Lecture 8 – Chapt 7 (first half)

Outline:

Average energy $\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$

Fundamental equations for S and U

T, p, and m

driving forces

Quick review:

Boltzmann – very important man

$S = k\ln W$ connects microscopic to macroscopic

also written as

$$\frac{S}{k} = \sum_i p_i \ln p_i$$

$$weight_i = e^{-\beta\varepsilon_i}$$

$$p_j = \frac{e^{-\beta\varepsilon_j}}{\sum_i e^{-\beta\varepsilon_i}}$$

the normalization factor is Q – the partition function

Since we know all the probabilities we can calculate the average energy

$$\langle E\rangle = \sum_j E_j p_j$$

Your book drops the partition function for a little while, but I would like to show you one more connection here at this time.

$$\begin{aligned}
\langle E\rangle &= \sum_j E_j p_j \\
&= \sum_j E_j \frac{e^{-\beta\varepsilon_j}}{Q} \\
&= \frac{1}{Q}\sum_j E_j e^{-\beta\varepsilon_j} \\
&= -\frac{1}{Q}\sum_j \frac{\partial e^{-\beta\varepsilon_j}}{\partial\beta} \\
&= -\frac{1}{Q}\frac{\partial\sum_j e^{-\beta\varepsilon_j}}{\partial\beta} \\
&= -\frac{1}{Q}\frac{\partial Q}{\partial\beta} \\
&= -\left(\frac{\partial \ln Q}{\partial\beta}\right)_{N,V}
\end{aligned}$$

So, if we know the partition function, then we can calculate the average energy of our system.

Now, that brings up a good question. **What do we mean by our system?** Whatever we are interested in. Very nebulous but convenient. Just have to be consistent.

Text does a nice job of defining a number of important things at the beginning of Chapt 7, make sure you pay attention to this. One thing I'll mention quickly here is extensive vs. intensive properties. **Extensive?** depends on the amount of stuff (*U, S, H, V, N, n*)
Intensive? doesn't (*T, P, concentration,* μ)

In last chapter Dill gave examples of how *S* maximizes with respect to *V, N*, and energy *U*. Not surprisingly then he reveals that *S* is often expressed as $S(U,V,N)$ Of course, *P* and *V* are related so we could change these variables around if we wanted to, but these three work out most naturally.

Similarly $U = U(S,V,N)$

These are called the **fundamental thermodynamic equations for entropy and energy**.

Very grand titles and they are important. Of course, there are other fundamental equations that we'll come upon later. Two is enough for today though.

Of course in chemistry we are often going to be concerned with how things are behaving when *S* or *U* is changing. We might like to understand how entropy changes as ice melts for instance. **How are we going to represent a small change in *S*?** with a derivative of course – *dS*. **What does this look like?**

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} dN_i$$

We are also going to want to know about energy in the same way...

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} + \left(\frac{\partial U}{\partial V}\right)_{S,N} + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

Ok then. If we want to know how, e.g., energy changes with respect to volume then, we need to know how that coefficient works, what it means. What do you think? If we are looking at some system and we cut the volume in half, that has some effect on the energy. **What should we call that?** Why not pressure. Kind of describes how the system pushes back on you if you are trying to compress it. Similarly for the others...

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$T = -\left(\frac{\partial U}{\partial S}\right)_{V,N}$$

$$\mu_i = -\left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

This leaves us with fundamental equation in differential form:

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

And similarly for entropy:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_i \frac{\mu_i}{T}dN_i$$

Recall our recent discussion of extensive and intensive properties. Notice where they lie? Intrinsics are all coefficients and extrinsics are all differentials in these two equations.

With respect to energy, T describes a system's tendancy to change entropy, p describes changes in volume and μ in the number of moles of whatever.

If we ignore entropy and # particles (i.e. $dS = dN_i = 0$), then

$$dU = -pdV$$

$$p = -dU/dV$$

Does this look familiar? **What is a force?** negative gradient of the potential. In other words it is the negative of the derivative of the potential energy.

So, pressure acts as a force with respect to energy and volume. Just as a traditional force acts with respect to potential and position.

I won't have time to work through any of his examples. They are good take time to understand them. (More lattice models – hopefully you aren't tired of them yet.)

So, very quickly here let's get back to entropy. Note that there is a more clear connection between our microscopic states and entropy (compared to energy), therefore Dill (quite rightly I think) focuses on entropy.

What does our second law say? Systems rearrange themselves to maximize the multiplicity (alias: entropy). So, then if $dS = 0$ **this implies?** equilibrium. If $dS < 0$ then we must be forcing something to happen, or if $dS > 0$ then the system is heading toward equilibrium.