

## Lecture 15A • 10/31/11

Le Châtelier's principle; Q versus K

I want to talk about the process of a system attaining equilibrium, because if we're going to talk about disturbing equilibrium, we first have to talk about attaining it. Instead of talking about a chemical reaction as my example, I want to take something that's a little bit easier to draw out, which is about vapor pressure. What is vapor pressure? Why is it that a liquid would produce a gas if it is not at its boiling point? Because some of the molecules have enough energy. Remember that energy distribution diagram. We have energy per molecule; number of molecules. The idea is that some fraction of molecules has enough energy to be able to evaporate. The reverse is going to be true as well, though, that at any particular temperature if you have a gas phase, the ones that are moving too slowly would condense again, then, depending on your temperature, depending on the energy distribution, some fraction of molecules would always, therefore, condense.

So you have this back and forth that goes on if you take a liquid into a container. We can discuss this as four different stages. In this discussion, the forward process is going to be evaporation, making the vapor. The reverse process is going to be condensation. Let's say that at the instant of time zero, you have a container that's under vacuum that you suddenly introduce liquid into. If we're talking about terms reactants and products, we only have reactants; there are no products. If there's only reactants, the rate of the reverse reaction is zero; you only have the forward process. So there's vapor that's forming, liquid that's evaporating, because a fraction of molecules have enough energy to be able to evaporate. Just after that starting point, you have formed some vapor. At any particular temperature, there's going to be some quantity of that vapor that then condenses. If you've just started the process of allowing the liquid to generate its vapor pressure, there's not going to be a heck of a lot of that product yet. So, the rate of the forward process is still greater than the rate of the reverse process, so some vapor is now condensing.

But, the liquid is still evaporating at a rate greater than the condensation of that vapor. At some point, when you reach equilibrium, you'll have enough vapor around that the rate of the condensation of that vapor matches the rate of evaporation. At that point, you'll have no more change in pressure, because every little bit that's evaporating is condensing at an equal rate. That is the point at which vapor pressure is measured, because vapor pressure is an equilibrium phenomenon. But now let's imagine one more case. Let's say that we somehow inject extra vapor into the system. Ignore how this physically occurs – all of a sudden, vapor appears. If we were already at equilibrium, but we now have too much vapor around, that means the rate of condensation is actually going to be greater than the rate of evaporation. We're going to be past equilibrium. The concentration of products will be too great; the rate of the reverse reaction will now be greater than the rate of forward reaction. Overall, condensation occurs.

Let me walk through this-step process again. If you only have liquid, you have no reverse reaction, so the only thing that can happen is the liquid's evaporating. As the liquid continues evaporating, though, we're going to build up vapor, and that vapor, some of it, is going to condense. At first, the rate of evaporation will still be greater than condensation, until you reach a point where the two are in balance with each other. If you suddenly mess with the equilibrium by putting more vapor, which in this case is a product, that means that suddenly the rate of the reverse process has increased, but the rate of the forward process hasn't. As a result, the equilibrium will shift.

Now that I've given you this physical example, let's now talk about Le Châtelier's principle, which is that when a system at equilibrium is stressed, changed, the system will respond in a way that relieves that stress. In discussing Le Châtelier's principle, if we're dealing with concentrations – if we change temperature, we're going to cause a shift in equilibrium as well, because temperature affects the rate of both the forward and the reverse reactions. If we ignore temperature changes, we're going to be looking mainly at concentration. So we're trying to figure out how changing concentration might affect equilibrium. That's what Q is. Q is called the reaction quotient, and Q is mathematically identical to K, except that K is only calculated at equilibrium concentrations, while Q can be calculated at any point in a reaction.

Let's see a graphical example of that then. What kind of diagram did I just draw? A reaction progress diagram. How is it different from a reaction coordinate diagram? We're looking at a solution, a whole bunch of molecules, as they go from reactants to products. A reaction coordinate diagram is just looking at one set of molecules, so they display two different things. No assumption about time is made here, because, in term of time, you'll never actually get to products, you'll get to equilibrium. Equilibrium is the lowest-energy point on this curve. Q is wherever you happen to be in a chemical reaction. Let's say that I put Q right at this point. Not worrying about specific reaction, in general, we could say that Q is a measure of products over reactants. In this situation, if  $Q < K$ , then not enough products have formed; another way to express it is that there are too many reactants around. Another possibility is if  $Q > K$ , then not enough reactants are present, or you could say too many products have formed. I'm going to use equilibrium to explain what happen when we have a strong base that neutralizes a weak acid. A weak acid is something that doesn't like to dissociate, and what we're going to talk about is if we force it to dissociate, we force it to get out of its equilibrium. What does that mean it's going to do in response?

When water is around, a ketone can undergo a reversible reaction with that water. An oxygen can become protonated, which can then cause some other event to occur. When that positive charge forms, water can come to attack. Because water started out neutral, the oxygen on the product will initially be positively charged. A proton comes off, and we end up with a neutral –OH group. This is a geminal diol, but because this was formed just by adding water to it, sometimes it is referred to as a hydrate. What if I tell you that this reaction is actually not that favorable; this doesn't like to move forward very much at all. Is there a way this reaction could be forced to happen? Acid is just a catalyst. It might help in terms of that initial formation, that rate, that it might not end up adjusting the balance of equilibrium. If we add base, we'd remove the  $H^+$ , and the reaction wouldn't happen at all. If we removed products, what does that mean?

If we suddenly removed products, we could think of that in a few ways. If we removed products, we're effectively going back uphill energetically towards reactants. The reaction would want to go back downhill again, make more products to get to that lowest-energy point. Another way of thinking about it: at equilibrium, you've got equal rates of the forward and reverse reactions. If you suddenly remove products, then the forward reaction is going to be greater all of a sudden, because by removing those products, you're reduced the rate of the reverse reaction. Because of that, the reaction's going to move forwards. If we suddenly remove products,  $Q$  has the form of products over reactants,  $Q$  will be less than  $K$ , so the reaction will again proceed forward to make more products. No matter which way I tried to explain it, when you remove products, the reaction tries to form more products. If you continually remove it, then you're going to force the reaction to completion. That's an application of Le Châtelier's principle. Le Châtelier's principle is that, you stress a system, it responds to the stress. If you remove products, more products form. If you add reactants, reactants are used up. If you pull out reactants, reactants form; remember, this is reversible. Whatever you do, it does the opposite. We're going to remove a product as it forms to force a reaction to go completion.

This particular reaction is reversible and non-spontaneous. Non-spontaneous means positive change in free energy ( $\Delta G > 0$ ). If I wanted to write a reaction progress diagram for this, it would look more closely to something like this. The equilibrium is going to lie close to the reactants side. If products are suddenly removed when the reaction is at equilibrium – so if we removed products, that means  $Q$  is going to be less than  $K$ . Since  $Q$  is an express of products over reactants, and the concentration of product just decreased. Another way you could say it is that the rate of the forward reaction is greater than the rate of the reverse reaction, since products have been removed, but not reactants. The potential energy of the system is effectively increased, therefore, the reaction will move forward to make more products to reestablish equilibrium. To complete this example, the practical upshot is that if products are continuously removed as they are formed, the reaction can be forced to completion, even though it is non-spontaneous.

We could tell exactly the same kind of story in different situations. For example, sometimes to push a reaction forward, it's easier just to add a ton of reactants. For example, for a similar reaction mechanism, instead of removing products, we just flood it with the solvent, which happens to be one of the reactants. If you push a whole bunch of reactants into the system, then that makes  $Q$  again less than  $K$ , which will push the reaction forward. Completion means 100% products. At equilibrium, you'll never have 100% products, if you truly have equilibrium. If you have 100% reactants or 100% products, then one of the reactions or another, you don't have, so it's not in balance, so it's not at equilibrium.

In some reactions, there are other tricks you can play. For example, in gas reactions, sometimes if you have one gas making another, then if you have a reaction that takes one gas molecule and splits it into two, then temperature can cause the reaction to shift one way or another, because it's trying to relieve pressure.  $K$  is only affected by temperature, not concentration.  $K$ , the equilibrium constant – equilibrium itself can shift back and forth; the position of where a reaction is can shift around. But the ratio of reactants and products itself is a constant. If you change a concentration, the reaction may move one way or another until you get back to the same proper ratios.  $K$  never changes because you change the concentration of something. In this example, if I remove products, I change concentration, so the reaction shifted to get back to  $K$ . So the change in concentration didn't change  $K$ , it just made the reaction have to do some work. The only thing that can change  $K$  is by changing temperature, because that changes the rate of both the forward and reverse reactions.

If you removed it but it was in the same reaction environment, then yes, it would try to react backwards and try to establish equilibrium. In this particular example, it's tough to isolated hydrates, because with even just a little acid around, they will go backwards.

#### Delocalization

I'll start with the allyl cation. Each carbon in this molecule is  $sp^2$ -hybridized. The discuss point that came up, therefore, was what do we do about the  $p$  orbitals that, the way we think about hybridization, would exist? The question could be – do we connect the two  $p$  orbitals on the left, or do we connect the two  $p$  orbitals on the right, and the answer ends up being: yes. We connect all three of those  $p$  orbitals. I want to talk about proper writing of resonance structures.

Resonance structures only exist because the system used to write structures (Lewis dot structures – line structures are just a modified form of Lewis dot structures) is unable to unambiguously represent bonds that cover more than two atoms.

A line, when we draw it, means a bond between two things. If we have three things that are overlapping, how do we write one bond that covers those three? If we had six things overlapping, like benzene, then how would we write benzene? There are dotted lines that are sometimes used, but that's a really poor way to do things if we are trying to count electrons. Part of the reason that Lewis dot structures can be useful, even in these situations, is that one line means two electrons. In these two resonance structures I drew for the allyl cation, at least we can count how many total electrons are involved. But, you have to know those are resonance structures. No single resonance structure correctly reflects the true structure of a molecule. The true structure of a molecule can be estimated by averaging all possible resonance structures together.

We could come up with some rules for writing resonance structures. There's one main rule – only lone pairs and pi bonds are able to move; single bonds can never be formed or broken. Why is that true? Let me draw a different example molecule. Let's say I had the allyl anion instead of the allyl cation. It turns out it has a pair of resonance structures as well. Mechanistically, I could write that resonance by showing that lone pair attacking the double bond and pushing the electrons over. If we were to draw a SMOG, we'd need to know the hybridization of each of these atoms. Let's take the second molecule I drew, where the negative charge is on the lefthand side. What is the hybridization of that carbon? If you said  $sp^3$ , then you weren't looking at the true molecular structure. Remember that resonance structures, individually, do not reflect the correct structure. That pair of electron does not exist in an  $sp^3$  orbital; that carbon is  $sp^2$  hybridized. If you are unsure given all the single bonds, what about the resonance structure on the left? Same molecule, isn't it? But in this same molecule, it is  $sp^2$ , so how could it go from  $sp^2$  to  $sp^3$  if it's really the same molecule? The answer is, it doesn't; it's just that the way that we write structures fails to properly show what the hybridization should be. This carbon is actually  $sp^2$ -hybridized. It appears  $sp^3$  in this structure; that is because resonance structures fail to show delocalized bonding. Delocalized – think of local, and then delocalized means it's somewhere not local. It's somewhere besides just right in one location. Delocalized gets this idea across that electrons are flowing across multiple atoms.

What would the SMOG for this look like? Identical to the allyl cation, it's just that there are now two more electrons floating around that pi system. Why is it that you can have one case where you have a positive charge, and then this molecule it's still fine to put two more electrons into? If we had two p orbitals and only two p orbitals interacting – underneath that really means that there's just two atoms interacting – how many molecular orbitals did we say exists in the case where two p orbitals overlap? In other words, if I had just a plain carbon-carbon double bond, what kind of orbital is the double bond? What kind of bond is it? It's a pi bond. If you have a pi bond, what else is there, but empty? The antibond. In the case of pi bonding, you always have one lower energy level and one upper energy level. How did that occur? Because you either had zero nodes between the two atoms, or you had one node between the two atoms. How come you didn't have more than that? Because you only had two atoms. In a pi system, the number of atoms tells you the maximum number of nodes.

If I now have three atoms, what does that mean my three molecular orbitals are going to look like? One energy level will look like this – no nodes. One energy level will look like this – one nodes. Then the last one, will have two. The maximum number of nodes in a pi system is equal to the number of atoms minus one. So, three atoms, three p orbitals – zero, one, and two nodes. These are what the molecular orbitals for this pi system are going to look like. These p orbitals are line up in a line. Imagine that phone cord example – the two ends [of the molecule] would be like the two ends of the phone cord. [max energy packets like max nuclear interactions] As we make more complicated orbital systems, the more orbitals we add in, the more nodes that are possible, but the lowest-energy version is always one orbital where the sign is equal across the molecule. Of course, these are just idealized representations. What we need to do is use p orbitals to estimate what these molecular orbitals are going to look like – that's exactly what we did with pi bonds and antibonds. Pi bonds and antibonds exist; we use p orbitals to describe them. The way we did it was, for the bond, we added two orbitals that had the same sign as each other, and for the antibond, we added opposites.

Same type of thing is going to happen in this case. If I wanted an orbital in which there was only one sign across the whole thing, then what way would I shade my p orbitals to achieve that? I'd have to shade them all the same way. That would be the lowest-energy configuration that you could have – no nodes. What about the highest-energy configuration? What if you had a node between each atom? That could be represented by the p orbital flipping signs each time. That's why the maximum number of nodes in a linear system is the number of atoms minus one. But what about this middle case, where the node effectively would pass through the middle of this p orbital? Then we wouldn't even use that p orbital to estimate what the molecular orbital looks like. We had have one orbital on one side, on orbital on the other, and so the molecular orbital picture would look like this. You might say: how could that p orbital disappear? That p orbital's not there; it's just our model to estimate what one of these systems looks like. But the p orbitals don't exist, so we could do whatever we want on paper. In the proper approach, we would just say the coefficient for that orbital ends up being zero.

Let me ask you in terms of energy: this bottom orbital, do you think this is bonding? Why? Why was a pi bond a bond? What was so good about it that made it a bond? Because electrons are between the nuclei. If these overlap with the same sign, then you're going to end up with the smear across the molecule; the electrons are spread out, that's putting electrons between positive charges, that's favorable, so this is a bonding orbital. Now the top one, where every other atom, the sign of that orbital changes. What's that going to mean as far as electrons between the nuclei? There aren't any; there are nodes there. So if there are no electrons between the nuclei, then they're exposed and that's unfavorable.

Unlike the pi star before that we had, this has two types of unfavorable interactions, so really not likely. This would be an antibonding orbital. What about the middle case? There's no interaction. These orbitals are so far away, they effectively don't interact, so it is a non-bonding orbital. In terms of relative energy, that non-bonding orbital would have an energy of zero. Zero is the energy of unreacted atoms. In other words, when you bring the system together, you had electrons in this non-bonding orbital, they're not higher or lower in energy, and so they don't really help or hurt the system.

In the allyl cation, we only had two [pi] electrons. We had a pi bond next to a positive charge. The pi bond only had two electrons in it. This system, because it has four electrons, you'd occupy the bonding orbital, and in this case you'd also occupy the non-bonding orbital. Because the non-bonding orbital doesn't hurt or help, doesn't matter if the electrons go there. This also explains why the electrons can delocalize. We had our one rule for writing resonance structures, which was that lone pairs and pi bonds can move around. This is one example of why.

There's a secondary rule that would help you choose between good and bad resonance structures. Better resonance structures generally have full octets where possible, lack of charge separation, and charges that match electronegativity. We could take something like acetone and because it only involves the pi bond, I could show the bond magically opening up. But, this would technically just be a resonance structure. The second structure I wrote is unfavorable, due to charge separation. I could have another example, where I did it the other direction. I could open that pi bond up towards the carbon. If I did that, I end up with a positive on the oxygen, a negative on the carbon. Oxygen certainly doesn't like being positive, so that's a worse structure than what I wrote above.

The main point is: when writing mechanisms, you need to know that both of these molecules really represent just one structure.

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forward – evaporation; reverse – condensation

@ t=0, liquid is introduced into a completely empty chamber (under vacuum)

Le Châtelier's principle – When a system @ equilibrium is stressed (changed), the system will respond in a way that relieves that stress.

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Q = products / reactants.

If  $Q < K$ , then not enough products have formed and/or there are too many reactants around. If  $Q > K$ , then not enough reactants are present and/or too many products have formed.

This particular reaction is reversible and non-spontaneous ( $\Delta G > 0$ ). If product are suddenly removed when the reaction is at equilibrium:

- 1)  $Q < K$ , since Q is products / reactants and [products] just decreased
- 2)  $R_f > R_r$ , since products were removed (not reactants)
- 3) Potential E of the system is effectively increased.

Therefore the reaction will move forward to make more products to reestablish equilibrium.

– If products are continuously removed as they form, the reaction can forced to completion, even though it is non-spontaneous K is only affected by temperature, not [].

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– No single resonance structure correctly reflects the true structure of a molecule.

– The true structure of a molecule can be estimated by averaging all possible resonance structures together.

Rules for writing resonance structures:

– Only lone pairs and pi bonds are able to move; single bonds can never be formed or broken.

This carbon is actually sp<sup>2</sup>-hybridized. It appears sp<sup>3</sup> in this resonance structure, but that is because resonance structures fail to show delocalized bonding.

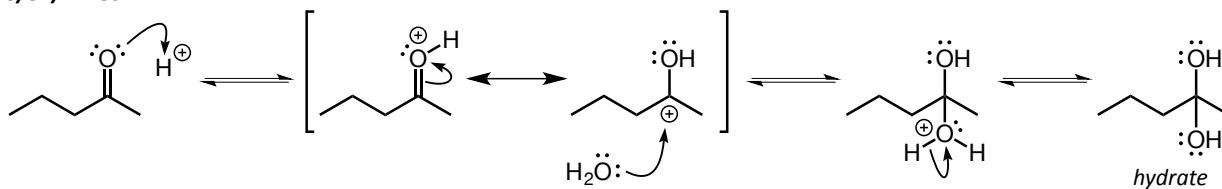
max # of nodes in a pi system is = # of atoms – 1

A non-bonding orbital is the same in energy as the atoms if they had never undergone bonding.

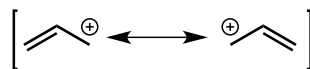
– Better resonance structures generally have full octets (where possible), lack of charge separation, and charges that match electronegativity.

Structures

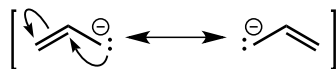
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