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RAFAEL JARAMILLO: Hi. Today we're going to introduce phase diagrams of unary binary, and ternary systems with a real focus on ternaries. The challenge of drawing phase diagrams is how to capture a phase equilibria with flat pictures on a piece of paper.

So before we begin, we're going to remind ourselves of the Gibbs phase rule. I'm going to keep this down here in the bottom of the board. Gibbs phrase rule says that the number of degrees of freedom in a system is the number of components minus the number of phases plus 2. So I'll keep this down here so we can refer to it.

We'll start with unary systems. I'll draw the phase diagram of a very well known unary system for iron, temperature on the vertical axis, pressure on the x-axis. So this is the very well known phase diagram of iron-- alpha phase, high-pressure epsilon phase, beta, gamma, and liquid.

So for a unary phase diagram, we have two independent intensive variables, and that's pressure and temperature. We also have two axes on a flat piece of paper. That means we can represent the full phase diagram as a flat image.

So for instance, in a unary system, the condition of two-phase coexistence implies 1 minus 2 plus 2. That is one degree of freedom. And we do indeed see that two-phase coexistence is represented as lines on the unary phase diagram that is geometrical objects with one degree of freedom.

Now we'll do binary systems. I'll draw the phase diagram for a eutectic system, something like the lead/tin system perhaps. We have lead, tin. The horizontal axis is the second component, in this case, tin.

The vertical axis is temperature. And we'll make this a eutectic. So there's our lead/tin phase diagram-- the lead solid solution, a tin solid solution, and the liquid phase.

So now we have three independent intensive parameters. That is, temperature, pressure, and x2. Or, if you like, you can choose x1. So if we only have a flat image, we have to represent a subspace. So what we do is we represent-- we represent a subspace of fixed pressure as a flat illustration.

And 99 out of 100 binary phase diagrams you encounter will be for 1 atmosphere of pressure. So unless it says otherwise, you can safely assume it's for 1 atmosphere of pressure.

So let's consider how Gibbs phase rule plays here. So for example, two-phase coexistence implies two components minus two phases plus 2. So we have 2 degrees of freedom. There's only 1 degree of freedom evident in this binary phase diagram.

So for instance, let's consider this two-phase region here. We have a timeline connecting that material, which is a solid solution with a fixed composition, and this material, which is a liquid solution with a fixed composition. The 1 degree of freedom that's evident in the phase diagram is that you can move along these lines. That's 1 degree of freedom.

The second degree of freedom is actually pressure. So it's coming out of the board. It's not apparent in this diagram. We consider three-phase coexistence. In this case, the number of degrees of freedom is 1. So the three-phase point in a eutectic diagram is, of course, the eutectic point.

The eutectic point is a point. It looks like an object with 0 degrees of freedom, but we know that the 1 degree of freedom becomes apparent when you come out of the board. So as you vary pressure, this point becomes a eutectic line, and you get your 1 degree of freedom.

Now we'll move on to ternaries. In this case, we have four independent-- four independent intensive parameters-- temperature, pressure, and two independent composition variables. We know that, by definition, the sum of the mole fractions or the weight fractions, if you like, is 1.

So we can rearrange this as a function for x2, a function of x1 with an intercept, and a constant slope of minus 1. Then we're going to draw that function.

So on the horizontal axis, we'll have x1 going from 0 to 1. And on the vertical axis, we'll have x2 going from 0 to 1. And we have a family of curves, which is parameterized by x3.

So there is the line of x3 is 0. And I'll draw a couple more lines. So here's x3 is 0.25, x3 equals equals 0.5, and x3 is 0.75.

OK, we're going to represent composition on the two-dimensional flat picture. But we want to represent-- we want to represent all three components on an equal footing, not give special status to x3. So we're going to deform our composition map into an equilateral triangle.

So we'll start with the composition map from the previous slide. And we're going to imagine taking this triangle and transforming it into an equilateral, recognizing now that this corner represented pure component one, this corner represented pure component two, and this corner here represented pure component 3.

So we'll label the corners as such, component one, component two, component three. And the lines of fixed component three mole fraction remain. This construction is called the Gibbs triangle.

On the Gibbs triangle, the points of pure component 3, 2, and 1 occupy the corners. As we've already seen, compositions, that is, materials with fixed x3, radiate, as it were, as lines from the x3 corner. I'll draw those lines.

So this, for instance, is a line of x3 equals 0.75. This is the line of x3 of 0.5. And this is the line of x3 of 0.25. The edge of the triangle here is, of course, is the line of x3 equals 0. In other words, this is the binary line between x1 and x2. This axis has become the x3 axis.

Similarly, lines of constant x2 emanate from the x2 corner. So we have lines which cross the diagram as such. And we can label them with tick marks-- 0.75, 0.5, and 0.25. This has become the x2 axis.

And finally, compositions with fixed x1 emanate as lines from the x1 corner. See how I've drawn this. So we have lines 0.75, 0.50, 0.25, and this here is the x1 axis. Of course, these lines didn't cross down here, but I'm not great at drawing.

All right, so for example, how do we evaluate the composition of any point on this diagram? Let's take that point. Call it point P. Let's first read x3. Well, what we do is we draw a dashed line parallel to these lines of constant x3 composition, and we see where that hits the x3 axis. That's at about 0.6.

All right, let's do x2. So here we look for the x2 axis. And we draw a line over. That looks like it's at about 0.3. Now, of course, we know that these guys have to sum to 1. So we know that x1 has to be 0.1. We can verify that by drawing a line down to the x1 axis. And we do see that it falls right about 0.1.

Now we're going to see how we represent phase equilibria on the Gibbs triangle. This is best done by illustration. So I'll start by drawing a fairly generic ternary phase diagram that shows both single, two, and three-phase regions.

Start by labeling our components. I'm going to put a three-phase region right in the middle. This is going to be bordered by two-phase regions and one-phase regions. The two phased regions will have tie lines.

And let me label my phases. I'll switch to pink to label the two-phase regions. Let's start by looking at this alpha-gamma region.

Gamma plus alpha, two-phase region with tie lines. You'll note that, in ternary phase diagrams, the tie lines themselves are straight. I drew them as close to straight as I could, but they're not necessarily parallel.

So there's the gamma plus alpha region. Here is the gamma plus beta region. Here, of course, is the alpha plus beta region. And right in the middle we have the alpha plus beta plus gamma region. Now let's see what the implications are of Gibbs phase rule.

So for instance, in a ternary system, we have three components. So 3 minus 2 plus 2 is 3. So in this case, we have 2 degrees of freedom-- 3, sorry-- 3 degrees of freedom. So take, for instance, this solid solution in coexistence with this solid solution.

1 degree of freedom is apparent in this ternary phase diagram just as, with the binary phase diagram, that 1 degree of freedom is represented by those lines of variable composition. But the other two degrees of freedom are in the third and fourth dimensions of this drawing, and they correspond to temperature and pressure.

Let's take another example. For a three-phase equilibrium, we have 2 degrees of freedom. On this phase diagram, the three-phase region is bounded by these points. And those are points of fixed composition.

So there are 0 degrees of freedom apparent in this ternary phase diagram. The two degrees of freedom of the system correspond to, again, pressure and temperature, which we can't show on a flat image.

Now, in a ternary phase diagram, analyzing phase fractions is exactly analogous to a binary phase diagram. We use tie lines and the lever rule. However, analyzing phase fractions in the three-phase region is a little more complicated, and we'll do that next. So we're going to analyze this three-phase region in a little more detail.

These are called tie triangles. For a given temperature and pressure, the compositions are fixed.

And since, of the four independent, intensive parameters, on the ternary phase diagram, we're showing the composition parameters, for typical ternary phase diagrams, the temperature and pressure are fixed. In order to determine the phase fractions, we use a generalization of the lever rule.

So let's consider a given composition, overall system composition. Let's say that my overall system composition is that point there. So the way to figure out the phase fractions is, you imagine this triangle as a solid triangular sheet.

And you have it balanced on a pedestal or a fulcrum. Here's my overall system composition. So we're going to try to balance it with the fulcrum at that position.

So you imagine a cone. This is now meant to be a real, three-dimensional object, like a three-person seesaw. And the way you determine phase equilibrium is you add material to the three corners until the triangle is level with the ground.

So if you want it to balance out this triangle, you'd probably add just a little bit of material over here because that has a large lever arm, a little more material over here that has an intermediate lever arm, and then a big pile of material over here.

That's the corner with the shortest lever arm. And you adjust these fractions until this triangular sheet is level with the ground, and the result is the proper equilibrium phrase fraction for the system with that overall composition.

We're going to illustrate ternary phase diagrams with a very well known case study of the ouzo effect. So ouzo, if you're in Greece, or pastis if you're in France, is a spirit made up of water, ethanol, and anise, anise essential oil.

So you need to know for this demonstration is that ethanol-- ethanol is a common solvent. Meaning, it's a solvent common to water and the essential oil. But water and oil are, of course, insoluble.

So first, let's see what happens.

[VIDEO PLAYBACK]

[MUSIC PLAYING]

What that video shows is that ouzo, itself, is a clear, colorless solution. That is, it's a single-phase solution. However, adding just a little bit of water causes it to transform into a milky substance that is a two-phase suspension. So we're going to figure out what the ternary phase diagram for the system has to look like in order to be consistent with the ouzo effect.

So let's start by drawing the triangle. I'm going to put water down here, ethanol here, and the essential oil here in this corner. All right, so when we add water, we don't change the ethanol-to-oil ratio. So let's draw lines of constant ethanol-to-oil ratio.

Those are lines that emanate from the water corner. So those are-- now, ouzo is a pretty strong drink. So let's say it's 100 proof. That is roughly 50/50 ethanol-water. So let's draw a line corresponding to 100 proof.

All right, so now we have a little bit of understanding how to navigate this diagram. There's our 100 proof line. That is 50/50 ethanol-water. And there's our lines of constant ethanol-to-oil ratio. So let's imagine that, when we buy it at the store, or we have it delivered to our table in the taverna, we start at this composition. It's mostly water and ethanol.

It has a little bit of essential oil. And we need to figure out a phase diagram such that, when we move along that line of constant ethanol-to-oil ratio, we move from a single phase to a two-phase region. I'm going to draw the boundary of a two-phase region that's consistent with that observation. There. I'll draw the tie lines.

Right, so here is a proposed phase diagram. We start with ouzo, single phase, solution of water, ethanol, and essential anise oil. When we add a little bit of extra water, we move along this line of constant ethanol-to-oil ratio until we enter into the two-phase region.

And now I have a cloudy, milky suspension with a water-rich phase co-existing with this phase, which lies roughly in the middle of the ternary phase diagram. All right, so now we have our cloudy, two-phase ouzo drink here represented by that point in the two-phase region.

That's at ambient temperature. Now, we know that increasing temperature makes solution-forming more favorable. So let's see what happens in practice

[VIDEO PLAYBACK]

[MUSIC PLAYING]

Right. So what we saw was that, at 41 degrees C, the two-phase regions seemed to be resolving into a single-phase region. And as we continue to increase the temperature to 47 and 62 degrees Celsius, we've recovered a single-phase solution.

Now, granted, you could have been changing composition as you have differential evaporation from the solution. But the cuvette was capped. So let's assume that the overall system composition of that liquid-liquid two-phase system did not change. Let's see how we represent the effect of changing temperature on the ternary phase diagram.

So I will start by labeling our initial two-phase region boundary by the temperature which that initial video was shot, 20 degrees C. Now let's draw a different boundary that's consistent with the observations at 41 degrees. They're just on the border. I'll label that 41. As we continue to increase the temperature, solution-forming seem to become more and more favorable.

So here, for instance, might be 47, and here is 62. So what we see is that, as we increase the temperature, our overall system composition at this point moves from being within the two-phase region to being back within the one-phase region.

So in this way, we can show you a little bit about what happens in the third dimension on the flat ternary phase diagram by drawing contours of the borders between regions as if they were contours on a topographical map and labeling those contours by the temperature.