

3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 34

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PROFESSOR: OK. So. Last day we started looking at phase diagrams, and we looked at unary phase diagrams, one component systems, and one component system P versus T , pressure versus temperature. And this is the situation for water. Water is an exception, because it's got this negative solid equals liquid coexistence curve, but otherwise, you have large, single-phase regions here, which I've designated circle p equals 1, and then along these lines, we have equilibria. So this is liquid goes to vapor, this is solid goes to liquid, this is solid goes to vapor. And we know that for water, if we take the 1 atmosphere, if this is pressure in atmospheres, the 1 atmosphere isobar, then that would put this point at 100 degrees Celsius, and this point at 0 Celsius. And then we have the triple point, which is solid equals liquid equals vapor at 0.01 degrees C, and p equals, I think it was 4.58 millimeters of mercury. So that's the triple point. And we looked at a variety of other one-component phase diagrams, and I think we came to a pretty good understanding.

And then up here, we have the supercritical fluids. So I've got a break in the line here. And for water, you reach supercriticality at 374 degrees Celsius, and up here at 218 atmospheres. So these are not phenomenal, these are not geological pressures at all. And so that's if we want to the decaffeinating of coffee and so on. And so what happens here, is you have a highly compressed vapor or a highly rarefied liquid, and you end up with solubilizing power of a liquid, but transport properties of a gas. So this stuff has really good diffusivity. So it can penetrate into interstices and do its work very quickly, to say nothing of the fact that you're up at 374 degrees Celsius or higher.

So today what I want to do, is I want to look at two-component systems. So component number is circle c , c equals 2. So that means now I have to deal with pressure, temperature, and lowercase c is composition. I want to know how things vary with composition.

So let me give you an example. Suppose I have two substances, A and B. So here's substance A, and I've got its one-component phase diagram. And in this case, I'm going to put solid-liquid vapor in the conventional setting, where the solid-liquid line is-- the coexistence curve has a positive slope. So this is A, and let's say I've got B over here, and it's got its solid-liquid coexistence curve, and so we've got its melting point, and whatever.

So now the question I want to ask is, what happens if I mix A and B? And let's just say, here's the melting point of A, so this is at p equals 1 atmosphere. And here's the melting point of B. And I want to ask the question, how does the melting point of the mixture vary? So let's say I'm going to connect these, and I want to ask, what happens if I've got an AB mixture? So I'm going to put lowercase c here, which is

concentration. So at the one end, I've got 100% A, and over here, I've got 100% B, and I know those melting points. Question is, what happens when I mix them? Does the melting point-- is it just a straight line? Is it a linear variation? Do you go through a local maximum? Do you go through a local minimum? Or do you go wild? I mean, what happens?

So a question you might ask is, suppose I made a 50-50 alloy of 50% A and 50% B. If I knew the end-member melting points, could I predict this? Or if not, do I have an archive? Remember the phase diagram compendium is an archive. What is the value of the melting point at 50-50 or 75-25? So that's the question I want to ask.

Now this is getting really messy, because now I have to plot pressure, and I have to plot temperature, and I have to plot composition. So this is really crazy, right? I've got pressure, and I'm going to have composition here, and I'm going to have to have now a third axis, aren't I? I'm going to have to have a third axis. I'm going to need a temperature axis. And I've got to make a three-dimensional drawing. And this is messy. But we're in luck, because 3.091 is solid state chemistry. So as solid state chemists, we're more interested in what happens in the solid here.

Now, I've drawn these lines with a slope, but they're really not to scale. It turns out that, you know, you can move 10,000 feet up or down in the atmosphere and have a huge variation in the boiling point because this line is shallow. But this line is virtually straight up and down. You have to go to geological pressures to change the melting point very much. And so, as a result, this is almost insensitive to pressure, to first order, right?

So we can say solid equals liquid is almost insensitive to pressure, whereas liquid equals vapor is very sensitive very sensitive to pressure. But we don't care about this so much. So what I'm going to do is throw it away. I'm going to throw it away, and just say, let's look at just T versus C. Temperature versus composition on the strength of the fact that the melting point and all of these things are mildly dependent on pressure. All right.

So now I'm going to give you three different types. There's many, many different types of binary phase diagram. So now we're going to be looking at C equals 2. So instead of a unary, this is going to be called binary. Binary phase diagrams. And they come in all shapes and sizes, but they can pretty much be classified in several bins. And I've made the classification.

So classify binary phase diagrams according to their bonding. It all comes back electronic structure and bonding. Vary by bonding. Because bonding, then, ultimately indicates solubility, and that's what we're looking at here. We're going to look at how well A dissolves into B, and how well B dissolves into A. That dictates solubility. So it all comes full circle.

So I've made this up. You're now going to find this in the book. So I just decided, for ease of teaching 3.091, is I'm going to just give the different types. And so I call them type one, type two, and type three. You're not going to find that in the books. I made that up, because it's simple.

So type one. What's type one binary phase diagram, according to me? What is the type one? It means complete solubility. So A and B are completely soluble in one

another as solid and liquids. That's the first thing that you'll see on a type one phase diagram.

And the second one is, a change of state is present. And you know the only change of state we care about here is solid goes to liquid. So we're going to show solid goes to liquid, and the thing is totally, as they say in California, totally soluble as liquids and solids.

Now, here's some bonding rules that you can think about. So what would be the characteristics of two substances A and B that would give complete solid solubility? Well, one thing is they'd have to have identical crystal structures. That would heighten the chances of this. Identical crystal structures. So if they're both FCC metals, you've got a better chance of making an infinite variation in solution composition than if one is an FCC metal and the other is a BCC metal because FCC will just sit on the lattice site.

But there's more fine structures. Second one is similar atomic volumes. So if we're going to have a substitutional solid solution, let's make sure we're replacing oranges with oranges, and not trying to put a grapefruit on a site that normally is occupied by a lemon, because there's going to be a size restriction there.

And the third thing is, even if they have identical crystal structures and similar atomic volumes, you can still run into trouble with respect to complete solid solubility if you have a large variation in electronegativity. And I'll show you an example of that. So if you have a small difference in electronegativity, it means there's a low propensity for polarity, and ultimately no chance of electron transfer.

So I think it's pretty cool. So I wrote those down, but was disappointed to learn that for metals, they were enunciated about 75 years ago by the British metallurgist Hume-Rothery. So I can't take credit for this. This is one name. It's one of these hyphenated British names. He's Sir da-da-da-da Hume-Rothery. So he has the Hume-Rothery Rule. And he called such systems that mix as binaries forming isomorphous, meaning they have the same structure.

So let's take a look at the prototypical isomorphous phase diagram, and it looks like this. We're plotting temperature versus composition. We threw away the pressure coordinate. So I got pure A on the left, pure B on the right. Little c is concentration, so it varies from 100% A to 100% B. And the vertical axis is temperature.

So one extreme, I've got the melting point-- this is a melting point of pure A. And at the other extreme, I've got the melting point of pure B. So that, we know. And now the question is, how does melting point vary as a function of composition? And for an isomorphous phase diagram, it looks like this: lens-shaped. Up here is all liquid. You see A and B mix in all proportions. And down here is all solid. And furthermore, it's an all-liquid solution. It's a mixture. And this is an all-solid solution.

And then comes the piece that if you take enough thermodynamics, you'll be able to rationalize. I'm simply going to tell you without proof that when you have a multicomponent system, when c is greater than 1-- so we're in that situation. Now, c is 2. When c is greater than 1, it is impossible to move from one field, up here, this is-- I'd better put the label on it-- this is a single-phase field. So up here, p equals 1, because it's homogeneous liquid solution, p equals 1. When you're in pure materials, you can go from solid to liquid. But when you're in a two-component system, you

cannot move from one single-phase field to a second single-phase field without moving through a two-phase field. And we'll get to that, what it means to move from one field of p equals 1 to another field of p equals 1 requires traverse or transit across a field of p equals 2. And so what's in here has to be the end member. So this must be liquid plus solid. So I'm going to call it slush. They have a slush in here.

The other terminology that people give this is, it's lens-shaped, right? Looks like a lens. So let's call this lens shape. So we're going to use the Latin word for lens, which is lens. But we want to make it adjectival. So we're going to use the adjective - what's the genitive form of lens? Lentis? So we will call this lenticular. This is lenticular. The phase diagram has a lenticular shape. Looks like a lens.

And you know, just as over here, I showed you, every line represents a coexistence curve, right? The lines are all coexistence curves. These lines are coexistence curves. The line up here is liquid equals vapor, so this one must be the coexistence of the two things on either side. So what do I have here? I have liquid. Here I have slush. So I'm going to write that. So I'm going to write the equilibrium, liquid goes to liquid plus solid.

And this line, this coexistence curve, it's called the liquidus line. This is the liquidus equilibrium, the liquidus coexistence curve, and so on. And so what's the liquidus? The liquidus is the lowest temperature. So you pick a composition. The liquidus is the lowest temperature at which you can have a single-phase liquid solution, OK? So liquidus equilibrium. And the liquidus is the lowest temperature at which all liquid is stable. You go below that temperature at that composition, you start making solid, because slush requires that there be some solid present.

And then the lower line, it also is a coexistence curve. So on the one side, I've got solid. On the other side, I've got slush. So I'm going to write that one down. That solid goes to liquid plus solid. And that's called the solidus equilibrium, or that's the solidus line, the solidus coexistence curve, and the solidus is the complement. The solidus is the highest temperature at which you can have all solid present. So you pick a composition, and I'll tell you what the highest temperature is at which you'll have a single-phase solid solution. So solidus is the highest temperature at which all solid is stable. All right. Good.

And I'm going to look at a few of these things. It's always fun to see if I'm on track with the Hume-Rothery rule. So here's copper nickel. They're both FCC metals. So we've got copper melting at about 1085, nickel melting at about 1455. And there's the phase diagram, lenticular phase diagram. So up here is all liquid, and then-- this is all metallurgy terminology. A solid solution of A and B, they call alpha. Metallurgist looks at that, goes oh, it must be a solid solution, OK? So there's p equals 2 in between, p equals 1, p equals--

Here's a ceramic system. This is nickel oxide, magnesium oxide. It's not metals, but they have identical crystal structures, very similar atomic volumes. They're ions, so we have nickel and magnesium substituting for one another on the cationic sublattice. So they must have very nearly equal sizes. If I look at this, and I see a lenticular diagram, it means they must have similar atomic volumes, which means the dominant defect in here must be Schottky, not Frankel because Frankel needs a big difference in atomic volume. If you have a big difference in atomic volume, we wouldn't have a lenticular phase diagram.

So here's-- mag oxide melts at 2800 degrees centigrade. It's a great refractory. You can hold molten iron in it. And here's nickel oxide down here.

All right. Here's an interesting one. This is gold nickel. Both FCC metals. Shade your eyes from the lower part. Just look at the upper part. It looks lenticular. It's what you'd expect, gold and nickel. They're both, you know, card-bearing metals. But you've seen already, with the cesium-gold, gold has a fairly high electronegativity. And what happens is that you get over here, at about 33 atomic percent of nickel in gold, you have an atomic ratio that allows to have something that starting to approximate electron transfer. So it's almost as though you have a lenticular phase diagram between pure nickel and this nickel-gold compound. But up in here, it's nice lenticular stuff.

All right. What's the next one? Oh, yeah.

So now I want to go in and I want to start talking about what goes on inside here. So what I'm going to do, is I'm going to blow this up. And I'm going to start at 40%, 40 weight percent nickel, and I'm going to say, what happens if we take a crucible that's 40 weight percent nickel and copper, and we cool it from all liquid at 1300, down to all solid at 1200, pausing in that slush zone at 1250? So we're going to take snapshots and say, what's the contents of the crucible look like at 1300, at 1250, and at 1200, and come out of it, have an appreciation for what all of this stuff means.

So let's start our experiment. So we're going to have three crucibles here. And we're going to start with 40% nickel in copper, and that's going to be the experiment we'll perform.

So I've got three crucibles. And so if I look at the phase diagram, here I am. This was 1300 degrees C, this was at 1250 degrees C, and then this was at 1200 degrees C.

So at 1300, that's trivial. 1300 for this thing, it should be just all liquid. And maybe it's copper. I know at this temperature, it's going to be blinding white heat. So it doesn't matter. I could use this. But I felt compelled, it's one of those rare opportunities to use colored chalk. So I want this to sort of be copper-colored. The meniscus is going to look like this, because the liquid metals have a very high surface tension. They want to ball up. So you're going to have a meniscus looking like this, and this is all single phase, all liquid.

And over here, I'm going to do the easy one. If we get down to 1200, it's all solid state, right? At 1200, I'm going to end up with something that's solid, and it's going to be polycrystalline, and these are all going to be grains of alpha. All solid. And I'm going to label all of these as alpha solid solution. They all have the same composition, which is 40% nickel in copper. And these are all 40% nickel.

Now, according to this phase diagram, when we get down into the center there, something else happens. We end up in a two-phase regime. And that two-phase regime is a regime in which certain compositions are forbidden because that's an equilibrium. It doesn't allow us to have what's in between. I think the next slide actually shows this.

So what I've designated as c_2 is this 40%. So c_2 is now going to park at that point in the middle. Whoops! Want to get into that.

So here's where we are. We're in the center of that two-phase regime. So this is the solidus. This is the liquidus. And we're at 1250. t equals-- And we're at this value. We started at c_2 , which is 40%. But in this regime, 40% is forbidden. If you stop at 40% at 1250, this says that the stable phases are a liquid and a solid. But the liquid has less nickel in it, and the solid has more nickel in it. It's like if this is a solubility limit.

In other words, if you started at pure copper, and you started adding nickel, you can keep adding nickel until you get to this concentration. You try to add any more nickel, it's like adding too much sugar to water. What do you have? The stuff just falls to the bottom of the cup, doesn't dissolve. That's this. It's the solid. Only instead of being pure nickel, it's still a copper nickel solution, but kind of rich.

So I'm going to call this c^* . It's the solubility limit on the liquid side. And this one here I'm going to call c^* on the solid side. In other words, I could start from this side, and keep adding copper to nickel, and I make a homogeneous alloy until I get to this composition. If I try to add any more copper, I jump across.

So we're here in the middle. But now, isn't there something strange here? It's saying I'm going to have a liquid that's nickel-poor and a solid that's nickel-rich. And I'm just putting up here what the diagram says. And we know that FCC metals, which is denser, the liquid or the solid? The solid. So down here I'm going to have α , OK, a bunch of grains of α solid solution, and up here, I'm going to have a liquid solution. And the composition here is c^* liquid, and the composition here is c^* solid. It's different composition from this. Here the composition is equal to c_2 , or the 40% nickel. So I've got disproportionation.

But the total mass, I can't have sources or sinks. So I have to conserve mass. So I'm going to ask you to just do the algebra. You've got two equations and two unknowns. I know what the n -member concentrations are. They're given by the n 's of this thing called the tie line. The tie line ties the two ends of the two-phase region together, and then we just do a mass balance.

Well, fortunately, the metallurgists have thought about this for a while, so we don't have to go through and figure out, well, if two apples cost 15 cents-- we don't have to do that kind of thing. We can just invoke the lever rule, and it will tell us how much of the liquid that's nickel-depleted and solid that's nickel-rich add up to this.

And so let's look at the lever rule. Basically what's going to happen here is that the stuff that started off as 40% nickel, 60% copper, that's my initial mix, it's going to break into two layers. It's going to break into a liquid layer, which, if you go to the phase diagram, looks like it's about 38% nickel and 62% copper, and that's what we're going to call c^* liquid. And then over here it's 45% percent nickel and 55% copper. And that's what we call c^* of the solid.

And so it's just a lever. So there's c^* . This is the c_2 that we want. And we want to ask, what's the relative amount of the liquid phase and the solid phase? And why they call it a lever rule is, look, if you cooled something that was at this composition, it would be 100% liquid. And if you cooled something at this composition, it will be 100% solid. And so it's going to be a constant variation across here. So you use, you

take this, and you know, and I want this amount, I'm taking this versus this, kind of thing. It's a lever construction. So we'll just put it down.

So the percent of the liquid in the crucible at 1250-- and then this is a general thing. Whenever p equals 2, you'll use a lever rule. Percent of the liquid is given by this one. The composition of the solid at the end of the tie line minus the composition that you started at. This is your bulk initial concentration, divided by the length of that tie line. $c_{\text{star solid}} - c_{\text{star liquid}}$. And then multiplied by 100%. So you get a percent, and the number here is going to be 45 minus 40 over 45 minus 32, and that works out-- going to multiply by 100, or else there will be complaints. And then this turns out to be 38%.

So what that means is that if you take this amount of liquid here-- pardon me-- based on conservation of mass, if you drop and hold at 1250, 38% of that volume is now sitting here in the liquid, which means 62% of it by volume has turned into solid. And the composition here is different from the composition here, but if you add up all the nickel in the crucible and sum it versus all the copper in the crucible, you still end up with 40% net nickel.

So this very powerful. Because what you can do here is you can separate metal. Because I started here with 40% nickel, 60% copper, and now I've got something-- the liquid face, I wrote here, the liquid phase is now 68% copper. So can you see that if I'm clever about this, I could use this as a technique for enriching. And if I'm thinking about recycling metals, maybe I need to know something about phase diagrams because it's a very simple way of concentrating impurities or concentrating the desirable stuff.

Let's look at one other thing here that's really very interesting. Suppose I had something, instead of c_2 at 40%, suppose I choose a c_1 . So this is 40% nickel. Now what if I take something that's 35% nickel, and I cool it down to 1250? What happens? If I park here at 1250 degrees, according to the phase diagram, that substance has to phase separate, and I'm going to end up with the same thing. I'm going to end up with liquid and solid.

Now, isn't there a contradiction there? How is it that whether I started with 40% or 35%, I end up with the same end members? What's the missing piece? The relative amounts will be different! The relative amounts. Here, look. As I'm getting closer to the liquid, can you see that axiomatically, I'm going to make more liquid and less solid if I ended up with something over here? But at 1250, those are the end members. That's the only stuff that's going to be present.

Ah! That's so good. I think I've got some other stuff here. Oh yeah. Oh, this was-- yeah.

So p equals 2. Lever rule. Whenever you see p equals 2, you have two things you think of. p equals 2 means phase separation. And that phase separation means you're going to get different amounts, and the lever rule.

And why I have this Manchurian Candidate-- it's this movie. I know there's a remake. The remake is horrible. The original, if you see the original, is about some fellows that were brainwashed. They were American prisoners of war brainwashed in North Korea and they're brainwashed to become assassins on cue. And the cue is the

Queen of Diamonds. When someone shows the Queen of Diamonds, they just go into automatic pilot, and they're supposed to assassinate the political figure.

So for you, your Queen of Diamonds is p equals 2. When you see p equals 2, you go, phase separation. Lever rule. All right? No guns, just this. I just want the formula. You go, phase separation, lever rule. Whenever p equals two. So what happens in here? Phase separation. Boom, boom. Right there. Oh, I'm not supposed to say boom, boom. Phase separation. Ta-da! You know, something. PC, whatever.

OK. So let's keep going. Now I want to look at a second type of phase diagram. So the first type of phase diagram was complete solubility. Now the second type of phase diagram has partial solubility. So let's look at that one. So I call this type two.

And you don't predict this stuff. We would give you the phase diagram and simply ask you, you know, you're the specialist. Tell me happens if I cool this to such and such a temperature? You can tell me you get phase separation, and the composition of the two end members, and so on.

So the characteristics, the bonding characteristics here, are partial or limited solubility of A and B. We're doing all of this for a binary system A and B, and no change of state. So that means either always solid, or always liquid. That's not to say that the A and B never become solid. I'm just saying that a type two diagram is limited to a single state.

So let's take a look at the diagram. The diagram looks like this. We're going to plot temperature versus composition. So pure B on the right, pure A on the left. Concentration is the abscissa, and then the ordinate, of course, is temperature. And so the shape of the diagram is this. There's the coexistence curve. It's called a synclinal coexistence curve.

So above, we have all solid. And in here, we have two solids. So using the metallurgical terms, this is alpha plus beta. Two phase regime, OK? So let's get those labels up right off the bat, so we know who's where.

So outside the coexistence curve, p equals 1. Inside the coexistence curve, p equals 2. And wherever I'm saying all solid, alpha plus beta, I could write all liquid, and then it goes to l_1 plus l_2 . So maybe we should do that, to show that we're multilingual. So it's either all solid, or it could be all liquid. And then this would be liquid 1 plus liquid 2.

And so why do we call it synclinal? What's this? This is an incline. If I put two inclines and I synchronize them, I get a syncline. And if I don't synchronize them-- these are two ladders. I could prop them up. That's called a syncline. And if I put two ladders like this, if I'm really stupid and I fail physics, if I do this, they fall down. So this is called an anticline, OK? That's an anticline. This is a syncline. It's not a U-shape, or a hump, or something like that. This is 3.091. This is a syncline. Synclinal coexistence curve.

All right. So what's on here? What's this equilibrium, then? Well, the equilibrium must be this equals this. So that would be, in the case of the solid, it's the solid solution goes to alpha plus beta, or it could be the liquid goes to liquid 1 plus liquid 2. That's the equilibrium.

You can think about it almost as a solubility. So let's start over here on the left. Let's pick a temperature. Let's call this T_1 . So I can put B into A, and I continue to get an all-solid solution, up to this concentration here. What happens at this concentration? I've hit a solubility limit. And if I try to put any more B into A, I get a tie line-- lever rule. In here is lever rule time, isn't it? Lever rule. p equals 2, OK? So it's solubility limits. Solubility limits.

All right. So let's look at some examples.

Oh, here's this one, actually. That's why I had a-- you know, if you go to lower temperature, gold, nickel-- look! They actually phase separate. That's shocking. I always find this one shocking, because you think gold, nickel, nice FCC metals, they should substitute for one another. Look what happens. If you start putting nickel into pure gold at 700 degrees, you get the 10 weight percent, you put any more in, boom. Right across here. So this is going to be two phase.

So if you look at the solid, what's that going to look like? If I'm at, say, 30%, now I look underneath and I've got a polygrain system, and I'm going to have an alpha and a beta, and an alpha and a beta. I'm going to have two different grains. And now, what's the relative amount of alpha and the relative amount of beta? It's given by the lever rule.

OK. Let's look at a few other examples. Here's hexane nitrobenzene. And so they've even put I-alpha, I-beta. They put the-- actually, that's probably a-- it's hard to read. But I think it's really an F, but it didn't come through very well, so it's the beta fraction, the alpha fraction. So you can see how you use the lever rule.

So up here it's all p . That's the not pressure, that's my circle p . Single phase, two phase. Drop down to 290 degrees, it separates into two liquids. With the hexane-- with two liquids, you'll actually have them floating on top of one another, right? Well, maybe. Depending if the density difference is tiny, you might get a dispersion. I'll show you that in a second. All right. So p equals 2, lever rule. OK? Hexane nitrobenzene.

Look at this one. This is surprising to me. Potassium chloride, sodium chloride. It's almost lenticular with a little bit of depression, but down here, it actually separates.

This is polymer. It's a polystyrene, polybutadiene, depending on what the-- at low index, polymerization index, they mix. At high polymerization index, the two are mixing. You get two phase, single phase. Changes the mechanical properties, too, doesn't it?

Now this one-- some systems actually have a lower critical point. Oh, I meant to tell you. You see, there's this temperature here. Above this temperature, they mix in all proportions. You can ever have phase separation. This is the maximum temperature at which you have no phase separation. So this is called the consolute temperature. And it's usually an upper consolute. The higher you go in temperature-- it's like saying, do you dissolve more sugar in cold water or warm water? You dissolve more sugar in warm water. And eventually, you get to a temperature high enough that you can mix in all proportions, right? That's the consolute.

Some systems, for entropic reasons-- and again, if you take 560 or some of the other thermal classes, you'll understand this, but for entropic reasons, you actually

have homogeneous solutions at low temperature, and at elevated temperature, you get phase separation. That's funny, isn't it. So this is water triethylamine, and they mix in all proportions at this zone here. And then above a certain-- it's called lower consolute temperature. It actually phase separates. Doesn't matter. All you care about is p equals 2, phase separation, lever rule. The rest is details.

This is a real hoot. This is water nicotine. It has a lower consolute temperature and an upper consolute temperature. So it's got a solubility bubble. You see? Out here, things are soluble. In here, they're insoluble. So they are immiscible. So we call this zone, this region here under the dome, so to speak, this it's called the miscibility gap, because things in there are not soluble in one another. But with nicotine, you have a lower consolute and an upper consolute, so you have a miscibility gap that's a complete ring. That's cool! I like this.

All right. So now I'm going to do a little experiment. We have a few minutes, so I'm going to show you ouzo water. I'm going to mix it, and I'm going to actually mix ouzo and water, and go into the two phase regime, and then out.

So this is what it is, all right? It's oily stuff, you know. If you're of Greek ancestry, you know what this stuff is. All right? But it's got licorice, it's got a fair bit of oil in it.

So what I'm going to do, is I'm going to come in here, and I'm going to start adding ouzo to water. And they're both clear, colorless liquids. OK, Dave. Let's go to the-- All right. So what we're going to do-- this is distilled water. So I'm going to put some distilled water in here. A little bit of distilled water. And this is ouzo. It's clear and colorless. OK. Can we show you this? Let's do this. OK. Ouzo, it comes from Greece. All right. So it's also clear and colorless. That was the point. Not to show you the label. See? It's clear and colorless. So this is clear and colorless, and the water, as you know, is clear and colorless.

So now what I'm going to do-- see, I don't have to wear a smock, or goggles, or anything. This is great. So what I'm going to do, is I'm going to add some of this stuff. Clear and colorless.

OK. It's turned milky. Why has it turned milky? Because we've now crossed into here, and the second phase is coming out. But the density difference and surface tension differences are so slight, that instead of having the second phase float on the first phase, we have a dispersion, G. If you go to the dairy case, and you look at something called milk, you'll have the same thing. Why is milk milky? Because the fatty phase is a fine dispersion, and the particle sizes is dadadada, versus the wavelength of visible light, et cetera.

Now if my phase diagram is correct, and I'm in here, if I keep adding ouzo, I should eventually emerge on this side, and instead of having a milky dispersion, I eventually should come here, and now I'll have a homogeneous, single-phase solution. But now it's going to be ouzo-rich, instead of water-rich.

You never thought phase diagrams were interesting. You don't know.

There we go. Je vous presente. There it is. So what we've done is, we've come across the thing. Yeah, that's good. Just put that there.

Now, David, please, back to the slides. May I have the next slide, please? That's a joke. When you have these terrible speakers at conferences, they get up there, really nervous, and they stand up there, and the first thing they say is, may I have the first slide, please? That's sort of a gag among scientists. What's your opening statement? May I have the first slide, please? May I have the next slide, please?

OK. So we've done this. All right. Now-- yeah, OK, this is just more.

All right. So now I'm going to show you absinthe. Absinthe is the same thing. Absinthe also comes from the same family. And there's a little culture here. It contains wormwood. The wormwood was up at around 200, 250 parts per million. And what wormwood does, it's got a hormone they call thujone. And thujone antagonizes the gamma aminobutyric acid, which moderates firing of the neural synapses. Basically, we've got this GABA that regulates how-- our brains could work much faster than they do, but the GABA regulates. If GABA doesn't work, you can start moving so fast that you get muscle thing, and you get epileptic, is one example.

But anyways, what it does, is if you drink this stuff, instead of being a stupid drunk, you become a very high-functioning, very alert drunk. And I'm going to show you what the consequence is in art.

Anyways, the cultural piece here was that there was a destruction of the French wine industry in the 1800s due to a blight called Phylloxera. It's like a beetle, and it ate the vines. And in fact, the French wine industry was saved by the American wine industry. Vines from New York state were brought over, grafts were made, and virtually all French wine today is on American stock with the exception, occasionally you'll see something says *vieille vin*. Old vines. There was some areas that were spared.

So what's that have to do with anything? It has to do with the fact that when the Phylloxera hit, the price of wine went very high, and the people at the bottom of the socioeconomic ladder couldn't afford wine. So they turn to absinthe. Absinthe was easily produced.

Thirty years later, when the vines come back, the French wine industry wants to recapture the market. So there's a Faustian bargain between the French wine industry and the Women's Temperance Union to try to disparage absinthe. And there were a few major show trials that involved vicious murders in which it was alleged that the killer was deranged on absinthe. And with this, they slandered the name of absinthe so badly that it was eventually banned and literally taken off the market.

I mean-- you know, we had the Rosalind Franklin commentary a few lectures ago. I hope I never read about you doing something like this in order to help your start-up company take over market share. That's not the way you're supposed to do it.

Anyway, so what-- now, how did they drink it? They drank it by mixing-- so it's now back, but it's got very low levels of thujone, so it's-- David, may we go to this? So we're going to make a mix called the *louche*. It's a-- OK, here it is. And this stuff here is beautiful. Because it's a green color, a soft green color. And the French even have a name for it. They call it the green fairy, *la fee verte*. So this is what absinthe looks like. Beautiful. Very nice. And it's got the same kind of licorice smell to it.

And so you make the louche by one part absinthe and five parts water. So this, at no upcharge, you get this glass. It's a beautiful piece of, you know, late Belle Epoque glassware. And the interesting thing is, these people were absolutely crazy, scientifically. And so what they did is, the markings on this glass are such that if you put absinthe up to this ring here, and then you put water the rest of the way, you get exactly the five to one ratio for louche. So you don't even have to measure. You just put like so. OK. Let's see. I'm going to get this right! It's science. Here's our distilled water. You see how it's milky? So there's the louche. And if you wanted to be a real hipster, you had this special Belle Epoque spoon. And what you'd put on top of this would be a sugar cube. You know, this is how it was done. You have to know some culture. You don't know. You've led sheltered lives. You pour it through here, like this.

So now I'm going to show you the art. So David, may we cut to the slides again? So there's the louche. All right. So here's the poster. Here's the man. He's pouring the water through the slotted spoon with the thing, and there's a very well-to-do lady, you can tell, she's got a beautiful hat, and she's well-dressed. And he's inviting her to join him for a glass of absinthe. L'absinthe oxygenee. That's the name of the company. The oxygenated absinthe. C'est ma sante. This is my health.

Van Gogh painted this.

This is Picasso. The absinthe drinker. There's the absinthe again.

This is Picasso after many absinthes. You can see the slotted spoon and the sugar cube. What else is there? That's up to you.

All right. When you saw Moulin Rouge, you may not have known all of this cultural history. So now let's take a look at what's going on here. There's the absinthe, and I think we've got a little--

[VIDEO PLAYBACK]

-I don't even know if I am a true Bohemian revolutionary.

-Do you believe in beauty?

-Yes.

-Freedom?

-Yes, of course.

-Truth?

-Yes.

-Love?

-Love? Love. Above all things, I believe in love. Love is like oxygen. Love is a many-splendored thing--

[END VIDEO PLAYBACK]

Love is like oxygen. Chemistry is everywhere! All right, so this is what happens eventually. This is the poster. This is from Switzerland. October 7, 1910. Gentleman, This Is the Hour! And there's the clergyman with the Bible, and there's the green fairy. And she has a wand. She's been stabbed, but she's lying here with a wand. The wand is an opalescent wand, because this stuff is opalescent.

Last thing I'll show you is some really, really cool chemistry that you must remember. When Toulouse-Lautrec drank-- let's go back, David, to the thing. So when Toulouse-Lautrec drank absinthe, and he drank lots of it, he didn't like the milky color. So he wanted to make the milky color disappear. So I'm in the two-phase regime, and I've got an oily phase. And so how do I get rid of the oily phase? What he did is he added cognac

And why did he add cognac? Not because he was a hard-drinking alcoholic. It's because if you've got a fat phase here, and you've got an aqueous phase here, and if you add alcohol, you've got $\text{CH}_3\text{CH}_2\text{OH}$. This can bond to the water by a hydrogen bond, and this aliphatic tail can stab the fat and bring them into solution. That's why you have these recipes. Do you ever wonder why the recipe says, add brandy, or add this, and then two steps later, it says flame? You say, geez, I just put the brandy in, now it's vaporizing away. Isn't that kind of stupid? No, it's not!

This is what you're doing. You're cosolvating. If you're ever making a cream sauce or something, and all of a sudden, everything just curdles? First you scream. You go, ahhh! Phase separation. The second thing you do, is you get some of this, and you cosolvate it.

All right. So let's see what Lautrec did. Lautrec-- I might have to dilute the volume here. We've got quite a lot in here. So just to make the point. So here's the louche, and now we're going to add cognac. He called this drink, Le Tremblement de Terre. The earthquake. He had a walking stick a meter long that was hollow, and it always had this in it.

Look! Look at that. Isn't that something? So now it's this beautiful blonde, golden color. It's clear. So this is all phase separation and so on. At the end, it's all about chemistry.

All right. We'll see you on Wednesday for our wrap-up. Good.

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