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**CATHERINE
DRENNAN:**

Cell potential-- cell potential ΔE_{cell} , and we're going to relate this back to ΔG . So as we saw with these cells, you have this flow of electrons through the circuit. They're generated at the anode from the oxidation reaction, and they go over to the cathode. And when your cell is running, it'll generate a potential difference, this ΔE_{cell} , between those two electrodes in the cell.

So ΔE_{cell} has a lot of different names. It's called cell potential, cell voltage, electron motive force, EMF. All of these names are valid, can be used. I'm going to try to call it cell potential. Hopefully, I'm not going to switch up. But if you see any of these, it's talking about the same thing.

So overall, then, if we know this cell potential, we can relate this back to ΔG . And so that will then be able to tell us whether the reaction is spontaneous or not. So the overall free energy, Gibbs free energy, of the cell is related to the cell potential by the following equation.

So ΔG for the cell minus n , the number of moles of electrons that pass through the system, Faraday's constant and that cell potential. So we can think about this at a particular time. We can also think about this equation in the standard states. So let's just think again about standard states so we can talk about ΔG° for the cell and ΔE° for the cell-- so ΔE° , the cell potential, cell voltage, EMF for the cell, in which the products and the reactants are in their standard state. And the unit here is volts. So we have a new unit that we haven't used before, I think-- volts.

So let's look at an example of how we would then calculate our ΔE° for a cell. And we'll do the cell we've been using this whole time, our cell with zinc at anode and copper at the cathode. And so we have our anode reaction. And again, this is our oxidation, anox. And our cathode reaction, cathred.

So we can write it out as the reduction reaction happening at the cathode. And the equation we're going to use for this is the following. So ΔE° of the cell, the cell potential, equals E° ,

and E here is the standard reduction potential-- and this is the standard reduction potential for the couple, the reaction, that's happening at the cathode-- minus the standard reduction potential for the reaction that's happening at the anode.

So now we can look those values in the back of the book. So we have for zinc the standard reduction potential, minus 0.7629, and the standard reduction potential for the copper, plus 2 two electrons to copper solid reaction, plus 0.3402 volts. So now clicker question, why don't you calculate for me what the cell potential is for this type of cell. So 10 more seconds.

81%, that's right. So let's take a look at that over here. So the correct answer involves putting the standard reduction potential for the reaction at the cathode with the sign, without changing it as plus over here, 0.3402, and then it's minus. And then you put the standard reduction potential in there, and this is a minus value minus, 0.7628. And minus a minus we get a plus, and so our answer is 1.103 volts. And this is very important, and it's important to think about the reaction at the cathode, which is the copper reaction.

The reaction at the anode is the zinc reaction. And a lot of people who try to be too clever with these. And they're like, OK, but this one's the one that's being oxidized, so I'll switch the sign and then put it in the equation and end up getting it wrong. So if you always remember standard reduction potential put here-- standard reduction potential put here-- the equation already takes care of the sign issue for you, so don't do anything with the sign.

Other people say, I looked through pages and pages of these potentials in the book, and the reaction I'm looking for isn't listed, because they're looking for an oxidation. They're not going to find the reaction written as an oxidation in a table of reduction potentials. So all of these are listed as reduction potentials. That's what you will find.

The trick is to remember which is happening at the cathode, which is happening at the anode, and then you will always get this problem right. And it's good to get this right, because as you will see later on, this can be step one in a multi-part problem. So when we successfully calculated ΔE of the cell, the cell potential, then we can ask, is the flow of electrons going to be spontaneous for this? Will it?

It will be. And the way we know that is that we can always come back to ΔG . So whenever you're asked if something is spontaneous or not, you always want to think ΔG . That's what I'm going to go for. I'm going to think about ΔG .

So here ΔG equals minus n , number of moles of electrons, Faraday's constant, times that cell potential. So if the cell potential is positive, ΔG will be negative. And is a reaction spontaneous when ΔG is negative?

It's easy to answer. It's on my shirt today. I'm giving it all the way-- yes. So when ΔG is negative, then you can be feeling spontaneous. It's a spontaneous reaction. So ΔE positive means ΔG negative. Reaction is spontaneous.

So now let's have a little reminder, review, of what types of cells have spontaneous reactions and what kind involve non-spontaneous reaction. 10 more seconds. Can anyone tell me what the correct name is of the cell that involves a non-spontaneous reaction? Electrolytic cell.

So if we look over here-- so people knew about the galvanic. That's good. So a reaction, if it's a spontaneous reaction that will produce an electric current, that's called a galvanic cell. If it's a non-spontaneous reaction that has to be driven by applying a current, that's called an electrolytic cell. So I just threw up another random name to see if people would go for it.

So it's important to keep these in mind, because a lot of the problems will say things like, in this galvanic cell. And you seem like you don't have enough information to solve the problem because the problem didn't tell you which reaction was at the anode or which reaction was that the cathode. So how do you do the problem?

Well, the fact they told you it was a galvanic cell, there's only one way to put the reactions in order for it to be spontaneous. So that's part of the problem-- figuring out which is at the anode and which is at the cathode based on the fact that it has to be a spontaneous reaction. So knowing these terms is really important. It's hard to do the problems without them.

Summary of this part, then, so a cell operate spontaneously. Whether it does or not can be determined by your cell potential. If it's positive, it's spontaneous. And that's because if it's positive, ΔG is negative. And ΔG is really what tells you about spontaneity. And you can calculate your cell potential from your standard reduction potentials that you will find in your book.

So now let's think about the meaning of the standard reduction potential. What's true if it's a large positive value? What's true if it is a large negative value? We can look at these values and know something about the reactions. So meaning of standard reduction potentials-- what do the values tell us?

So a large positive standard reduction potential means that the element is easy to reduce. So let's look at an example. So we have fluorine F_2 gas plus two electrons going to 2 fluorine minus ions. And this has a standard reduction potential of plus 2.87 volts.

So large positive number means that it's easy to add electrons. And we can think about this in terms of what we know about these reactions. So again, if it's a positive standard reduction potential, E^0 , that's going to mean a negative ΔG for this reaction as written, written as the reduction reaction. And so it's favorable or spontaneous in that direction.

So the reduction is spontaneous or favorable. So when you have a large positive value here, you can think about, yes, fluorine wants those electrons. It spontaneously will grab those electrons and become F-minus. And this also makes sense to you if you think about your periodic table trends.

You have fluorine wants to be F-minus. It will have its noble gas configuration then. It likes getting an extra electron. So this should make sense from other things that we've talked about. So now I could ask the question, and I will, and it's a clicker question, does that make F_2 a good oxidizing agent or not? 10 more seconds.

So the answer is yes. F_2 is easy to reduce, which makes it a good oxidizing agent. Remember, it's an agent of oxidation. It wants to go out there and oxidize other things. It wants to itself be reduced.

So something that's a good oxidizing agent is easy to reduce. It wants to be reduced. It wants to be an agent of oxidation, bringing oxidation to the world. So it's easy to reduce. It's a good oxidizing agent.

So in general, you can think about this the following way. Let's just like bring the noise down a little bit. I know it's a clicker competition day.

So we have a large positive value here for a reaction. For a reduction reaction is written large positive standard reduction potential. And the couple here, F_2 to F-minus is the couple we're talking about. And we'll say that the oxidized species of that couple is very oxidizing. And again, F_2 here is the oxidized species. So the oxidized species F_2 is a good oxidizing agent. It's very oxidizing because it has a large positive standard reduction potential.

So I don't know how well this copied. But here are some standard reduction potentials. They're

all in your book, so it's OK if they look terrible. But the important point here is that the top.

We have large positive values. So if you can see that in your handout, this is the reaction we just talked about, or the couple we just talked about-- F_2/F^- and so large positive. And then there's a gap here. There are pages and pages and pages of these standard reduction potentials. And at the very bottom, you have a large negative number, so large positive on the top large, negative on the bottom.

So at the very top, the oxidized species of that couple is very oxidizing. And we'll see it in a minute, that at the bottom the reduced species, when it's a negative number here, the reduced species is very reducing. So let's look at the reduced species, and this is lithium on the bottom.

So a large negative standard reduction potential means that the element is hard to reduce. So example, lithium plus 1 plus 1 electron going to lithium solid. The standard reduction potential for this reaction is minus 3.045 volts. So it's hard to add electrons to lithium-plus.

We have a negative standard reduction potential, which means a positive delta G for the reaction is written for the reduction reaction. So it's not favorable. Lithium-plus does not want electrons. It doesn't want to go to lithium solid.

So lithium-plus, if it loses an electron, it gets its nice noble gas configuration. It's a group-one element. It likes to be in the plus-1 oxidation state. It doesn't want to be reduced. So is lithium plus 1 a good oxidizing agent? No, it's not. It does not want to be reduced.

But lithium solid is a good reducing agent. It's a good reducing agent because it wants to reduce other things. It wants to itself become oxidized. So lithium solid will reduce other things. Lithium solid wants to be oxidized. It wants to be lithium plus 1.

So the rule here for those large, negative standard reduction potential couples is that with a large negative standard reduction potential, the reduced species is very reducing. The reduced species here is lithium. So lithium is reduced compared to lithium plus 1. This, then, is very reducing. It is a good reducing agent.

Do you think lithium plus 1 would be a good reducing agent? What do you think? So if it was a good reducing agent, it wants to reduce other things and become oxidized. Do you think lithium plus 2 is a good thing? No.

So again, in this couple, it's the reduced species that's very reducing. And so you have to think

about this a little bit. Make sure that you pick the right one. Often you'll ask about rank the order of these as reducing agents. And people remember this, but don't remember which species of the couple is going to be doing the thing.

So think about what's happening. Lithium solid, does it want to become lithium plus 1? It sure does. Does lithium plus 1 want to become lithium plus 2? No. So again, back to just our table just for a second, on the top-- large positive, oxidized species very oxidizing, negative value, reduced species very reducing. And now if we look at this, I don't know how well this came out in your handout either, but part of the periodic table for you kind of compressed.

Over here we have fluorine, large positive, standard reduction potential, easy to reduce over here, good oxidizing agents. If they get an electron, if they're reduced, they get their noble gas configuration. Over here, we have these big negative numbers, easy to oxidize the solid or the neutral to their plus 1. So they would be good reducing agents. And so this all makes sense when you think about trends in the periodic table.

So today we're going to have two examples of why all of this is important across disciplines. So often these units are really talked-- you talk about making batteries and things like that. And that is important. In fact, with energy initiatives, making batteries is a really hot area right now.

But all these things you're learning are also related to biology and to medicine as well. And so we have one more of the "In Their Own Words" segment. And John Essigmann studies DNA damage as related to cancer. And people are like, what is DNA damage and cancer have to do with oxidation reduction potentials? But it's not all about oxidation reduction. That's what a lot of the damage is.

So why don't you hear from John Essigmann.

[VIDEO PLAYBACK]

- My name's John Essigmann. I'm in the Department of Chemistry and Biological Engineering MIT. I'm a toxicologist by training, so I study how cells respond to toxins, and in particular, the kinds of toxins that cause nucleic acid damage.

Some of these are chemicals from out in the environment, organic compounds, that cause DNA damage. But I'm also interested in how chemicals inside our body, for example, reactive forms of oxygen, the molecule that we breathe, also cause nucleic acid damage. Oxidation is the process by which we convert our metabolic fuels into energy.

This is a gummy bear being oxidized by potassium chlorate. This is exactly the kind of chemical reaction that goes on in your bodies. But in your body, it goes on at a much lower rate.

Oxygen is a double-edged sword. There are two aspects to its use that is good for us. The first one is by acting as an electron acceptor, sort of like an anode in a battery, it completes the circuit and allows us to be able to generate free energy that we can use to power vital processes. That's good.

The second good thing is that it's the ammunition of our innate immune system.

[COUGHING]

Oxygen is used to charge the system to produce one, two, or three electron-reduced species that themselves can react with reactive nitrogen species to create a host of very damaging oxidants. Our innate immune system uses these to protect us against invaders and oftentimes, we believe, developing cancer cells.

The bad thing is that the second system I described doesn't have a lot of accuracy in how it focuses that chemical warfare. So not only are the, let's say, invading bacterial cells or the cancer cells hit, but surrounding cells as well. And that creates oxidative damage in the genomes of those cells, those innocent bystanders.

If those cells divide, the oxidative damage that's in them can cause mutations, and that sets the cell along a path. If you accumulate enough mutations in enough genes, you're going to convert that normal cell into a cancer cell that will grow out into a tumor.

[END PLAYBACK]

**CATHERINE
DRENNAN:**

So that was one of, I think, the only video, besides mine, that involved a faculty member. But I thought it's nice to have a sort of a collection of different folks talking about their research. And this relates to free radical species as well as to oxidation and reduction.

So now I have another bio example, which hopefully we'll get to at the end. But I want to introduce a very important equation for this unit and oxidation reduction, which is the Nernst equation. So here, and this happens, I think, to all of us all the time-- our exhausted batteries.

So when you have a battery or you go to turn on your headphones or use your laser pointer or

things like that and the battery doesn't work anymore, it's because the cell reaction has reached equilibrium. So equilibrium is a state of calmness. It's also a state of batteries not working anymore. And so at this point, when it's at equilibrium, the cell generates zero potential across its electrodes. It's not working anymore.

It is a dead battery. And we need to think about when it reaches equilibrium, what state it's in at any given time compared to its equilibrium state. So this really brings us back to some of the ideas that we had in the chemical equilibrium unit, where we were thinking about composition of a reaction at any given time compared to the equilibrium state.

So how does cell potential change with cell composition? So again, we know a lot about this. And exam three on Friday has equilibrium on it. So we already know a lot about what happens in relationships between equilibrium. And we know that ΔG changes as the composition changes in the cell. And until equilibrium is reached-- so again, reactions going forward and back in equilibrium-- the forward direction equals the reverse direction. But at some given time that is not always the case.

So the equation that we know from before is that ΔG equals ΔG^0 plus $RT \ln Q$. And so if you know ΔG and Q , you can talk about what the ΔG is going to be at a particular composition of the cell with a particular value of Q . So now we can think, well, OK, here's what we know about Q , that reaction quotient, and ΔG .

What do we know about ΔG and E , the cell potential? And we just talked about that. So we know that ΔG^0 equals minus n , the number of moles of electrons, Faraday's constant times that cell potential.

So now we can do a rearrangement of terms. We can combine and come up with the Nernst equation. So here are the two equations. One we knew before. One we just learned about today. And we can put those together. We can plug in for ΔG here without the 0, and for ΔG^0 with the 0 over here. And then we can divide both sides by minus the number of moles of electrons and Faraday's constant, come up with the Nernst equation.

So the Nernst equation compares our cell potential under standard conditions with our cell potential at any given time based on that reaction quotient Q . So let's do an example with the Nernst equation. So let's calculate the cell potential at a particular time when the zinc plus 2 ions are 0.1 and copper plus 2 is 0.0010 molar. And we're same cell as we've done before.

So step one, very easy, we want to calculate the cell potential under standard conditions. And this is particularly easy because we already did this today. So you already told me it's plus 1.103 volts. So we could look up our standard reduction potentials for our copper couple and our zinc couple and calculate this.

So we already did this, and that's why I said you want to make sure you get this right because it's often just step one of a multi-part problem. So we want to get that right. Step two is calculating Q, and this is a clicker question. 10 more seconds.

I tried to make the math not that hard. So Q, products over reactants, so one thing you want to do is make sure you have the reaction written correctly. So you know what the products are and what the reactants are. And here we have the zinc ions over copper.

Copper solid and zinc solid don't appear in the equilibrium expression or in the Q expression also because they're solids and their concentration is not changing. So there is enough information that was given because we don't include the solids. So it's just the concentration of zinc ions over the concentration of copper ions, or 1.0×10^{-2} .

Now we need to know n. So n is the number of moles of electrons that are involved in this reaction. This reaction involves how many electrons? How many? It involves two, right. So the zinc to zinc plus 2, copper plus 2 to copper, so it involves two electrons. So this is two, and sometimes you can just look at this and realize it's two electrons involved.

Other times you have to balance the reaction to figure out how many electrons are involved. It's not obvious by looking at the reaction. This is a simple one, but some of them are not. So that's we're balancing reactions comes in handy. so

Now we have everything we need to plug it into the Nernst equation. So we can put it in. We calculated this standard cell potential over here, the plus 1.1 value. We can look up R. Everything, again, room temperature. Natural log of Q, we calculated Q. We have two electrons and Faraday's constant. And we can multiply this out, get this value.

In terms of significant figures, this also is a lot of fun. We have log rules of significant figures, multiplication and division rules of significant figures, and adding and subtracting rules of significant figures, and also in terms of units. All of a sudden, volts appeared. That was nice because our answer should be in volts. But where did they come from?

So we had our kelvins are going to cancel out. But we have joules over here. And we have coulombs. But luckily, a joule per coulomb equals a volt. So we're all set to get our appropriate units.

So just a couple of things that I'll mention about this as well-- since almost all these problems are at room temperature, I try to make your lives a little bit easier on the exam and multiply this out for you, because these are all constants, and they're big constants that involve plugging a lot of numbers in. So I will give you this combined value. And if you use log instead of natural log, you need to change that value here. And so what I actually put on equation sheets are these equations.

I'll also put the full equation there as well but just to make your lives a little bit easier. It's horrible to make mistakes up there. So just briefly, what about at equilibrium, what does Q equal? Q equals K. Delta G equals 0. And so we can rewrite this expression again, which we've done before. And if we take this and look at this expression now, we can again combine these-- we have two expressions for delta G0-- and combine them and solve. And you can see that you can also calculate K from standard reduction potentials.

So all the things that we have been learning here, we can always come back to chemical equilibrium. So I'm done with everything but my second bio example. So you'll have to wait until next week to find out how vitamin B12 gets reduced in the body.

Let's just take 10 more seconds on the clicker question.

Does someone want a nice T-shirt to tell me how they got the right answer? Pass this back.

AUDIENCE: So when you're looking at the Pb--

CATHERINE DRENNAN: Let's all quiet down.

DRENNAN:

AUDIENCE: [INAUDIBLE] and zinc, zinc is going to reduce--

CATHERINE DRENNAN: Let's quiet down.

DRENNAN:

AUDIENCE: --Pb because it goes from a 2 plus charge to no charge at all. So that's reducing its charge. And then in the reverse reaction, Pb does the same thing to zinc 2 plus and takes it from 2

plus to a neutral charge.

**CATHERINE
DRENNAN:**

Yep, great. So the trick to this is just look at the equations and figure out what is being oxidized and what is being reduced in both directions. Oxidation reduction, it's not just about batteries. Batteries, of course, are very important.

There's a lot of active research right now in trying to make better batteries that are more environmentally friendly, just solving the energy problem every single possible way. But even if you're not interested in solving the energy problem, oxidation reduction is really important in medicine. So I'm just going to give you another bio example for this.

So there's a vitamin in your body, vitamin B12 It has one of the largest negative reduction potentials of any biological molecule. So we ask the question, how can something like that be reduced in the body?

So let me introduce you to vitamin B12. You're going to see this a couple of times today. So vitamin B12 needs to be reduced to be active. But it has a low reduction potential.

This is the vitamin B12, and you'll see several more views of it, and it's in pictures in your handout of today's lecture. There's an enzyme that requires vitamin B12 and another B vitamin called folic acid. And if this enzyme is not functioning properly in your body, it leads to all sorts of things.

It's connected to heart disease. If women don't have enough folic acid while they're pregnant, it can lead to birth defects, neural tube disease, where the brain doesn't form properly. Also, there is rising evidence connecting a vitamin B12 deficiency with bringing on Alzheimer's disease. And some people actually buy little B12 squirt bottles and squirt it into their nose before exams. I'm not sure that helps. But as you get older, I would seriously consider taking extra vitamin B12.

So since we're talking about this, we'll have a little nutrition quiz. Where do you get vitamin B12 and folic acid in your diet? First let's think about vitamin B12. Does anyone know where you get this, besides vitamin pills, in food? Where do you get vitamin B12 in food, yeah?

AUDIENCE:

Broccoli?

CATHERINE Broccoli, no. We had a hand up there. Anyone else? Yeah.

DRENNAN:

AUDIENCE: Meat?

CATHERINE Meat, yes-- red meat, actually any kind of meat. But hardly ever is red meat the answer to a
DRENNAN: nutritional question. So I thought I'd put it up there in big bold red letters. Yeah, you get B12 in meat.

Plants don't use vitamin B12. So you can eat as many plants as you want. Unless they're covered with bacteria that do use B12, you will not get any in your diet. So if you're vegetarian, you should take a vitamin tablet. You don't need much, so it's not really your problem. But it does come from red meat.

What about folic acid? Any guesses where folic acid comes from? Yeah.

AUDIENCE: Broccoli?

CATHERINE Yes. Very good. So it's the fall in New England, and hopefully some of you have gone out and
DRENNAN: seen the foliage. So folic acid does come from green leafy things. And if you're Norwegian, you will also say the following.

So Norwegian scientists claim that the great longevity of Norwegians has to do with the fact that their beer is rich in folic acid. And somehow they even got a grant from the Norwegian government to study the correlation between beer and health. Everyone signed up for that study, I'm sure.

So red meat and beer for good health. But yes, leafy green vegetables, yes, folic acid, foliage, also orange juice is really high. And at one point, they had this commercial for orange juice. It's not just for breakfast anymore. It's good for your heart. Well, that was because of the folic acid in there. And that's actually true.

So there was a commercial that actually provided you with valuable nutritional advice. Not so sure about the beer, but I'd go buy the leafy greens and the orange juice. So you need both of these to be healthy.

But again, we have this problem that vitamin B12 has this low negative redox potential. So how is it reduced? Well, in the body it's reduced by a protein called flavodoxin, which has a flavon,

which is another B vitamin. So there's lots of B vitamins going on here.

So the standard reduction potential for vitamin B12 is minus 0.526. That's a really low number for biology. And for flavodoxin, it's minus 0.23. So we ask, which is the better reducing agent? And that's the clicker question. Let's just do 10 more seconds.

Yep. So the better reducing agent wants to reduce other things and get oxidized itself. So vitamin B12, with its low negative potential, is very reducing. It wants to reduce other things. It wants to be an agent of reduction.

But that's not what's supposed to happen. It's not supposed to reduce flavodoxin. It's supposed to happen the other way around. So we could ask, is the reduction, then, of vitamin B12 by flavodoxin spontaneous if this is the case, yes or no? No. It shouldn't be spontaneous. It's not going the way that it should go.

So we can just calculate how exactly non-spontaneous it is. So we can calculate both what the change in potential is, and we can also calculate ΔG^0 from this. So we saw how to do this before. But we were talking about different kinds of galvanic or electrolytic cells.

But now we can use the same equation that we saw before but talk about it in terms of a biological system. So before we saw to calculate E^0 of the cell, the cell potential, we had the standard reduction potential for the couple at the anode minus the standard reduction potential for a couple at the cathode.

We can do the same thing here but just put reduction and oxidation over here. So we can make this a generic equation. And we can plug our values in. So the thing being reduced is vitamin B12.

So we want to put the reduction potential of B12 in there. And the thing being oxidized is the flavodoxin. And so minus 0.526 for the B12. Standard reduction potential would be 12 minus the standard reduction potential of flavodoxin. And we get a negative number, minus 0.0296 volts.

So then we have a negative value, which should tell us that ΔG is going to be positive. But we can also calculate that value from the equation you saw before. So just because we are talking about these equations in terms of cells before, we can also talk about it's same exact equation that we use in biology.

So minus n , number of moles of electrons-- this is a one-electron process. I would have had to tell you that. You wouldn't necessarily have known it's one electron. But that's our one.

What is this term here, this kind of weird-looking F term? What is that again? Faraday's constant. Then we plug in our cell potential or potential difference. And we get out a value positive 28.6 kilojoules per mole-- big positive number. So is this spontaneous? Why don't we all have heart disease?

It is not a spontaneous reaction. So how is it driven forward? This happens in our body. This reaction happens. So clearly something has to happen to make it spontaneous.

So when we were talking about the different kinds of cells, we had electrolytic cell, where we could put in a current to drive a non-spontaneous reaction. Same thing happens in biology, and the current in this particular case is a molecule known as adenosylmethionine.

So it's the methionine amino acid within a denosyl group attached to it. And the cleavage of this molecule is very spontaneous. It has a ΔG of minus 30.6 kilojoules, which is greater than what we need. And we can even calculate the net ΔG for this reaction, the coupled reaction, of the cleavage with the reduction. And if we do that, we have minus 37.6 plus 28.6, so minus 9.0 kilojoules per mole.

So we can drive this unfavorable reduction reaction with a very favorable reaction, the cleavage of adenosylmethionine. And that's how it works. So that's why we're all healthy. So this is the end of our oxidation reduction example.

We'll transition to transition metals. But we're not moving very far away from oxidation reduction. Because to do problems that are effective transition metals, you have to know how to determine oxidation numbers and all sorts of things.