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PROFESSOR: All right, so we're going to try to finish up oxidation reduction today. The next unit we're heading into is transition metals. So, in the last class we were talking about delta e knots of cells, so the standard potential of a particular electric chemical cell. And as we ended class last time, you had a clicker question, which you told me what the reaction was at the anode and the reaction at the cathode for this particular electric chemical cell.

So, now we're going to consider, we're going to calculate what this delta e nought is for this cell. So we have an equation that we can use to calculate delta e nought of a cell, and that is that the delta e or the potential of the cell, is equal to the standard reduction potential for the reaction that's occurring at the cathode, minus the standard reduction potential for the reaction that's occurring at the anode. So you told me which reaction was occurring at the anode and which at the cathode last time. So we can just go ahead and use that information in here. So the reaction that's occurring at the cathode is the copper reaction, and the reaction and the anode is the zinc reaction, and note here, I have these written as reduction potentials, because we're going to be plugging in the standard reduction potential into this equation.

So, where do we get our standard reduction potentials? Well, your textbook has tables of many standard reduction potentials. And, of course, on an exam you would be given that information. And the standard reduction potentials were measured against the standard hydrogen electrode. So, now we talked last time about what some of these abbreviations mean. So we can look up the values and they're all going to be listed as reduction reactions, because they are standard reduction potentials. So all the reactions, if you're looking for ones written as oxidation, you'll be out of luck, they'll all be written as reductions.

So here, written as a reduction, zinc plus 2, two electrons to zinc solid, copper plus 2 plus two electrons to copper solid, and you can look up those standard reduction potentials. And then you can plug them in to your equation. Again, the equation is the standard reduction potential for the couple at the cathode minus the standard reduction potential for the reaction at the anode. So the reaction at the cathode is the copper reaction, and so we have -- we put in here 0 . 3 4 0 2, and then minus, and the zinc reduction potential's negative, so it's minus a minus 0 . 7 6 2 8, and then if we add that together we get a positive value of 1 . 1 0 3.

And so in doing these, this is a pretty easy thing to do, but I'm sort of emphasizing it because a lot of people out-clever themselves in doing this. They say, well, one thing's being oxidized in this reaction, one thing's being reduced, so I'm looking up a standard reduction potential, I'm going to change the sign, and then plug it in and

change the sign again. And so they change the sign so many times and they come up with the wrong answer. So just a hint in doing these problems, if you always think that the equation is asking you for the standard reduction potential, look that value up and put it in. Don't do anything fancy with signs, just use this equation as written, plugging in the standard reduction potentials, and you'll be all set and you won't have any problems getting it wrong. So try not to out-clever yourself and flip signs around many times in doing these problems.

All right, so we have a value, a positive value then for our potential for the cell. So we can ask the question, in this type of cell, would the flow of electrons be spontaneous? What tells us if something is spontaneous? ΔG tells us if something is going to be spontaneous. And we mentioned last time a connection between ΔG and ΔE_{cell} . So, ΔG tells us if something will be spontaneous, and we talked last time of this equation that ΔG for the cell is equal to minus n , n here being moles of electrons times Faraday's constant, times the ΔE_{cell} for the cell. So here again, we're relating back to thermodynamics, back to ΔG , and we're thinking about whether things are going to be spontaneous or not.

So, if we have a positive value for ΔE_{cell} of the cell, what's going to be true then for ΔG ? It'll be negative, and so will it be spontaneous? Yes. So, if ΔE_{cell} is positive, ΔG will be negative, and if ΔG is negative, the reaction will, in fact, be spontaneous. So the answer, then, is yes.

So now let me introduce some more terms to you. Galvanic cell is an electric chemical cell in which a spontaneous chemical reaction is used to generate an electric current. So on a problem, which you may have on your problem-set and have already looked at this, it'll say something about for a galvanic cell. Well, that wasn't just kind of random information they're throwing out, they're telling you that the reaction's going to be spontaneous in that cell. So that will often tell you what reaction had to be happening at the anode, and what reaction had to be happening at the cathode. Because you need to have it be spontaneous, you need a value for ΔE_{cell} , then it's positive. So, the information that it's a galvanic cell tells you a lot about the problem.

In contrast, we have electrolytic cell, and in this case, we can put in energy to provide, to be able to drive a non-spontaneous reaction. So you can generate a current to then force and non-spontaneous reaction to go. So these are 2 different kinds of cells. So again, whether something's spontaneous or not comes back to our friend ΔG . So if a cell is operating spontaneously, that means you're going to have a ΔE_{cell} of the cell that's positive, which means that the ΔG of the cell will be negative. And we can calculate these ΔE_{cell} of the cell from the standard reduction potentials, which some nice person measured for us against the standard hydrogen electrode. And so we can look up those values and then we can calculate ΔE_{cell} of a cell, we'll know something about whether it will be a spontaneous reaction or not.

So now let's think about the size and the sign of standard reduction potentials and what they tell us about a

particular reaction. So the meaning of the standard reduction potential that you can look up in your book. So first let's think about what happens or what would be true if we had a large positive ΔE° . And that's going to mean that the element is easy to reduce. So let's look at an example. At the top of your table, you're going to see this particular reduction with this particular reduction potential. So we have $F_2(g) + 2e^- \rightarrow 2F^-(aq)$. And the standard reduction potential for this is measured at plus 2.87 volts. So, as written, that's the value of the standard reduction potential. That's a large positive number, so that's going to mean that it's easy to add electrons to F_2 . The ΔG° would be favorable for that.

So then, you can tell me, does that make F_2 a good oxidizing agent or not and why? OK, let's do 10 seconds. Good. Yes, it is easy to reduce. So it's easy to add electrons, which makes it a good oxidizing agent. So let's go back to the slides.

So, a good oxidizing agent is something that oxidizes other elements and gets reduced itself. So it goes around oxidizing things, it's an agent of oxidation. So something that easy to reduce is going to be a good oxidizing agent. And something that's easy to reduce is going to have a large positive standard reduction potential.

So, one way to sort of remember this is for a particular couple. If something has a large positive ΔE° , the oxidized species, the oxidized species here is the F_2 , it's, of these two things, it's the one that's oxidized. So the oxidized species is very oxidizing. So that's one way to remember it. Large positive ΔE° , oxidized species is very oxidizing.

So, here is a list that is similar to what you would see in the back of your book, and we just talked about this couple between fluoride gas and a fluoride ion up here with this large positive standard reduction potential, and as it says up here, oxidized form is strongly oxidizing. Now, here we have positive numbers, and now we start to go to small negative numbers, and by the time we get down here, we have a large negative number for the standard reduction potential, and this is between lithium ion and lithium metal.

So, let's consider what would be true down on the other end of the table. So a large negative ΔE° means that the element is hard to reduce. So let's look at this reaction with lithium. So we have $Li^+(aq) + e^- \rightarrow Li(s)$. When you add one electron to it, you get lithium metal. And the standard reduction potential for doing that reaction is minus 3.045 volts. So, that's hard to add electrons to lithium ion -- lithium ion is very happy being lithium ion, it doesn't want that electron back, and so that would be a non-spontaneous, unfavorable reaction. So, is lithium ion a good oxidizing agent? No, it's not a good oxidizing agent, but something around here is going to be a good agent. Lithium metal is a good reducing agent.

So, lithium metal likes to reduce other things, lithium metal likes to be oxidized, lithium prefers to be lithium ion. So it's very happy to be lithium ion, so the metal form is a good reducing agent.

So, if we think about what's true at the bottom of the table, then if we have a couple of plus 1 to the solid, then if you have a large negative standard reduction potential, the reduced species is very reducing. So the reduced species here is the lithium solid, it is a good reducing agent. So, large negative reduced species is reducing. And if we go back to work table then, up here we have the big positive numbers. The oxidized form of this first couple is very oxidizing, at the bottom you have the large negative numbers, and the reduced form of that couple is very reducing.

And you're going to be asked questions, given different elements in problem-sets or on exams and saying which of these is the better oxidizing agent, which of these is the better reducing agent, and be able to compare, and you need to think about where it is, which are the bigger positive numbers, bigger negative numbers, and you can make those comparisons, and if you remember on the top, big positive, oxidized form very oxidizing, big negative, reduced form very reducing, you'll be all set to answer those questions.

And some of this should be sort of intuitive of the things that we've talked about already in this course. So we think about the periodic table for a minute, and here are some of the potentials, lithium is easy to oxidize, it's a good reducing agent. If it's lithium plus 1, then it has a noble gas configuration, it's very happy there. Whereas fluoride can get its noble gas configuration if it's f minus, so it's easy to reduce and that makes it a good oxidizing agent. So you can think about this in terms of it's sort of intuitive if you think about what you know about those elements going into this unit.

So now, let's think about calculating a standard reduction potential for this particular electric chemical cell. So we're given equations and we want to calculate a standard potential for this. So, in doing this then, we're going to use our standard reduction potentials on this table, it's a little hard to see, so I'll go back over there. So now we have to figure out if we see this equation, what's the reaction that's going on at the cathode? First tell me what's happening at the cathode -- is it an oxidation or reduction happening at the cathode? The reduction is happening at the cathode. Now look at that equation up there and tell me what is being reduced -- which element is being reduced in that equation? The iron is being reduced. So we're going to write the 1/2 reaction, that's balance, so there were two iron 3's. And on the other side there's two iron plus 2's, and how many electrons am I talking about here? two electrons. So we have the reduction reaction.

Then at the anode, the anode has an oxidation going on, and we only have one choice left of what's being oxidized. So, we have -- and again balanced. We have 2 i minus, and this is an aqueous solution going to i 2 solid plus two electrons. So we have now our two 1/2 reactions written out, and we can look at the potentials for the standard reduction potentials, which we'll need to calculate the e for the cell. So now we want to calculate e nought for the cell, and that's going to be equal to the e for the cathode reaction. And that particular couple at the

cathode, we're looking then at iron 3 plus going to iron 2 plus -- that's the reduction potential that we're going to be looking up. And then we also need another standard reduction potential, the one for the couple at the anode, and the couple at the anode that we're looking up is i_2 to i minus.

So, if you can see that up there, it's also in your handout, then we can plug in those values. So, for iron, we have plus 0.770 volts minus plus 0.535 volts. And that's going to equal 0.235 volts, which is a positive number. So what would be true about this reaction in terms of it being spontaneous or non-spontaneous? Right, so it would be spontaneous, because you have a positive value for Δe , so we'd have a negative value for Δg .

All right, so now, let's think about what the good oxidizing and reducing agents are here, and let's have a clicker question for that. So, which is the better oxidizing agent, iron plus 3 or i_2 , and which is the better reducing agent, i minus or iron plus 2? So think about that one.

All right, let's take 10 seconds. Very good. So the trick here is to, again, think about these two different potentials. Now, unlike the example we had before, we had a big positive and a big negative value, these are both positive values. But one of them is bigger than the other, and so the better oxidizing one is going to be the one of these two, these are both the oxidized form. So the one with the bigger positive number, the oxidized species will be better at oxidizing, and so that would be the iron plus 3, that's the bigger positive number. Whereas here, when we're considering which is the better reducing agent, we're looking at the two reduced species here, and here the thing with the smaller a positive number, the reduced form will be a better reducing agent, more reducing. So again, you can look at where those are in the table and the size difference between them to get the right answer. So, very good.

OK, so now, I want to consider a biological example for a minute, and I'm going to ask a question that we we'll then answer at the end of class. So in cells, things have reduction potentials. Vitamin B12 has a reduction potential. In fact, it has one of the largest negative reduction potentials of any biologically occurring molecule. And so it has to be reduced to be active in the body. So how can something with a very large negative reduction potential be reduced? That's the question. Why should you care? Well, because vitamin B12 needs to be reduced to be active. And the proper functioning of enzymes, there's only actually two that you have in humans that require B12 -- one that requires B12 and folic acid is thought to be important in preventing heart disease, birth defects, and B12 has recently been linked to mental health. In particular, a lack of B12 has been linked to dementia. So, these are all pretty significant things.

So, one thing that I think is kind of interesting here when they talk about heart disease, how many people have heard of cholesterol? How many people have heard of homocysteine? Would you be surprised to know that homocysteine is a better indicator of whether you'll have heart trouble than cholesterol? Yes. You would think that

you would have heard of the one that was a better link. Well, homocysteine is actually a better link to indicate whether you might have heart problems, but the thing is that there's not a whole lot of money to be made there, whereas there's a lot of money to be made in drugs that lower cholesterol. So you may realize, if you think about where you get your medical information, it's often from commercials where someone's trying to sell you something. And so if there isn't much money to be made, say, the treatment for a condition might be taking vitamins, which there's not a whole lot of money to be made there, you don't hear as much about it. So, it's important to consider the source of information about your health, and as scientists, you can all evaluate information about your health now.

All right, so vitamin B12 is very important, you really need vitamin B12 to be a healthy person. And most people at MIT are maybe at this stage are not that worried of heart disease. Many of you are probably not worried yet about having children with birth defects, but maybe some of you are worried about mental recognition of particular facts for exams coming up, and so you may be concerned about B12 to keep sharp mentally. So, where do you get vitamin B12 and folic acid in your diet and how is it reduced? So let's first consider where you get it in your diet. So, does anyone know where you get vitamin B12 in your diet? I heard vegetables. Anyone agree with vegetables? I didn't say if anyone liked vegetables, does anyone agree that vitamin B12 come from vegetables. It doesn't. Where does vitamin B12 come from?

So, red meat is a good source of vitamin B12, all meat is a good source the vitamin B12. Plants do not use vitamin B12 at all. So, people who are vegan are in trouble in terms of how much vitamin B12 they get, but luckily there are vitamin tablets that can help take care of this. So meat is really the best source of vitamin B12.

So, I'm always looking for good references to vitamin B12, and I saw one recently. Has anyone seen the HBO series, True Blood. One person. OK, if you watch that, you will notice that if you date a vampire, you have to make sure you get extra vitamin B12, and that Sookie, of True Blood is taking vitamin B12 tablets just to be on the safe side.

So, vitamin B12. What about folic acid? Anyone know where you get folic acid? In the fall, what happens, people say let's go outside and look at the trees or look at the pretty foliage. Any suggestion of where folic acid comes from? Oh, wait a minute. I was at a meeting once where there was a whole lecture about how Norwegian beer was the best source of folic acid, and it was, perhaps, not coincidentally reported by Norwegian scientists. They would not vouch for any other kinds, but some -- but it does come from barleys, vegetables, this kind of thing.

So, here is a secret for healthy diet. Have some of you seen the orange juice commercial that says "Drink orange juice, it's good for your heart." That's because of this, so that actually is potentially true. So you get a lot of folic acid in orange juice, and folic acid is, in fact, good for your heart. So, who would have guessed, some of the

claims are actually true.

All right, but we still have a problem, we still need to know how it's reduced in the body. And so we're going to come back to that at the end of the lecture and answer that if we get that far.

All right, so we need to do a couple more things first so everyone can finish their problem-sets, and the things we're going to do is we're going to look adding and subtracting $1/2$ cell reactions, and then get to one of my favorite things, which is the Nernst equation.

All right. So, some of you may have encountered this problem on the problem-set already. Suppose you need you know a standard reduction potential and it's not given to you in the back of the book, but other things are given to you in the back of the book. Can you calculate the thing you need from related equations? So suppose you really want to know the reduction couple for copper 2 going to copper 1. But that's not given. You find copper 2 with two electrons going to copper 0, and you find copper 0 going to copper plus 1 with one electron, and you'll realize that if you combine these equations, you'll get the desired one. So if you add these together, you have copper 2 with one electron, one electron cancels out here. The copper solids cancel out and you're left with copper plus 1.

So you add these together, and you know the potentials for these. How do you get the standard potential for the thing that you've come up with, for the sum of those? So, as someone actually asked me before class, you have to go back to free energy, and you do, but I'm going to derive an equation so that you don't have to go all the way back, but this is, in fact, how you do the problem, you think about the different free energies.

So, the new reaction, the new ΔG for that new reaction will be equal to the ΔG for the reduction minus the oxidation reaction here. But we can substitute for ΔG this minus n , Faraday's constant times our reduction potential, and put it in to this equation here. And so we have it for the new reaction, and then the 2 reactions that we're adding together.

So we have Faraday's constant in common, so that's going to cancel out. And we can also move n to the other side, because we want to solve for this new E value, this new standard reduction potential. And so that's going to be equal to the number of moles that are involved in the reaction that's the reduction times its reduction potential minus the number of moles involved in the oxidation reaction with its reduction potential, and then the number of moles for the reaction that -- this new reaction in question. So we can use, then, this equation to look for a $1/2$ cell reaction that is the sum of two other reactions.

So let's go and use that equation, then. So here we have the known values -- we know the couple for copper 2 to copper 0, we know the couple for copper 1 to copper solid, and this is what we want to know. So we can use this equation. Which of these reactions is the reduction, what value am I going to put in here? Which of these goes

into the reduction? Which of these is a reduction reaction? Yeah. And how many moles of electrons are involved? So, we put in 2 times 0.340 volts, and then over here in the oxidation, there's one electron involved, and we put in our other potential. So 1 times 0.522. And what are the number of moles of electrons for our desired, final reaction? 1. And so, then we can do the math and come up with an answer of 0.158 volts. And so now we've just come up with a new reduction potential, we've calculated a new reduction potential for this 1/2 cell reaction right here.

So, this equation will be given to you on an exam and all you need to do is know how to use it. So we've calculated now the standard reduction potential for copper 2 to copper plus 1.

So, just a little note about when you're going to use this and when you're going to use the other equation that I showed you. So, if we're talking about a whole electric chemical cell, the number of moles that are released at the anode are going to equal the number of moles taken up at the cathode and be the number of moles involved in the overall equation. So this equation is not necessary, and for a full electric chemical cell, we're going to use the equation that I gave you before for this ΔE° for the cell, so we just use this. But if it's not a whole electric chemical cell you're talking about, if you're talking about calculating a 1/2 cell potential, then you need to use this equation. Both of these equations will be given to you on sheets for the exam. This one's for an electric chemical cell, this one's for calculating a 1/2 cell potential. So again, if it's 1/2 cell potential, you want to use this equation.

OK, so now the Nernst equation. So, some of you may have encountered in your life where you go to turn something on and you discover that the battery is dead. So, an exhausted battery is a sign that your chemical reaction has reached equilibrium. At equilibrium, you're going to have a zero difference potential across your electrodes, and the battery will be not useful to you at that point. So, if you -- instead of getting annoyed next time you have a dead battery, you can think about all, ah, it's finally reached equilibrium.

So, we need to think about, then, to think about how these cell reactions are happening, how the potential is going to change with the composition of the ingredients in those electrochemical cells. So, we know something about equilibrium and components of reactions again. So this is a nice lecture to give coming up with a week before the exam, because now we're going back and reviewing the first material on the exam from chemical equilibrium.

So, we know that ΔG is going to change as the components change until equilibrium is reached. And when equilibrium is reached our ΔG is going to be equal to zero. Before equilibrium is reached, ΔG will depend on the ΔG° for the equation, RT and the natural log of q , where q is what? What's q ? The reaction quotient. So we saw this before and we're back to using it again.

So what do we know about the relationship between ΔG° and ΔE° ? We know that ΔG° is equal to minus n , moles of electrons times Faraday's constant times ΔE° . So, we can combine some

things around. So we can take our equation that we saw in chemical equilibrium and substitute in values that are related to standard reduction potentials. So we can put in, for this ΔG , minus n Faraday's constant times the ΔE . And for ΔG° , we put in the same thing but now we have ΔE° . And we have $R T$, gas constant times temperature times the natural log of Q , our reaction quotient. Now we can divide both sides by n and Faraday's constant and we come up with the Nernst equation. So the Nernst equation tells us the potential for a cell at any given time, at any given component of ingredients in the cell, any amounts of, say, your zinc plus 2, compared to the standard potential for that cell, which you're going to calculate from your standard reduction potentials in the table, and then you have this term, gas constant times temperature, number of moles of electrons involved, Faraday's constant, and you need to know Q , the particular composition of the cell at that given time.

So, just a hint in doing Nernst equation problems, if you're given a problem and it's giving you concentrations of things at a particular time, that should be a clue that the Nernst equation is going to be what you're going to want to use here.

So, let's look at an example. Say we have a -- we want to calculate the cell potential at a given time at 25 degrees, and we know our zinc plus 2 ions are 0.10 molar and copper 2 ions are 0.0010 molar, and this is the equation for that cell. So we can look up, again, our values in the table, and the first thing we're going to do, if we're going to use the Nernst equation, is to calculate the standard potential for that particular cell, and here are the values from the table, and why don't you go ahead and calculate that for me.

All right, so let's just take 10 more seconds on that. OK, so let's see if we can get into the 90's pretty soon, because we should be able to do that for this particular one. All right, let's go back to the presentation here.

So it was actually, this was pretty easy. I didn't actually mean for these two things to show up, to help you out of what the reaction at the cathode and the anode was, so that was an easier question than I had intended. So, first you need to think about if you're given an equation here, what's happening at the cathode, what's happening at the anode. As it's written, you can look and see so copper plus 2 is going to copper solid, zinc solid's going to zinc plus 2, so you can think about which is the cathode reaction, which is the anode, which has a reduction, which has an oxidation going on, and then once you know which couples you're talking about, then you can plug in your values. So, at the cathode, we're going from copper plus 2 to copper solid. We put in our standard reduction potential, using the equation we have a minus, and then the standard reduction potential at the anode, so we have the oxidation from zinc solid to zinc plus 2, and we put in this value and we calculate the number here.

So then, we have that, we also need to know Q . So why don't you tell me what Q is now? OK, let's just do 10 more seconds on this. OK. So here, if we go back, Q is going to be equal to products over reactants, except things that are solids are not changing during the equilibrium so we leave those out. So it's going to be concentration

of zinc plus 2 over the concentration of copper, which gives you a value of 1.0×10^{-2} . So, just a review of q , if you need help calculating q 's, we're going to have to extra problems for the exam coming up to be posted on Friday. So, this'll be used in several units. So then you need to know n , and then we have everything to go back to the Nernst equation. So how many moles of electrons are involved in this? 2. Sometimes it's not so obvious, so this can trick people, so make sure that you pay attention to this. This one is a pretty obvious one. All right, now we have everything that we can put in. You calculated the standard potential for the cell, you calculated q , and you told me how many moles of electrons there are. So we can go and put this in. So we calculated positive 1.03 volts minus the gas constant times the temperature, it was at room temperature, natural log of q . We had two moles of electrons and Faraday's constant here. And now if we do the math, this whole term comes out to 0.0592 volts, and we get our answer, which is a positive number there.

So, just a note about units and constants. Where did volts come from here? Well, the moles canceled out, and the kelvin canceled out, and we are left with joules per Coulomb, and conveniently for us, joules per Coulomb is a volt. So, all our units add up here.

And just a note about a significant figures in doing these problems, the Nernst equation, boy, significant figure fun. If you want to make sure you know significant figures, here you go. Significant figure rules for logs, we have significant figure rules for multiplication and division, and then significant figure rules for subtraction. So, one equation gives you every type of significant figure rule. So, that can be a lot of fun as well.

All right, but I'm going to try to make it easier for you on an exam and avoid some math mistakes. All the problems I'm going to give you are at room temperature. And so, the gas constant is a constant, temperature for these problems is going to be a constant, always room temperature, Faraday's constant is a constant. So, all of these, I'm going to give you the value that they all add up to, and if you use log instead of natural log, there's this value as well. So, these will be given to you on an exam, so you'll see these equations on the exam as well and you can use them. So, this is for natural log, this is for log, so we are not going to test your ability to multiply room temperature times the gas constant divided by Faraday's constant. So that's going to make it a little easier in doing these problems.

All right, so what about at equilibrium. What does q equal at equilibrium? So, q equals K at equilibrium. What does ΔG equal at equilibrium? Zero. And so that means that we knew before, from this equation, when this is equal to zero, then $\Delta G^\circ = -RT \ln K$, so q equals K at equilibrium. And so we had this equation that we used before. We now have this equation, so here it related ΔG° to the equilibrium constant, here we relate ΔG° to ΔE° . And so, I think you can see what's coming. We are going to relate these two together and come up with an expression where you can calculate equilibrium constants from standard reduction potentials. So, you may be asked to do this as well. So everything in these units are, in

fact, related to each other.

And the only thing we have left today, the answer to this question about how B12 is reduced in the body. So, you're just going to have to wait to find out, don't worry you won't get heart disease between now and Friday, and I'll let you know how it all works out on Friday.