded by the hydrogens in water.
 3. Dipole-dipole
 - a. Polar compounds consist of at least one polar bond (bond has an EN_{diff} between 0.4 and 1.7 – ammonia (NH_3), water (H_2O), etc.) and is asymmetrical. This creates a dipole moment where the particle has a permanent negative region and positive region.
 - i. Molecules align themselves so that the negative end of one is near the positive end of another.
 - ii. This interaction creates an intermolecular bond called a dipole-dipole bond and increases the boiling and melting points of polar compounds.
 - b. Hydrogen bonding
 - i. Bonding in compounds containing hydrogen and a highly electronegative element such as O, F, or N.
 1. Strongest dipole-dipole force
 2. Strength due to the highly polar nature of the bond between H and O, F, or N. This creates a large partial charge on the hydrogen and a large partial negative charge on the other atom. In addition, the distance between the dipole is very short to the very small hydrogen.
 3. The combination of large bond dipole a short dipole-dipole distances results in a very strong dipole-dipole interaction.
 4. London dispersion forces (LDF)
 - a. All liquids and solids have these forces, but LDFs are the ONLY force in atomic (He, Ar, etc.) or nonpolar (H_2 , Cl_2 , CH_4 , CO_2 , etc.) liquids and solids.
 - b. Instantaneous dipoles created when the electron cloud of one atom or nonpolar molecule interacts with another atom or nonpolar molecule.
 - i. Strength of LDF increases with size of particle (MM is good indicator of size; the higher the MM , the stronger the LDFs.
 1. The bp of $\text{SnH}_4 > \text{GeH}_4 > \text{SiH}_4 > \text{CH}_4$
 2. The mp of $\text{I}_2 > \text{Br}_2 > \text{Cl}_2 > \text{F}_2$ (I_2 is large enough to be solid at room T)
 - a. The larger the atom, the larger the electron cloud, the easier it is to induce a dipole (polarizability).
 - b. I_2 is more polarizable than Br_2 , Cl_2 , or F_2 .
 - c. In addition, large nonpolar molecules (like oils) have stronger LDFs because they have an increased surface area.

- i. Neopentane (C₅H₁₂) is almost spherical in shape while *n*-pentane (C₅H₁₂) is long. Both have a *MM* of 72g/mol.
 1. *n* – pentane has a higher bp (36.1°C) than neopentane (9.5°C) due to the shape alone.
- ii. Chemical Bonds
 1. Macromolecules (crystal is essentially a single unit connected through chemical bonds; continuous chemical bonding throughout the entire structure)
 - a. Metallic
 - i. Very strong intermolecular force with high mp and bp
 - ii. the metallic bond results from a “sea of electrons.”
 1. The atomic cores (nucleus + inner electrons) and the valence electrons.
 - a. The overlapping of the outer orbitals gives the valence electrons places to move freely throughout the solid. These electrons are called “delocalized,” which means the electrons are attracted to all of the positive nuclei in its vicinity. Valence electrons are not exclusively associated with one atom.
 - b. The strength of a metallic bond is reflected in its heat of vaporization (ΔH_{vap}) (how much energy needed to change the liquid into a gas; boiling point)
 2. Covalent network (covalent bonding through structure)
 - a. Very strong intermolecular force with a relative high mp and bp.
 - b. Actual covalent bonds between the particles in the solid.

C. Changes of State

a. Phase Changes

- i. Vaporization (*l* to *g*) and condensation (*g* to *l*)
 1. Involves the addition of *E* and removal of *E*, respectively.
 2. In a closed system at constant *T*, an equilibrium will exist between the liquid a gas state.

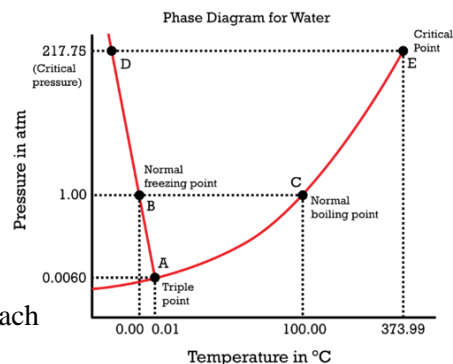
$$\text{liquid} + \text{energy} \leftrightarrow \text{gas}$$
 - a. Equilibrium is a dynamic state where opposing changes occur at the same rate.
 - i. For this case, as one gas particle condenses into a liquid particle, a liquid particle vaporizes into a gaseous particle.
 1. Equilibrium vapor pressure is the pressure of the vapor when equilibrium has been established.
 3. Boiling is when a liquid turns to a gas inside the liquid.
 - a. Boiling point occurs when the vapor pressure of the liquid equals the ambient pressure (surrounding pressure). Normal bp for water is 100°C at 1atm (760torr/101.3kPa).
 - i. To keep a liquid boiling a constant supply of energy must be added.
 1. Molar heat of vaporization, ΔH_{vap} .
 - a. Amount of energy needed to vaporize one mole of a substance.
 - i. Molar heat of vaporization for water is 40.79kJ/mol.
- ii. Freezing (*l* to *s*) and Melting (*s* to *l*)
 1. Involves the removal of *E* and addition of *E*, respectively.
 2. Normal freezing point (fp) – *T* at which the solid and liquid are in equilibrium at 1atm (760torr/101.3kPa).

$$\text{liquid} \leftrightarrow \text{solid} + E$$
 3. Molar enthalpy of fusion, ΔH_{fus}
 - a. The amount of energy needed to melt 1 mole of a substance.
 - i. For water, $\Delta H_{\text{fus}} = 6.009\text{kJ/mol}$
- iii. Sublimation and deposition
 1. Involves the removal of *E* and addition of *E*, respectively.

$$\text{solid} + E \leftrightarrow \text{gas}$$
 - a. Example, CO₂(*s*) in a closed container.

D. Phase Diagram

- Curve A-E – liquid gas interface
- Curve A-D – solid liquid interface
- Curve A-(y-axis) – solid gas interface
- Triple point (A) – point where all three phases exist in equilibrium
 - For water the P is 0.0060atm and the T is 0.01°C
- Critical point on a phase diagram where the liquid phase and gas phase have the same density making them indistinguishable from each other.
 - Critical temperature – above this T a gas cannot be liquefied by pressure alone.
 - Critical pressure – the pressure of a gas in its critical state (the P needed to liquefy a gas at its critical T)
 - For water, the critical temperature is 373.99°C and the critical pressure is 217.75atm



E. Water

- Polar, bent (105°), two unshared pairs of electrons, crystalline solid
 - Dipole moment – permanent positive and negative areas on the molecule
 - Dipole-dipole forces hold the liquid and solid form together
 - Special type of dipole-dipole bond called hydrogen bonding.
 - Unusually strong, due to its shape (bent), polarity of its bond (the H-O bond has a $EN_{\text{diff}} = 1.4$), and its relatively small size.
- $d_{\text{liq}} > d_{\text{sol}}$ ($1.0\text{g/cm}^3 > 0.917\text{g/cm}^3$) (solid floats)
 - Usually, four to eight water molecules linked through hydrogen bonding in liquid water. If not for these molecular groups, water would be a gas at room T .
 - When water freezes it forms in a hexagonal arrangement which has many empty spaces resulting in a lower density than liquid water.
 - As the ice is heated up, the rigid structure breaks down allowing for the molecules in liquid water to have fewer and more disordered hydrogen bonds. This results in the liquid water molecules to crowd together with it being the most tightly packed at 3.98°C where water is at its densest.
- normal mp = 0°C and normal bp = 100°C
- Compared to nonpolar molecules similar in size (CH_4 ($MM = 16.05$) vs. water ($MM = 18.02$)), water has a high heat of fusion, $\Delta H_{\text{fus}} = 6.009\text{kJ/mol}$, and heat of vaporization, $\Delta H_{\text{vap}} = 40.79\text{kJ/mol}$.
- High specific heat, S , of 4.184J/mol-K.