

[SQUEAKING]

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[CLICKING]

RAFAEL

JARAMILLO:

OK, so today we are starting a new topic. We're done with unary phase diagrams. We are going to start reacting gas systems. And it's useful, not just because it's useful and it's all right, but because it's an entree for solutions. So just a bit of topic here, we have start, and then we went to-- we did some heat engines. We did a little bit of heat engines, a little bit.

And this is where the course-- this is where the course do people get off the bus, at the engines. But we stayed on the bus, and then we're going to do a little bit of reacting gas reacting gases. We're going to do a little bit of that. And after this, this is where the course 10 people get off the bus. They get off the bus here, but we stay on the bus.

And reacting gases-- we're doing it because in addition to being useful, it sets us up for solutions. And I mean mixtures, not answers. So this is where this goes. And I find this interesting because thermo is a weird topic in that it's taught by, like seven or eight different courses at MIT.

You don't have that with multivariable calculus. You don't have seven different classes teaching their all multi and others. But thermo is really unique in that we have so many different disciplines teaching thermo, and we each have our own flavor. So that's that.

So anyway, let's get started. Gas mixtures-- and what do I mean? Homogeneous now, homogeneous multi component. So this is a complement of what we just did. We did unary. Unary was one component, multiple phases. Now, we have multiple components, one phase. So let's get that clear in our head.

So let's talk about air. Air, what's in air? Here's my bucket of air. What's in my bucket of air?

AUDIENCE:

Primarily oxygen, then nitrogen.

RAFAEL

JARAMILLO:

Primarily nitrogen-- about 80% by mole than oxygen. So it's a mixture of those. What else is in there? Just kind of curiosity, what else do you know to be in air? What's the third dominant component?

AUDIENCE:

Argon maybe.

RAFAEL

JARAMILLO:

Sorry?

AUDIENCE:

Argon.

RAFAEL

JARAMILLO:

Argon, yes. Yeah, sorry, I had a hard time understanding you for a minute. Yeah, argon is the third major-- the third-- it's not a principal component because 1% or something. But it's, I think, the third most prevalent component. H₂O, we know H₂O is in air. We talked all about humid air. CO₂, of course, is in there. And there are others.

So let's say that that's air. So there we have our bucket of air. So the phase is gas. The components-- the components are what we just mentioned. There's nitrogen. There's oxygen. There's argon. There's water. There's carbon dioxide and so forth.

Those are the components. And the components are not to be confused with elements, OK elements are nitrogen, oxygen, argon, hydrogen, carbon, OK, so don't confuse elements and components, although sometimes they overlap.

All right, let's get right into Dalton's law because this is important. We've talked about it in the previous lecture. This is a little bit of a preview. Apparently Professor Carter has been talking about it. So it's in the air. Get it? That was an air pun.

Dalton's law of partial pressures-- Dalton's law of partial pressures. All right, so I'm just going to write it out. In a gas mixture-- so gas mixture-- each component contributes a partial pressure in proportion to its mole fraction.

All right, so this is full of thermodynamics terms here. Let's highlight on component, mole fraction, partial pressure. It's also a mixture. It's full of thermal concepts in here. And I won't circle gas because that's not really new for us. But, all right, so what does that mean?

So, for example, if I have two components, this is how we label it. The pressure of the system equals pressure 1 plus pressure 2 I think you'll remember that we use subscripts for components. Subscripts are for components.

We won't have any phase labels here because it's one phase. It's only gas. So we don't have to worry about phase labels, but we do have subscripts for components. And in order to find the partial pressure for component i , you take the total pressure, and you multiply by the moles of i over the total moles of gas in the system. And we already have seen that we have a symbol. We use X for the mole fraction-- mole fraction sub i .

All right, so there's a lot here actually. It may look simple. That's sort of a deceptively simple question. Are partial pressure real? Are these real measurable things or are these concepts that we just use out of convenience?

AUDIENCE: Aren't partial pressure is just like different pressures at different places within like a material?

RAFAEL JARAMILLO: So we're assuming that the pressure is everywhere uniform. So it can't be different places, not exactly. But maybe you're on to something.

AUDIENCE: I think I've have seen, like the pressure is uniform, which is kind of like force over area. So if we take any random area since like very small fraction like 50% or like 80% is nitrogen, 80% of the like momentum heading that area is from nitrogen molecules.

So it's kind of like having 80% contribution to the total pressure. But it's because of a small fraction. Maybe like we have a chemical reaction that's only permitting one, it would only work as a spare as, like 80% pressure of the nitrogen that penetrate.

RAFAEL JARAMILLO: OK, that's good. So here's a gas mixture, red and green. And those gases're in a box. So one thing you can think is pressure is forced by area. So these gases-- the molecules hit the side of the box, and they bounce off. And maybe 80% of the force experienced by any given patch of the wall comes from nitrogen and 20% comes from oxygen. If it's air, 80 20.

So that's a good way of thinking about it. Or you could say 80% of all the molecules that hit the wall are nitrogen and 20% are air. So the pressure is proportional to the mole fraction. That's exactly what we're saying, that-- but that-- that's the right way to think about it.

But you can really go down the rabbit hole. Because if you have a force transducer, it measures force. It doesn't measure chemistry. It doesn't know whether what hit it was a nitrogen molecule or an oxygen molecule. So you can really head down this path.

And you can convince yourself that partial pressure-- although it's very adjacent to a lot of measurable things, and it's very, very adjacent to electrochemistry-- it may not seem that we're close to electric chemistry. We really are. We're very close to electric chemistry. Itself is kind of an immeasurable concept. Anyway, I don't want to go down that rabbit hole, but it's worth thinking about. It's interesting.

So let's move on with foundational concepts here. We did partial pressure. Let's talk about reactions. Reactions can change. They can change components. Or they can change phases or both, but not elements. So right now, we're doing multi component unary.

So now, we're dealing with reactions that can change components, but everything is remaining in the gas phase. So phases, that's later. I mean, we actually did that already when we did unary transformations, but we didn't talk about them like reactions. But you can. It's fine.

And this is course 22. So if you're changing the elements, go to course 22. But the formulism is the same. It actually is. It's just-- all right. So reactions can change components and phase.

So here's an example. Let's see, here's an example-- a reaction that changes components but not phase. Reaction that can change its components but not phase. $\frac{1}{2}$ nitrogen gas-- I'll carry the phase labels here just in a simple way just for-- since we're just getting started-- $\frac{1}{2}$ oxygen gas equals NO_2 gas. So same phase-- this is a mixture changed components, but not the phase.

Here's another example-- a reaction that changes components and phase. A reaction that changes components and phase. You can have H_2 gas plus $\frac{1}{2}$ O_2 gas go to H_2O liquid. So that's a common reaction.

We're not going to deal with reacting heterogeneous systems for weeks and weeks. So we're not going to deal with that yet, but I just wanted to let you know that everything we're writing down here-- the formalism for reactions-- will apply to more complicated situations.

Now, before I move on, I want to-- the attendance is low today. So if there are reasons for that that I should know, please tell me. You won't hurt my feelings. I'm really curious. Why do I bring that up now? I want to remind you, those who are here today, that the reading for today and on Monday is in Denbigh. So the PDF is on the website.

So we're changing books because Denbigh treats reacting chemical systems much better than DeHoff. Denbigh is a chemical engineer. This is an exceptionally well-written text. So don't be put off by the fact that it's got some years on it. It's exceptionally well written.

And as with the rest of the class, if you're not doing the reading associated with lecture, if you're not doing the reading ahead of time, and if you're not working the problems in the text, you're not getting your money's worth. So please do keep up with the reading, especially on a topic like this where it's a little bit-- it's just a little bit outside of the mainstream of material science. It's not just covered in DeHoff.

And there are so many textbooks on this topic, and I picked the one that I think is just the most elegantly written, really intellectually very clear. So I hope that you find the same. Also, some of the problems on the p set are straight out of Denbigh. So there's that too.

All right, so let us move on, more really foundational concepts. Ideal gas mixtures-- and throughout this course, I often use mixtures or solutions interchangeably. They're always going to mean the same thing. All right, so we're going to set up a little bit of a toy problem, sort of a thought experiment here. Here's the thought experiment. It's a really simple one.

We've got a box. And as so often happens in thermodynamics, we find ourselves with the box that's been partitioned. And we have now two components in their pure state, not mixed. Let's call this pure number 1. You can think of this as a nitrogen, pure nitrogen gas if you like. It's at some-- it's at a temperature. It's at a pressure. And it is at a volume, and I'm using that tag there for an extensive quantity of volume. So there's pure number one.

And then we've got in the other part, pure number 2. It's orange and green. I'm like three days delayed for St Patrick's Day, but I got there. All right, temperature, pressure, and volume. And although it may not look like it in my drawing, I intended for those volumes to be equal.

So here's a very simple situation. And this really brings us back to the baby book almost. We've got these gases, and we're going to mix them. Are there any other national flags that combine orange and green? Those colors have nice contrast, orange and green.

AUDIENCE: Ireland, I think.

**RAFAEL
JARAMILLO:** I think there's orange in the Indian flag.

AUDIENCE: This-- yeah, I think some country too called, like the Ivory Coast that's basically just the Irish flag reversed.

**RAFAEL
JARAMILLO:** OK, OK, all right. Any others? Ivory Coast, I think India had the orange and green in the flag, Ireland. Anyway, all right, so now we've got a mixture of these things. So they mixed. There we go. And so we have a mixture of 1 and 2.

I'll claim or just postulate for this model system that temperature didn't change. The pressure didn't change. And we have twice the volume. And if you don't believe me, it's $PV = nRT$. You solve for the moles of this. You solve for the moles of this. You add them together, a very simple situation.

Why is it so simple? It's because ideal gas molecules don't interact. That's why it's so simple. They don't interact. Each component behaves as if it undergoes-- and here is kind of the less intuitive part. Each component behaves as if it's undergoing an isothermal expansion.

And you could either choose to believe this or disbelieve this. It may or may not make sense. If it doesn't make sense, that's fine. Just treat it as a model. I'm showing you a model. It may apply. It may not. All right, so we know how to treat that. ΔG of component i equals $n_i RT \log$ its partial pressure over the pressure.

This is a really critical equation that comes from this assumption. We're using an expression for ΔG for an isothermal process and ideal gas. And we are modeling that as an expansion from pressure P to partial pressure P_i . So the Gibbs free energy is its starting value plus the change where G_i have $0n_i P$ because it's some standard state, however it started off. So they started off in a standard state. And they started off in a standard state.

So this slide here-- this board-- there's a lot of intellectual content here. The equation might look simple, but there's a lot of intellectual content here. So it's going to take a little while and some practice to understand this fully.

But I'll restate the assumption here. This model is that each component behaves as if it undergoes isothermal expansion. And if you buy that, then you can use the apparatus which we've already established, which is calculating the change in Gibbs free energy for an isothermal process as each gas expands from initial pressure P to partial pressure P_i .

To follow up on my earlier comment that we're really close to electrochemistry-- and for those of you who have seen the Nernst equation or done any batteries research, this looks a lot like the Nernst equation actually. And it's just a hop, skip-- it's a little bit of a stutter step from here to get to talking about electrochemistry. So if you don't care about electric chemistry or haven't been exposed to that yet, don't worry about it. But I think those connections are kind of neat for those of you who have been exposed to that.

So now, let's talk a little bit about notation. To remind you here, this is a reminder. G_i is an extensive property of component i . That is the total Gibbs free energy of all the stuff in component i . G_i without the prime is a molar intensive property. That is Gibbs free energy of i per moles of i . So you could read that Gibbs per mole of i .

Here's a new concept-- G_i^0 molar Gibbs free energy of component i in its standard state. What is that? I'm going to define it for gases-- standard state for gases. It's a pure gas that's unmixed at standard pressure-- 1 bar-- and same temp as the solution or mixture in question.

So concept, concept, concept, concept-- these two are not new to you today. They are-- they can be confusing, but they're not new today. And all of this is consistent with DeHoff. This is new today. We're introducing standard states. And standard states are defined somewhat differently than you might have seen than before.

Standard states for gases, to be specific for today, is the pure gas non mixed at one pressure but at whatever temperature the problem you're analyzing is. So it's not the same thing as STP. It's not standard temperature and pressure. It's not one bar 25 degrees C. It's whatever you have before you make the mixture.

And the process of making mixtures is so central to material science, I'm going to slide backwards here. We have a pure gas and another pure gas, a pure substance and another pure substance. They're both at the same temperature. I don't know what temperature that is. It's just a parameter, but they're at the same temperature.

The standard state of pure component 1 is this temperature and one bar. The standard state of pure component 2 is this temperature and one bar. And those are standards because it's what you have before you make the mixture. So I'll use this analogy often in this course. You imagine you have a beaker of A and a beaker of B.

And you're at whatever temperature you want to make your solution at, whatever temperature you're processing your material at. Beaker of A beaker of B-- they're at temperature. And you mix them, stir it around. That's material science. The standard state of a substance is however it's found when it's pure at one bar at the temperature that you're doing your solution form.

All right, let's move on. Chemical potential-- chemical potential and ideal gas mixtures. So we know that for any sort of change of temperature, and pressure, and mole number, this is the change in chemical potential. So $\mu_i - \mu_i^0 = \Delta G_i$ at fixed temperature, fixed pressure, and fixed moles of everything else.

All right, this is now. From before we have $\mu_i = \mu_i^0 + RT \ln \frac{P_i}{P^0}$. So chemical potential is molar Gibbs free energy. We calculated the change in Gibbs free energy for the mixture process. And so we can write an analogous equation for chemical potential.

So again, how to read this. Chemical potential of component i-- chemical potential of component i relative to its standard state at temp T and partial-- so the chemical potential component i relative to its standard state at temperature T and partial pressure P_i . That's how to read that. And we're going to use this so very, very much. I think it deserves a purple square.

I'm going a little fast through this material, so I remind you to please interrupt me with questions. Here, let's get a question. Do ideal gases mix spontaneously? Right, do ideal gases mix spontaneously? Here's my setup from lecture 1. These are ideal gases, two different components. Are they going to make spontaneously?

AUDIENCE: Yes.

RAFAEL JARAMILLO: Yes. Yes, they do. OK, so that you knew on day one, I think. Most of you sort of got that on day one. But now, we can answer this question. Why? What is the driving force? On day one, we talked about randomness and entropy, and it just sort of seemed like what would happen.

And we said oh, this is going to be an entropy-driven process, which is true. That's true. But now we have a more useful way of analyzing this problem in general, which is what is the driving force? At fixed T and P, the driving force is to lower the Gibbs free energy, the total Gibbs free energy.

So Gibbs free energy equals the sum of the molar Gibbs free energies-- and the molar Gibbs free energies are their reference values plus the change. I can combine these, and I find that the Gibbs free energy is the Gibbs free energy before mixing plus ΔG due to mixing and ΔG due to mixing the change of Gibbs free energy when this spontaneous process happens.

And you can plug and chug here. It's $\sum_i n_i RT \ln \frac{P_i}{P}$. And here's the kicker-- positive or negative? What should it be? Without-- forget the math. What should it be? Should this be positive or negative? The process will happen spontaneously.

AUDIENCE: Negative.

RAFAEL Got to be negative. If a process happens spontaneously at fixed temperature and pressure, the driving force is lowering the Gibbs free energy. The change of Gibbs for that process must be negative if it is to be spontaneous. Does the math work out? This is strictly positive. This is strictly positive. This is strictly positive. What about the partial pressures?

AUDIENCE: The i is strictly lower than P , so it's like a negative mole.

RAFAEL P_i equals $x_i P$. x_i is less than or equal to 1 by definition. You can't have a mole fraction greater than 1. Therefore, P_i 's are less than or equal to P . So $\log P_i$ over P is less than or equal to 0.

This is our driving force for mixing. The driving force for wave mixing is that the chemical potential of each and every component is lowered by mixing. So we're just a little more than 30 days past the start of the semester. And at the start of the semester, you knew this would happen, and you sort of-- we were able to discuss why it would happen in a hand way to be an intuitive way.

And now, a little under five weeks later, we now see the same result. But we have a formalism attached to it. We can calculate the change of strategy for this process, and we can see that it's negative. And we can quantify and count things. So I guess you could say we've come full circle.

All right, for the remaining 10 minutes or so or eight minutes, I'm going to talk about balancing chemical reactions, which gets back to-- for those of you who took chemistry in high school, it would be high school chemistry. And I'm just going to remind you of some basic facts. So this is probably the most opportune time for questions on this mixing process and the thermodynamics of mixing ideal gases.

Now there's a chat. Again, I'm very slow on the uptake when it comes to chats when I'm lecturing-- so much work in this circle. Well, it took five weeks. If not, then let's remind ourselves about how to balance chemical reactions. All right, here we go-- balancing chemical reactions.

So, for example, a gas-- sorry, give me one second. I want to remind you of something. Not a reminder, it's a public service announcement. Here's a PSA. PSA-- can ignore fugacity in Denbigh. It's the only count against using Denbigh at this point in this class is that Denbigh admits to the existence of something called fugacity. Fugacity is the same as activity. We haven't gotten there yet.

Fugacity is a chemical engineer's term. Activity is a material scientist's term. They have the same meaning. And as I said, we haven't gotten there yet. And you can completely ignore the discussion of fugacity in that relevant chapter of Denbigh. Don't let it trip you up. Don't sweat it. And you got to remember-- public service announcement.

OK, back to balancing chemical reactions. So let's have a gas phase reaction $A + B \rightleftharpoons 2C$. Everything's gases. So the reaction balance can be written in another way. $0 = 2C - A - B$. And so this is pretty familiar.

The only-- here's something new, but it's not that new. We're going to use stoichiometric coefficients. We're going to define them here. Plus, this defines stoichiometry coefficients ν_i . So maybe you've seen this before. Maybe you haven't, but it's a pretty simple concept.

This way we can just generalize. So we have these stoichiometric coefficients $U_{sub\ i}$. The $U_{sub\ i}$'s, they come from conservation of atoms, balancing chemical reactions. Conservation of atoms-- and by convention, $U_{sub\ i}$'s are less than 0 for reactants because they're consumed. And $U_{sub\ i}$ is greater than 0 for products because they're created.

So that's balancing chemical reactions. And I want to just remind us. When we see this, this is what we should think. We should think-- well, let me not use a bunch of different colors-- we should think of at some fixed temperature and pressure of volume of A, A, A, A, A, A, B, B, B, B, B, C, C, C. This is meant to be more gas molecules in a box.

This isn't I took A and B, and it went totally to C. We'll actually see that never happens, except in 0 Kelvin. Instead, it's a system that's fluctuating back and forth. Reactions go to the right. Reactions go to the left. Nature doesn't care what you wrote in the left-hand side.

You could have easily written $2C$ equals A plus B . Nature doesn't care. It's a reacting mixture of gases and, in our case, at a fixed temperature and pressure. So that's a little bit about balancing chemical reactions. Let's keep going.

We have constraints on the $d n_i$'s. If you remember, dG at fixed temperature and pressure equals $\sum \mu_i d n_i$. The total-- all the changing in Gibbs free energy at fixed temperature pressure comes from changing of mole numbers. It's going to come from these reactions as some components are produced and other components are consumed.

So we want to figure out what are constraints on the $d n_i$'s. And I'll just write this down for the reaction, which we saw in the previous slide-- $d n_A$ -- it's not meant to be DNA, like dinucleic acid. It's just $d n_A$. Here is $d n_V$ over ν_V equals $d n_C$ over ν_C . So this is just true in general for any chemical reaction. The term $d n_i$ over ν_i are constant.

And this defines for us a new variable. It's just C , which is the reaction extent. So it's a unitless, generalized parameter to describe whether the reaction runs a little bit to the left or a little bit to the right. And maybe some of you have seen this before, and probably most of you have not.

So this is a series of $M - 1$ equations in M variables. M here is a number of components in the reaction-- A, B, C, three components. How many equal signs? 1, 2. $M - 1$ equations in M variables-- what does that mean?

If I have $M - 1$ independent linear equations and M variables, how many independent variables do I have? Linear algebra again-- how many independent variables do I have describing the change in moles as this reaction proceeds?

AUDIENCE: One.

RAFAEL JARAMILLO: One. One independent variable, that's right. So instead of having to sum a bunch of different $d n_i$'s on the right-hand side of my expression for dG , I can simplify and have only one. And I think you probably have an intuition for that.

If I have a reaction, it can go to the right. It can go to the left. It's like one variable. There's sort of one variable that tells you what's changing. It can go to the right. It can go to the left.

So that comes out in the analysis, one independent variable. So, for example, I can express dn_A as $\nu_A d\xi$ over $\nu_C d\xi$. And I can express dn_B equals $\nu_B d\xi$ over $\nu_C d\xi$ and write dG totally with respect to $d\xi$. That's just an example. I can eliminate n_A and n_B and write the differential of Gibbs free energy totally with respect for one independent variable.

So again we're back to counting independent variables to set up problems. All right, another concept from introductory chemistry-- coupled reactions. Coupled reactions-- so, for example, 4 ammonias is plus 5 oxygens can turn into 4 nitrous oxides plus 6 waters. I'm going to call that reaction 1.

And that is the same thing as 4 ammonias splitting into nitrogen and hydrogen. I'll call that reaction 2. 2 nitrogens plus 3 oxygens becoming 4 NO molecules. I'll call that reaction 3. 6 hydrogens plus 3 oxygens-- did I get my numbers right here or did I not-- becoming 6 waters. And that is reaction 4. And reaction 1 is simply the sum of reaction 2, reaction 3, and reaction 4.

This is a reminder of how you can break down chemical reactions into subordinate reactions. Why am I telling you this? I'm telling you this because of thermodynamics, of course. The overall change in state variables is the sum of changes between intermediate states. This is super useful. And, again, it's introductory chemistry, so this hopefully is a reminder.

So, for example, ΔG for equation 1-- reaction 1, I should say-- is the same as ΔG for reaction 2 plus ΔG for reaction 3 plus ΔG for reaction 4. And this is something that you'll use on the p set. And preview for next time-- each reaction obeys its own equilibrium balance. And we will talk about equilibrium balance on Monday. So that's it for today.