[SQUEAKING]

[RUSTLING]

[CLICKING]

RAFAEL JARAMILLO: All right, so today is the last lecture of new material. We're going to talk about reactions between gases and condensed phases. So we're going to talk about that, and then, we'll make it specific to oxidation. And then, on Friday, I'll do an extended practice problem, I suppose, on reactions between gases and condensed phases.

So in general, some reaction-- I'm going to write this really generally. aA plus bB going to cC plus dD. And these are not just for ideal gases. So the last time we've seen reaction like this in 020, it's been for ideal gases reacting. And we're going to move away from that and do this more generally.

So let me just quickly remind you of how we get to the action coefficient. We have a general expression for the change in Gibbs free energy with these unconstrained internal variables, and we can re-express this in terms of the reaction extent, remembering that DNI over mu I is a constant for all I reaction extent. I don't need to have an I there. Just xe.

And reminding us that mu of I, the chemical potential of a given species is its reference chemical potential plus [INAUDIBLE] activity. So this is still completely general. We take that expression and we write d of g equals-- let's see, mu of I not mu of I plus rt log a of I to the power mu of I. And this is all times dt. And this is d G0 plus RT log product a of I mu of I. Again, whole thing times dt.

And of course, this is 0 at equilibrium, because at equilibrium, Gibbs free energy is optimized. So the coefficient is 0, and we get, at equilibrium, this product, a of I mu of I, which we call the equilibrium constant, equals e to the minus delta G0 over RT. So that's just a reminder. But this is why I wanted to take three minutes for that because we're going to make this specific to metal oxidation. That's what we're doing.

So equilibrium constant for metal. And what you're going to find is that it simplifies a lot. So that's good. Metal oxidation. As we started the last lecture, we have some metal reacting with a modal of oxygen gas going to MzO2. Remember, z here has to do with the fact that we don't know what the oxidation state of that metal is. So potassium would be 1, iron has a couple of different oxidation states.

Copper would be 1 or 2-- so there's different oxidation states. So this is to do this generally. So all right, now, we're going to write the equilibrium constant for this reaction. So we have the activity of the oxide MzO2. Sorry, the writing is getting a little bit small there.

The activity of the oxide over the activity of the metal to the power of z times is the activity of O2 gas. The products of the numerator, reactants, and the denominator. The metal is z modal of metal. So we have that activity to the power of z. And straightforward to write down.

Everyone with me so far? All right, this oxidation reaction at equilibrium. We're going to come back to that. This is the metal and oxygen and the oxide all coexisting at equilibrium.

And now come the approximations. We're going to treat O2 as-- how are we going to treat oxygen, anybody? How will we model oxygen?

AUDIENCE: Constant pressure? [INAUDIBLE] question.

RAFAEL JARAMILLO: Not constant pressure, but we have a--

AUDIENCE: It's a gas.

RAFAEL JARAMILLO: --as a-- what kind of gas?

AUDIENCE: Ideal gas. Ideal?

RAFAEL JARAMILLO: Yeah, because it's the only model for gases that we know. [INAUDIBLE] So an ideal gas-- the activity of an ideal gas is just as partial pressure by atmosphere for 1 atmosphere reference statement. Good. That's easy.

And we're going to assume that condensed phases are pure. That's big. If we assume the condensed phases are pure, that's equivalent to saying that their composition is unchanging, all right? That's saying that this metal does not dissolve any oxygen, and it's saying that this oxide is what?

What kind of a compound is always at fixed stoichiometry?

AUDIENCE: Like, perfect crystal?

RAFAEL JARAMILLO: Sorry?

AUDIENCE: The perfect crystal?

RAFAEL JARAMILLO: No, well, not perfect. No, not a perfect crystal, actually. Be something else. We learned this just two days ago.

AUDIENCE: [INAUDIBLE] ?

RAFAEL JARAMILLO: Mm, yes. It's a pure oxide, meaning that stoichiometry is ideal. It's a line compound. It doesn't deviate from that. So if we can assume the condensed phases are pure, what is the activity of a pure phase?

We've got to think back. What's the activity of a component in its reference statement?

AUDIENCE: 1?

RAFAEL JARAMILLO: Right. Thanks, that's recalling material from the middle of the semester, so it goes back a little bit, but the activity of the material in its reference date is 1. So now, I have some really handy approximations. The activity of oxygen gas. We're treating it like an ideal gas, so it's just Po2 by atmosphere.

And the activity of the metal and the activity of the oxide are both 1. So it's equivalent to assuming that there's vanishing oxygen solubility in the metal and that the oxide is a line compound. So with those approximations, we have the equilibrium constant is Po2 by atmosphere, so minus 1, and this is going to be equal to the E minus delta G0 over RT.

So you see this simplified quite a lot. Simplified quite a lot. All right, I want to share some slides on binary metal oxygen systems to convince you that they do tend to be pair of materials. So let's look here. I grabbed a couple.

OK, so here's the tin oxygen system. And you could see that an oxygen-- well, it's just a gas here. Tin down here is a metal until it becomes a liquid. In the liquid phase, it dissolves some oxygen. You can see that the liquid phase here has a solution region.

So you can dissolve oxygen in liquid tin, but what about in solid tin? I know oxygen is off. So you see solid tin will just coexist with this line compound tin oxide. So this is what we're talking about, a line compound of an oxide and a metal that doesn't dissolve any oxygen.

Here's another example, copper oxygen. Again, copper. It's written here as a parentheses as if it's a solid solution, but really, there's vanishingly small oxygen dissolution and copper. There's some. There's some, but it's so small as to be invisible on this part.

I'll tell you that when you're making a component for cryogenics or for space applications, you want oxygen-free copper. You can buy it from McMaster, and you want it, because oxygen is magnetic when it freezes, and so a lot of times you want non-magnetic copper. So you have to get oxygen-free copper, but it's there at the parts per million level.

It doesn't show up at all on the spot. So again, oxygen not dissolving in copper and these oxides being line compounds. Here's more examples. This is a little counter example. This is manganese.

Manganese actually does dissolve some oxygen. So you see it dissolves 1% or 2% of oxygen. So maybe the activity of manganese should be not quite 1. Maybe it should be 0.99. And making these oxide similarly to not quite long compounds. They have some solid solution region, so that's a counterexample.

Another example a titanium oxide oxygen system is titanium dissolves a lot of oxygen. So this is an even counter counterexample. This is a titanium, so funny system. It dissolves a lot of oxygen into solid titanium, but its oxides here are line compounds.

So what to make of it? It's good to understand where the approximations are and where they might not. Questions on these faith diagrams before I go back to the board?

AUDIENCE: Does this dissolving all owe to the molecule or just oxygen in general?

RAFAEL JARAMILLO: I'm sorry, I didn't quite-- could you repeat?

AUDIENCE: Going back to the solution, is this like dissolving oxygen as auto form or other forms of oxygen?

RAFAEL JARAMILLO: It almost certainly disassociate. So this would be dissolving oxygen atoms. Well, I mean, how do you dissolve oxygen atoms? You expose the material to oxygen gas, and there's some catalytic process by which the oxygen gas splits into oxygen atoms at the surface and the oxygen atoms diffuse into the metal.

It's almost certainly not dissolving O2 molecules. Metals that do dissolve oxygen are the basis for a lot of interesting technologies, but we won't have time for that. So let's move back to-- sorry, any other questions on these phase diagrams and interpreting them or applications and so forth before I move back?

All right, so we have this really simple expression for the equilibrium constant, and now we want to evaluate delta G0 equals delta H0 minus T delta S0 for metal oxidation. So we're going to evaluate that. So we're going to start with enthalpy.

Enthalpy delta H0 equals delta H0-- let's say 298 plus 298 temperature D-- temperature and you can have a delta Cp for the reaction. So this is general, but here's the-- and you know what's coming is an approximation. So I'm going to tell you for most metal oxides, delta H0-- let's say 298-- is large.

These are energetic reactions. Why would the enthalpy of formation of an oxide be large? Does somebody have the sense for why that should be?

I'll give you a hint. It's large negative. It's large in the negative direction. What reaction are we talking about here?

AUDIENCE: Oxidation?

RAFAEL JARAMILLO: Oxidation. So what kind of reaction is an oxidation reaction other than just-- you could say it's an oxidation reaction, but what's actually happening? Maybe somebody who hasn't replied yet today. What's happening on the atomic level during an oxidation reaction?

AUDIENCE: Does it include a favorable transfer of electrons?

RAFAEL JARAMILLO: Yeah. Yeah, this is due to-- so thank you to the two of you. Due to exothermic nature of electron transfer during metal oxygen bond formation. And I could-- I get to ionic.

So it's an ionic bond formation. You have very electronegative element, and that's oxygen, and less electronegative elements, those are metals. And that bonding mechanism is electron transfer, and it's very exothermic. So as a result, delta H's tend to be very large and negative.

And this allows us to neglect temp dependence. Neglect temp dependence. We'll just say that it's whatever it is at 298, because that's a convenient reference point. And these are tabulated. The enthalpy of oxidation reactions at standard condition, those are tabulated.

So that takes care of the enthalpy. What about the entropy? Entropy delta S is delta S at some reference temperature, 298 plus integral. OK, so who knows-- who has a guess on what we're going to do?

We're going to approximate this as what? What am I looking for? I want to justify what approximation.

AUDIENCE: Aren't entropy values usually much smaller? So if the enthalpy is already so big, we could assume entropy is 0?

RAFAEL JARAMILLO: I see. So you're right that entropy values tend to be much smaller, but the thing is they're multiplied by temperature. So they do matter quite a lot, because the temperature number can get large. So we're not we're not going to neglect it completely, but I'll tell you-- I'm sorry?

AUDIENCE: Neglecting its temperature dependence?

RAFAEL JARAMILLO: Yeah, we're going to neglect its temperature dependence. So I'm going to write this before I write this. It's just the why we get to do that. So let me write neglect the temperature dependence, and now, somebody please tell me why we might be able to do this?

And it's not just that we really like to make our lives easier. It turns out to be a really good approximation in many cases. What about this oxidation reaction?

What's the dominant entropy change? What's the dominant contribution to delta S?

AUDIENCE: Could it be when the phase change happens? So when the temperature is constant?

RAFAEL JARAMILLO: The phase change meaning from metal to metal oxide?

AUDIENCE: Yeah.

RAFAEL JARAMILLO: That's true, but maybe tell me what part of that?

AUDIENCE: [INAUDIBLE] condense it?

RAFAEL JARAMILLO: Yes, thank you. That's what I'm looking for. The reaction entropy is dominated by-- I didn't see who said that, but thank you so much. By condensation of O2 from the gas. That's it.

So here's metal. There's a chunk of metal, and then I have O2 gas. Gas is very high entropy, as you know. O2. And this reaction pulls the oxygen out of the gas and makes a metal oxide.

So the reactants have much, much higher entropy than the products, simply due to the fact that the reactants included a mode of gas and the products don't include any gas. And in almost all cases, that change dominates the reaction entropy. And since we're modeling oxygen as an ideal gas, the entropy of this gas is temperature independent. It's configuration entropy.

It's the thing we've been talking about pretty much the whole semester, which is the entropy of randomly configured gas molecules. Good. Thank you. So now we have waved our hands, although we've done it scientifically. Scientifically waving of hands has happened, and we figured out that we can neglect the temperature dependence of the enthalpy and we can neglect the temperature dependence of the entropy, and this is going to make our lives even easier than they already were.

We can solve for this thing. We can solve for that oxygen partial pressure. PO2 by atmosphere equals e the delta H0 over RT. e the minus delta S0 over R. This is the oxygen pressure at which a metal and its oxide coexist at equilibrium.

All right, so you've got a metal. They've got it's oxide, and this is the oxygen partial pressure, so there's some oxygen here. This is the oxygen partial pressure at which this kind of situation is that equilibrium.

What happens if the oxygen partial pressure is higher than the equilibrium value? What do you think happens spontaneously in this system? Think Le Chatelier's principle. I have the system in equilibrium and then I shove more oxygen gas in. I increase the oxygen partial pressure.

What do you expect to happen? How will the system respond?

AUDIENCE: Spontaneously oxidized?

RAFAEL JARAMILLO: One more time. I'm sorry, I didn't quite hear that.

AUDIENCE: Spontaneously oxidized?

RAFAEL JARAMILLO: Yes, fantastic. Metal spontaneously. So you're going to have spontaneous conversion of more metal into oxide. We've already established that the oxygen can't dissolve in the metal and the oxygen can't dissolve in the oxide. They're pure components, so all we can do is convert metal to oxide, metal to oxide, metal to oxide.

Excellent. Thank you. What about at lower? At lower oxygen pressure pressure? If we're below this value, what do we expect to happen spontaneously?

AUDIENCE: We will see the reverse reaction happening. So more O2 gas will form?

RAFAEL JARAMILLO: How does it form?

AUDIENCE: Through the oxide decomposing back into a metal and O2 gas.

RAFAEL JARAMILLO: Exactly, thank you. I'm going to use this term the oxide is reduced, but your expression of spontaneously decomposing is exactly the right thing. So if we pull down the oxygen pressure below the equilibrium value, the system will respond by converting oxide into metal and oxygen gas. And you can think of this in terms of Le Chatelier.

If I add more oxygen, the system will try to counteract that by condensing the oxygen into more oxide, so it'll take more metal, convert it into oxide by pulling some of my extra oxygen out of the atmosphere. If I pull down the oxygen pressure, the system will try to counteract that by giving off more oxygen gas from the oxide. The oxide will decompose into more oxygen gas and more metal.

That's right. So that's what happens. So for example, let's imagine Ti oxidizing. That's a nice reaction. At 298 Kelvin, I looked it up. The PO2 at this equilibrium is-- anybody have a guess?

Forget the guess. It's completely naive. 10 to the minus 150 atmospheres. A completely silly, make believe number. It's 0. It's 0. It might as well be 0.

What does that mean about titanium metal?

AUDIENCE: It's very favorable for it to oxidize.

RAFAEL JARAMILLO: Very favorable with oxidized. Titanium metal, if you see it in the air, will actually be titanium metal with a thin layer of its own native oxide on top of it. Because if you were to remove the oxide and wait a split second, the oxide would spontaneously reform. And so this spontaneous oxide formation process is really important for a lot of reasons.

It's important for microelectronics, it's important for stainless steel. That's how stainless steel remains stainless. You have spontaneous formation of a passive rating, or you can think of it as a protecting oxide layer and the engineering of those materials continues. It's all interesting stuff.

All right, so that is enough to take us to Richardson Ellingham diagrams. So we're going to do this. I can't really motivate this, because it sounds kind of random what we're going to do. So I'm just going to tell you what it is, and at the end tell you why it's useful.

We're going to plot delta G0 as a function of temperature for metal oxidation reactions. As you know, it's like this. And so this is a pretty simple thing. This is a line with slope minus delta S0 and intercept delta H0.

This is a really, really simple line. So here's is temperature. Let's see in Kelvin. Here's 0, here's 0. Here's delta G0, and we have line. We have a line, the slope, and an intercept.

Slope, intercept. That is a Richardson Ellingham diagram. Now, why did we do that? A couple of reasons.

Let's start by talking about the PO2 scale. What's that? The equilibrium constant is PO2 by atmosphere to the minus 1, which is equal to e to the minus G0 over RT.

So I'm just going to rearrange that and write delta G0 equals RT log PO2 by atmosphere. This is a line on delta G0 by t plot with slope our log, PO2 and 0 intercepts. Let's draw that. All right, here is temperature in Kelvin. 0 is 0.

Here's delta G0. I'll draw the oxidation of a given metal just to have something on there. And now, I'm going to draw these two contours, right? Delta G0 equals RT log PO2 over atmosphere. So I'm going to draw a series of lines all with 0 intercepts in varying slope.

So there's a series of lines with 0 intercept and varying slope. And as I move in this direction, I'm increasing PO2. So that's what a Richardson Ellingham plot is. Now, I get to tell you why it's useful. All right, so if I rush through the explanation what it is, because it's just like, I have to tell you what it is.

But now, I can show you why it's useful. So why is this useful? It's useful for materials processing. Let me illustrate that.

Let's consider two metals, and I pick these just because they appear nicely separate on the plot. Let's consider tin in manganese. If I look up the Richard Ellingham diagram for tin and manganese, I could do that, but I'll just draw qualitatively what it looks like.

It's temperature in Kelvin. It's delta G0. And I'm just here to tell you that the tin line sits well above the manganese line. So that's just a fact about these metals. This here is tin plus O2 going to tin O2. That's what that is, and this is 2 manganese plus O2 going to 2 manganese oxide.

And here are my PO2 contours. What is this plot telling me? It's telling me that, at a given-- I have a typo on my scan lecture notes, I'm sorry. At a given temp at any given temperature, PO2 for the manganese oxidation reaction is lower than for the tin oxidation reaction.

That's a useful fact. How do I see that? Let's say at a given temperature, let's see that temperature here. I have this point on the tin oxidation line. And this point on the manganese oxidation line.

Well, the PO2 contour that runs through the manganese oxidation line intercepting of that temperature corresponds to a lower partial pressure than the PO2 contour that runs through the tin oxidation line for that given temperature. Again, at its given temperature, the PO2 partial pressure contour for manganese oxidation is a lower partial pressure than the contour for tin oxidation.

What does that mean? Manganese metal will reduce tin oxide. So if you were to put tin oxide-- let's say an ore into a furnace in the presence of manganese metal and heat it up, the manganese will convert to manganese oxide and then tin oxide will convert to tin metal.

Why is that? Manganese has higher affinity for oxygen than does tin. Or saying the same thing, the enthalpy of oxidation is more negative for manganese oxidation than for tin oxidation.

So you can see that from the plots. The intercept of these plots is delta H. So you can see the intercepts for the manganese oxidation-- that's at this point down here-- is lower. Let me extend these lines.

The intercept of the manganese oxidation reaction is lower than the intercept of the tin oxidation reaction. The enthalpy of manganese oxidation is more negative. Or if we are speaking a little bit colloquially, manganese metal pulls-- in quotation marks-- oxygen out of tin oxide.

So everything I just wrote, these are all saying the same thing about metal oxygen bonds. All right, these are all equivalent statements. They're just ways of interpreting metal oxygen bonding and the implications of that for materials processing. If you're going to be processing manganese in the presence of tin, you need to know which one is going to have a higher PO2 at equilibrium for oxidation, because it's going to determine your process outcome.

I want to share with you some pictures of Ellingham diagrams. So there's lots of Ellingham diagrams out there. Here is one representation that's a little busy, but you can see lots of things here. You can see many metals which are all represented.

Let me grab my laser pointer. Sometimes the laser pointer is stubborn. So here's iron. Oxidation reaction is a nickel reaction copper. As you move down, you're going to metals that have higher affinity for oxygen.

So copper is sometimes considered noble. So it doesn't readily form an oxide. You remember we talked about roof flashing. It takes a long time for it to turn green. As opposed to calcium, right?

If you have calcium metal around, you should look out, because it's going to explosively oxidize. So down here, you have calcium, magnesium. Aluminum. Aluminum is a very energetic oxidation reaction, but we know it forms a passivating oxide.

So you don't have exploding aluminum all over the place. You have almost instantaneous formation of aluminum oxide on the surface of aluminum. Titanium silicon manganese chromium. So this is a limited Richardson diagram, Ellingham diagram, because it only shows about a dozen or so metals. Of course, you can get very, very busy plots.

I want to point out one more thing, which is the PO2 scale. PO2. And you see it's a series of numbers running from 1 atmosphere to 0 to the minus 200 atmospheres. And each of these numbers has a little tick mark, and the tick marks all point towards the origin.

You see these tick marks, they're at different angles. Why is that? Because it's asking you to imagine a series of straight lines connecting the origin to those values. Those series of straight lines connecting the origin to-- I've never done this before.

I draw the line. So here is-- oh, there we go. Look at that. So this would be a line of 10 to the minus 50 atmospheres of oxygen. So for example, you might say that zinc and its oxide are equilibrium at 400 degrees C and 10 to the minus 50 atmospheres of oxygen. That would be one way to read this plot.

And you also see that the delta H of formation here is correlated to the electronegativity. So this idea that metal oxygen bond formation is energetic, well, we know that, but it's more energetic for less electronegative metals. So we expect noble metals like silver and copper to be fairly electronegative. They like their electrons, 1.9, 1.93.

And we expect alkaline, alkaline Earth metals-- let's say alkaline earth-- alkali metals. Alkaline Earth metals like magnesium, right? They are happy to give up their electrons to oxygen. And that has a lower electronegativity calcium is down here at 1.

So there's some solid chemistry here. There's one more thing I want to tell you about Ellingham diagrams, and that is the effect of phase transitions. So let's consider melting of metal or its oxide. Metal's metal-- oxide's also metal-- causes-- it causes discrete jumps in those values.

So for example, let's consider solid metal plus O2 going to MO2 solid. Reaction one. This says standard entropy 1. It's negative. It's negative, because we're pulling oxygen gas out of the gas, right?

Solids. Solids. Now, consider case where metal melts at lower temp than MO2. So metals have a lower melting point, which is true for most but all oxides. And raise the temp until then the metal solid becomes liquid metal.

So that's what we're going to do. We're going to consider that, and now we're going to consider the oxidation again, except now we're oxidizing liquid metal. So the oxide is still solid but the metal is now liquid.

And we'll call this reaction to have delta S02 Well, we know that the liquid metal has higher entropy than solid metal. We know that. So what that means is that delta S02 is going to be smaller than delta S01, and they're all less than 0.

In other words, it's going to be even more negative. On a plot, it looks like as follows. There's temperature. This is delta G0, and we have a kink in the plot.

The kink happens at the melting point. So here is metal melting at that temperature. The lower curve is a solid oxidation reaction-- solid metal oxidation. The upward curve is liquid metal oxidation.

This intercept is delta H0 for solid metal oxidation, and this intercept is delta H0 for liquid metal oxidation. So let's go back to some real plots. So now we can understand why there are break points in these. There are break points in these curves, because at these transition points, the standard enthalpy and entropy of these reactions changes.

So this melting point here of aluminum, it changes the slope very slightly. You can't really see it. You can't really see it, but there is a slope change. Then up here, the aluminum boils. So there's another break in the slope. Here, manganese melts.

Here, the manganese melts. Here, zinc melts and zinc boils. So forth and so on. And if you want to really lose your mind, you can look at more complete Ellingham diagrams. So this is posted on the website. And this is a very, very, very thorough Ellingham diagram now with so many elements and melting points and boiling points and so forth.

And you can start to look at these and learn what the melting points and the boiling points of the metals and the oxides are, and you can see how they change the slope of these curves. There are cases where the slope actually dips downward for a little while. That's typically a melting point of an oxide and so forth. And if you really like to explore this a little more, which I encourage you to do. It's a nice way to learn.

Go to DoITPoMS page with Ellingham diagrams. For those of you who don't know DoITPoMS, you should know DoITPoMS. It's a really excellent resource for learning material science concepts. It's maintained by University of Cambridge, and it's a nice complement to things like OpenCourseWare and MIT. Let me share that just to show you where you might go to play with this a little more, get a feel for it.

So here is the DoITPoMS page for Ellingham diagrams, and if you click on oxides, there's a whole bunch of oxides. And so let's go at random cobalt oxide. See Ellingham diagram. So it now shows you Ellingham diagrams for cobalt for its two different oxidation states. And it will give you data, you can mouse around, get the actual numbers.

Change the temperature. It gives you free energy information, and so forth. And it's a nice learning tool. So now I will call it a day and stop recording.