LECTURE 22. STATISTICAL THERMODYNAMICS

So far we have discussed thermo in fairly simple terms that allowed us to do two useful things:

- Predict reaction spontaneity from $\Delta G = \Delta H - T\Delta S$
- Perform simple calculations of ΔG, ΔH, ΔS, B.E., w

This was all put together in worksheets and permitted the ability to quickly feel useful with thermodynamics.

But--It really played fast and loose with the underlying theory of thermo. It is all fine, it was just sloppy. Kind of like you didn't earn it.

So now you will earn it, with more sophisticated lectures on thermodynamic theory

- Statistical thermodynamics

- Internal energy

- Entropy, equilibria, and free energy

To this point in thermo we have dealt entirely with bulk properties of a system
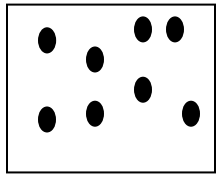
 ──────────► Provides a bulk V, T, P, G, H, S, E of a system

But what about if we deal with the system one molecule at a time and ask questions about is E or S one molecule at a time. This is the study of **statistical thermodynamics.** And the short answer to the question is this:

To find internal energy:
$E = \frac{1}{2} kT$
Which is the energy per
molecule per degree
of motion freedom
in a system

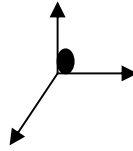**To find internal entropy:**
$S = k \ln W$
which is the absolute entropy
per molecule in a
system.

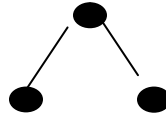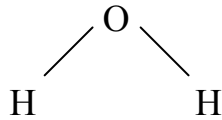The constant, k, in both equations is the Boltzmann constant $= 1.38 \times 10^{-23}$ J/K

The Origin of Internal Energy

Consider an atom → ●   It can move 3 ways in a 3-D coordinate

Now hook that atom up to other atoms to make a molecule.

O
H   H   →

If each atom has three directions in which to move, then N atoms will have 3N ways to move. So for example, water has 9 total different kinds of movement. If you start playing with the vextors, you see that some times all the vectors for the atom are going in the same direction, and the molecule can translate. Other times the vextors oppose each other and you get vibrations.

In fact there are three fundamentally different kinds of motion.
- Translation- the molecule change location

- Rotation – the molecule spins

- Vibration- the molecule twists

 If you are bored, try to visualize these movements

Translation: water moving to the left because all 3 atoms move left. There are 3 ways all molecule can move.
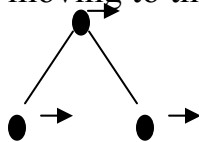
Rotation: is water spinning counterclockwise. There are 3 ways most molecules can rotate. Linear molecules can only rotate 2 distinct ways.
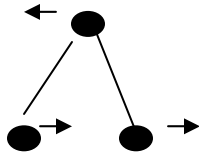
Vibration: is water vibrating. There are 3N -6 ways most molecules vibrate (6= 3 trans. + 3 rotates)
3N-5 ways linear molecules vibrate (5=3 trans.+ 2 rotates)
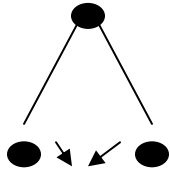
How much energy is associated with each movement? The amount is dependent on temperature. From **equipartition** theory we learn the average energy per motion is,

E= ½ kT   T= Kelvin
                K= Boltzman constant

So, the

Translation of a molecule are	3 x ½ kT	= (3/2) kT
Rotation of a non-linear molecule are	3 x ½ kT	= (3/2) kT
Rotation of a linear molecule are	2 x ½ kT	= (2/2) kT

So a **non-linear molecule** (most molecules) have

$$3/2 \text{ kT} + 3/2\text{kT} = \textbf{3kT of motional energy at room temperature.}$$

A **linear molecule** (like CO_2 or I_2^-) has

$$3/2 \text{ kT} + 2/2 \text{ kT} = \textbf{5/2 kT of motional energy at room temperature.}$$

But what about **vibration**?

For our purposes, at room temperature there isn't enough energy to excite vibration so we ignore them.

So what if you have more than one molecule? Just add up the motional energies of the individual atoms. Look at the example below for a mole of molecules.

******Time out for something utterly fascinating:
    Did you know R (the ideal gas constant) is actually $= kN$ where N is, Avagadros' number. *****

So one molecule $= 3/2 \, kT + 3/2 \, kT = 3kT$ of energy but one mole $= 3/2 \, RT + 3/2 \, RT = 3RT$ of energy
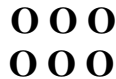
Therefore, A mole of non-linear gas molecules at room temperature has $3RT = 7.5$ kJ of motional energy.

Absolute Entropy

As temperature, K, decreases, the motional energy of matter, J, decreases. At that point, in the absence of motion, we start to form perfectly ordered crystals.
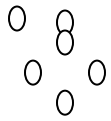
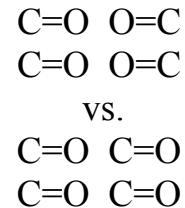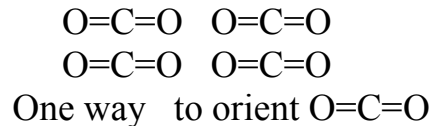O O₈   T → 0   O O O   And we see that S decreases as well.
 O   O
    O   →   O O O

We can think, though, about how the complexity of an individual molecule figures into the order.

O=O,   when flipped,   is still O=O
O=C=O,   when flipped ,   is still O=C=O
but, C≡O,   when flipped,   is now O≡C

So in terms of the ability to order a compound, we would say that O=O and CO_2 have a lower absolute entropy then CO. For example, there is only one way to order molecules of CO. But there are two ways to order molecules of CO.

O=C=O O=C=O   C=O O=C
O=C=O O=C=O   C=O O=C
  One way   to orient O=C=O   vs.
                                                     C=O C=O
                                                     C=O C=O
                                          Two ways to orient C=O

This means that there are $1^4 = 1$ possible orientations of four molecules of CO_2
And there are
This means that there are $2^4 = 16$ possible orientations of four molecules of CO

Boltzmann generalized this way of describing the extent of the disorder:

S (Absolute Entropy) = k ln W where W = the number of possible orientation = # of orientations $^{\text{#of molecules}}$

So when I have
4 molecule of O2, I have $1^4 = 1$ orientation
4 molecule of CO, I have $2^4 = 16$ orientations

And calculating the absolute entropy, S, for those four molecules:

$S = k \ln W = 1.38 \times 10^{-23}$ J/K ln $1 = 0$ J/K   for O_2

$S = k \ln W = 1.38 \times 10^{-23}$ J/K ln $16 == 3.8 \times 10^{-23}$ J/K for CO

If I have a mole of molecules it works the same way.
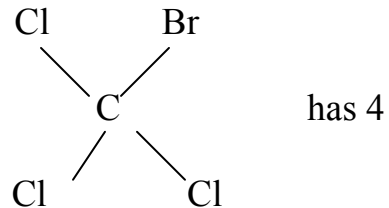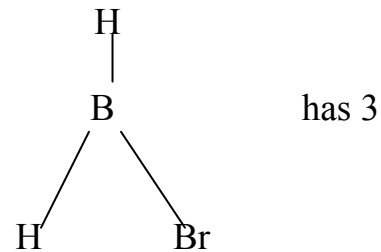
What is the S for a mole of BH_3, which has 1 orientation?
$S = 1.38 \times 10^{-23} \ln (1^{6.02 \times 10^{\wedge}23}) = 0$ J/K

So we now have a way to find the absolute entropy of a system just by knowing

- How many particles are involved
- How they orient.

Unfortunately this latter consideration is complicated by the physical system.
Consider:
- I can look at a symmetrical molecules and figure there is one way to pack it.
- I can look at an asymmetric molecules and figure its orientation.

- But some molecules achieve levels despite different shapes because of preferred physical orientations. **For example,** HCl has two possible orientations, so we would expect $W = 2^n$

But H- bounding makes it move likely to form H-Cl ......H-Cl so it actually has $W < 2^n$

And a lot of interesting information about how packing occurs in solids can be determine by comparing experimentally measured entropy to the statistical thermodynamic value.