CHEM 1035 – Lecture 37

Intermolecular Interactions

The mixing of the atomic orbitals of the bonding atoms leads to the formation of molecular orbitals. Many properties of molecules can be explained with molecular orbitals that cannot be explained by the Lewis structures, or through orbital hybridization.

Intermolecular forces

- Covalent bonds occur between atoms within a single molecule. The observable physical properties of compounds (e.g. the state of matter, density, melting point, etc.) are a function of the attraction between the molecules of a compound.

Covalent molecules demonstrate many different physical properties. Some are soft, some are hard; some are gases, some are solids; some have very high melting points, some have low melting points. These properties are a function of the strength of the “Intermolecular forces” acting between the individual molecules of the compound.

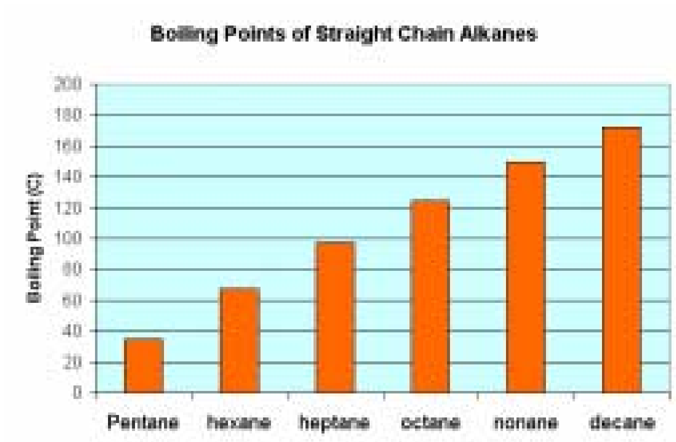
Perhaps the easiest measure of the intermolecular forces is to look at phase changes (e.g. conversion between solid-liquid-and gas phase)

Phase Changes

- Consider the changes in matter when going from one state (e.g. solid) to another (e.g. liquid)
- How can we characterize the different states of matter on a molecular scale?

What, on the molecular scale, defines something as a solid, or a liquid, or a gas? When looking at the ideal gas law, we presented a Kinetic Molecular theory of gases to explain why all gases had physical properties that were virtually identical despite the fact that they had different chemical properties. Let's extend the Kinetic Molecular theory to include a description of other states of matter

Consider a series of related molecules



Looking at the boiling point of these related molecules, we can see a general trend that the more massive the compound, the higher the boiling point. How can we relate this to the Kinetic Molecular theory?

All compounds, at any temperature, have the same Kinetic Energy. Consequently, their velocity is inversely proportional to the square-root of the molar mass. Compounds that are liquids at a given temperature, therefore, have velocities that are so small that the molecules tend to associate with each other. Taken one step further, things that are solids have a even smaller velocity relative to the other molecules in the solid, and they tend to have even greater association with each other.

Phase changes

- Solid to Liquid – fusion, melting
- Liquid to gas – vaporization
- Gas to Liquid - condensation

To change the phase of a material, you need to alter the velocity of the molecules of the compound relative to one another. This can be done by changing the temperature.

Changing the temperature implies that these processes involve an change in the Enthalpy of the system. Are these processes Endothermic or Exothermic? What is your rationale?

Enthalpy changes with Phase change

- Heat of Vaporization : ΔH^o_{vap}
- Heat of Fusion : ΔH^o_{fus}
- Heat of sublimation : ΔH^o_{sub}

What is sublimation? – the process of converting directly from a solid to a gas. CO_2, naphthalene (moth balls) both sublime. How to get the heat of sublimation? Hess's law of heat summation. Example with water.

How much heat is required to change the temperature of 20.0 gm ice (solid water, c = 2.09 J/gm·K) from -10^{o} C to 0^{o} C?

Q = cm(delta)T

Is this a exothermic or endothermic process?

Once at 0^{o} C, what happens? Does the temperature continue to change while the ice melts? Why/Why not?

Heat and temperature change during phase changes

- Within a single phase, changes in the heat are accompanied by temperature changes.
- During a phase change, the temperature of the system stays constant, and the heat flow is associated entirely with the changes in the kinetic energy of the molecules in the system.

Example Problem

How much heat is required to change the temperature of 15.0 gm of ice from -20^{o} C to 15 gm of liquid at 35^{o} C?

c_{solid} = 2.09 J/gm·K

C_{liquid} = 4.184 J/gm·K

Process: heat the ice from -20^{o} C to ice at 0^{o} C. Convert ice at 0^{o} C to water at 0^{o} C . Then heat the water from 0^{o} C to 35^{o} C.

Liquid-Vapor Phase Transition

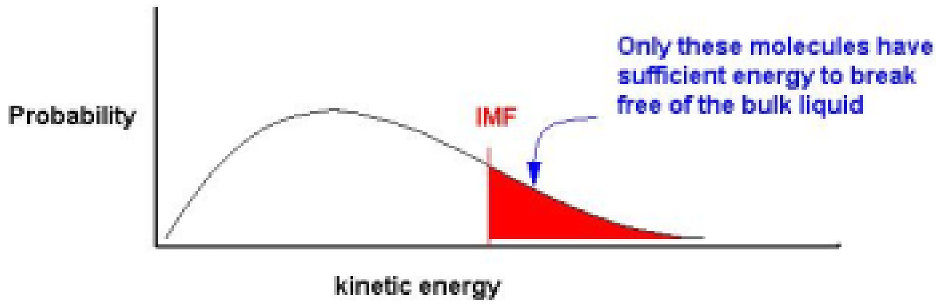
Vaporization (evaporation) of a liquid, like melting (fusion) of a solid occurs by heat transfer without changing temperature.

How does the vaporization occur?

Demonstration with chloroform in open container and closed container.

Why is there a difference? Phase change equilibrium, and vapor pressure.

Kinetic Energy Relationship to vapor pressure



Frequency distribution plot of the fraction of molecules in the liquid phase and the associated kinetic energy of those molecules. The IMF (intermolecular force) indicates the energy equivalent that corresponds to the Intermolecular forces that hold the molecules together in the liquid phase. If the kinetic energy of the molecules in the vapor phase exceed the IMF, then they have sufficient energy to escape the liquid phase and become vapor.

We can see from this relationship, that the amount of material in the vapor phase will depend on the kinetic energy of the molecules. From the kinetic molecular theory, we can change the kinetic energy by increasing the temperature of the system. What happens to this plot?

Vapor Pressure

- In a closed system, the vapor pressure of a pure material is the partial pressure of the vapor phase of the molecule that exists in the space above the pure liquid.

Temperature-Vapor pressure Relationship

- Clausius-Clapeyron Equation

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

From the Clausius-Clapeyron equation, the vapor-pressure at one temperature can be related to the vapor pressure at a second temperature, provided that the Heat of vaporization is known.