Notes on teaching Chemistry 126 using *Introduction to Molecular Thermodynamics*

Bob Hanson

Day 1: Chapter 1, Sections 1.1-1.8

Probability: Six Ideas

On hand: deck of cards, dice

Summary: I don't spend much time talking about the syllabus, which is available on the web. We get going, and I pose lots of questions and try to encourage students to come up with all the answers.

1. P_x = (# of ways of getting x)/(total number of ways of getting anything)
   example: prob of drawing an ace? (4/52)=8%

2. "AND" probability MULTIPLIES
   example: draw two cards, one after the other. What's the probably of the first one being an ace AND the second one also being an ace? (4/52)x(3/51)=0.45%

3. "OR" probability ADDS
   example: What is the probability that the top card is either an ace or a king? (4/52+4/52)=8/52=16%

4. "AND" and "OR" probability can be combined
   example: What is the probability that the top two cards are an ace and a king? Well, this is tricky, because it could be Ace-King or King-Ace. So we get (4/52)x(4/51)+(4/52)x(4/51)=1.2%

5. $P_{\text{not } x} = 1 - P_x$
   example: What is the probability that the first card is *not* an ace? Well, since the probability of it being an ace is 4/52, then with this idea the probability of it being not an ace is 1 – 4/52 = 48/52 = 92%

6. There are two interpretations of all of this.
   1. gambler's interpretation: "*This next card* will probably be…." "My chances of winning *this time* are…"
   2. casino interpretation: "Over the long haul, we will win *this* many times."

So, what does this have to do with chemistry? Well, in chemistry we are generally working with HUGE numbers of molecules. We basically take the casino's perspective. The casino knows that over time—over many, many games—it will come out ahead precisely because probability works so well with large numbers of things. For us, given a mole of atoms, we can be confident that the statistics will work. We'll see how this works with a simple reaction next time.

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Day 2: Chapter 1, Sections 1.9-1.16

Distributions and Equilibrium

On hand: brown/silver H/D cards; PC with WINEQ.EXE ready to go. What this program allows us to do is do much larger systems, much like they will do in lab next week.

Summary: Four major points are presented: (a) There is something called a *distribution*, (b) there is typically one *most probable* distribution, (c) when the system gets large, this most probable distribution describes what we will see at *equilibrium*, and (d) the concept of an *equilibrium constant* falls directly out of thinking about chemical reactions in terms of probability. You don't need anything else.

1. Distributions. Consider the "equilibrium" that arises when 24 "H" (brown cards) and 24 "D" (silver cards) are mixed. As I shuffle, there is a constant rearranging going on, and at any time I can take a look and see how the cards are arranged. In particular, I want to take two cards off the top at a time and see what I get. [DEMO: separate them into stacks of H_2, D_2, and HD. I do this three times and tally on the board my results.] The question is this: What is the probability of getting the *distributions* that I got? Tricky problem, eh? Actually, it's too hard.

2. The most probable distribution. Maybe it would be easier just to answer the question, "What's the *most probable distribution*?" This turns out to be a pretty manageable question. Still tricky, but manageable. [DEMO here to introduce the WINEQ program and show all the distributions for 24H/24D and their probabilities. (Don't worry about Q yet.)] It turns out this is an easier question for big systems, which is what we are most interested in anyway.

3. Determining the most probable distribution. The method for doing this is given in Section 1.10. I go through, step-by-step, for 1 mol of H_2 and 2 mole of D_2. We think of it as fish in a pond and we want to know what kinds are there, so we sample the pond. What's the probability of an atom being H? (1/3) Of being D? (2/3). A molecule being H_2? (1/3 x 1/3 = 1/9) What's the probability of a molecule being D_2? (2/3 x 2/3 = 4/9) Of HD? Two ways to do this: Either (a) "not H_2 or D_2" (1-5/9 = 4/9) or (b) "HD or DH" (1/3 x 2/3 + 2/3 x 1/3 = 4/9). So the most probable distribution is (remembering that we have 3 moles of molecules total) 0.33 mol H_2, 1.33 mol D_2, and 1.33 mol HD.

4. The effect of large numbers is to make probability more reliable (Section 1.11). [DEMO: using WINEQ, try 240H and 240D. Notice the narrowing. If you try more, better start with a 1:1:2 mix of H_2, D_2, and HD, perhaps 1000:1000:2000 or 600:600:1200] Notice that the range of distributions around the most probable is narrowing dramatically. At a mole of H and a mole of D, for example, it would be a sharp line. *This is a key point*, that for large numbers of atoms, the most probable distribution describes the *only observable outcome*.

5. Equilibrium (Sections 1.12–1.16). Another way of looking at this is as an equilibrium between “H_2 + D_2” and “2 HD” [DEMO: take two brown cards in one hand, two silver in the other, and “react” them. Do this back and forth a few times. Look out! Sometimes the “back” reaction won’t result in a change!] We can write:

$$H_2 + D_2 <====> 2\ HD$$

This is fundamentally what is going on when we shuffle the cards. Over time, although there are fluctuations, the system will be found in a certain “most probable distribution” most of the time. Amazingly, it does not matter how many cards/atoms we start with of each type (H or D), as long as we have plenty of them, the following calculation will always come out the same (roughly—with some fluctuation):

$$n_{HD}^2 / (n_{H2}\ n_{D2})$$

It will be 4, or thereabouts, every time! We call it the *equilibrium constant*. Section 1.13 – 1.15 discuss the implications of this, and Section 1.15 proves that the number is a constant regardless of the number of H and D initially—provided we are working with large numbers of atoms.

Well, this is a lot for one day! But hopefully the main points are there: Probability is fundamental to chemical reactions. What we call equilibrium and the “equilibrium constant” are both direct consequences of the fact that we are dealing with huge numbers of particles that are acting randomly. In simple isotope-exchange reactions, we can actually predict the equilibrium constants and (if we know how many atoms of each type there are) the equilibrium “distribution” of atoms into molecules. What we’re missing is energy and how *its* distribution among molecules and atoms influences the final equilibrium position in real chemical reactions. So energy is next.

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Day 3: Chapter 2, Sections 2.1-2.7

The Distribution of Energy

On hand: Overhead of Figure 2.1. Also fun is
http://www.stolaf.edu/people/hansonr/imt/intro/banana

Summary: The essential things to present include: (a) Not all equilibria behave like the H2/D2/HD equilibrium—and even that one doesn't have a K of 4 exactly, Temperature, for example, has a dramatic effect on the value of an equilibrium constant. (b) energy is quantized and enters systems in "packets" called *quanta*. For small systems it isn't too hard to calculate all the different ways energy can be distributed.

1. In general, the equilibrium constant for a chemical reaction can't be determined as though the atoms were playing cards. The actual K for the H2/D2/HD equilibrium is 3.25 at 25ºC and rises slowly with temperature. Figure 2.1 shows other reactions and how their equilibrium constants change with temperature. Some decrease, some increase. How come?

2. Basically, reactions that absorb energy (heat) when they occur tend to "go better" at higher temp. This should seem reasonable. On the other hand, reactions that release heat tend to "go better" at lower temperature. By "go better" I mean further to completion. Mostly we'll see why this is in Chapter 3. For now it's just an interesting observation.

3. Energy is quantized. That is, it is absorbed by atoms and molecules ("particles") in distinct "packets" of energy, called quanta. Once the energy is in the system, it can be exchanged back and forth between particles ad infinitum. We can see this with a simple system of 3 particles with 3 "units" of energy. [Work out all possible cases with them. Notice that the ten possibilities can be grouped into three distinct sets. DEMO: banana] Each possible way is called a **microstate**. Notice that one of these "distributions" of energy is the *most probable* because it has more microstates than the others. Over time, the system will mostly be observed with this most probable distribution of energy—at least more times than the other two distributions. The number of different microstates a particular distribution involves is called *W*.

4. If we want to know which distribution will be the most probable, we'll have to do some work. Either (a) work out all the possibilities as above or (b) find a way to calculate *W* for each possible distribution. For small systems it isn't too hard to figure out what all the possible distributions are. Calculating the number of ways (microstates) for each possible distribution is also not particularly difficult for simple systems such as this. (Sections 2.5-2.7. I do NOT derive this in class.) Of course, if more energy or more particles are involved, well, this can get out of hand. That's where Boltzmann comes in (tomorrow).

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Day 4: Chapter 2, Sections 2.8-2.14
The Boltzmann Distribution

On hand: PC with WINTROPY.EXE ready to go. (Or http://www.stolaf.edu/people/hansonr/imt/intro/boltz) What these programs allow us to do is quickly see how energy is distributed in larger systems. WINTROPY.EXE will be used in lab for Experiment 5.

Summary: The essential things to present today include: (a) When you have lots of energy in a system involving lots of particles, there's no hope of even counting all the possible distributions, much less figuring out W for each. (b) The most probable distribution has a very interesting property that makes it possible to predict. (c) As for the H2/D2/HD equilibrium, as the number of particles increases, the probability of observing anything *other* than the most probable distribution is incredibly small.

1. I like to start the day with the WINTROPY program, because it gets the point across about the geometrical series without getting temperature involved. I just give it 200 or so particles and 200 units of energy and go from there. I get the students involved in seeing the pattern. It's interesting to pull out some calculators and get people to calculate ratios from one level to the next to the next. We quickly see that except for a few top levels that only have a few particles, the ratios are pretty similar. This TRULY is the essence of the Boltzmann law. Then I separate the levels to 2 units and try again. Interestingly, the ratios are now the square of what they were before.

2. The point is that the most probable distribution has this interesting characteristic that, when the levels are evenly spaced, n1/n0 = n2/n1 = n3/n2, etc. (a geometric progression, like those Russian jars that have one inside another inside another….)

3. The Boltzmann law allows us to relate these ratios to the energy level spacings in (in Joules) and the temperature (in Kelvin). Now you can play with temperature and see the effect. What happens if you double the temperature? What happens as T approaches 0? [There is a very cool relationship here when you take every other level as "reactant" or "product" but that will have to wait for later.]

4. Sections 2.11-2.13 have useful information, but I wouldn't dwell on them. The proof in 2.11 is NOT something to get into in class, I think. The calculation of the population of the lowest level is interesting and useful for homework, but again not something particularly important. The calculation of the number of levels occupied in Section 2.13 will be used in Chapter 3, but if you dwell on it, they will think they have to know it.

Chapter 3 is a particularly difficult chapter because of all the math. Three days is barely enough time to spend on it, especially with the added Sections 3.9-3.13. I will suggest strongly that they give it a brief scan, then read the summary, Section 3.14, carefully. Only THEN go back and read the chapter more carefully. Still, don't get too bogged down in the math.

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Day 5 (Mon 2/18/2002): Chapter 3, Sections 3.1-3.5

Energy Levels in Real Chemical Systems; Electronic Energy

Summary: The main points of this chapter include: (a) There are four relatively independent ways that real molecules can absorb energy: We speak of a molecule's "electronic energy," "vibrational energy," "rotational energy," and "translational energy." (b) While quite different in terms of what's going on, these energies have something very interesting in common: They all are related to some sort of "constraints." In the equation describing the energy levels, there is a distance term, which shows up in each equation as $1/(\text{some distance})^2$, and a mass term, which shows up as 1/(some mass). (c) For very understandable reasons, electronic energy levels are the furthest separated, followed by vibrational levels, rotational levels, and, finally, the incredibly closely spaced translational levels.

1. The four forms of energy dispersal in molecules:

   a. **Electronic**: The electron primarily is the actor here due to its very small mass relative to the nucleus. Due to the 1/m term, this sort of excitation requires way more energy than is generally available at any reasonable temperature. Result: at equilibrium, all molecules are found 100% in their "ground electronic state."
   b. **Vibrational**: defined as anything that moves one atom relative to another in a molecule. (So you must have at least two atoms.) Mostly we think of bond stretching. In this case the masses are larger, and now the approximation that only the particle with the lesser mass moves is not good enough. We need **reduced mass**. In addition, the equation can be recast to refer to a **force constant** for the "bond." Vibrational levels get closer and closer together as the energy increases, ultimately leading to dissociation and molecular destruction. (Thus, high temperature leads to chemical reactions.)
   c. **Rotational**: a "tumbling" around a center of gravity—so again reduced mass is important. The masses are larger, and the levels are considerably more closely spaced. Hundreds of levels occupied at room temp.
   d. **Translational**: the ultimate in closeness of energy level spacing. It's that $1/d^2$ term, where now d is on the order of cm or meters. Only gases here. That's the essential point. Just unfathomably close energy levels.

2. Mostly new here is the idea that there are many different integer "quantum numbers"—we know about *n*, *l*, and *m* in terms of electronic orbitals for the H atom, but there are others. A little familiarity with the equations is all we are asking.

3. OK, so we get a little practice in this chapter with our calculators and with units. I wouldn't illustrate more than one calculation in class. Mostly we are just going for the qualitative result that comes out of solving the equation, not the exact answer itself. This is a different approach most students are unfamiliar with.

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Day 6: Chapter 3, Sections 3.6-3.9

Energy Levels in Real Chemical Systems, Continued

Summary: I use this day to do some calculations in class and *discuss* the results. Exactly why are vibrational levels so much closer together than electronic levels? Remember, students won't necessarily have incorporated the words "vibrational," "rotational," and "translational" yet. So any discussion is good. I think the real challenge is to picture what those energy levels represent, and how we can even begin to show the idea in black and white on a page in a book. Main points:

1. Reduced mass is important in vibration and rotation because those are the two that involve multiple atoms of similar mass doing something around a "center of mass." Picture playing paddle ball. Anyone have one? Just you and the ball there. Notice that both move, but the smaller mass REALLY moves. Same for the H—Cl bond. Mostly it's the H, but the Cl is involved, too. Note that in reality (something like Figure 3.5 on page 3.13) the levels get closer and closer together. Point out that it's not the frequency of vibration that changes, it's the *amplitude* as energy is put in. Get them to sound out a nice steady tempo. Try a nice slow tempo with your two fists, then add energy and KEEPING AT THE SAME TEMPO, make the bond stretch. Then add more energy. This is really very dramatic. It doesn't take long before you can imagine that bond just flying apart.

2. The action in vibration is over a pretty small distance—about 1/10 the distance of a typical bond for low-energy vibrations. Rotations involve considerably bigger distances because the entire molecule is tumbling. That leads to much more closely spaced energy levels for rotation than for vibration.

3. Translation is just amazing in its closeness of levels. It's all due to the distance term, which is 8-10 orders of magnitude larger *and squared as well*. So here's the point: We can use equations for more than just getting numbers. We can use them as a basis for *understanding* what is going on. This is a very new idea for most students. Professor, should I memorize this equation? Well, maybe, if it helps you remember what type of energy levels are more closely spaced and why. But don't expect me to make you do that calculation on an exam!

If you can get these points across, you have taught them something quite valuable, I think. It's really the fundamental goal—to see through the math to the essence of the problem and to make those equations *mean* something. It's a challenge for sure.

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Day 7: Chapter 3, Sections 3.10-3.14

Energy Levels in Real Chemical Systems: Applications

Summary: This is a good day to catch your breath and get some feedback. How are they doing? What can we make of all this? These sections are simply there to give them something to walk away with that relates to the real world. After all that math, we need to see how we can use our findings without getting bogged down in the nitty-gritty. Pick the applications you like the most and run with them. My notes, below.

1. We can build a little diagram that shows electronic, vibrational, and rotational energy levels all in one go. Each molecule is in *one and only one* of these “states” at a time (presumably, sort of, anyway).

2. When a molecule absorbs energy, it can go from a lower electronic state to a higher electronic state and maybe even be vibrationally excited at the same time. Really emphasize getting a mental picture of what is going on here as best you can.

3. Chemical reactions aren’t terribly hard to imagine. Given enough energy, a bond will break. That’s pretty much what it’s all about.

4. Equilibrium will turn out to be simply the case where some of the energy levels “belong” to one sort of molecule and some “belong” to another. It will all come down to which has the lower ground (electronic) state, and which has the more closely spaced energy levels. (Gases, in particular, are going to have really close energy levels, right?)

5. Fluorescence and phosphorescence are very cool. A little tricky, but very cool.

6. Lasers and stimulated emission are also very cool. At least, I think so!

After this, we focus on heat, work, and the First Law.

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Day 8: Chapter 4, Sections 4.1-4.5, possibly 4.11

Internal Energy and the First Law: The Microscopic Perspective

Summary: *Heat* and *work* are essential concepts in the study of thermodynamics. The key point here is that they relate to *processes* rather than *states*. Especially interesting is that there is a simple way of looking at heat and work in terms of energy levels and quanta. *Heat* is the energy transferred to a system that goes into moving individual particles from lower energy to higher energy levels. *Work* (at least in a *PV* sense) is the energy transferred to a system in such a way that the translational energy levels themselves are made further apart. There is a great demo here. Take a tank of CO_2 with just the top of the dry ice maker attached (the venturi). Point the nozzle over the heads of the group and let ‘er rip. Pretty soon you will see “snow” falling in the room. What you have done is expanded a gas adiabatically (faster than there is time for energy transfer between molecules). The expansion leads to a decrease in the separation of translational energy levels without a decrease in populations. According to the Boltzmann law, this results in a decrease in temperature. (The energy is being transferred to the air molecules as they are pushed aside.) All of what is presented today can be illustrated using the WINTROPY program if desired.

1. We define internal energy (U) and introduce the idea of a *state function*. It doesn’t matter how you get from one state to another. This is pretty easy to see in terms of particles and energy levels. What does it matter which particles are moved first, as long as in the end we have the same distribution each time?

2. Microscopic heat (q) and work (w). If you think about it, there are only two basic ways to change the internal energy of a system: Either move particles up to higher levels, or move the levels themselves. Some discussion needs to be made relating to the colloquial use of “heat” and “work.” These terms are very specific. Unfortunately, as a verb, “to heat” simply means “to raise the temperature of.” What’s new here is that applying work can also raise the temperature of a system without any heat involved. The classic example is a bicycle pump. It only takes a few pumps under pressure to make a bicycle pump rather hot. Yet no heat is involved. (Another demo?) This takes some getting used to.

3. The natural expression of the above idea, that there are only two ways to increase the energy of a system, is the First Law of Thermodynamics, $\Delta U = q + w$. Note that we’re using the more recent standard of w applied TO the system as positive.

4. If you have time, the engine description in Section 4.11 is interesting. Through a sequence of changes, the system is returned to its original state. Overall there is no change in internal energy, because U is a state function, but if you do the math, you find that heat is converted to work.

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Day 9: Chapter 4, Sections 4.6-4.12

Internal Energy and the First Law: The Macroscopic Perspective

Summary: In lab, students are going to be measuring q using a simple styrofoam cup calorimeter. Because there is no volume change (we deal with that later), $\Delta H = \Delta U = q$. Not something to mention yet, of course, but something to at least keep in mind. One of the most difficult aspects of this story appears to be the relationship between a real chemical system, involving some number of moles of reactant going to product, and the chemical equation for that reaction, which involves a certain integer number of moles of reactant going to product. I've been careful in the book to remove the "per mole" designation when writing amounts of energy associated with chemical equations. This avoids the "per mole of *what*?" issue and fits very well with our standard treatment of units. It's a convention used throughout the book, but it may not be one you are comfortable with. You decide.

1. Heat capacity (C) is not a difficult concept to get across. On a microscopic scale there is a connection between the heat going into a system and the populations of energy levels. That has to affect the temperature if energy level positions are not being changed (either through work or chemical reaction). What may not be obvious is the approximation that $q = C\Delta T$. This can actually be demonstrated using the WINTROPY program using 100 particles and a 1000 units of energy. You can easily demonstrate, for example, that putting x units of energy into a system with energy level spacings of 1 unit leads to a different temperature than putting the same number of units of energy into a system with energy level spacings of 2 units. Thus, each real chemical system has its own unique heat capacity.

2. Macroscopic PV work relates (pretty much) only to gases, where we use the ideal gas law to bypass units of liter-atmospheres $-(P\Delta V)$ and go directly to Joules $-\Delta(nRT)$. Note that in some cases this is $-(\Delta n)RT$ and in other cases it is $-nR(\Delta T)$. The main point is that generally work is a minor component and can be ignored even for the most dramatic chemical reactions. (Chemists ignore their work?)

3. Calorimeters require careful discussion. It's very important to make the distinction here between system and surroundings. Always ask the question, "Where is the thermometer?" (Probably—but not always—in the surroundings.) The other point here is the distinction between the actual system and the equation we write for the chemical reaction. You can't overemphasize the need to be careful here and write your units. "Per mole of *what*?" is the essential question!

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Day 10: Exam over Chapters 1-3

To the student:

No calculators. One year I gave this exam as a "no calculator" exam. That may sound crazy, but I think it emphasized that we are not focusing on answers so much as on solutions. By now everyone should have completed Experiments 1-3, including probability/equilibrium, atomic spectroscopy, and molecular spectroscopy. You should be well prepared for an hour of examination over these topics. Fundamentally all I'm interested in finding out is the extent to which you understand the concepts discussed in class.

Communicate effectively. Communication is a key challenge. Thus, laying out a problem is more important than plugging it into your calculator. You need to show me how you would arrive at the solution. Mostly this is just a matter of being careful with units and writing the math out in a consistent way. Make sure that you have an equals sign and that what is on the left in each case really equals what is on the right. Some of you are probably somewhat sloppy on this, so you will have to be extra careful. I give lots of partial credit as long as I can detect that behind a mistake is a reasonably good understanding of the situation.

I'll provide equations. I'll provide equations, but you will be expected to understand where you might use them. So, for example, you may see the equations for vibrational, rotational, and translational energy, but I won't necessarily indicate which is which.

Not everything is math. Some questions will not directly involve calculation. These are the "why" or "how" or "which" questions that get at the principles directly and bypass the math. Many times, though, you will find that illustrating an answer with a simple example involving a little math works better than a long discourse with lots of fancy words.

There will be some challenges. I wouldn't be doing my job if I didn't provide a challenge to you. That's the nature of the game, so expect the unexpected. Much of what you see on the exam should look pretty familiar, but there are going to be a few places where you'll see something that you probably have never thought about before. The goal is to see if you can extend what you know—to see if you can apply what you know to new situations. I would argue that this is the final goal of all education, and it takes practice. So here's your chance to shine. You can study for this by imagining how what you have learned might be extrapolated.

Studying for the exam. Everyone is a little different here. But I'd suggest: (a) rereading the summaries for each chapter, particularly for key concepts; (b) going through representative examples; (c) asking the question in each case, "Why is this so important it was included here?"; (d) looking over the laboratory experiments to make sure you understand the concepts there; (e) sitting down in a quiet spot and seeing if you can put it all together into one consistent story; and (f) asking me, a tutor, or a friend for help understanding the parts that you think are important but you don't feel comfortable with.

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Day 11: Chapter 5

Bonding and Internal Energy

Summary: We introduce Hess's law here for two reasons: (a) They need it for lab, and (b) it applies to all state functions, not just enthalpy (where it is typically introduced). Probably the single most difficult thing for students is getting the sign right for ΔU. It's just so tempting to use "products minus reactants" here. But that is not what Hess's law says. Hess's law says that the overall change in a state function is the *sum* of changes for each step in any hypothetically equivalent change.

1. Hess's law. The main point here is that there has to be a reference point X, usually just a hypothetical one, such as "sea level" or "isolated atoms." Then going from A to B can be calculated as "A to X" plus "X to B." The diagram is most useful here. For internal energy, the reference is at the top of the diagram, where there are no bonds. It's very important to understand that Hess's law relates to the *sum* of changes for the component steps, not the *difference.*

2. Mean Bond Dissociation Energies. This is a great application of Lewis structures. Students feeling unsure about this should review the rules. There is a web-based quiz that may help in the tools section for Chapter 5. The key is to add up the bond dissociation energies of both reactants and products. Then, because the path "X to B" is going down in energy (making the bonds of products), we must remember to reverse the sign of the sum for products before *adding* it to the sum for the reactants. I do NOT recommend using the form "sum for reactants minus sum for products." That's not Hess's law. That's just confusing, since all changes in state functions are related as "products minus reactants" not "reactants minus products." Also, note that I always use the word "dissociation" between "bond" and "energy." That's to point out that bonds don't have "energies" associated with them.

3. The "high-energy phosphate bond" and "acid dissociation." This is an opportunity to emphasize that bond creation always *releases* energy. So the term "high-energy bond" is worrisome at best and downright misleading at worst. That phosphate bond is *weak*, allowing the reactant ATP^{-3} to be at a "high energy" relative to products ADP^{-2} and $H_2PO_4^-$. See Figure 5.6.

4. Computational chemistry. The point of this humorous section is that much better ways of estimating ΔU exist.

5. Not done yet. The problem with using mean bond dissociation energies is that there's no consideration of phases. Thus, melting, freezing, evaporating, and condensing all give 0 for ΔU by these calculations. Considerations of hydrogen bonding, ionic bonding, electrostatic forces, and the like all need to be factored in some how. (We'll see how in Chapter 9, when enthalpy is discussed.)

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Day 12 (Wed 3/6/2002): Chapter 6

The Effect of Temperature on Equilibrium

Summary: This chapter goes well beyond Davies' discussion to put all the concepts together from Chapters 2-5. The program used to produce the diagrams is KAB.EXE. It's fun and very easy to use. There are six places you can click and drag: on the thermometer, to the left and right of each of the energy levels, and the temperature line on the lower graph. Try it!

1. Equilibrium constants from Boltzmann distributions. The amazing thing is that all you have to do to model equilibrium is imagine a case where some of the lines of the Boltzmann distribution are "A" and some are "B." Then the effect of temperature on equilibrium is to change the relative populations of A and B.
2. Two extremes. At very low temperature, particles are in the lowest levels, and if those levels are of A, then A will be "favored." At very high temp, the particles tend toward even distribution among the levels, leading to the idea that the substance with relatively more energy levels "per unit of energy" will be favored at high temperature.
3. Plots of K vs T . These graphs are very important, as they introduce a sort of graph that will be used throughout the book (and was mentioned at the beginning of Chapter 2). The key reference line is $K = 1$. I always make a point of drawing this line. Above it, products are favored; below it reactants are favored.
4. Evenly spaced energy systems. When the levels are evenly spaced, one can prove mathematically the ideas presented qualitatively in this chapter. I wouldn't focus on this in class—it takes too much time, but I encourage the interested student to look it over. Really, I think, a demo using KAB.EXE works much better for convincing students how it all works.
5. Example cases. The point is that we can combine mean bond dissociation ideas from Chapter 5 with energy level spacing ideas from Chapter 3 to good effect to predict whether reactant or product will be favored at low or high temperature.
6. The solid/liquid problem. Ah, now here is a grand problem. In melting and freezing there is no equilibrium constant. Understanding this one requires adding the surroundings (Chapter 4) to the puzzle, which involves introducing entropy (Chapter 7).

There is a web-based quiz at http://www.stolaf.edu/depts/chemistry/courses/toolkits/126/js/quiz that students can use to review this material. I fire it up the *next* day at the beginning of the hour to help students see if they've gotten it. For now, just use the "I'm a beginner" level.

Notes on teaching Chemistry 126 using *Introduction to Molecular Thermodynamics*

Bob Hanson

Day 13: Chapter 7, Sections 7.1-7.6

Entropy and the Second Law

Summary: Building on Chapter 4, this chapter emphasizes that change occurs in the surroundings as well as in the system. Entropy is defined, and it is argued that the entropy change of the surroundings is very important.

1. Entropy. The fact that energy is conserved argues that energy changes cannot possibly "explain" chemical reactivity. Rather, the "most probable distribution" has to include changes in the surroundings. The universe tends toward maximum W for the simple reason that anything else is "less probable."

2. The connection between ΔS_{sur} and q_{sur}. The result that $\Delta S_{\mathrm{sur}} = q_{\mathrm{sur}} / T$ is another amazing property of Boltzmann distributions. Again, I wouldn't do the proof in class, but perhaps a little demo using WINTROPY.EXE would be in order. (They do this in lab as part of Experiment 6.) For example, if you set up a system with 1000 particle and 1000 units of energy, you might get T = 104 Kelvin, W = 4.83E+592, ln W = 1364.646, and $S = k \ln W$ = 1.884E-20 J/K. (It may take some time to find the most probable distribution. I think this is the "final" number, but I'm not sure.) Then, adding 20 units of energy, so q = 20 and there are 1020 units of energy, you might get T = 105 Kelvin and W = 3.75E+598, which gives ln W = 1378.267 and $S = k \ln W$ = 1.902E-20 J/K. Then ΔS is 1.88E-22 J/K. OK, now q = 20E-21 J (because each quantum unit is 1E-21 J) and the temperature is roughly 104.5 K. So q / T is approximately 1.91E-22 J/K. What do you know, it works!!!

3. Measuring entropy changes. The obvious problem is that heat usually results in a change in temperature, so it's not clear what "T" means in the equation $\Delta S_{\mathrm{sur}} = q_{\mathrm{sur}}/T$. The proper way to handle this is using calculus, but for our purposes we can consider only changes where the temperature change is small.

Notes on teaching Chemistry 126 using *Introduction to Molecular Thermodynamics*

Bob Hanson

Day 14: Chapter 7, Sections 7.7-7.12

Entropy and the Second Law—Day Two

Summary: Standard molar entropies allow us to calculate the change in entropy for a chemical reaction. The logarithmic nature of entropy allows us to sum up the entropy of a system as due to electronic, vibrational, rotational, and translational components. What this allows us to do is make some broadly useful generalizations relating to structure and phase. Building on Chapter 3, we can now quantify the effects of different energy level spacings.

1. Standard Molar Entropies. W for a system depends upon the number of particles, the energy level separations, and the temperature. We define the standard state as for a mole of particles at 1 atm pressure (to take account of the changes in energy level separation for the translational energy of gases when the volume changes). The standard state, expressed with a superscript ^{o}, *does not include the temperature.* Indeed, we also need to specify the temperature, because S^{o} has to change with temperature. 298 Kelvin is used in these tables.

2. Trends. The most important discussion today revolves around trends that can be extracted from the information in Table 7.1. Standard molar entropies increase in the order solid, liquid, gas for any real substance, For gases, increasing mass leads to increasing standard molar entropy. The atomic gases have relatively low standard molar entropies. One trend that is tricky to explain involves the unusually high standard molar entropy of O_2. See page 7-11 for a summary of these trends.

3. Standard change in entropy for a chemical reaction. Notice that when this calculation is done, the “per mole” part cancels out. Again, I emphasize that writing ΔS for a reaction depends upon how the equation is written—exactly what coefficients are used. Sure, for some simple reactions, you might write “J/K per mole,” but that just begs the question, “Per mole of what?” and isn’t really defensible based on unit analysis. (The correct answer is, I think, “Per mole of reaction, whatever that means.”)

4. Another way to look at ΔS. The units “J/K” suggest that entropy changes have something to do with “heat per degree.” Indeed, for a reaction to be spontaneous, ΔS gives us the maximum amount of heat that can be extracted from the environment in the process of making the reaction happen *at a specific temperature*. A bit bizarre, perhaps…. Just an idea I had. Skip it if you care to.

Notes on teaching Chemistry 126 using *Introduction to Molecular Thermodynamics*

Bob Hanson

Day 15: Chapter 8

The Effect of Pressure and Concentration on Entropy

Summary: This chapter presents the essential concepts for understanding the origin of the rules for writing equilibrium expressions. Entropy is reduced when the pressure of a gas or the concentration of a solute are increased. (Really what we are looking at are volume effects, but it is more convenient to talk about pressures and concentrations than about molar volumes.) We find that the reaction quotient, Q, arises from a combination of logarithmic terms that are based on comparison with a standard state. Once again, it is important to emphasize that the “standard state” does *not* include temperature. Or, to put it another way, just saying something is in its “standard state” doesn’t say a thing about what temperature it is at. You still have to specify the temperature. Ideally, there would be two days to discuss this chapter. Do the best you can. We’re moving pretty fast here.

1. The volume effect on entropy. We present Einstein’s “gedanken” experiment for the effect of increasing the volume on thermodynamic probability, W, and from that on S.

2. The entropy of mixing. Mostly, this section is for the instructor’s benefit. We’ve heard of this; if you want to introduce mole fractions, this is a time to do it. I pretty much skip it.

3. Pressure and concentration effects. Using the ideal gas law or the definition of concentration, we can get rid of the volume ratio in the equation $\Delta S = nR \ln (V_2/V_1)$. The purpose isn’t immediately obvious, but it has to do with our definition of standard state and our focus in chemistry on pressures and concentrations rather than volumes.

4. Entropies in relation to a standard state. Using a standard state as reference that puts a “1” in the denominator of the logarithmic term simplifies the picture but introduces a units problem. Technically, the units are still there, but of course no one shows them. “P_x / bar” means, in effect, “Use the number for pressure (in bars), without its units.” It doesn’t take long before one gets tired of writing that “/ bar”! We drop it on page 8-12.

5. Reaction quotients. For a reaction, we want ΔS, and the reactions quotient, Q, provides us a means by which we can get adjust the standard entropy, ΔS^o, to give us the entropy change under the actual conditions of the reaction.

6. Rules for writing Q. These pop right out of the way ΔS comes from ΔS^o. Seeing that all this comes from consideration of entropy ONLY sets the stage for the argument that all equilibrium is based on probability.

7. A bizarre calculation? You have to wonder why we would want to calculate the entropy change for a reaction while at the same time demanding that the concentrations of reactants and products are all *constant*. It’s definitely something to ponder. See page 10-5.

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Bob Hanson

Day 16: Chapter 9

Enthalpy and the Surroundings

> Summary: So we have argued that $\Delta S_{\text{universe}}$ should be positive for a process to be observed, because that represents going toward the most probable distribution. (Or, more precisely, if $\Delta S_{\text{universe}}$ is positive, at least it means that the outcome is more probable than the starting point.) We have learned that it isn't too hard to get at the entropy change for a reaction system, but we have to be careful to factor in the actual concentrations of reactants and products. The final piece of the puzzle is getting the entropy change for the surroundings. The trick here is to use q_{sur}, which, under the conditions of constant external pressure, is $-\Delta H$. (It would be $-\Delta U$ if the total volume were kept constant.) Notice that under these conditions the path is defined explicitly, so, effectively, q becomes a state function.

1. Enthalpy. All we are looking for is a simple way of getting at q_{sur}. That's because we know that for the surroundings, since there is no reaction going on, we have that $\Delta S_{\text{sur}} = q_{\text{sur}} / T$. By defining our path as "at constant pressure and temperature" we are all set: $\Delta S_{\text{sur}} = -\Delta H / T$ when the overall pressure is constant. Note that ΔH and ΔU are closely related, so we can think of ΔH as a measure of bonding changes in a reaction.

2. Standard enthalpies of formation. Here's another opportunity to talk about bonding as a *loss* of energy for a system. Note that the standard reference state in this case is "elements in their predominant phase at room temperature." This is a bit different from the standard reference for internal energy, U, which is "isolated atoms." Using the elements makes life MUCH easier, and we don't have to assume anything about how the atoms are actually connected in terms of single or double bonds. A great application of Hess's law. This time it is the *reactant* arrow that is reversed. Several examples are given.

3. About Figure 9.2. This figure summarizes the main point of the chapter and ties in strongly with Chapters 5 and 6 . While ΔS for a reaction is relatively independent of temperature (OK, not quite[*]), ΔS_{sur} is HUGELY dependent upon temperature. That "$1/T$" term in how ΔH relates to the change in entropy of the surroundings is critical. At low temperature, the effect of dumping heat into the surroundings or extracting heat from the surroundings is the dominant factor in whether the predicted $\Delta S_{\text{universe}}$ is positive or negative. This is consistent with the idea that ΔH is a measure of *bonding*. At high temperature, the ΔS_{sur} term becomes much less important, and it is the ΔS term that dominates. That is, at high temperature it is the change in entropy of the *system* that is important. This is consistent with our idea that it is the spacing of the energy levels that is most important at high temperature.

[*] That's because the effect temperature on populations of products won't ever be exactly the same as the effect of temperature on populations of the energy levels of reactants. But the effects largely cancel. In the next chapter we allow for this difference in effect to a certain extent.

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Bob Hanson

Day 17 (Mon 3/18/2002): Exam 2, Chapters 4–8

These chapters cover a lot of territory:

4a. work and heat

4b. calorimetry

5. estimating ΔU for a reaction based on mean bond energies

6. K vs. T and the effect of temperature on equilibrium

7a. the definition of entropy

7b. estimating ΔS for a reaction using standard molar entropies

8a. the effect of volume changes on entropy

8b. relating volume changes to changes in pressure and/or concentration

8c. adjustment to the standard molar entropy based on nonstandard pressures and concentrations

8d. the reaction quotient arises from reactants and products not necessarily being in their standard states

Notes on teaching Chemistry 126 using *Introduction to Molecular Thermodynamics*

Bob Hanson

Day 18 (Wed 3/20/2002): Chapter 10, Sections 10.1–10.6

Free Energy

Summary: The statement that $\Delta S_{\text{universe}} > 0$ for a process to be observed, can be rewritten as $\Delta S - \Delta H / T > 0$, or $\Delta H - T\Delta S < 0$, since T is always positive. That puts the expression in units of energy and suggests the definition of free energy: $G = H - TS$. THAT then suggests plotting G vs. T to see what happens. This turns out to be amazingly informative way to approach the subject. It goes beyond a strictly mathematical definition and allows an intuitive understanding of the role of free energy in equilibrium.

1. The entropy change of the universe. Our emphasis on the most probable distribution leads to the idea that a "system+surroundings" that is *not* in the most probable distribution, given the opportunity, will progress naturally to one of the many microstates that are characteristic of the most probable distribution. Sure, there will be fluctuations, but the large number of particles involved in real chemical systems argues for those fluctuations being unobservable. The direction toward that most probable distribution is in the direction of increasing entropy (increasing thermodynamic probability) of the system and its surroundings. The connecting link is the heat transferred between the system and its surroundings. Thus, $\Delta S_{\text{sur}} = q_{\text{sur}} / T = -\Delta H / T$, at least when pressure and temperature are kept constant.

2. Free energy. There is no particular need for another state function. But what free energy does is allow us to express a demand relating to the universe (that the entropy of the universe must increase) to a demand relating to the system alone (that free energy must decrease). Now rather than maximizing something ($\Delta S_{\text{universe}}$), we are minimizing something (ΔG). It's all just a trick.

3. Graphs of G vs. T. The real message here is that although G is unnecessary, it turns out that it is quite convenient. It isn't hard to rationalize what a graph of G vs. T would look like for any substance. Here H is the y-intercept (which, for a single substance is placed at an arbitrary position along the y axis). The slope is simply $-S$. The slope becomes more negative with increasing temperature, because as the temperature of a substance increases, particles are spread out over more energy levels (energy is distributed in more ways), and W increases. We use these graphs as another opportunity to emphasize the difference in phases. Melting, for example, always involves an increase in entropy of the system.

4. Back to equilibrium. Most important, equilibrium is when $\Delta G = 0$. The entropy of the universe is maximized at equilibrium, and neither forward nor reverse reaction is favored over the other.

5. The "Low Enthalpy/High Entropy Rule." This comes from Davies's book. Notice that on a graph of G vs. T, at low temperature we are basically looking at enthalpy differences, while at high temperature, the $-TS$ term takes over, and the lower curve will always be the one associated with higher entropy, S.

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Bob Hanson

Day 19 (Fri 3/22/2002): Chapter 10, Sections 10.7–10.10

Free Energy, day 2

Summary: We take a quantitative look at free energy. In particular, we focus on those crossing points and set $\Delta G = 0$.

1. Melting points. In this case there is no significant effect of concentration or pressure on the analysis. We simply set $0 = \Delta G = \Delta H - T\Delta S$, consider both enthalpy and entropy to be their standard values, and solve for T.

2. Gas curves. Due to the effect of pressure on the molar entropy of a gas, the curves for gases are "adjustable." Now at any temperature we can find a vapor pressure for which $\Delta G = 0$. Higher vapor pressure leads to less entropy and a flatter curve. Some sort of demo is nice here. Could be the rotvap, could be balloon in an Erlenmeyer.

3. Boiling and vapor pressure. Mainly the point is that there should be a "normal" boiling point, and it's not hard to calculate. But we can also calculate the vapor pressure of a gas over a liquid at equilibrium with its vapor (as opposed to boiling). It's the same equation.

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Bob Hanson

Days 20 and 21 (Mon/Wed 3/31 and 4/2, 2003): Chapter 11

The Equilibrium Constant.

[I don't have notes from 2002 on these two days. So I'm writing this in 2003 without much sense of how much time anything took.]

Summary: Our whole focus now is on those crossing points, where $\Delta G = 0$. Now we allow for multiple gases and multiple solutes. We have to think about which curve will adjust and in what way as the reaction proceeds. The key equation I use for everything is Equation 11.1 on page 11-5.

1. Reaction quotients. Never hurts to go over this again. Students may not feel very comfortable with pressures and concentrations in the same expression, but I think it's good for them to see those and know where it's coming from (entropy, of course!).

2. The concept of an equilibrium "constant" was introduced in Chapter 1. Now we return to this idea, seeing that it is derived simply from Equation 11.1 when solving for $\Delta G = 0$. They need to understand the reasons behind the rules on page 11-5.

3. Experimental determination of ΔH° and ΔS°. The web site should be very helpful for this. The main information is in the "Temperature and Equilibrium" script.

4. Qualitative picture of equilibration. See the "2NO2/N2O4 Example" script.

5. Equilibrium calculations. Students have already slaved over equilibrium calculations of the type "What are the final equilibrium concentrations…" You can do that if you like, but I'm more interested in their now focusing on temperature and its effect. Equation 11.1 in an equation-solving calculator just can't be beat!

6. Entropy of the Universe. I think it's kind of cool that $\Delta S_{\text{univ}} = R \ln K/Q$. What a marvelously simple expression! So only when $Q < K$ will ΔS_{univ} be positive. How elegant!

7. I would spend whatever time is available the second day looking at data, perhaps doing Quiz problems (I just display "all") and answering questions. The second day, Day 21, might also be a great day for some sort of workshop activities.