Thoughts of the Day 11/16/10

Real gases

A way to try examine real gas behavior is to compare it to ideal gas behavior. This is essentially what the compressibility factor does. Z=(PV)/(nRT)

If $Z > 1$ then for the same P & T the volume of the gas is greater than it would be if the gas were ideal. This is in the limit in which the repulsive IMF dominate

Conversely if $Z < 1$, the volume is less than ideal. Thus the attractive forces are dominant.

How to quantify this.

1. Just use the exact data. Nice. It's exact. Cumbersome. We can't really get physical insight staring at tables of numbers.

2. Fit the data to an empirical model. For example we could plot Z as a function of P for a real gas and then fit the curve to a polynomial. This would give us an equation of state. Downside is there are an infinite number of terms. We could just drop a few off. Also, our Z data is taken at one temperature. We now have a different equation for every temp.

3. Find a model which tries to incorporate IMF into the ideal gas law. This is the van der Waals equation.

The van der Waals equation (VDW) takes the ideal equation and modifies it to include the effects of IMF. For repulsions it changes the volume. Rather than the using the volume is uses a modified volume that subtracts out the "volume" occupied by the molecules.

For the pressure it adds and extra term for the "internal" pressure that comes from the attractive IMF.

The final result is

$$\left(P + \frac{an^2}{V^2}\right)\left(V - nb\right) = nRT$$

where a and b are constants.

In the limit of low P (large volume) this reduces to the ideal gas law.

The b constant is essentially the molar volume of the “molecules” (not the space between them). Thus big molecules should have larger b values.

The a constant deals with the attractive IMF. Thus molecules with dipoles or large polarizabilities should have larger a values.

Solids and Liquids

We talked about different properties

Isothermal (constant T) compressibility (change in volume with pressure).

This is given by

$$\kappa = \left(\frac{-1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \approx \left(\frac{-1}{V}\right)\left(\frac{\Delta V}{\Delta P}\right)_T$$

That is the change in volume (deltaV) divided by the change in pressure (delta P). This is normalized to 1/V to make the properties intensive (independent of the amount of stuff). The negative sign is to make kappa positive since deltaV and deltaP will have different signs (increases in pressure will lead to a decrease in volume).

Gases are very compressible. Solids and Liquids are not. They are different by factors of nearly a million. Liquids are slightly more compressible than solids.

We also looked at the change in volume with temperature at constant pressure.

This is the thermal expansion coefficient.

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P \approx \left(\frac{1}{V}\right)\left(\frac{\Delta V}{\Delta T}\right)_P$$

Change in volume for a given change in temperature with pressure held constant. Again normalized to the total volume. (no negative sign now as deltaV and deltaT will have the same sign). Increase T things expand. Decrease T thing compress.

Gases have huge thermal expansion. Solids and liquids do not. Again liquids have larger thermal expansion than solids.

Fluid vs Rigid

Fluid take the shape of the container they are in. Rigid substances do not. Liquids and gases are fluids. Solids are rigid.

Diffusion

In fluids the molecule move around a lot. We can quantify this by diffusion. This is the propensity for the molecules to “wander” and is a direct result of entropy. Given the chance, the molecules will wander away from each other. Diffusion is usually thought of for systems in which there is a gradient (difference) in concentration and can be measured by watching that gradient change. For example, you could put a drop of red food coloring in a glass of water. Now where the drop was there is a high concentration of dye compared to the other areas of the glass. Diffusion is slowly eliminate that concentration difference as the molecules wander. The distance of diffusion is given by the diffusion constant. For this we look at the root mean square displacement since on average the molecules are not moving (same number moving in each direction). The rms displacment is given by

$$r_{rms} = \sqrt{6Dt}$$

Where D is the diffusion constant and t is the period of time over which you are calculating the displacement. The diffusion constant depends on what molecule is diffusing, what it is diffusing in, and the temperature. So for example, there is a diffusion coefficient for water in water at 25°C. There is a different coefficient for a sodium ion in water at 50°C. The larger the molecule the slow the diffusion. The lower the temperature the slower the diffusion. And finally the more viscous the solution the lower the diffusion. We’ll try to hit viscosity next time.

Surface tension

Molecules at surfaces have high energies than those in the bulk as they have fewer molecular neighbors and thus fewer IMF. This means they have higher potential energy. Thus liquids will adopt conformations that minimize surface area. For drops this means making a sphere. For liquid surfaces this means avoiding ripples and remaining flat. Thus the idea of tension. The surface holds its flat shape to maintain a low energy.

We ended class thinking about h-bonding.

H-bonding

Is a special case of dipole interactions that occurs when an H-atom is bonded to a highly electronegative atoms (O,N, or F). The large deltaEN leads to large partial charges. The loss of electrons around the H nucleus also make the H atom very small allowing it get to very short separations from the atom with the partial negative charge. Smaller distances = lower energy = big IMF.