[SQUEAKING]

[RUSTLING]

[CLICKING]

RAFAEL JARAMILLO: So we've motivated solution modeling. And now we're going to start to see how it's done. So this is the outline of today's lecture because we're going to cover a lot. I don't mind covering a lot here. It's covered well in the text as well. So this is basically a-- I'm being a tour guide here.

So we're going to start by introducing the ideal solution model. Then we're going to talk about nonideal solution models. We're going to talk about two particular types of nonideal solution models, dilute solution model and regular solution model. And I hope folks are ahead of me and have read chapter 8 in the book. And if you have, it will help.

I flipped this upside down-- better. OK, so let's talk about first ideal gas solutions. We've already done this actually. We've already done this. Ideal gas solutions, we have pure A at temperature, pressure, and some volume. And we have pure B at some temperature and pressure-- same temperature same pressure-- and a general different volume. And we mix them.

And if these are ideal gases, PV equals nRT tells us that we get A and B at the same temperature, same pressure, and a total volume that is simply the sum of the two volumes. So this is for ideal gases, all right. So we know this.

And we've seen that we can model this process, this process of making the mixture, as an isothermal, an isothermal expansion for each gas. So we've seen this. And this is the result that we got. Isothermal change in chemical potential is molar Gibbs free energy.

That means the total change in the chemical potential of each component throughout this process is going to be the integral of its partial pressure times v. And making this a little bit more explicit, this is from P to P sub i, dP dummy variable, RT over p. And this equals RT ln partial pressure of i over the total pressure. We already worked on this. We derived this already. And this is the change of chemical potential for isothermal expansion.

This is also-- and here's the new part-- this is also delta mu of i for the mixing process. Well, that's actually not new. We use this in the previous unit on reacting gas systems. But we're going to really focus on this. This delta is now going to correspond to the mixing process. So this is delta for the mixing process.

OK, so what is the Gibbs free energy of this mixing process? We know how to write that down now because we've done the rudiments of solution modeling. It's the sum, weighted sum by mole fraction of the partial molar property. And we just take from the previous board.

So what we're going to do is we wrote down-- sorry about that. We wrote down the partial molar properties, the partial molar Gibbs free energy-- that is the change of chemical potential with mixing. And now we can write this using the formulas that we already have seen.

So it's a sum of the mole fractions and the partial molar property. And we just borrow from the previous slide. This xi R of T log P of i over P. And we're going to use Dalton's rule to re-express the arguments in the log as a mole fraction. And so this is a solution model. We've talked about solution models. But we haven't actually seen one written down mathematically before. So this is one. This is actually an important one.

So let's graph this and see what it looks like. So in a graph delta G of mixing-- and the first thing is that it's strictly negative. And you can see that by the log expression. Mole fractions are less than or equal to 1. So this sum is less than or equal to 0. And so that's an important thing to observe. You have a family here with increasing temp.

So the first thing to observe here is that there are very few parameters in this model. This is a composition, x sub i. And there's temperature. And that's it. So if I plotted this solution model versus composition, I'm going to have a family of curves in varying temperature.

And the way this is going to work is with increasing temperature, delta G mix gets more negative. So we're going to note that. Note, delta G mixture is less than 0, and d squared delta G mix dx2 squared is greater than 0 everywhere. So that is, its negative and it's curved up everywhere.

And what we're going to see in a couple lectures is mathematically, this ensures that the mixing is always spontaneous. Which is good because we expect that to be the case for ideal gases mixing. This goes back to the baby book.

When you have these two populations of gas molecules, and they don't interact with each other, then you remove the barrier between them, you expect them to mix spontaneously. And that's what this math is enforcing. So, OK, so now what we're going to do is we're just going to abstract this a little bit and call everything we just did the ideal solution model, the ideal solution model.

And we can write it down very compactly. So this model, it's motivated, motivated by or derived from ideal gas mixing. But it approximates a broader class of real-world systems.

So this is very typical in science. You have some simple case. You treat it as a model system. You develop the model. You study the model. And then you say, oh, well maybe this model applies elsewhere. Maybe it does. Maybe it doesn't. So here are some properties of the ideal solution model-- the partial molar entropy of mixing.

We can get this from the combined statement. And this derivative is really easy. It's just a partial with temperature of this thing. And we have minus R ln x sub i. And this is everywhere positive. That's good. So entropy of mixing is positive.

Another thing which we have, the partial molar volume of mixing-- and, again, we get this from the combined statement, going back to chapter 4 in the text. And there's no pressure dependence here. There's no pressure dependence in this model. So there's no volume of mixing. That's good. That's what we expected.

What about the enthalpy of mixing? This is delta mu of i minus T delta S of i, going way back to the definition of our potentials. And if you write this out, you see that 0. And likewise, the partial molar energy of mixing equals the partial molar enthalpy of mixing minus P and the partial molar volume of mixing. And that's also 0.

So this is simply using the stuff, which we did a couple of weeks ago, definitions of these potentials and the combined statement of the first and second law, and applying those operations to these quantities in mixing. And I encourage you to work through these on your own.

And so the results here are what we want. That's what we want to see. What, the entropy increases on mixing. So this is a process driven by entropy increase, which is-- we postulated that back in lecture 1 with a baby book. There is no volume of mixing for ideal solutions. The final volume is sum of pure component contributions.

That's good. And there are no interactions between molecules. That was the foundation of the ideal gas molecule, right-- no bonds made or broken by the mixing process, no change in enthalpy for energy. So what we're seeing here is, again, what we intuitively have known now for weeks. We're just seeing it in this formalism. OK, so this is the ideal solution model. Great, let's move on.

STUDENT: I have a quick question, sorry.

RAFAEL JARAMILLO: Yes, please.

STUDENT: Is there a reason why we write the bar for entropy, enthalpy, et cetera, but then we don't write the bar for the mu's for the chemical potential?

RAFAEL JARAMILLO: Yeah, Gibbs is special. And the reason-- the chemical potential is the partial molar Gibbs free energy. We don't have a special term for partial molar entropy, partial molar volume, partial molar H, and partial molar u. It's just, historically there's not. I mean, you could imagine coming up with new words and using different Greek letters.

But Gibbs is so important that the partial molar Gibbs free energy has been named chemical potential. And so it's special, good question.

STUDENT: OK, thank you.

RAFAEL JARAMILLO: Yeah, Gibbs is special. OK, all right, so what happens if the molecules do interact? What happens if we're not mixing ideal gases? Well, we want to capture the deviation. We want to capture the deviation from the ideal model. And what you're about to see is a very familiar thermal thing, which is more bookkeeping.

Your pattern recognition might start kicking in soon that this is a thermal thing. This is what thermodynamics does. We let delta mu equals R of T log of A of i-- I'm going to introduce that in a second-- equals RT log gamma of i x sub i. Just bear with me. These are just definitions. A i is being defined as the activity of component i. And it's further defined by the product of gamma of i and x sub i. And gamma of i is known as the activity coefficient of component i.

And why do they do this to us? What is with all these terms? If we rewrite delta G of mixing in terms of these activities and activity coefficients-- let me just pull what we know to be the case. This is x sub i delta mu of i equals product of i x sub i RT log gamma of i x of i.

And we're going to use the property of the log function. And we're going to see that this turns into x of i RT log x of i plus x of i RT log gamma of i. So the reason why they do this to us is because when we model solutions in this particular way, we have this neat separation between the ideal case and deviations from ideal, deviation from ideal.

And we can see that nonideal behavior is captured by gamma of i not equal to 1. So if you have ideal solution, ideal behavior, the activity coefficients of all the components is 1. And this thing, which we call the activity, is just equal to the mole fraction.

And if the solution does not behave ideally, if it deviates, we just dump that deviation into this term over here. And we say it's captured by these activity coefficients being not equal to 1. And we can figure out what they are later-- so, again, just a bookkeeping exercise at this point, and also introducing essential terms.

Now, this activity, if you're in course 10, this is equal to fugacity. And that's not exactly true. Fugacity sort of is activity in certain cases. But, anyway, if you've heard that term fugacity, or you wondered what it was when you were reading the Denbigh book, here effectively we have it. It's the activity.

And so we now have this mathematical framework to capture nonideal behavior. And so what we're going to do next is introduce two solution models for nonideal solutions. The first one is going to be the dilute solution model.

OK, so this is the dilute model. It's based on some physical reasoning, which is always a relief after all this math-- so we have solvent and solute. OK, so what does dilute mean? Not concentrated. So these are the assumptions. We're going to make two assumptions about these physical systems-- one, each solute molecule is surrounded by solvent. And solute-solute interactions are negligible.

So this has physical implications. So this is like, someone drops you in the middle of the woods very, very, very far from civilization. And you start acting the way you do when there's no one else around. And there's not a chance of you running into somebody. And however you act, that's up to you. But this is the point. You are acting as if there's not another soul on Earth. You're in the middle of the woods.

And now let's say that somebody else gets dropped into the same woods 10 miles away. All right, that person will also act as if there's not another soul on Earth, however they act. And if we populate the woods in this very dilute way where there's not anybody within miles and miles and miles of each other, then each individual person will act as if they're the only person in those woods until we get to a point when they start becoming aware of each other.

And just as you might if this were you in the woods, if you started becoming aware of somebody else where before you didn't think there would be anyone else, your behavior might change a little bit. It's the same with dilute solutions. We're in the dilute limit when each solute is acting as if it's the only one, completely surrounded by solvent, and all of its thermodynamics are dominated by solute-solvent interactions.

So that's the first assumption and the second assumption is that each solvent molecule on average on average is surrounded by pure solvent, and therefore act like a pure substance. So this is a little bit harder to justify. And actually, on the P set, we asked you to take this and justify this. We don't put it that way. We'll cover that in three minutes. But, effectively, what you're asked to show on the P set is that given this, this follows.

So, yeah, there's some solvent molecules here that are near solute. And, yeah, they know that there's solute. But if you averaged over all the solvent molecules, the average solvent molecule is surrounded also by only solvent molecules. So these are the physical assumptions. And so here are the mathematical implications of that.

So assumption number 1 leads to something called Henry's law, Henry's law of the solute. And that's the following. In the limit of mole fraction x_2 going to 0-- so the second component here is the solute-- the activity of component 2 approaches this quantity, where gamma 2 0 is called Henry's constant.

This mathematical form results in what we want, which is that thermodynamically, each additional solute molecule thinks it's the only one in the forest. Assumption number 2 has the following implication called Raoult's law of the solvent. And Raoult's law of the solvent is that the limit of x_1 going to 1, that is the solvent becoming increasingly concentrated, the activity is simply equal to the mole fraction.

So these are Henry and Raoult. I don't know whether they were contemporaries, whether they were BFFs or whatnot. And I have a really hard time remembering which one is which. Just a note for the P set, this can be derived from Henry via Gibbs-Duhem integration which is discussed in detail in section 8.20.3. So that's relevant for the P set-- Raoult's law solvent, and Henry's law of the solute.

All right, so let's plot how those look. Variation of activity with composition, it could look like this. This is an example. And I'm just going to copy this figure from DeHoff figure 8.4, because I think it's useful. So I'm about to copy here. All right, so it could look like this.

What I'm trying to plot here is as a function of x of 2, the activity of the first component and the activity of the second component. So this goes between 0 and 1. This goes between 0 and 1. On this plot goes between 0 and 1. It doesn't have to. You can have activities greater than 1. But we're going to keep it simple here.

And so the ideal solution model is that. Those are the ideal model, slope minus 1, ideal; slope, 1, ideal. So the ideal solution model is like that. Henry's law here is going to have a slope not equal to 1. So this is a slope of gamma 1 0 Henry. And, similarly, we can have some slope gamma 2 0, and this is Henry. That's Henry.

And the reality could be something like this. When x_2 is concentrated, x_1 is dilute. And you start up Henry's law there. And then it deviates. And at some point, you asymptote, so Raoult's law. So this might be reality. There's lots of different ways that this could shake out.

But as drawn here-- and, again, you have for dilute x_2, you start along Henry. And then at some point, asymptote Raoult's. So this could be what you get. All right, Raoult's law, Henry's law; Henry's law, Raoult's law, and one implies the other.

All right, so that's dilute solutions. And I ask you one problem on dilute solutions on the P set. We're not going to spend a lot of time on dilute solutions in this class. The reason why we took this time, these 15 minutes of lecture and a little bit of time on the P set, is to set you up, for those of you who are going to do aqueous chemistry or electrochemistry. You'll want to know this. So that's why we did that.

There is another type of solution modeling, which is much more useful for 3.020. And those are called regular solution models. So these are models that we're going to spend the next couple of lectures on, at least the lectures that are new material. And you spend more time on the P sets on.

So regular solution models are like this. We also start with some physical assumptions, and then we develop the implications of that-- one, the entropy of mixing. The entropy of mixing is captured by the ideal model delta S mixed ideal. That gets a little bit fuzzy over there. I'm sorry for that.

OK, so we're going to assume that the ideal model captures the entropy of mixing. And as we'll see later when we do statistical thermodynamics, we will show later that this is what's called configurational entropy. Configurational entropy is entropy associated with the spatial configuration of things. And, again, you can recall the pictures in the baby book, mixed up in this represented by where things are in space. So that's configurational entropy. And that's the ideal model.

But we're also going to allow intermolecular interactions. Intermolecular interactions are nonzero or finite, I don't know-- exist. So there you have it. What that means is going to be this, nonzero enthalpy of mixing.

So in this model, when you make a mixture, some bonds are made. Others are broken. And there's going to be an energy cost to that. So this is what we get. We get delta G of mixing equals delta H of mixing, general nonzero, minus T delta S mixing where this is ideal. That's ideal. And that is equal to the following. OK, so this is what's called a regular solution model.

And I'll give you one more piece of information, which is the simple regular model. The simple regular model is the simplest case of regular solution models for binary systems. And we can write it down really easily. This is it. Delta H mixing equals a0 x1 x2. So it's a model with one parameter. It's a mixing term parameterize by a0, which typically has units in joule per mole.

If A0 is greater than 0, this is an endothermic mixing. Endothermic mixing, we have to put in heat energy. So maybe some bonds are broken. The molecules end up in a higher energy state. In less than 0, this is exothermic mixing.

OK, and so with that model for the enthalpy of mixing, we have the full solution model, which is a0 x1 x2 plus RT sum i x sub i natural log x sub i. OK, so this is the simple regular model. And we're going to spend some time on this. You're spending some time on the P set.

Yeah, it's got two parameters. It's got enthalpy, a mixing parameter. And it's got temperature. And from these two parameters, you can generate a nice diversity of physical behavior. And we'll see that in the weeks ahead.

OK, today's lecture covered a lot of essential information. And I went rather quickly. So I have plenty of time for questions. And I will keep the recording on for some time now and then switch it off at 10:55. And before we start that, I'll remind you my office hours have switched to Wednesday at 12:00. So that's in about an hour, an hour and 15 minutes from now. Office hours switched to Wednesday at 12:00.

And there's a very slightly revised syllabus for thermo. None of the due dates change or anything like that. It doesn't really change your life substantially. But it is a little bit of a more accurate view of where we're heading in the next couple of lectures.

The exam is Monday. And it will cover unary phase diagrams and reacting ideal gas mixtures and the rudiments of ideal solutions. But none of this really involves solution modeling apparatus that we're working on now. What that means is that the P set that's due on Friday is only minimally covered on the exam. So you can focus on slightly earlier material for the exam-- exam Monday.

And we will get new thermo next Wednesday-- not this Wednesday, but next Wednesday. And what is that, the ninth-- is that the ninth-- next Wednesday, 4/9. this Friday-- sorry, next Friday. This Friday, we're going to work some problems. And then I guess it will be new thermo. But we're going to walk through the Nernst equation just for your own curiosity and interest. That won't be tested or covered formally in this class.

And then Monday is the exam. And then Wednesday we're going to talk-- we're going to spend an hour talking about social implications of material science. And so we won't really see new, hard-core course content until next Friday. OK, this is time for questions.

STUDENT: Can you explain the delta H of mixing and how you got that?

RAFAEL JARAMILLO: Yeah, so the way I got it is I just told you that's the model. It doesn't apparently come from anywhere right now. But I'm glad you asked because we do have something called-- here, let's do this.

OK, that's basically what asked. And the answer is that you can say, oh, it's empirical. I made a bunch of measurements and this fit the data. And, historically, that's probably the most accurate answer. But it also comes from something called the quasi-chemical model. And we are going to, I believe next Friday, start right here where we try to justify that.

And as a preview, what we do is we imagine-- green and red, this is never good. Red and blue is OK. We imagine atoms or molecules on a lattice like this. I'm not drawing a nice lattice here. We imagine molecules on a lattice where we have two different components on the lattice.

And we say, OK, all the energy is nearest-neighbor bonding. So we have blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue, blue-blue blue-blue, blue-blue, blue-blue, blue-blue. This is a lot harder to say this over and over again than it would seem. And, oh, here we've got some blue-red bonds. And just for completeness, let's say I have a red over there. There's a red-red bond.

And what we're going to do is we're going to count up these bonds. And we're going to do some combinatorics. And we're going to end up with this expression. So it does come from somewhere. I would be willing to bet a cup of coffee that historically it comes from empirical data, comes from data and fitting and people making reasonable guesses as to what empirical-- what model will empirically fit the data. And then at some point somebody worked out this model and said, oh, this is neat. This justifies what we've been using all these years-- forgot a blue-blue. Does that help?

STUDENT: Yeah, thank you.

RAFAEL JARAMILLO: How would you get that? How would you get that? Well, you'd have a beaker. And you would have inside of that beak-- it doesn't have to be a beaker. It can be a crucible or anything. And inside of that you'd have another little beaker or crucible. And this beaker would be full of something which has a large heat capacity like water. And it's easy to measure the temperature of this thing. So you've got a thermometer in there. So we've got a big thing of water and we've got a thermometer in there.

And what we're going to do is we're going to make mixtures. So we're going to take some of A. And we're going to take some of B. And we're going to add them-- just mixing up my colors here-- we're going to add them in in different quantities. And we're going to end up with different solutions in this little beaker.

And we're going to measure the temperature rise. And so for every composition that I have, we're going to have something like this. We're going to have x of A, x of B and a temperature rise. And we measure. Let's see, 0.99, 0.01, 0.98. We're doing a bunch of experiments, right.

And I'm going to have numbers for temperature rise. Why does that help me? Well, the temperature rose in this big bath of water. So I can estimate the heat evolved from this mixing process because I know the capacity of water. So the heat evolved are going to be numbers. And then I can say, oh, well this is a constant pressure process. So heat and enthalpy is about the same.

And, OK, I can model the heat evolved is a function of composition. And maybe it fits this functional form. That's how this actually would go. That's how this actually does go when we do calorimetry in the lab. This isn't like stuff relegated to the distant past. I mean, we do this every day in the lab, especially those that have been focused on thermochemistry and such things, so.