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**RAFAEL
JARAMILLO:**

Right. So this is the last lecture before an exam. And so what I'm going to do is walk through a case study just look at reacting systems of ideal gases in a little more detail. And then if there's time remaining, I want to do Nernst in a nutshell, just for fun.

So we're going to start with reacting systems of ideal gases. And this pen is on its way out so I'm going to switch. And we're going to consider our reaction of the form $A + B \rightarrow 2C$. And later on, I'm going to plug in some numbers. And I plugged in numbers for hydrogen plus chlorine goes $2HCl$, which is all in the gas phase.

And this is also generically discussed in the textbook, so that's very convenient. And here's what we're going to do. We're going to ask, what can we learn-- what can we learn from plots of free energy versus composition, free energy versus system composition?

So free energy, Gibbs free energy is the sum of partial molar Gibbs free energy weighted by the moles. And we know that we decompose this into the sum of the contributions of the pure components before they were mixed, and then we have this ideal solution model.

So composition is expressed by those n of i 's. We have per component i at pressure p . That's the reference state.

And then here, we have a system that was mixed at fixed T and total p , so just remembering what those terms are. Now we're going to start analyzing this in a little more detail.

All right. So for a univariate reacting system-- univariate, that meant that there's only one variable, univariate. And that's a system with only one reaction. So the reaction can run to the right or run to the left. There's only one reaction coordinate. We saw this in almost all of the examples that we did.

The composition can be expressed with respect to a single variable. So we saw this before. And right here, we're going to write with respect to n_c . So I'm just going to arbitrarily choose the third component.

And so we know that dn_a equals dn_b -- equals, in this case, minus $1/2 dn_c$. Remember, this is $A + B \rightarrow 2C$. And we get these from $dn_i / \mu_i = \text{constant}$. Good?

And so that means that n_a equals n_a^{initial} plus the total change of n_a . And we just plug that in, n_a of a initial minus $1/2 n_c$ minus n_c^{initial} . So this is stuff we've seen before in one form or another.

n_b^{initial} minus $1/2 n_c$ minus n_c^{initial} . That's just integrating those changes. That's good. And, of course, n_c , well, that's our independent variable, so n_c equals n_c . So that's good. Now we've expressed this univariate system with only one variable, n_c . Everything is in terms of n_c . That's good.

We're also going to need, also going to need n total equals-- and for this particular system, this happens to equal n of a initial plus n of b initial plus n of c initial. And that's not always guaranteed, that the total number of moles is fixed.

But for this reaction, for this one that we're doing, you have the destruction of two moles and the creation of two moles, so the number of moles is fixed. So this just makes the math a little easier in this particular case. And we're going to need n of total in order to write my p of i 's, which are total pressure over n of i over n total.

So that's what we're going to need our n totals for. All right. So now we have everything except for the reference data. We wanted to write the Gibbs free energy as a function of composition, and we're well on our way.

So now we can now write out the Gibbs free energy as a function of n of c and plot it. So this is what we get. Gibbs free energy is n of a initial minus $1/2$ n of c minus n of c initial.

Chemical potential a is reference state, plus n of b initial minus $1/2$ n of c minus n of c initial, times the chemical potential of b and its reference state, plus n of c times the chemical potential of c and its reference state, plus the contribution from the ideal entropy of mixing $RT \sum n_i \log \frac{n_i}{n_{\text{total}}}$.

All right. So this so far, none of this is new. I'm just writing things out a little more than I have in the past. So in order to go any farther, it's helpful to put some numbers in.

So what we're going to do is, we're going to consider, again, this reaction, the gas phase reaction, hydrogen plus chlorine going to hydrogen chloride. And we're going to consider this at 298 Kelvin. And I'll tell you, this reaction is really annoying.

And this reaction is annoying for me personally because in my lab-- and a lot of labs that are doing similar research-- we would really like to use hydrogen-containing precursors and chlorine-containing precursors to grow certain semiconductors. It can be a very effective way of growing certain semiconductor thin films.

The problem is that the reaction byproduct is hydrogen chloride, or hydrochloric acid. And if you're making hydrochloric acid, you really can't have any metal in your system, especially downstream. And what that means is, you can't use a lot of common semiconductor-processing equipment. You have to use less-common equipment. You have to use a lot of [INAUDIBLE] and so forth.

And it stands as a pretty substantial barrier to running processes like this in the semiconductor industry, where no one's really interested in swapping out stainless steel reactors for nonmetal reactors. It can be done. But anyway, it's a problem-- so a little bit of an aside there.

So let's see. The chemical potential of hydrogen, what is that? We need to get this from databases. So we're going to have a standard enthalpy of hydrogen minus T times the standard entropy of hydrogen. And by convention, the standard enthalpy of elements at 298k and 1 bar is 0.

By convention, by convention or definition, elements in their standard state at 298 Kelvin, 1 atmosphere have H^0 set to 0.

Similarly, for $\mu_{\text{chlorine } 0}$ -- chlorine 2 -- this is $H^0_{\text{chlorine}} - TS^0_{\text{chlorine}}$. And we don't need to look anything up there. And then we have the chemical potential of HCl in its standard states.

And this is going to be $H, H_{T0} \text{ minus } T_{S0} H_{Cl}$. And this is nonzero because this is a compound. This is the formation enthalpy for one mole HCl from the elements in their standard state. That's what that is.

So you might see this like this, $1/2 H_2 \text{ plus } 1/2 Cl_2 \text{ going to } HCl$ with an enthalpy, a formation, sometimes written as ΔF_H . All right. So what do we do? We get data.

And so you can find data for the standard entropy of these components and the enthalpy of formation of HCl. You can find that data-- I'd say on NIST WebBook or pretty much anywhere else. These are all pretty common materials.

So I plotted some things, so we're going to look at the plots. So I plotted the function. This is what it looks like. So this is plotted for the case of-- let me put a grab a laser pointer here. This is plotted for the case of-- initial moles of A and B is 1, and initial moles of C is 0.

I could have plotted-- I could have chosen any starting conditions here, just made it simple. So you start with a stoichiometric mixture of A and B and no C. And I plotted this Gibbs free energy of the system as a function of n of c using data for hydrogen chlorine and hydrogen chloride.

I did cheat a little bit. I reduced the formation enthalpy of HCl just because it makes the plot easier to read by eye. So don't take these numbers to the bank. Don't use these in your future engineering and research endeavors. But the science lesson still stands.

So what is this plot telling us? Would somebody just please interpret this? What does this mean? What's the meaning of it.

AUDIENCE: Well, we can see that g is minimized approximately at 1.5 moles of n_C . That is HCl. So that being the lowest point, that's where the reaction will settle at equilibrium at this temperature.

RAFAEL JARAMILLO: Great. Thank you, So yeah, that's exactly right. The reaction, if you start over here on the left-hand side with number of moles of C, the reaction will proceed to the right until the Gibbs free energy is minimized. And we see that point right here. Good.

We also see it curved back up. So there is a problem on the P set about this curvature. And this curvature is always here, even if it gets pushed really close to the y-axis. This is to say that at equilibrium, no reaction ever runs all the way to one side at equilibrium. There's always a little bit of mixing, and that comes from the singularity of $x \log x$. So that's another thing to see.

You could see here that, in this case, the starting Gibbs free energy on the left-hand side is higher than the Gibbs free energy if you had full conversion. So there's a driving force here for the reaction to run to the right initially. I don't know.

I'm not sure what else to say here. All right. Now, what I did is I repeated the calculation for 328 Kelvin. And so how did I do that? Let me switch back to the camera for a minute. We'll come back to this data, but I want somebody to remind us how I would have calculated this for a different temperature.

So we have here the Gibbs free energy. And now I want to calculate this for a temperature other than 298 Kelvin. What do I need? What data do I need?

I have temperature here. So obviously, I can change that number from 298 to a different number. But is that the only thing that I need to keep track of, or is there something else?

AUDIENCE: There's also the heat capacities for H center.

RAFAEL
JARAMILLO: You need the heat capacity for each component. That's right, Can you tell me why? What do I do with those heat capacities?

AUDIENCE: You can get the H T of, that the H-- the enthalpy as a function of time.

RAFAEL
JARAMILLO: Right. I need to change the enthalpy from enthalpy of 298 to enthalpy at a different temperature. I also need to update the entropy. So I integrate heat capacity here. I integrate heat capacity over temperature here. I also have to change the temperature here.

So what I'm doing is I'm using the heat capacity data to calculate the standard chemical potential at some other temperature. That's right, so just a reminder there. So I need a heat capacity data for all three components. And I did those calculations. I just programmed this in MATLAB, so it did it for me.

And I updated H's, and I updated S's, I updated mu's, and I plugged that all into this expression. So I have an updated mu, updated mu, updated mu. And, of course, I just changed the temperature there. And then I reapplied it.

So let's see. Let's go back to the graphs here. So I replot it. So let's see. Can somebody speak to-- what is this plot telling us? The 328 Kelvin plot is below the 298 Kelvin plot. Can somebody offer an explanation as to why that is?

Why did it overall drop instead of rise?

AUDIENCE: Could it have to do with this reaction being either exothermic or endothermic?

RAFAEL
JARAMILLO: So I love that, and we're getting there. But in this case, that's not the dominant effect. In this case, that's not the dominant effect. Somebody else?

AUDIENCE: Could it be because the temperature is higher, so the formation of enthalpy-- sorry, the delta G has to be lower?

RAFAEL
JARAMILLO: Yeah. It has to do not so much with any reaction or formation, but it has to do with this functional form. dG for any system equals minus SdT plus PdV plus ba, ba, ba . So the trend in temperature of Gibbs free energy tends to be negative because Gibbs varies with temperature with a slope of minus S , and entropy's strictly positive.

Now, there could be other things changing. You can have volume changing-- sorry, VdP . You can have volume changing. You can have number of moles changing. But just as a rule of thumb, for almost any system, Gibbs tends to go down as the temperature rises. And it comes simply from that coefficient. OK.

All right. So now we can see that the overall thing shifted down. But it's a little bit hard to compare these two curves when they're so shifted. The dynamic range of the plot is kind of too big. And so what I'm going to do is, I'm going to do what they do in the textbook. And I'm going to plot this arbitrarily, the Gibbs free energy minus 2 times the Gibbs strategy of C_0 .

So what I'm basically doing is I'm pegging these plots to 0 on the right hand side. You could peg it to 0 on the left hand side and same thing, basically. And so now I can zoom in a little bit. Now I can draw another conclusion from these plots by comparing them.

You see I have them now on the same plot, so I get the full dynamic range of the plot. And then I'm going to zoom in even further. So now we're zoomed way in around the minima. Would somebody like to point out an observation about these equilibrium points? Can you draw any conclusions about this reaction from what's plotted here?

AUDIENCE: Increasing temperature drives the reaction to the left.

RAFAEL JARAMILLO: To the left, yeah. So Samuel is pointing out that as you heat up, Sam is pointing out that the minimum in Gibbs free energy at 298 Kelvin is over here, and it seems to shift a little bit to the left as we increase the temperature. It's a little subtle. You need to look closely. But it's visible if you zoom in-- Zoom in. Thank you, Zoom.

All right. So I'll ask a couple of questions. And these are the questions which we're going to analyze, two questions. First, is the reaction endothermic or exothermic? And two, can you estimate the reaction enthalpy from the data on the screen?

So who wants to tackle number one, question one, is this reaction endothermic or exothermic?

AUDIENCE: Is it exothermic?

RAFAEL JARAMILLO: Is it exothermic? And OK, why?

AUDIENCE: Because we see that with an increase in temperature, it shifts to the left. So we would expect it to be a product of the reaction so that when it increases, by Le Chat principle, it will shift to the side. That reduces the amount of heat.

RAFAEL JARAMILLO: Yes, exactly. Thank you. That was very clearly said. So Le Chat says systems-- I should say reacting-- says that reacting systems, quote unquote, "resist"-- they don't have bumper stickers. They don't actually know what they're doing.

But they, quote unquote, "resist" the temperature rises by running in endothermic direction. They try to soak up that heat-- the endothermic direction.

So this reaction is observed to run to left with increasing T. So running backwards is endothermic. So as written, it's exothermic. Good. That's good.

And well, also, just remember Van 't Hoff said $d \log k_p / dT$ equals $\Delta H_0 / RT^2$, which is basically saying the same thing. All right. But what we're observing is that this is negative, right?

The reaction at equilibrium is shifting to the left, so k_p is getting smaller as we raise temperature. So this slope is negative. And indeed, we have an exothermic ΔH . Good. So that's a concept question.

All right, but what about number 2? This is a little bit more involved, so I'm just going to step through this. Using Van 't Hoff, using Van 't Hoff, if we can estimate $d \log k_p / dT$, then we can estimate the enthalpy of the reaction.

So that's useful. So here's what we're going to do. I'm going to ask the class, how would I estimate this? How would I estimate this quantity?

AUDIENCE: Isn't K_p equal to the partial pressures of the products over the partial pressures of the reactants?

RAFAEL Right, right. But this is the data I'm given. So is there something you could do with this?

JARAMILLO:

AUDIENCE: Well, given that it's an ideal gas system, we have the number of moles at equilibrium of HCl. And from there, we can extract the number of moles of the reactants, which would be a substitute for the partial pressures.

RAFAEL Great, that's fantastic. That's exactly what I'm looking for. Thank you. So I just showed that plot again just to jog

JARAMILLO: your minds. And that's right. So what we're going to do is, we're going to look at these two temperatures for which we're given data, 298 and 328. And we're going to eyeball-- we're going to eyeball the equilibrium number of moles of C.

And I did that. You could do it if you were still looking at the plot. It's not hard to do. I eyeballed it. I didn't solve it numerically or anything. I just sort of did it to two decimal points, 1.55 and 1.53. So that's it. That is the data that we need.

From there, everything is calculations. And C at equilibrium is 1.55 and 1.53. We already have expressions for n_a and n_b in terms of n_c . And you can figure out from the stoichiometry of the problem, it comes out to 0.225 and 0.235.

So now you have the mole numbers. And what we just heard from-- was basically Dalton's law, that we can get the partial pressures, and therefore, the equilibrium constants from the mole numbers. So I went ahead and calculated those from these numbers, 47.5 and 42.4.

And just as a reminder here, this is using p_i equals n_i over n_{total} . And again, just to make it very, very clear what I did, for example, 47.5, what is that? That's 1.55 divided by 2 squared over 0.235 divided by 2 times another factor of 0.235 divided by 2 reaction coefficient.

So that's an example. All right, so these are-- as usual with thermo, the actual calculations are exceedingly simple. It's just figuring out what goes where. OK, good. And then what? Then what do we do?

Using these estimates-- well, we don't have a derivative, but we have some changes. The change in $\log K$ of p , we calculated it. It's minus 0.114. The change in temperature was 30 Kelvin. So those are the two data points we were given.

And so we will just say, well, I'm in a rush, and this is all the data I have. So let's say that this derivative is approximately equal to rise over run. And this comes out to -0.00379. The units here are inverse Kelvin. And there, that's it.

So ΔH equals $RT^2 \frac{d \log K_p}{dT}$. And I'm going to say it's approximately equal to-- OK, I estimated that. R is a constant. What temperature should I use? What temperature should I use?

AUDIENCE: Maybe, like, the average temperature, so the one in the middle.

RAFAEL Yeah, that works. Anything will really do. Yeah, you remember this from calculus, when you take a derivative, you can evaluate a function in the left or the middle of the right, stuff like that. So I'll use midpoint. Anything will do. You just have to use a number. You can't just leave it as T.

So we'll use a midpoint. And if I do that, I say minus 3.09 kilojoules. And that's the answer to the question that was given, estimate the enthalpy of this reaction. It's exothermic, as expected. That's good.

And I'll let you know that when I generated that plot, I used minus 2 kilojoules. So the plots are generated from minus 2 kilojoules and the heat capacities. And this rough estimate gets us minus 3 kilojoules. All right. Well, anyway, it's a starting point. The idea was an estimate.

I will leave you-- I want to move on, but I'll leave you with just some ideas, how to find temp. You want to make sure that you know how to calculate the temperature dependence of mu of i's. I think answered that a while ago. I want to make sure we do this.

And this is an interesting question. Can we estimate the heat capacity difference across this reaction from a temp series of G of m of c? So we didn't see just now a temperature series. We really just saw two temperatures.

But if you had a bunch of temperatures, if you had a whole family of curves at different temperatures, you could estimate heat capacity differences from that. And it's interesting to think about how you might go about that-- at least, formally. All right. So in the time remaining, I'd like to move on to Nernst-- unless there are really burning questions about this, in which case I'm happy to stall.

AUDIENCE: I had a question about-- I guess going back towards the start of working on this problem. So in this particular reacting system with HCl, we do have the n total is equal to a constant because for two moles of reactant, we have two moles of product. How would you deal with that not being the case?

RAFAEL It's formally not hard. It's just get a little annoying. The computer will take care of it for you. Basically, what you do is, you have these expressions here for n_a , n_b , n_c , and it's all in terms of n_c . So we reduced everything to one variable, right?

All that means is that the n total, which is the sum of n_i 's, will also then, in general, have an n_c dependence.

AUDIENCE: OK.

RAFAEL Everything else follows. It all follows here. That'll general have an energy dependence there in the denominator. **JARAMILLO:** But plug it in and plot it, it's-- in general, here, I have n total here when using Dalton's law. I just went ahead and plugged in 2's there.

In general, you'd need to calculate n total, and it would be other than 2 so that there'd be another place where you'd need to keep track of it. Good question. OK. Anything else?

It's a nice reaction form to analyze to just understand the math and the formalism and the fundamentals of this because of that conserve mole number. Adding a very mole numbers is a complication. Of course, it's realistic. There's lots of systems you'll analyze in your careers that will not have fixed mole number, but it's a complication.

And so that's why I chose here to do $A + B = 2C$. Likewise, in the textbook and lots of other textbooks, we like to take the simple cases first. All right. So now I want to just switch gears and take you on a very quick walk through the Nernst equation.

And you can just sort of stop taking notes if you like and just let this wash over you. It's just for context. It's just for context. All right. So what we're going to do, we're going to take a redox reaction, take a redox reaction.

And why I'm doing this now, by the way, is because it couples nicely to some stuff which we have done in this class recently. And it couples nicely to what you're going to be doing in 023. So that's why we're doing this now.

OK, so we take a redox reaction. I'm going to use this one. It's a very well known reaction. This is called a Daniel cell. There's a guy-- I had to look us up-- JF Daniel. And we're talking about the 1830s. He's making batteries out of zinc and copper and sulfates. So it's a very-- so we take this redox reaction. Great.

And this is key. We're going to separate the reduction and the oxidation half reactions in a device-- this is about making stuff, making devices-- in a device engineered such that electrons and ions follow separate paths.

So you have to know something about plumbing. You have to know something about electronics. This is fine. This is fine. So this is an example for the demo cell. This is what that would actually look like. What on Earth does that actually look like? This is what that would actually look like.

We're having two beakers here, two beakers, these two beakers. And what are we going to do here? We're going to have a rod of zinc metal, rod of zinc metal. And we're going to have a rod of copper metal.

And then we're also going to have something called a salt bridge, which can be a U-shaped pipette, a pipette but a u-shaped tube, filled with brine, basically. And this is aqueous. So these are aqueous systems.

And what do we have here in solution? We have zinc sulfate aqueous, aqueous zinc sulfate, and aqueous copper sulfate. And so we have a system where ions can go this way. But we still need somewhere for electrons to go.

And so electrons, we pull out through external circuitry. Put two terminals there, and these are the voltage current terminals.

And what I've just drawn, if you abstract away the details, is every battery ever made or every electrochemical reduction system ever made. But anyway, we don't have time for everything ever made. We're just going to step through this example.

So that's what we did. Now I'll keep on going. The electrostatic work-- you guys remember introductory physics? The work of moving charge nF across potential E -- we tend to use this sort of scripty E . This is also known as electromotive force, but it's also sometimes just written V .

What's nF ? n equals moles. F equals the number of coulombs per mole of electrons, 96,485 coulombs per mole. This is known as Faraday's constant.

The [INAUDIBLE] work of doing that is-- I'm going to call this W star, which is also the change in energy of the system. And this is from introductory physics. We have displacement, dot product with the electric field. So this is a force dot product with a distance field displacement, displacement fields-- let's see-- dot product.

And if you remember how voltage is defined, it's a spatial integral of a directed field, so nFE . So the work, the negative work, which is the minus change in energy of a system, of moving n moles of charge across potential ϵ is nFE .

We're also going to take something called the generalized work theorem, which I don't have time to derive. But hopefully, it's a little bit intuitive. The change of energy is W_{star} , where W_{star} is any reversible work.

So, so far in this class-- and really, for the entirety of this class-- we only deal with mechanical work, PdV work. And that's fine. But just for this one 20-minute segment, 15-minute segment, we're going to deal with electrostatic work. We're going to admit that there are other ways-- other than mechanical ways-- of changing the energy of the system through work.

And this is electrical work, electrostatic work. So if we take this and we combine it with this, we get something called the Nernst equation. And the Nernst equation is very simple. The change in Gibbs free energy of a system is minus nFE . That's the change in Gibbs free energy for moving n moles through a potential of E .

But we're going to keep going here. We're going to use stuff we already know, formalism of reacting systems, to write ΔG with respect to activities-- or, if you like, concentrations. So, for instance, in this case, ΔG equals ΔG^0 plus $RT \ln q$ and-- remembering the form of our reaction here-- zinc sulfite activity, copper activity, copper sulfate activity, zinc metal.

This here is the reaction quotient. All right. So what we're going to do is, now we're going to use Nernst to couple electrostatics-- that was from the previous board-- we're going to couple electrostatics and chemistry.

So this was thermochemistry. This was electrostatics. And so what happens when electrostatic and chemistry get married? You get electrochemistry. And it's written as followed.

nFE equals minus ΔG^0 minus $RT \ln q$. And this is also sometimes called the Nernst equation. This is a cell voltage, something you can measure easily with a voltmeter. This is a reference. And this reaction coefficient depends on concentrations.

So for the Daniel cell we have-- for example, for a Daniel cell, we have ϵ -- not, ϵ sorry-- electric potential is a reference potential minus $RT/2F \ln$ concentration of zinc sulfate with a concentration copper sulfate.

What are these? x 's are concentrations in aqueous solution. E^0 are reference potentials, reference potential defined for a reference state. And in this case, it would be concentration of the two aqueous components equals 1 mole.

And I made n equals 2 because this particular redox, it involves two electrons if you remember the formal charge on sulfate or copper or zinc here. OK. So that was very fast, but I think it was worth it because now you've seen this stuff. And then as you see it again in other classes, hopefully, there'll be some connections to some material from 020.