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5.111 Principles of Chemical Science, Fall 2008  
Transcript – Lecture 19

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PROFESSOR: We're pretty much ready to get started. Let's settle down and take a look at the clicker question. So take 10 more seconds. Very good. Most people had this right, and the trick here is just to think about the sign of  $\Delta G$ , whether it's negative and positive, and think about the equation and the influence of temperature on that equation. So whether it's going to make  $\Delta S$  a bigger factor or a smaller factor and how that will play out. So you can look at the equation and figure out what the signs have to be and then the influence of temperature.

All right, so let's move to the first slide that I have today, which is welcome to the middle of the semester. So I'm Kathy Drennan and this is lecture 19 of 36, which means that you are halfway through the course. And so what you heard on Monday before the exam was about thermodynamics, and if you don't have all your  $\Delta G$ 's and  $\Delta H$ 's and if you don't have entropy full in mind, that's OK, we are not really leaving thermodynamics, we're going into chemical equilibrium, which is all about thermodynamics. So you're going to hear a lot more about  $\Delta G$ ,  $\Delta H$ , temperature, and about our friend, entropy as we go along in the second half.

So it's the middle of the semester. That means that you've had two of the sort of four hour exams -- remember the fourth hour exam is actually combined with the final exam. So the final exam is 200 points of cumulative material, and 100 points of new material, so you've done two now of those four sort of hour exams.

Just to remind you of some of the topics you have seen and the topics coming ahead, this is on the syllabus, and we're actually where we're supposed to be on the syllabus, so if you want to take a look at that ever to see where we're going, we're actually on track. So the first half of the course are a lot of basic principles, and we're moving today into chemical equilibrium, so a lot more  $\Delta G$ 's,  $\Delta H$ 's coming on. And then we're going to move into acid base, which is acid base equilibrium.

So we're not going to be leaving equilibrium or thermodynamics. Then we're going to go into oxidation reduction, which is also about equilibrium, and then transition metals, and end with kinetics. And so, these altogether represent the fundamentals needed for the study of biochemistry, organic chemistry, any kind of chemistry, biology, the life sciences, many things -- so you're getting all the fundamental principles of chemistry in this class.

So along those lines, I just thought I would share something that happened to me on Wednesday when I was riding the T, the Silver Line, in particular. So I don't know if any of you have had this kind of experience yet where you're on public

transportation and someone next to you says, "So, are you a student?" Maybe you have a notebook out or a book out or something. And you say, "Yes," and they said, "Oh, what are you studying?" And then you say "Well, you know, chemistry, math, physics." And they're like "Oh." And then they go busy themselves doing something else. Or they tell you "I didn't really like those subjects in school." And then they stop talking to you. So how many people have had that experience so far, that you scare the person next to you by what you study? OK, a few people. If I ask that question four years from now, I think it'll be like half the class, eight years from now it'll be everybody. So this is kind of common.

But what happened to me on the Silver Line was actually pretty exciting, because I've had that other experience many times. So, I was wearing my keys around my neck, because women's professional clothes, no pockets, with a little MIT cord, and the person next to be on the Silver Line said "So, do you go to the Georgia Tech of the east?" And I said "Well, I am a professor at MIT." And he said "Well, I'm a mechanical engineer and I went to Georgia Tech." And so he said, "So, what do you teach?" I said, "Chemistry." And he said, "Chemistry -- I really wish I had paid more attention in chemistry." I said, "Well, what do you do now?" And he said "Well, I work for the army, and I'm part of a team that has mechanical engineers, electrical engineers, and chemists, and we're trying to figure out ways to detect explosives." So I said, "Oh, well have you heard of the head of the Chemistry Department at MIT, Tim Swager who works in the area, and he said, "Yes," he knew the name.

And so he said that one of his problems on the team, and in talking to the chemist, his chemistry language is not really good enough, and so he was really struggling, and that the best results of this team effort would be if everyone could really talk to each other. So he wished that he had paid more attention in his chemistry class. And so I, of course, my connection with chemistry was by wanting to understand biology, but for everyone it might be a little bit different.

So, as I mentioned in the beginning of the class, one challenge that you have this semester is figure out what your connection to chemistry is. What are you going to use chemistry for? How does this fit into what you want to do? And maybe for some of you, you're not going to know that yet. Hopefully it won't take till you have a job doing something to realize that you're lacking something in your education. And so, probably if you stay in science and engineering, need chemistry, good to learn it all now. And from exam 2, we see that you are learning it now and that's really great. So, some day maybe someone in this room will be involved in national security, and if you're not a chemist, you'll be able to talk to the chemists and make really good progress toward that work. So, chemistry -- it's important in medicine, national security, the economy, energy initiatives, a lot of the big things going on now. It's a fundamental, and you will get in this course, the fundamentals.

So if you have any good tea or bus or airplane conversations, let me know -- I'll catalog those for future reference. It's always a touch of how what we do here connects with the real world.

All right, so we're not going far from thermodynamics, we're going into chemical equilibrium. And we're going to be talking a lot about  $\Delta G$ . So if  $\Delta G$  is not your friend yet, don't worry, you can still bond with  $\Delta G$ .

All right, so chemical reactions, chemical reactions can go into a state of equilibrium. And it's a dynamic equilibrium, the reaction is still happening, but if a reaction is an

equilibrium, the rate of the forward reaction will equal the rate of the reverse reaction, so there'll be no net change in composition.

So let's take a look at an example. So let's look at a reaction in which we have nitrogen gas, and we have hydrogen gas, and they are reacting to form ammonia. Suppose we just start with nitrogen gas and hydrogen gas and we don't have any ammonia left. So if we consider concentrations versus time. So say we start with, we have some nitrogen gas, some concentration of nitrogen gas. As it reacts with hydrogen, the concentration will decrease and then level off. We'll start with some amount of hydrogen gas, and its concentration will also decrease and level off. And in the beginning we won't have any of the product, any of the ammonia, so its concentration will increase and then level off.

So when these reactions level off, you're reaching equilibrium. The reaction is still happening, but the rate of the forward reaction is equal to the rate of the reverse reaction, so there's no net change. So the concentrations are staying the same, but there's still -- the reaction is still going forward.

So let's think about the case when we have pure reactants when we haven't formed enough products yet to reach equilibrium. So if we have pure reactants, the reaction is going to be spontaneous in the forward direction. So we'll have a reaction that is spontaneous in the forward direction. And what will that mean about our friend  $\Delta G$ ? Is it going to be greater or less than zero? So it'll be less than zero -- so  $\Delta G$  or the forward reaction will be less than zero. So when  $\Delta G$  is negative, the reaction is spontaneous in the forward direction.

So what about when you have pure products, then the reaction should be spontaneous in the reverse direction. So you have spontaneous in the reverse direction, and what does that mean about the sign of  $\Delta G$ ? Greater or less than zero? Greater, so it'll be positive. So, we can think about that in terms of a plot. We can think about free energy versus the progress of the reaction. So, the progress of the reaction is going this direction as you go along. So in the beginning if you have pure reactants,  $\Delta G$  is going to be less than zero. And you're going to proceed along in the forward direction spontaneously. If, on the other hand you have pure products,  $\Delta G$  will be positive, so you'll be spontaneous in the reverse direction, and the reaction will go in the reverse direction until what happens? Till you reach equilibrium. And what would  $\Delta G$  be at equilibrium? Zero.

So you see, there is a great relationship between  $\Delta G$  and equilibrium, so we have not left  $\Delta G$  behind. So,  $\Delta G$  is going to change as the components of the reaction change. As you have more products or more reactants, you're going to have a different  $\Delta G$ . So let's look at some equations. So  $\Delta G$  is the change in free energy, the difference in free energy, at some point in the reaction at any time with amount of composition. We also have  $\Delta G^\circ$ , which talks about  $\Delta G$  under particular conditions, so it's sort of the standard free energy. We have a term called  $Q$ , which is the reaction quotient, which tells you about products and reactants. We have our friend  $R$ , which is the gas constant, and this depends on temperature. So temperature is a term involved here.

So the  $\Delta G$  at any point in the reaction is going to depend on the  $\Delta G^\circ$  for that reaction, and the reaction quotient, products and reactants, and we'll define this in a minute, and then the temperature as well. So we need to know more about what  $Q$  is, what this reaction quotient is.

So this slide looks a little bit scary, but it's going to be fine, because a lot of the terms are going to cancel out. So we're going to talk about  $q$ , this reaction quotient, and we're going to have different types of problems -- some where we're talking about gases, and others we're talking about solutions. So you can see two different kinds of  $q$ 's, one that depends on partial pressure of the gas, and another that depends on concentration.

So here is our equation again that we just saw --  $\Delta G = \Delta G^\circ + RT \ln q$ , and here we've expanded the term for  $q$ . So  $p$  to the sub  $x$  is the partial pressure of a particular gas, and so in this equation, we have a plus  $b$  going to  $c$  plus  $d$ , the top of the line or the products. So we have the partial pressure of gas  $c$ , and this is over a reference, partial pressure, raised to the power  $c$ , the coefficient, and then also we have  $d$ , the partial pressure of gas  $d$ , over a reference raised to the small letter  $d$ . On the bottom of the terms for the reactants, partial pressure of gas  $a$  over a reference raised to the coefficient  $a$ , partial pressure of gas  $b$  over the reference raised to the coefficient  $b$ . Now what's great is that the partial pressure is one bar, and so that basically cancels out as far as we're concerned. And so the term for  $q$  is much simplified. You won't see problems that have the reference in them, so you can just think about  $q$  in terms of products over reactants. And you just have to remember that the coefficients in the reactions do matter.

If you're talking about solutions, the only difference is that we'll be talking about molar, so we have one molar, so the reference term here also cancels out. When you see something in brackets, like  $c$  in brackets, here that telling you it's a concentration term. So here,  $q$  is the concentration of  $c$  raised to its coefficient. The concentration of  $d$  raised to its coefficient  $d$  over reactants. Concentration of  $a$  to  $a$ , concentration of  $b$  raised to  $b$ . So the thing in  $x$  indicates it's a concentration term.

So  $q$  is just products over reactants, considering the stoichiometry of the particular reaction. So what about the equilibrium constant  $K$ ? So at equilibrium you told me that  $\Delta G = 0$ , and at equilibrium  $q$ , the reaction quotient equals  $K$ , the equilibrium constant.

So we can consider that in terms of this expression, if we're talking about this expression at equilibrium,  $\Delta G$  is going to equal zero. And so, we just set this whole term equal to zero. We can rearrange the equation bringing  $\Delta G^\circ$  to the other side. And so we have  $\Delta G^\circ = -RT \ln K$ , because at equilibrium,  $K$  is equal to  $q$ . So now we have another term to solve for  $\Delta G^\circ$ , and an equation that relates  $\Delta G^\circ$  to be equilibrium constant  $K$ .

So  $K$ , the equilibrium's constant has the same form as  $q$ , but we're only talking about the concentrations or the partial pressures of things at equilibrium. So it's the same, it's product over reactants, same expressions as  $q$ , but in the corner you say at equilibrium. So you're only talking about the concentrations of things at equilibrium if you're solving for  $K$ . If you're solving for  $q$ , it's the concentration or the partial pressure at any time in that particular reaction. Important thing, products over reactants.

All right, so, we can rewrite the equation one more way. So I just told you that  $\Delta G^\circ = -RT \ln K$ . So we can substitute into the expression  $\Delta G = \Delta G^\circ + RT \ln q$ , and now we can rearrange this equation. And so, if we rearrange it, we have  $\Delta G = RT \ln \frac{q}{K}$ , the  $\Delta G$  at any particular point in the

reaction equals  $r \cdot t$  natural log of  $q$  over  $k$ . And this equation is helpful for people if they're thinking about what is the equilibrium constant, what concentrations do I have now -- we're not at equilibrium, what concentrations do I have now, what is  $q$  now in the reaction, how does that compare to  $k$ ? And when you know what those values are, you'll know something about the direction of the reaction because you'll know if  $\Delta G$  is positive or negative. It'll be spontaneous in the forward direction or in the reverse direction. So this is a handy equation for thinking about the relationship  $q$   $k$   $\Delta G$ .

So let's think about that relationship for a minute. If  $q$  is less than  $k$ , what is the sign of  $\Delta G$ ? So it would be negative, which means the forward direction of the reaction will occur. So if you think about it, you can think about in terms of products and reactants. So at equilibrium then, if  $q$  is less than  $k$  at equilibrium, there are more products than there are right now, so you need to make more products. So you would have  $\Delta G$  would be negative, you'll see that mathematically, and you can think about it in terms of whether you're going to make more products or less products.

If  $q$  is greater than  $k$ , what is  $\Delta G$ ? So it would be positive and the reverse direction would occur. So you think that at  $q$ , if it's larger than  $k$ , it has more products in its terms, and at equilibrium there are less products, so you need to go in a direction that will get rid of some of those products so you'll reach equilibrium again. So this equation is very helpful in thinking about the direction of the reaction - - which direction will it be spontaneous.

So let's look at an example.  $K$  is given in this example, and then we have a bunch of partial pressures. And we're asked which direction the reaction will go. So what do I need to do to answer this question, what do I need to calculate? So if I'm given  $k$ , and a bunch of partial pressures, what do I first need to calculate?  $Q$ , right. So let's calculate  $q$ .

So  $q$ , we're going to talk about products over reactants, so we're going to talk about be partial pressure of the ammonia, and there are two of them being formed. Our reactants, we want to talk about the partial pressure of the nitrogen, and the partial pressure of the hydrogen gas, and again include the stoichiometry, so we have three there.

So now I can plug in my values, so I'm told I have  $1 \cdot 1$  bar, and down here I have  $5 \cdot 5$  and  $2 \cdot 2$  to the 3, again, considering the stoichiometry. And if you do the math, you get  $2 \cdot 1$  times  $10$  to the minus 2. That's your  $q$  value.

Now given your  $k$  value, which the problem states, and this  $q$  value, let's do a clicker question, tell me which direction the reaction will go. All right, 10 seconds.

So, 77%, pretty good. So,  $q$  is greater than  $k$  here. And if  $q$  is greater than  $k$ , what will be true about  $\Delta G$ ? I have another clicker question for that -- yell out the answer. What is it? Positive, right. So you're going to shift towards reactants, so you're going to go in the reverse direction. So you think about whether there are more products or less products at equilibrium, and so there are more products, so we have to think about which direction it'll go, and here, ammonia will dissociate until equilibrium is reached again.

OK. So let's think more about what  $K$  is going to tell us. So  $K$  tells us about the mixture of products and reactants at equilibrium, whether we can expect low or high concentration of reactants at equilibrium. So let's look at another example. So when you have  $K$  that's greater than one, so more products than reactants at equilibrium, you can think about this in terms of higher products at equilibrium.

When you have  $K$  less than one, we're going to have lower products. So again, think about  $K$  in terms of products over reactants at equilibrium. So if  $K$  is greater than one, there are more products than reactants. If it's less than one, there will be less reactants than products. So let's look at an example of that. Let's look at when  $K$  is greater than one. And I have the equation up there and I'll write it here as well. So we have  $2\text{NO}_2$ , and two double arrows, and  $\text{N}_2\text{O}_4$ . So we have a  $K$  value here of  $6.84$ , so that's greater than one value. So let's think about this reaction. So over here instead of concentration, we're going to talk about partial pressure because we're talking about gas, and we have time.

So initially we have a reactant. And the reactant starts at some concentration and decreases and then reaches a straight line, so reaches equilibrium. So we have our reactant here. Originally we have no product, and so product is going to go up and be formed and then it's going to level off as you reach equilibrium.

So initially, what is true about  $Q$  and  $K$ ? So with no products, what is true about  $Q$  and  $K$ ?  $Q$  is less than  $K$ . And so what's true about  $\Delta G$ ? Less than zero, it'll be negative, so it'll be spontaneous in the forward direction. So you're going to be spontaneous in the forward direction and you're going to make your product.

So now let's calculate what the concentrations are going to be at equilibrium. So initially, so you have your initial pressure for the reaction,  $2\text{NO}_2$  going to  $\text{N}_2\text{O}_4$ , and our initial concentrations are given as one bar, and we have no product. Now we talk about the change as we go toward equilibrium, how much does the reactant change? What do I write here? What change? Minus  $x$  minus something  $x$ ? Minus  $2x$ . So again, we're considering the stoichiometry, and what's over here? So just plus  $x$ , and then at equilibrium we now have  $1 - 2x$  and  $x$ .

So we're talking about equilibrium concentrations, so we're talking about  $K$ , so  $K$  equals  $6.84$ , which is going to be equal to the partial pressure of the product over the partial pressure of the reactant squared. So it's going to be equal to  $x$  over  $(1 - 2x)^2$ . So  $x$ , if you calculate it out, should equal point  $0.381$  bar. And then if we do  $1 - 2 \times 0.381$  bar, we get  $0.238$  bar. So if we go back over here, our products at equilibrium -- oh, I guess I should write what -- so  $x$  is our product and this is our reactant. So the product we have  $0.381$ , and our reactant at equilibrium is going to be  $0.238$  bar. So we have more product than reactant at equilibrium, which is consistent with the value of  $K$  being greater than one.

So, when you know something about the equilibrium constant, you know something about the reaction and whether you would expect more products or reactants at equilibrium. So again, you can think about this in terms of  $Q$  and  $K$ .

All right, so now we are going to go toward our next clicker question. So if we can rewrite the expression for  $\Delta G$  equals minus  $RT$  natural log of  $K$ , and express it in terms of  $K$ , and now we can think about then what is that relationship. If you have a large value for  $K$ , what do you expect to be true about  $\Delta G$  nought? All right, let's give that 10 seconds.

OK, why don't you discuss for a minute with your friends whether you agree with that 78% or not. All right, now we're going to re-poll, so click in again. Now give the right answer. Interesting. It actually usually goes the other direction, that after there's a discussion, more people come to the same conclusion. So I guess it's a matter of if the professor asks that, you assume that that must have been the wrong answer. Was that people's logic?

So what are the points of doing this, and we're going to actually do this kind of thing a few more times in class, is that collectively, and I was actually just at an education meeting about science down at the Howard Hughes Medical Institute, that statistics show that if you have a group where everyone in the group has the wrong answer and they're allowed to discuss it, there's a good chance they'll come up with the right answer. So that it's not just about one person in the group having the right answer, convincing everyone else that they're right, that the act of discussing often leads to new answers. So now that you know that it's not a trick on my part to tell you you got it wrong, we'll see next time whether this, in fact, holds, that the act of discussing helps give the right answer.

Anyway, so if  $K$  is large, it is true that  $\Delta G^\circ$  would tend to be negative and more -- it would be negative and more on the large side. So one can think about if there's more products over reactants, that's going to indicate something about the  $\Delta G^\circ$  for the reaction, and the  $K$  -- the  $K$ , if it's greater than 1, if it's a big number, then there are more products than reactants, and  $\Delta G^\circ$  would be negative and would tend to be a large number.

All right, so this is more actually kind of simple bookkeeping involved that if you know steps in the reactions and you know equilibrium constants, you can calculate an overall equilibrium constant for that reaction. So you can write a reaction as the sum of different components. And so up here, we are going to try to add these first two equations to get this net equation.

So we have  $2 \text{ gas } + 3 \text{ c l } \rightarrow 2 \text{ p l } + 3$ , and that's equilibrium 1. And so then in the next reaction, some of that is being consumed reacting with another  $\text{c l } \rightarrow 2$ , giving you  $\text{p c l } \rightarrow 5$ , and the net reaction we're interested in has  $2 \text{ p } + 5 \text{ c l } \rightarrow 2 \text{ p c l } + 5$ . All right, what do I have to do before I can add these together effectively and have things cancel out? I need to multiply what? Second equation by 2, yeah. So to get that to work I would need to have 2's there, then this is going to cancel out and these will add up, so we have 5 and then we have two of the main products. So if I do that, and I have the equilibrium constant for one and for two, how am I going to get equilibrium constant for three?

I'm going to multiply  $K_1$  by  $K_2$  and  $K_2$ . So I'm going to have to multiply  $K_2$  in there twice, because there's two of those -- we'd multiply that up. So if you have different parts of reactions and you can sum them together, then you can multiply out the individual  $K$ 's to get the new value of  $K$ . So that's something that's just useful that you'll run into in doing these types of problems.

All right. Now we're going to think about how equilibria respond to stress. And I always feel like I need to pause. MIT students, you guys are some of the smartest, most talented scientists in the world. I don't know if you fully appreciate how smart you all are. But this concept is tough for MIT students. So Le Chatelier's principle says that a system in equilibrium that is subjected to with stress tends to react in



such a way to minimize that stress. I have advisees coming to my office saying, "I'm double-majoring in this and that and I'm taking five classes and I have UROP and I have this lab exercise -- I don't know what's going on, so I've been thinking a lot about it and I think I should add a third major." Le Chatelier would be very unhappy with that. Le Chatelier would say that the appropriate response is to drop one of the majors, to minimize the stress. So in doing these problems, what I want to encourage you to do is think the opposite of what you would do. Minimize the stress. If you think about that you'll be all set.

All right. So Le Chatelier's principle actually is very useful. If you think about minimizing the stress, you'll be able to predict the direction that the reaction will shift. So the reaction's going to shift in a way to minimize the stress, so you can predict it. If you're thinking along these lines, you say, oh, that system was stressed, and then you can think about how that reaction or that system is going to respond. So let's give some examples.

So, we have a system in equilibrium -- we started out, we had our nitrogen and our hydrogen and we had no product. We reacted the hydrogen and the nitrogen, their forming products, and eventually they reach equilibrium, their  $\Delta G$  equals zero there's still the reaction going on, but there's no net change. All right, now the system is going to be stressed. So we're going to add more of a reactant. How will the system react to minimize that stress? What is it going to do? It now has too much of one of the reactants. You'll form more products, and that's going to use up some of your other reactant, which will go down, and you're going to form more product until equilibrium is reached again.

And one thing that I'll mention that the ratio has to be the same. The equilibrium constant is a constant given the same temperature, but you're not necessarily always going to have the same concentrations, but you should have the same ratios, the same value of  $K$ .

All right, so what about if you add more product, what's going to happen? What direction will the reaction shift? Right, it's going to shift toward the reactants, so you're going to make more of each of the two reactants until again, you find your equilibrium again. And then the reaction's still going but there's no net change anymore.

All right, so let's think about this -- let's think about this in terms of the math as well. If you want to stick with the math, that's OK, you can think about calculating  $\Delta G$ 's here. So if you're a system in equilibrium and you add more hydrogen, the system will respond to minimize that increase. So it's going to make more product that will minimize the increase, it shifts to the right. And this can be explained in terms of  $Q$  and  $K$ . So, you can think about, again, do you have more products now or did you have more products at equilibrium, and if you're adding more reactants, momentarily  $Q$  will become less than  $K$ . And so, you would get a negative  $\Delta G$ , which would make it spontaneous in the forward direction. So some people like to think about this in terms of  $\Delta G = RT \ln \frac{Q}{K}$ . So you think about if  $Q$  is less than  $K$ , what sign you have for  $\Delta G$ , and that's tells you whether the reaction is spontaneous in the forward or the reverse direction.

And let me just give you one hint for taking exams in this unit. That use of the arrow is really good, or saying "toward product" or "reactant." I can't tell you how many people write -- know what the answer is and write left when mean right, or write

right when they mean left. But if you draw an arrow you never really get it wrong, and when you say products or reactants it's a lot harder to make that mistake. So if you're not good with right or left, which let me tell you a large fraction of people are not, hedge your bets, you can write everything, more products, arrows, and then write if you want, then you're pretty sure that you have it all in there.

OK. So again, we can explain this in terms of  $q$  or  $k$ .

All right. So let's just quickly talk about adding more products. We did this already. If more products are added, then  $q$  is going to be greater than  $k$  momentarily, and you would shift toward reactants, shift toward the left, and again, we saw that down there.

So tell me a final clicker question and then we're done. What happens if you remove products and why? OK, 10 seconds. See if we can get in the 90's. No, no 90's today, we'll have to do it next time, but we got 73 right. So we're going to make more products as well.