[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK. So here we are. We're just starting. Yeah, we're a bit late. OK. So today, we talk about liquid-vapor equilibrium in mixtures. We have seen something already when we did the Gibbs phase rule.

And you remember that if we have-- if we consider the list of these properties like temperature, pressure, the compositions of, say, two phases-- for example, a liquid and a gas phase, depending on how many components you have-- r is the number of components-- plus 2 minus the number of phases, this was called the variance, namely the number of these variables that are independently changeable so that you remain in the same kind of equilibrium.

Like in this case, we are talking about liquid-vapor. But we also talk a little bit about solid-liquid. And you could also do it for solid-vapor and so on. Of course, the chemical potentials, as usual, will play a major role, as they did in order to derive the Gibbs phase rule.

So the first result that we want to derive is the Raoult's law. Raoult's law has to do with-- and we'll do it for the simplest situation. So the simplest situation will be one like-- one of these two cases. This one is a liquid. It's a liquid solution with components 1 and 2.

For example, you can think of water as being component 1 and 2 could be salt. So this is salt water. And it is in mutual equilibrium with the gaseous phase, in which there is also water, so 1. And there is another component, 3. For example, it could be air because humid air-- air has some humidity. And humidity is water vapor. So this is, for example, salt water and humid air, moist air in mutual equilibrium.

We are considering the case that-- we will do this as a major example-- in which the other component-- in this case, air-- so the molecules of oxygen and nitrogen in air are non-condensable. So you do not find them in the liquid phase. And conversely, the other component in the liquid phase, salt, is non-volatile. So you don't find it in the vapor phase.

That means that, for mutual equilibrium, it is required only that the chemical potential of the component that can be exchanged between the two phases be equal. So it means that the chemical potential of water in the liquid must be equal to the chemical potential of water vapor in the gaseous phase.

And this is one example. The other is liquid over a solid. So again, think of water and salt. And this is ice. So again, salt, we assume, is not freezing. So it's a solute of the liquid solution, but it doesn't freeze. And therefore, we need only equality of chemical potential of component 1 between this and this. And this actually is not a mixture. It's just a pure component. I mean, this is just pure ice.

And of course, this example is very practical-- for example, when you put salt on the sidewalks for avoiding freezing, for changing the temperature at which freezing occurs. And this is also you put salt in water. And that will change the boiling point of the solution. So when you make pasta and you have salted your water, the boiling point is not 100 degrees Celsius. It's just a little bit more, depending on how much salt you put.

So how do we derive Raoult's law? As usual, we only need to apply the equality of chemical potentials, and then manipulate the equations somehow. So let's say that we have two phases that, for a moment, we call A and B, just generic two phases. So the chemical potential of component 1 in phase A-- you're going to assume, to derive Raoult's law, ideal mixture or solution behavior for all components-- or actually, for this component, not for all components, for this component.

And so this is the pure-- phase A pure component 1 plus RT, the log of the mole fraction of component 1 in the phase. And then we rewrite the chemical potential at pressure p. We rewrite it by integrating the derivative of the chemical potential with respect to p from p to p-sat, p-sat being the saturation temperature (I meant saturation pressure) at which the pure substance at that temperature changes (phase), or boils, or freezes.

So we rewrite this as chemical potential at another pressure. And we pick the saturation pressure. And then we integrate the derivative. And remember, the derivative is just the specific volume. And then we do exactly the same also for the other phase B, just change the A's in B's.

Then we recall that when we have a pure substance-- this is the reason why we decided to use the saturation pressure. When we have a pure substance, the saturation pressure is defined precisely by that pressure at which, at the given temperature, the two chemical potentials of the two phases are equal, so they are in mutual equilibrium.

So liquid and vapor, for example, at the boiling point, have equal temperature, equal pressure, and equal chemical potential. But the three are not independent. And the equality of chemical potential defines the saturation pressure at that temperature.

So that means that this and that cancel because they are equal. The moment we equate the two chemical potentials. These two will cancel. And we are left with just the remaining terms. And so these remaining terms. The part with the logarithms that we put together. The logarithm becomes the logarithm of the ratio of the mole fractions. And the integral, you can put it in this form. It's the integral of the difference between the specific volumes of the pure phases, pure substance in the two different phases.

So this is what you would call vfg, for example, or vjf. It's the volume of vaporization or freezing and so on of the pure substance. So this connects the compositions of these mixtures to properties of pure substances.

For example, if we take this case, where we have moist air on salted water, then, for air, we can assume-- for the specific volume, we can assume the ideal gas law. For the liquid, we can assume-- liquid water-- assume incompressible fluid model so that the volume is constant, specific volume is constant.

Remember, these are molar specific volumes. And then you do the integral here. So do the integral for the-- this is the part contributed by the fact that the volume is constant. So it's just the difference of the limits of integration. And the other is you integrate dp over p so you get the logarithm of p. So this is the result.

Now, it turns out that this term here is much smaller than 1 and therefore much smaller than this other value, which is the logarithm of-- RT times the logarithm. So if you neglect that-- and you can compute it and find that, for example, even for very high pressures and normal temperatures for liquid water and typical temperatures, this is of the order of less than 1/100, which is definitely enough lower than 1 to be negligible.

And so you neglect that. If you consider that, it would be called what is called the Poynting effect, the Poynting contribution. So what we are doing currently is normally described as neglecting the Poynting correction. And Poynting is the name of a person.

So the end result-- this is a square bracket too many. We find that log and log can go away. And you get that the ratio of the mole fraction of water in the air-- so that's the moisture content-- over the mole fraction of water in the solution. And here it is a solvent. So it's the predominant.

You could also apply it for pure water. In this case, y1f is equal to 1. Then that is equal-- and this is Raoult's law-- to the ratio of the pressure over the saturation pressure of pure water. This is a formula-- You can also remember then that since for an ideal gas mixture-- ideal Gibbs-Dalton mixture of ideal gases the partial pressure of the component is equal to the mole fraction times the pressure of the mixture. This can also be written as the partial pressure. And so the partial pressure of the component 1 in the mixture is equal to the mole fraction in the liquid times the saturation pressure of component 1.

If you apply the same formula here, equation 1, for the case of liquid and solid-- f and j for solid-- so that means ice-- both the volumes can be considered constants. So they get out of the integral. And so you have the difference. So the volume of freezing, the change, that little change in density between pure water and ice that makes it so that ice floats on water, that's the volume of freezing.

And so Raoult's law takes this other form. So it gives you the mole fraction of water in the solution in terms of the difference in pressure. Saturation pressure this time-- this is the saturation pressure, of course, of the liquid-ice transition-- times that volume of freezing divided by RT. So with this, you can compute these relations. And these have to do with the phase rule. For example, in this case, we have-- since it is a binary mixture, it has just two components.

Of course, the second mole fraction is 1 minus the first. And so you have one relation between these two and the same, another relation between these. And then we have the relations between the chemical potentials that remove two other relations. And so you are left with the fact that the moment you fix the temperature and the pressure, everything is set.

So the mole fractions are fixed, like here. You cannot change arbitrarily the mole fraction and still stay in mutual equilibrium. And here also, you cannot-- the ratio of the mole fraction of the liquid and the vapor is fixed by the given temperature and pressure.

You can interpret, in a molecular way, the Raoult's law. See, Raoult's law says, for example, here we are considering a different situation than the one before in which not only component 1, but also component 2, can go-- can cross phase. For example, in the fg case, it can be both volatile and condensable.

This would be, for example, wine. Wine is a solution of alcohol and water. And when you boil that, you'll get a vapor in which you have both alcohol and water. But they are in different compositions. So when they are in mutual equilibrium, the mole fraction of alcohol in the liquid phase is different from the mole fraction of alcohol in the vapor phase.

So Raoult's law gives you-- which is written here again-- partial pressure of, say, water is equal to the mole fraction times the saturation pressure. And if you have two components, you have to Raoult's law, one also for the second component, because now also component 2 can be exchanged, you should write also the equality of chemical potential for that component. So you get the second equation.

And you see here the idea, the molecular interpretation, is this. And if you have a pure substance at equilibrium, there is somehow an exchange-- an equilibrated-- a balanced exchange of molecules that are in the vapor phase that go down in the liquid and an equal amount of molecules that, from the surface of the liquid, go up in the vapor phase. And this is for component 1. And this is for component 2.

Now, when you have a mixture, you see that, on the surface, you have some dark and some gray particles. So this dynamic exchange that occurs between the liquid and-- occurs only proportional to the amount of dark particles for the dark ones that are on the surface.

So if you assume that the fraction of particles that are on the surface is equal to the mole fraction in the liquid phase, then you see that the partial pressure, which is driving this exchange with the black particles, is only limited by a fraction, which is the mole fraction, by the fraction with which they occupy the surface and equally the other ones. And therefore, since the pressures add up, that's the relation. And that is one way of interpreting this.

In any case, when we have the two Raoult's equations, we can usefully combine them by using the obvious fact that the mole fractions add up to 1. So for example, I could add this and that. If I add these two, you see y1g plus y2g is 1. So I'm remaining with p. So I obtain this pressure-- this expression that the pressure is equal to this plus that.

And of course, instead of y2f, I write 1 minus y1f. This is called the bubble line. It expresses, for a given pressure and temperature, the composition of the liquid phase. So if I give you the temperature and the pressure, you can compute the mole fraction y1f because you can go on the tables of the pure substances for the p-sat of the two substances. And then with this equation, you solve for y1f.

Or, if you solve this equation for y1f and y2f and then sum up so that it's equal to 1, this is the other expression that you obtain. This is the dew line. It contains the relation that gives you-- that allows you to solve for the mole fraction of component 1 in-- so the composition of the vapor in the two-phase state.

And of course, once you have the bubble line, this is really an equation of a line. So you see that if you plot pressure versus mole fraction-- in this case, we're talking about-- if you're doing this equation here, it's the mole fraction of the liquid. You get this straight line that we call the bubble line. An so for a given temperature and a given pressure, you go here and read the mole fraction of the liquid.

The dew line is not a straight line because it's 1 over p that is linear in y. So it has this shape. And so for that temperature and the given pressure, you go down here and read the mole fraction of the vapor. Of course, you can eliminate pressure from the system of these two equations. And then you get a direct relation between the composition of the vapor phase and the composition of the liquid phase, where what counts is the ratio between the saturation pressures of the two substances, which is called the relative volatility.

And here is a plot. So this is y1f. This is y1g. And this is how that equation looks. Of course, remember that here, if we have written this for both substance 1 and substance 2, it means that we have assumed that at all compositions, the liquid behaves as an ideal solution, as an ideal solution, yes.

And so this is a very strong assumption because most liquids do not behave like that. But still, this is a starting point. So that's how the bubble line and the dew line look for an ideal model, a completely ideal model.

And that is enough to give an idea of what is done when we do distillation. You see, this plot is done at constant temperature because it's easy, because you fix the temperature. You go and read the saturation pressures from these lines. Of course, I can do also numerically a plot in which I fix the pressure, and then for each temperature.

So if I fix the pressure for each temperature, I have to go and read the values that will give me the mole fractions. And I do a plot. And a plot will generally not produce straight lines any longer, if it is a plot at fixed pressure. This is more useful because mostly you boil things at a fixed pressure.

So here is the idea. So we've got the bubble line and the dew line, sorry-- the dew line here and the bubble line here. So suppose you start with a mixture in the liquid phase at this composition, say 50/50. And I heat it up. At a certain point, I reach the bubble line. And the first bubble gets boiled off.

That bubble is in equilibrium with my saturated liquid and has a composition, which is here. It has a different composition. And we compute it by that formula that we have derived based on the relative volatility. Of course, you can express the relative volatility as a ratio of pressures. But it's also related to the ratio of the saturation temperatures because this T-sat of p is the inverse function of p-sat of T.

If I keep heating up-- for example, I have an equilibrium at this temperature. And for an equilibrium at this temperature, the bubble line gives me the mole fraction of the liquid. And the dew line gives me the mole fraction of the vapor, again following this expression. If the temperature goes up to here, I have saturated vapor, which is in equilibrium with the first or, say, last drop of liquid, so this is saturated vapor. Then if I still heat it up, it will go up.

So the idea is this. If I start with a composition like 50/50 and I want to separate, what I could do is to go up to this temperature here, like an intermediate temperature between the temperature-- the saturation liquid temperature and the saturation vapor temperature.

And notice that whereas for a pure substance, the dew line and the bubble line coincide and there is only one temperature at which the pure substance becomes liquid and is also saturated. So this lens-shaped thing will reduce to just a line.

But here, the boiling occurs over a range of temperatures between this and that. This is not only for liquid and solid. For example, in also metals, if you go metallurgy, this would be solid, this would be liquid, and this would be the "solidus" temperature. And that's the "liquidus" temperature. And this gap is like here.

OK, so let's say we put the temperature-- we added the temperature intermediate between the "liquidus" and the "vaporus," so to speak, temperature. Then you see that the two phases are one enriched in component 2 and the other enriched in component 1. So this is what happens in one stage of a distillation column.

Then what you do is you take the liquid and you send it down to another stage, which works at a different temperature. And then you take the vapor and you send it up to condense into the upper stage and so on so that eventually you can-- since in the upper level, you collected a mixture, which is more rich in alcohol.

Then you could play the same game, go to an intermediate temperature, like this one. And then you generate an even more enriched vapor and so on. You can continue as much as you need in order to obtain up to 99%. For example, this is how they get 96 volume percent alcohol that is used to make liqueurs.

All right, so this is for the distillation principle. Now, another thing that can be explained by Raoult's law is, as I mentioned, this idea that-- this fact that when you add salt on water, that water will freeze at a lower temperature than 0 Celsius. Or when you add salt in water, that water will boil at a higher temperature than 100 degrees Celsius.

How do we derive that? OK, we start from the Raoult's law for the specific case. So this is the Raoult's law for the liquid-ice case that we have seen a couple of slides ago. And we take the differential of this. And then realize that when we take the differential of p-sat, we actually-- this is p-sat of the pure substance.

So for the pure substance, we can remember the Clausius-Clapeyron relation that gives you the slope of this curve. On the pT diagram, this is the saturation pressure curve. And the slope of that curve is given by the Clausius-Clapeyron relation. And it is related to the enthalpy of the change of phase divided by the volume of the change of phase. Actually, it should be the entropy of the change of phase divided by the volume. But the entropy of the change of phase is equal to the enthalpy over the temperature of the change of phase.

So you use this in this relation. Neglect this term here, which is good if you have a dilute solution. Therefore, the mole fraction is close to 1. And therefore, the logarithm is close to 0. And you're left with these three terms. Then if you consider that you're not changing the pressure-- so if you remain at constant pressure and change the composition of the solution, this tells you how the temperature will change.

So essentially, from this equation, the p, you can compute the derivative of T with respect to a change of mole fraction of constituent 1. But the change of mole fraction of constituent 1 is also equal to the negative of the change of the constituent 2, in this case the salt. And then you have h and RT.

So in the end, you find that if you add a little bit of salt to the liquid solution, the temperature at which you have equilibrium, therefore the freezing temperature, changes from before by an amount that is related by these things-- RT squared, the enthalpy, so all properties that you can look up for the pure substance with a minus sign. So this is the freezing point depression case.

You can also plot it on this diagram. So if you have a solution-- here, I enlarged this area. So the black curves are the pure substance. If you add a little bit of salt in the solution, then this black curve shifts to the blue curve at lower temperature. And then also the same for the other side, for the other case, liquid over vapor, so boiling of a salted solution.

Here, we have to start from the Raoult's law written for these two phases, f and g, which is this one. Again, we do the differential. Again, we use the Clausius-Clapeyron relation. And again, we obtain a partial derivative of T at constant pressure, how that boiling temperature changes when you add a little amount of component 2, which is the salt.

This time, you have a plus sign. The ingredients on the left-hand side look similar, except that, of course, you have to put here the enthalpy of vaporization, whereas here you have the enthalpy of melting, and the plus sign. So the curve, the shift is on the right. So the boiling temperature is higher.

Actually, these boiling and freezing effects can also be used as means to measure-- are actually used as means to measure the salt content. For example, if you take seawater and if you want to measure the salt content, you run the experiment of freezing it and boiling it. And then with that, you can compute-- you see here, by measuring the delta T, that is related to the amount of salt content. And therefore, you infer from those measurements, these composition and salt content.

OK. Again, the problem is that, of course, ideal mixtures are good models for the gaseous phases, not so good for the liquid phases, and therefore not so good for the liquid equilibrium cases that we are interested in because the reality is more complex than the ideal models.

So we remind ourselves of some results that are useful in any problem with mixtures. They're going to be useful here. And they are going to be useful also from, I think, the next time when we start the systems with chemical reactions. And these expressions are important, namely that the properties are given by the weighted sum weighted on the amounts of the partial properties, denoted lowercase with a single subscript.

And then these partial properties can be related to the specific properties of pure substances if you add what we called the mixing property. But now, what I want to go back to, is this result that we haven't used yet. It's the Duhem-Margules relation that we obtained when we did this for the simple system. It was one of the various, say, byproducts of this derivation.

So the Duhem-Margules relation is this one. And it is important when you try to develop models for non-ideal behavior of the stable equilibrium state properties of mixtures. Why is it important? Because it imposes rules about the interrelations that must exist.

You see, this is a system of equations. It's not just one. There is one for every component. And so it's not that you-- you see, when you want to model properties of substances, you have to come up with correlations for these functions. And you might be tempted to use any sort of analytical form of these interrelations.

But Duhem-Margules says no or, at least, you may try, but you should check the consistency with this relation because not all relations are good for that purpose because some violate this condition. Actually, this condition-- remember that mu i comma j is the derivative of the chemical potential of component i with respect to the amount of component j. And so it is the second derivative of the Gibbs free energy with respect to two different components or also equal components.

Now, you can view this system of equations as a homogeneous system of linear equations in the unknowns, n, where mu i j is the matrix of the linear coefficients. And if you go back into your math courses, you will find that the system of homogeneous equations has a solution only if the determinant of the matrix of the coefficients is equal to 0.

But this determinant-- this matrix is the matrix that we call the Hess because, you see, it's the matrix of the second derivatives. And its determinant is also something that we have encountered. It's the Jacobian of the chemical potentials with respect to the compositions, of course, done at constant T and p. So you need that Jacobian to be equal to 0. So that is the condition. So you cannot arbitrarily select these functions. You have to check that the Jacobian be equal to 0.

For example, as you know, we have decided to call this functional relation the ideal. And in fact, we're going to call this mu i ideal of T, p, and y. This is a particular functional relation. So we have to check that it satisfies the Duhem-Margules relation.

So here is the ideal mixture assumption. So in order to do this derivative, computing this derivative, you have to be a bit careful in doing those derivatives. I forget now if we have done this already. But the key point here is that you have to take the derivative of mu with respect-- at fixed temperature and pressure, so this doesn't contribute. It's only the logarithm of the mole fraction.

So the logarithm of the mole fraction, you have to take its derivative with respect to the nj's. Now nj, it's easier to write it this way. So I'm taking the derivative with respect to nj of the logarithm of the mole fraction. The mole fraction of component i is ni divided by the sum of all the n's. Let's use another subscript, k.

All right, so that means that sometimes you find you have a contribution of the numerator when j is equal to i. And that's why I use the Kronecker delta. And then that contribution is simply 1 over the mole fraction, something like that.

Sorry, not correct. It's n sub i because it's the logarithm. The derivative of the logarithm is 1 over the argument. And then sometimes, the derivative picks up something from the denominator. The denominator, this could be viewed as-- that is a constant. So that is minus log of this. So it would be minus 1 over n. Yeah, so that's written here.

Now that you've taken this derivative, you can substitute into here. So you sum over n and verify that, indeed, that is equal to 0 identically. So obviously, people have been careful in-- people and also ourselves, when we derived this, we did it using the rules of the game. And therefore, it does obey the Duhem-Margules relation.

But when you start correlating experimental data for non-ideal behavior, you have to be careful in cooking up functional relations that are compatible. And if you remember now that-- so here it is. So if we are going to decide to write the actual chemical potential as a sum of the ideal plus an excess.

So in other words, we are going to call excess chemical potential the difference between the actual chemical potential and what is this ideal one. So essentially, we're going to say, for the real substance, for the real mixture, we need to define how the behavior departs from ideal. And this is called excess chemical potential.

Remember also this-- chemical potentials of the pure substance are equal to the Gibbs free energy, to the specific Gibbs free energy. This will come up. Also, since we have defined these properties of mixing, by the way we define them, it turns out that what we decided to call the excess chemical potential is equal to the difference between the enthalpy of mixing and the entropy of mixing multiplied by the temperature.

Not quite, only the part of the entropy of mixing that is not already included in the RT log of y. So you see, here, we call that delta s ex. So it is an excess entropy of mixing because, in the ideal solution, there is a mixing effect that accounts for that. Remember the surprise discussion? It accounts with R log of y. This is the surprise. And this is a part of the entropy, of the mixing entropy. It's the only mixing entropy that we have under ideal behavior.

And you may have some extra, some excess one. So that's why we say here chemical potential excess is equal to the entire enthalpy of mixing because, for the ideal mixture, there is no enthalpy of mixing and only this excess part of the entropy of mixing.

So with that in mind, of course, another thing that we should remember is that the Gibbs free energy, if we are interested in the Gibbs free energy of our entire mixture, that is equal to this. And so if you want, you can also define parallel with the fact that we decided to write the chemical potential as mu i ideal plus mu i excess. You can also plug that into here and obtain an overall mixture, Gibbs free energy as a sum of an ideal part and an excess part.

With that in mind, here is-- for example, for a binary mixture, let's fix these limit for ourselves. Binary mixture, here is the expression for the specific Gibbs free energy. So now, if I take this G and divide it by n, that gives me G over n. Of course, that summation becomes the mole fractions' weighted chemical potentials. And this becomes gid plus gex.

Now, gid is therefore the weighted sum of the ideal chemical potentials weighted on the mole fractions. And the ideal chemical potentials are these ones. So if I take that-- let's see if I can do this game like this. Take the weighted sum of these ones, that gives me g small id.

So you see that in this summation, I have two contributions. One is the weighted sum on the mole fractions of the pure component chemical potentials, which are equal to the pure component Gibbs free energies. And that is this plus this because, in this case, binary mixture, the sum is just limited to two components.

And then I have this other summation that is here. It's RT times the sum of y log y. That's the entropy of mixing, isothermobaric mixing. So that's the gid. And these are the ideal chemical potentials. And then we recall that.

Now, below here, I have listed some of the historical-- guesses or semi-empirical theories that have been developed in order to come up with ways of representing the excess part, so the non-ideal part of the behavior of mixtures.

The simplest one, by Margules-- you see, this is 1895. Yeah, my grandfather was 1889, so he was six years old. So gex is-- so it's assumed to be-- it's like symmetric-- a single parameter which may depend on temperature and pressure. But the dependence on composition is just the product of the two mole fractions.

And if you do the proper derivatives in order to obtain the excess chemical potential that derives from that, you find that the excess chemical potential of component 1 is equal to that function-- to that-- let's call it constant A, constant in terms that it doesn't depend on composition, times the square of the mole fraction of the other component and the same here.

If you go down below here, I have written an expression that we have derived a while ago that relates the enthalpy of mixing to the chemical potential. Now, actually, since for the ideal chemical potential there is no enthalpy of mixing-- OK, if I take this expression here and do this derivative, I obtain-- let's see.

So that's A y2 over T with respect to 1 over T. So it's equal to the chemical potential itself. Yeah, there it is. Because you divide by T and take the derivative with respect to 1 over T, it's just the 1 over T. So the derivative is simply 1. The enthalpy of mixing is Ay2. So in the limit when y2 is equal to 1, it means that the constant A represents the enthalpy of mixing.

And remember, the enthalpy of mixing is the change in enthalpy when you add a little bit of substance 1 into a mixture in which the predominant component is 2. That's why we evaluate it at y2 equals 1.

But you can also find the same for the component 1. So it turns out that constant A is also equal to the mixing enthalpy of component 2 in pure 1. So essentially, this says that the Margules one-parameter model is able to model only liquid mixtures in which the effect of adding component 1 to pure 2 is equal to the effect of adding component 2 to pure 1. So in other words, this mixture is very symmetric. Molecules are very similar to one another.

So he developed a two-parameter model. It's slightly more complicated. But at least, I have two parameters. And these two parameters turn out to be related to the mixing enthalpies of the two components, which makes more sense because, if I have a bunch of water and put some alcohol in it, I obtain a different effect than if I had a bunch of alcohol and I put some water in it.

And so this is Margules two parameters. Van Laar also is a two parameter, some sort of an inverse of Margules two parameter. It also, of course, satisfies the Duhem-Margules condition. And again, this A and B are related to the delta-- when you write it this way, they are related to the mixing enthalpies.

But two parameters, for many mixtures are not enough because molecules may be very different. You may have long molecules, small molecules. You have to account for the fact that maybe a long molecule is surrounded by many small molecules. And so you need more parameters for reality.

And people over and over have developed models with more parameters. They all satisfy the Duhem-Margules relation. For example, this one was considered by Guggenheim. And then it became famous under the name of Redlich-Kister. This other one was developed by Wilson. It's not the same Wilson as the cloud chamber. And based on this model, developments and improvements of the Wilson model, by Prausnitz and co-workers.

You have the models that you find now in your softwares that do modeling, which have several parameters which are related-- these epsilons are related to the Lennard-Jones potential, to the strength with which molecule 1 is attracted by molecule 1. And this is molecule 1 attracted by molecule 2 and 2 by 2. And so you see, there is some-- the physics behind this model is still related to the fact that we're trying to describe intermolecular forces and their effects. And these are the specific volume of the pure components.

So in practice, you describe chemical potentials and, therefore, the Gibbs free energy of a mixture in this way, by adding up contributions. So here are some examples, I mean examples of how these contributions look, for a binary mixture, as a function of the mole fraction of component 1.

For example, just the term y log y is this pinkish curve here. If you add also this other term-- and of course, it depends on what assumptions you take for the Gibbs free energies of the pure components. Here, I assumed 0 for component 2. And this number here may be 0.5 or 0.6 for component 1, just to make this.

And this is the linear part. The first two terms are linear in the mole fraction. And that's the blue curve. So you add up the blue curve and the pinkish one. And you get the red curve. That is g-ideal, just like that. And then here, I plotted the Margules one parameter, that's the green; Margules two parameters, the black; and van Laar, the orange.

Now, when you add up the ideal and the excess Gibbs free energies-- see, this is negative, this is positive-- they add up. And here is what you obtain. These are for the three cases-- Margules one parameter, two parameters, van Laar. You obtain shapes that are non-trivial.

And actually, in some cases, they're also no good in the sense that they violate the stability conditions because the second derivative of g must always be positive. We'll come back to this in a short while.

So here, we will find where the convexity is-- the second derivative is negative, this will have unstable states. And this will drive us to exactly the same ideas that we have seen for the van der Waals case, for the pure substance. Unstable states and also metastable states are possible. But we postpone that for a while.

When we are in the business of mixtures, there are other terms that I only want to mention because they are used by the practitioners. And that might be confusing. So I want to link to what we're doing. These are called-- for the condensed phases, we use activities and activity coefficients. It's just another way of writing the chemical potential, so to speak.

You could define the activity this way. So you take the chemical potential, this one. You subtract the same at some reference conditions of pressure and composition, so not necessarily the pure substance, divided by RT.

And that means that essentially you're rewriting your chemical potential as a term evaluated at those reference conditions plus RT log of the activity so that you have an equation that resembles this one, except that here you have the activity and here you have taken a reference chemical potential not for the pure substance, but for the mixture at some conditions that you decide to be useful as a reference.

And you can also define the activity coefficient, which is the ratio of the activity to the mole fraction, so that here you have the logarithm of y, which represents the ideal part of the contribution. And the non-ideal, or the excess, is all contained in these activity coefficients. So it's just changing names, defining variables. But the substance of the matter is what we've done.

In the same way, people sometimes use fugacities. This is useful for the gaseous phases. So fugacities play the role of generalized partial pressures. But the idea is that here you-- so you define-- you see these relations. Let's start from this relation here.

The chemical potential, you write it, again, as usual, like we did. We take as reference the pure substance. Then you have RT log of y. And then you have plus RT log of p over p0 plus RT log of phi. So essentially, you rename the excess chemical potential in terms of this fugacity coefficient.

Or if you wanted to start from the chemical potential, you define the fugacity by selecting, again, a reference condition for your mixture, not necessarily like we do here, the pure substance. You select this coefficient, this prefactor here as something that in the limit of ideal gas behavior reduces to the partial pressure.

So the fugacity in those limits is the partial pressure times the exponential of this. So again, this is just because I wanted to mention it. For example, if you compute the activities for the Margules, van Laar, and Margules two parameters, here are the expressions. And here they are for the van Laar. I think this is for the van Laar and how the activity depends on mole fraction and on that parameter that characterizes the model-- or the parameters A and B that characterize the model.

Now, that means that when we talk about liquid-vapor equilibrium-- for example, let's suppose we use the van Laar model. And you remember that we have to apply-- if we have two substances that are both volatile and condensable, we have to apply twice the Raoult's law.

Now, Raoult's law rewrites for a non-ideal mixture-- well, you substitute the mole fraction with the activity, the mole fraction for the components in the liquid with their activities. And we've given the expressions for the activities in the previous slide, also for the van Laar. So if you do that substitution, here is what the equation of the bubble line is. And this is for the dew line.

One of them used to be a straight line. But with this non-ideal model, it becomes very different. And the dew line also becomes sort of interesting. So just two parameters introduce a lot of structure in the behavior of your mixture, including the possibility of this, which is called the azeotrope.

The azeotrope is a condition in which you go from liquid to vapor. And that change is not across a finite temperature difference, but at a single temperature. So it behaves as if it were a pure substance. Like a pure substance it boils and condenses at the same unique temperature. But this occurs only at that particular composition. At other compositions, instead you have a range of temperatures. So the temperature of the "liquidus" is different than that of the "vaporus."

This is done by combining these two. You can construct a plot at a constant temperature. But you can also, the same equations, construct the plot at constant pressure. And of course, you can eliminate the pressure between the two and construct, for a given temperature or for a given pressure, the relation that you have between the composition of the vapor phase and the composition of the liquid phase.

So these are all things that you can implement in an Excel file and so on and very easy if you have few parameters. There is also a Lennard-Jones model of the mixture, of the binary mixture. So here, this model is taken again, from this article on Wikipedia from which I take these plots, very nicely done.

It explains that you can assume for the sigma-- you remember that in the model of-- in the Lennard-Jones model, sigma is representation of the diameter, essentially, of the particle. So when they collide, the two centers of the two spheres are at a distance, which is equal to their diameter.

If you have spheres of different sizes, the diameter at which they collide is the sum of the radii. So the radii is half of the diameter. So the sum of the halves is just the average diameter of the two proper diameters.

So you assume a Lennard-Jones curve or potential characterized by a sigma12 for the interaction between two unlike particles, that is equal to this mean value. And then for the depth of the Lennard-Jones valley, you use the geometric mean of the pure component ones. But then you also use an adjustable parameter, xi.

Now, the geometric-- if xi is equal to 1, this geometric mean gives you the equivalent of the ideal solution model. And in fact, you get that the bubble line is straight. It's a straight line. And this is with xi equal to 1.

If you change instead xi to greater than 1, you get a non-ideal mixture behavior with an azeotrope at this composition. If you change xi from 1.2 to 0.85, it goes on the other side. So it's an azeotrope-- upper azeotrope, lower azeotrope.

And also, if you play with the ratio-- this is wrong. This should be an epsilon 2 over epsilon 1, of course. I need to correct that. So if you change that from this one to very different, you may find a critical region, in other words that could allow you to go from liquid to vapor without a phase change, similarly to what happens in a pure substance. Where if you go above the critical point, you can take a liquid to vapor and vice versa (without a phase change).

So this case is one, let's see, for example here, in which you have a-- well, if you were in liquid-liquid, this would give you partial miscibility. But we'll do that in another occasion. So now, let's talk about-- a bit of the stability conditions.

So as we have seen, we can go-- see, the business here is to go from the properties of a pure substance to the properties of the other substance, and all the way to all the compositions in between. And when we do these diagrams here, everything is fixed by the condition-- This is a binary composition. So it's fixed by the fact that mu1f must be-- at T p y. Let's say y1f.

So for component 1 in the phase f, I have to have the same chemical potential of that component in the phase g. And that's one condition of mutual stable equilibrium. The other, mu2f-- Yeah. Well, let's call it again 1f. Let's choose for variables the mole fraction of one of them.

But I need to impose the condition for equality of the chemical potential also of the other component. So mu 2 must be equal to mu 2. So I have a system of two equations here. And that system of two equations can be solved, in general, to give me this, to give me-- for a given temperature and pressure, I can solve this system for the unknowns that are the mole fractions of component 1 in the gaseous and in the vapor phase.

So here, I have pressure and temperature. I fixed the pressure and the temperature. And then that system of equations gives me the mole fraction of the liquid and the mole fraction of the vapor. So I have this surface. So that equation here is an equation of this surface here. Actually, this is on the liquid and on the vapor. So it's on the other side. But you can do it for all the phases.

And you have these gaps here, these empty spaces between these surfaces, which doesn't represent any state, any stable state, because if you are there, the system likes to find stable equilibrium by separating and generating the two phases. So that's the idea.

And yeah, I think we'll stop here because there's not enough time to do Henry's law. But we can-- yeah, so next time, we will finish up this part. And we'll start the systems with chemical reactions.