Thoughts of the Day 11/18/08

Boyle's Law (Constant T)

PV = Constant

Simple enough.

$$V \propto \frac{1}{P}$$

Charles's Law

$$V \propto T$$

as long as T is in absolute scale. Using °C we find the T=0 absolute is at T = -273.15°C
This is the extrapolation point to find the T at which we expect the volume to be zero.

Avagadro

$$V \propto n$$

Volume depends on the number of particles (atoms or molecules). Not their type. Just how many. Twice as many, then the volume is double….

Let's put this all together.

$$V \propto \frac{nT}{P}$$

The proportionality constant is R. The value of R depends on the units you'd like to use.

Therefore

$$V = \frac{nRT}{P} \quad \text{or} \quad PV = nRT$$

You now know the ideal gas law.

When will we have trouble? What happens as P goes to infinity at constant T? The volume must equal zero. This is not physical. How can we cram all the molecules into the same space? How can they occupy zero volume!

Why problems at high P? Because the moelcuels get close together and start to interact. The IG law is the result for no interaction between the molecules. NO IMF. This is why it is the same for all gases. You don't have an ideal gas law for nitrogen and another for oxygen. The IG law assumes they are all the same. The difference between the different compounds is how they interact with each other. If there are no interactions, then there are no differences.

Except one key one. The ideal gas law depends on the number of particles. Not there mass. Therefore if there are the same number of particles for the same volume, pressure, and temperature. They must have different densities since different molecules (atoms) have different masses. Thus a helium balloon floats. It is as if you have replace the N_2 molecules in the air with He atoms (the exact same number). Since each weighs less, the balloon is much lighter than the corresponding volume of air.

Dalton's Law

Since the molecules don't interact, for a mixture we can imagine it is composed of subsets of molecules that each contribute according the number of molecules each has. This is the partial pressure.

The partial pressure of a gas is simply its molecular fraction (what percentage by number of particles) time the total pressure.

Add up all the partial pressures and you get the total pressure

Kinetic Theory of Gases.

We can relate the pressure to force from molecules. We can relate P x V to temperature via the IG law. Therefore we can relate temperature to molecular properties.

KEY RESULT

The T is proportional the average kinetic energy of the IG.

$$\overline{K.E.} = \frac{3}{2}RT \quad \text{per mole}$$

$$\overline{K.E.} = \frac{3}{2}k_bT \quad \text{per molecule}$$

The avereage speed is related to the kinetic energy

The root mean square velocity is

$u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}$ where M is the molecular weight.

Thus heavier molecules are moving slower and lighter molecules are moving faster at the same temperature.

There is a distribution of speeds (energies) at the same temperature. As you raise the temperature up the average speed (energy) increases and the distribution broadens.

Real gases

Ideal gases have no intermolecular interactions. This is not physical. However it does a reasonable job of explaining most gas behavior as gases have such low densities at typical room temperature and pressure that the molecules never interact any way.

Real gases have attractions and repulsions.

I tend to think of this as having an effect on the volume at constant temperature and pressure. Replusions make the volume larger (than would be expected for no interaction) and attraction make the volume smaller.

This can be quantified by looking at the quantity PV/nRT This is called the compression factor. For an ideal gas it is 1 at all temperatures and pressures. For a real gas it is not.

Typically gases will exhibit attractive forces first (Z dipping below 1) and then at high pressures be dominated by repulsions. At higher temperature repulsions also tend to dominate.

This affect is largest for gases with large intermolecular forces (H_2O, NH_3,…) compared to (He, H_2, ….)