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5.112 Principles of Chemical Science, Fall 2005  
Transcript – Lecture 34

Welcome, everybody, on this snowy Friday.

At the end of last hours, and I just want to take a minute or two here to finish this piece up, we were talking about ways of writing kinetics expressions for a particular type of assumed ligand substitution mechanism.

In particular, we were looking at dissociative substitution.

And now I would just like to take you through what happens if you don't make the major assumption that we made last time, which was that every time our intermediate five coordinate complex  $ML_5$  was formed it would go onto products.

That was our assumption last time, one of them. And this steady state approximation is one that allows us to simplify the rate expression. If we don't make that assumption, what we say is that the change with time of the concentration of the intermediate is approximately zero.

We know that at the very beginning of the reaction we have this  $ML_5X$  species.

$X$  is the ligand that dissociates to give  $ML_5$ , so at time zero there is zero  $ML_5$  concentration. And let me just remind you of this plot of what happens in a reaction like this.

We have our initial  $ML_5X$  species that decays away and we have our product  $ML_5Y$  that grows in.

And if this reaction goes by dissociative ligand substitution, which would certainly be consistent with a  $d_4$  high spin electron count, as we saw last time, then there may be some intermediate  $ML_5$  that at time zero has zero concentration.

And it may never really build up very much concentration. And then at the end it goes down to zero, too, because when the reaction is over all of our  $ML_5$  has a  $Y$  attached and is a six coordinate again.

If the concentration of the ML5 intermediate never really builds up very much, which is quite often the case, it may not be observable, the amount of which is produced during the reaction then this approximation is pretty valid and allows us to derive equations for the change with time of the species that we can observe, namely the starting material that is going away and the product that is coming in.

And so this is our concentration versus time plot for the reaction.

And with this approximation we can then set equal to zero the expression for the formation of the intermediate, which is  $k_1$  times ML5X.

This quantity  $k_1$ , if you remember back to the diagram we were using last time,  $k_1$  is the rate constant associated with surmounting that first energy barrier,  $k_1$  times ML5X.

That produces ML5, so this is producing it, but when you are in the middle of the well where the intermediate lies there are two ways to destroy ML5. You can go  $k_{-1}$  times ML5 times X.

This brings you then back over to where you started.

And you can also lose it in a productive sense by  $k_2$  times ML5 times our species Y, which brings us onto products. And we are still making the assumption that once you get to products the reaction is done and you never go back.

That assumption is built into this analysis.

And if we look at this, we have set it equal to zero meaning that ML5 is not building up. And so now what we can do is we can rearrange this expression and solve it for the concentration of ML5.

And you will see that you can do that here. ML5 becomes equal to  $k_1$  times ML5X.

That is the expression for the formation. These two brackets should be done. ML5X times  $k_{-1}$  times Y plus.

Sorry.

That should be X here. Plus  $k_2$  times Y. The expression in the denominator here are those two quantities that take us out of the well. And on the top we have the one quantity that takes us into the well from the starting materials.

And so now we have an expression for ML5 that we can plug into our expression for the rate.

The rate overall expressed as the appearance of the final product is going to be equal to  $k_2$  times ML5, this is going over the final barrier, times Y.

And so if we take the expression here for the rate, this is the value that we expect for the appearance of products.

We take that substitute in this expression for the unobserved intermediate ML5 into this.

Then we have an expression for the rate entirely in terms of things that we can either observe, namely the starting material, the concentration we would measure by some technique like spectrophotometry as a function of time, watching an absorbance band for it decay away, for example.

And then also in terms of the concentration of Y which we were talking about as the solvent, so it would have a large invariant and known concentration.

And then, of course, since X is being produced in the reaction whenever it dissociates from the starting material there is a relationship between the concentration of X at any time and the concentration of our starting material at any time.

Now we get an expression that we need to be able to integrate in order to actually produce, given these parameters,  $k_1$ ,  $k_{-1}$  and  $k_2$  to produce a predicted dataset to compare with the experimental.

And what one normally does is you take an experimental dataset, you have the equations that arise from your mechanistic hypothesis and you do a least squares fitting procedure to obtain the values of the parameters, which are these phenomenological rate constants associated with each step in the mechanism.

Extract the values of the parameters and see what you get, see if the mechanism that you have assumed can give you a good fit to the data or whether it cannot.

That is the end of my discussion of an introduction to kinetic analysis of chemical reactions, a really important subject where differential equations really become very important. Today I want to get onto the top of extended solids, and so I am going to talk about dimensionality here.

And materials.

And I want you to keep in mind the framework with which we have been discussing chemical bonding all throughout this semester because we are going to extend that today to try to understand some of the properties of systems that are not molecular but extend infinity in some number of dimensions.

We talked about the H<sub>2</sub> molecule.

This is a very small molecular system that we have described and talked about quite a bit. This system has a radius here of about 0.64 angstroms, or internuclear distance of about 0.64 angstroms. And then we can also consider molecules that become more extended.

There is an example of a polyene.

And my use of a polyene here should lead you to think that when we consider polymer chemistry, in some cases we will be talking about systems that are extended, maybe not infinitely but very greatly in one direction, or maybe more than one direction.

But polyenes are interesting species because if this thing had all the double bonds, trans as I have drawn here, then what we have perpendicular to the board would be a set of p-orbitals, one p-orbital perpendicular to the board on each of these carbons.

And all of those p-orbitals can overlap. And then we can start talking about the transport of electrons down a chain like this in one dimension.

So I put H<sub>2</sub> up here as an example of what is approximately a zero-dimensional system.

Here is a system that extends somewhat in one dimension. And then as an example of a two-dimensional system, let me just draw up here a piece of one of the sheets of the graphite structure.

Graphite is one of the allotropes of carbon.

And graphite is a really nice 2d structure. I can draw in some of the unsaturation here. And I don't mean to suggest that this thing stops here. These carbons on the parameter of the graphite system have bonds, and the structure looks very much like what I have drawn here if you repeat outward, up, down, left or right.

And what that leads to are two-dimensional planar arrays of carbon atoms that, as with the polyene structure, here this polyene that I drew with six bonds is about 13 angstroms long.

And then the problem that you get to with graphite is that these graphite sheets can have dimensions of millimeters.

You have gone from something short to something very, very large. And we are going infinitely.

I am going to show you a little bit more about this. I am going to let you look at this website yourselves. You are going to find that I did put into the notes for today the website that we are going to look at.

And it is for you to go ahead and look at in three-dimensions at the structure of the graphite.

And also, in particular, I want you to be able to look at the structure of the diamond framework. One of the things that I want you to be thinking about in association with today's lecture are the way that atoms pack in three dimensions when you make up a solid material.

You will see why that is important in just a moment.

And so we are going to have to go from bonds to bands in order to make this transition.

And that means we are going to have to talk about band structure today and where bands come from.

This, by the way, the title for this panel from bonds to bands is actually the inverse of a title that was penned for a beautiful article

written by Professor Roald Hoffmann. And he was actually one of my teachers as an undergraduate at Cornell University, and he also won the Nobel Prize for his contributions to theory.

And I refer you to his article from bands to bonds if you want to learn more about this topic because, although the concepts of solid state physics are often discussed with very different terminology than the concepts of electronic structure theory for molecules there are a lot of very important parallelisms.

And one of the things that Professor Hoffmann is very good at is in bridging the gap between different branches of science that talk about the same things but don't realize that they are talking about the same things.

And so here we have a system with a single orbital.

We are going to look at the number of orbitals. And here is a system with one. And this is an energy level diagram. We have used energy level diagrams for a lot of things. Last lecture we used them to discuss potential energy surfaces of chemical reactions, in addition to all these other properties.

Here is a system with one orbital.

And then, as you know, when you have a system with two orbitals you can get bonding and antibonding. This is the hydrogen problem. This might be a hydrogen atom, for example. Here is an H<sub>2</sub> molecular orbital diagram.

And then we can consider a system that might have three orbitals populated like this.

And then, if we have a system with four orbitals, it might be something like that, four electrons and so on. We see that one of the features is that the energy levels are starting to come closer together as we get more and more of them.

There are five. Here is six.

And then onto seven. And you start running out of room to draw them. And so what people do then with this problem, we are only up to seven and we have almost run out of space to draw these things.

So what do we do? We draw them, when we get out to infinity here, as a band.

What the idea is, is that we have here this band diagram, as we are going to call them, a type of diagram in which we are representing field orbitals down here as some kind of continuum.

Because there are so many of them, an infinite number of orbitals that are all interacting in some extended solid material, we are going to be talking today a little bit about silicon and germanium and things like gallium nitride in which you have a lattice that extends periodically in three-dimensions.

And so these molecular orbitals spread out and cover the whole material.

Electrons can be anywhere at once within this entire extended solid by virtue of these delocalized orbitals. And then, just like in molecules, there are empty orbitals.

And they occur also in a continuum.

I would like you to get your mind around going from both ends to the same place in that type of continuum. And the idea that these band structure diagrams that people use to describe the electronic structure properties of extended materials are really molecular orbital diagrams.

And so let's take a typical metal where  $N$  equals principle quantum number three.

The atom has a 1s orbital. It has a 2s and a set of 2p orbitals. It has a 3s orbital and a set of 3p.

And so there is an atom, like a sodium atom, for example. And here is our energy axis. What happens is that each of these orbitals that when you put all these atoms together into a piece of solid sodium metal, we talked about that earlier in the semester, these orbitals overlap, spread out and form bands.

And there is a band very low in energy that is derived from the 1s electrons in a metal-like sodium.

And it is completely full. And then there is a band from the 2s and there is a band, accordingly, from the 2p.

And then there will be a band from the 3s and a band from the 3p that I have run out of room to draw there. And notice that the bands that originate from atomic orbitals having the same principle quantum number here, 2s and 2p, are overlapping.

In the case of a sodium atom, this 2s band is completely full with electrons and the 2p band is completely full.

And this 3s band here, in the case of sodium, is half full. Furthermore, we are going to call these filled bands that are at the highest energy. This corresponds to our highest occupied molecular orbital.

That will be called the valance band.

And then up here the lowest unoccupied band is called the conduction band.

And so, in the case of sodium metal, this 3s band is half full.

And, if we go over to magnesium, this same 3s band is now full.

And if we go to aluminum that 3s band is full and the 3p band is partly full.

And it is a consequence of the fact that the electrons in the valance band are right here at the same energy as the lowest part of the conduction band in a metal that gives metals their luster.

It gives them their 100% optical reflectivity.

These properties that we very much associate with metals. And so from analyzing band structure diagrams, even simplified ones like the ones you will find here and in your textbook today, you can really say a lot about the properties of different materials.

When you have a meeting of the valance band and the conduction band then your material is a conductor and is metallic.

And then there are other possibilities, of course. You may have a valance band that is separated by some energy gap from the conduction band.

And if that is that is the case then you have a semi-conductor such as silicon.

And then, finally, you can have a large gap between your valance band and your conduction band.

And, in all cases, like with an MO diagram, we are putting these things on an energy axis. We are filling up electrons from the bottom in this material from the standpoint of energy, and so you have a large gap here.

And you have a material that is an insulator.

And I think you will appreciate why that is in a moment, but I want to bring Boltzmann's law to bear on the issue of electronic structure in extended networks like we are talking about today.

In materials like the ones I have drawn over here, the ability to conduct electricity is related to the probability of electrons being in the conduction band.

So we need to know something about electrons in the conduction band.

And, using a Boltzmann distribution, we can write that probability as being related to one over  $E$  to the  $\Delta E$  over  $RT$  plus one.

And, with an expression like this, this  $\Delta E$  here corresponds to our gap.

And so it is possible then to go ahead and estimate the number of electrons that would be present in a cubic centimeter of your material in the conduction band as a function of this energy gap.

And so we can consider that for materials like carbon or silicon or elemental germanium.

In the case of carbon, I am talking about diamond. And you should definitely go to that specified website and look at the diamond structure and try to get an appreciation for how the carbon atoms in diamond pack in three dimensions.

From a hybridization standpoint, all the carbons in graphite are  $sp^2$ .

Whereas, in diamond all the carbons are  $sp^3$  and tetrahedral. And completing this table --

-- we can write down  $\Delta E$  in kilojoules per mole.

The gap for diamond is 524 kilojoules per mole, for silicon 117 kilojoules per mole and for germanium 66 kilojoules per mole.

And here is the number of electrons per centimeter cubed in the material in the conduction band.

And, based on this large energy gap in the diamond structure, this value is on the order of  $10$  to the minus 27th.

Very small. This is an insulator. Diamond is an insulator.

And, on the other hand, silicon, the number of electrons per cubic centimeter that are in the conduction band are on the order of  $10$  to the 9th.

This much smaller gap in the case of silicon, despite the fact that the silicon atoms also are tetrahedrally disposed with respect to their bonding, just as in the diamond case, we have a much smaller gap,  $10$  to the 9th.

And that makes silicon, as you know, a semiconductor.

And then germanium  $10$  to the 13th, so even more. It is getting closer and closer to being metallic as the gap shrinks as we compare these materials.

And, having said that, we need to talk about the different types of materials that we can have.

I want you to understand the difference between intrinsic and extrinsic semiconductors.

If a semiconductor material is an intrinsic semiconductor that means it is a semiconductor in its pure state.

And why would we make that reference? I mean normally we are always talking about pure things.

But, actually, you will see in a moment that people do purposely make impure semiconductors for very good reasons.

And we will discuss semiconductor when pure. And what that means is you have a system like this with some kind of a small band gap, as we have suggested.

Here is our energy axis. And what can happen is that either thermally or upon absorption of light energy, we can have promotion of an electron from the valance band into the conduction band.

And so I will draw that new situation over here.

In other words, we may have thermal population of our conduction band. And we general, accordingly, a hole.

In this intrinsic semiconductor, for every electron that jumps up into the conduction band and can then provide conductivity by electron transport.

Down here, in the valance band, the missing electron generates a hole.

And that hole can move around freely in the valance band. How does it do that? Well, it is a little bit like the mechanism that we studied earlier for translocation of protons in acidic water. If an electron that is nearby the hole jumps into the hole, it creates another hole.

The hole thereby moves. And so here we can have hole transport in our valance band.

You can have conductivity occurring freely, both in the valance band and in the conduction band for an intrinsic semiconductor of this type where the number of holes is equal to the numbers of electrons.

And you might begin to suspect that for an extrinsic semiconductor the number of holes does not equal the number of electrons.

How does that work? In these extrinsic semiconductors wherein you have differing numbers of holes in electrons, you are purposely adding a small percentage of impurities to your material.

Let me draw two pictures to represent this.

Here I would like to draw just a simple tetrahedron. We are looking at a very small part of the silicon structure.

Let me put the silicons in here in color. Each silicon is coordinated to four other silicons in elemental silicon.

It is tetrahedral silicon all through this three-dimensional material in which these bands have been created and in which we have valance and conduction bands. But what if we have synthesized our silicon with a little bit of boron impurity?

If we do that then boron goes into a position in the crystal lattice that is normally occupied by silicon, so boron finds itself surrounded by four silicons, each of which wishes to donate an electron to the boron to form an electron pair bond.

But boron only has three of the needed for electrons to make those four 2-electron bonds and to generate the octet.

And so what happens is it wants to get an electron. And where can it get an electron from? It can get an electron from the valance band, from the HOMO of the system, from what would be able to donate an electron in the system.

The way this then works is as follows.

You should think about the structure of elemental silicon with a small number of boron atoms dispersed throughout that structure as creating localized negative charges that cannot move because they are localized on these borons.

And that generates for you a band structure diagram like this. You have bands, but then you have slipped in there a little orbital from the boron, a little electronic state here, an intermediate between the valance band and the conduction band.

So you have to choose your impurity correctly so that it has the right energy with respect to the valance band and the conduction band in order for the process that you want to occur.

Here is our boron-derived state here, and it needs that extra electron because it is electron deficient when you put it in there. And so an electron jumps onto the boron, we will represent that this way, in the material like that.

And this electron is fixed in position --

-- because it is associated with a negative charge that has formed on the boron. And a corresponding hole is formed down in the conduction band, and this hole transport can give rise to conductivity.

And so notice that in this type of semiconductor, and this, by the way, is a P-type semiconductor.

P for positive. You are putting in a hole on that boron, so this is a P-type of semiconductor.

This thing is stuck on the boron, and it generates a hole that is free to move in the valence band and giving rise to conductivity.

And so in this extrinsic-type of semiconductor, you are not necessarily getting any conductivity up here in the normal conduction band but down in the valence band due to the creation of the hole. And then the parallel situation to that would be where you have something that you dope into the structure that has one more electron than what is normally in the structure.

Normally you are putting in silicon atoms each of which has four valence electrons.

You put in a phosphorus atom, which isn't nearly the same size as silicon but has five valence electrons. So you have this phosphorus in here, and it is tetrahedrally coordinated to four silicons. And there is only a few percentage of phosphorous atoms doped into this silicon semiconductor.

And the phosphorus, what happens is it goes in there.

It has an extra electron. It wants to give it up so that it can have just an octet and form these four bonds to the four silicons. And when it gives up that electron, the electron goes out and that forms a positive charge that is localized and fixed on the phosphorous center in the structure.

And so we can represent that as follows.

Where we have a phosphorus state that we had chosen appropriately in energy to go ahead and give up that electron. It gives up the

electron to the lowest unoccupied orbitals in the system, which is the bottom part of your conduction band.

This electron jumps up off the phosphorus and into the conduction band. And that leaves behind a hole.

So you have a hole or a positive charge there fixed in position. And now you can have electron transport as your mechanism of conductivity up in the conduction band.

It is really, I think, quite fascinating to think about the way in which the concept of the octet rule and our understanding of bonding in tetrahedral centers can actually lead us to understand the mechanism of conductivity in solid materials that are either n-doped or p-doped.

Here it is quite clear.

And then, finally, I just want to take you through the way in which you can put the positive and negative doped materials together to create a device like a light-emitting diode.

LED materials, these are obviously great things because you can generate light with a lot more efficiency in terms of energy than you can with incandescent bulbs.

You can get them in all different colors. These are finding application in so many different ways.

One of the challenges that chemists have taken on is the discovery of light-emitting diode materials that are made of organic molecules, actually, conducting organic molecules that have properties correct for giving you very narrow emissions in the part of the spectrum that you want to have coming out of your light-emitting diode material.

So chemistry is really very strongly involved in making next-generation LED materials.

But I just want to tell you a little bit about how these things work. The idea is that you have these two types of semiconductors and you just oppose them at an interface.

Let me make the interface with blue. You have a solid chunk of material here. This will be our N-type semiconductor.

And over here they have a continuous possible two-dimensional interface here in this three-dimensional chunk of material.

And you have a P-type doped part of the system over here. And, in fact, normally this would be the same basic semiconductor material on both sides of the interface. And it would be just the doping that changes on the left versus the right.

This material might be something like gallium nitride.

Now, notice that this is a 3/5 type of material. And this is gallium in Group 13 and nitrogen in Group 15 of the Periodic Table. You add three and five together and you get eight, just the same number of valence electrons you would if you had silicon and silicon.

But these materials have the property that they are a direct band gap material.

And, as direct band gap materials, when the process that we are going to talk about here takes place at the interface then out of this interface comes the light.

And if your semiconductor material is an indirect band gap material like silicon is then that is not the case. And that has to do with the solid state physics of electronically where is the conduction band located relative to that valence band?

Has it shifted horizontally in solid physics-speak relative to the valence band? That's what makes a semiconductor an indirect band gap material.

If the conduction band is vertically situated above the valence band then you get a direct band material. And so solid state chemists are interested in designing new materials that have a direct band gap and that can release light when this process takes place at the interface.

And on both sides I just want to sketch the band structure for the materials.

And I mean the gap, actually, to be the same on both sides here. And the difference is what we have doped it with. In the case of the negative material, we have an electron up here in the conduction band that came in with, for example, our phosphorus atom and left behind a hole there that is fixed in space.

And down here we have our valance band all full.

Over here similar, except our material starts out with a hole down there because the electron has jumped up onto the doped atom and become fixed in space as a negative charge. And that left behind a hole in the valance band down there like that.

What you have is your n-doped material here on the left, your p-doped material on the right.

And, of course, what do you do then? You attach leads so that you can connect it to a potential difference. And, when you do that, you want your anode to be over here so that the electrons can flow that way up to the n part of the device.

And then electrons can flow this way, which means, of course, that holes go that way.

And here is your cathode. And so you can think of putting on your potential difference in a system like this. And that has the effect of ripping electrons out over here.

And, if you rip an electron out, let's say you take that negative charge back off of that boron atom, you pull an electron out to go ahead and reduce something down here in solution, if you are using a battery for this sort of process, well, then another electron can jump up here to take its place.

But you are building up a potential here. And so what happens? The highest lying electron in the system over here in the N-type semiconductor is sitting there right at the junction right next to where electrons are needed.

It jumps across.

Electrons flow downhill here. And you can look at it like this, electrons flow down here across the interface. And when you hook this LED up to your potential difference supply, the electron flow is unidirectional.

As the electrons jump across the interface, they are going from the conduction band of the N-type semiconductor, they are going down in here, holes are being created, maybe electrons are being pulled right

off of that boron and they are moving right across here in a process that leads to the emission of light right at the interface.

It is like a waterfall of electrons taking place all along this 2d interface.

Electrons are just moving across this interface and dropping down in energy. As they drop down in energy, a photon that is the energy of this energy difference between the gap of this material, those photons are released for each electron that transits this barrier.

And that is the principle of an LED.

And I hope you are enjoying seeing this connection between molecular orbital theory for molecules being taken all the way to solid state physics. Have a nice weekend and we will see you on Monday.