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PROFESSOR: All right. So today we're going to start the last section. We're going to do three lectures on phase diagrams. And I've given this the label here of Stability, Sustaining the Solid State.

We've talked a lot about the solid state in 3.091 as the vehicle for teaching the rudiments of chemistry. One of the things we have not talked about, is what are the conditions that sustain the solid state? How do I know whether something's going to be a solid, or a liquid, or a gas? This is very important. For example, if you're in a foundry, you're running places, making auto parts, you have to know what the solidification temperature is of the alloys, so you can get the parts out quickly and keep productivity high.

It's even important in failure analysis. You know, when they were looking at things like the rubble from the World Trade Center by understanding phase stability, the thermal history was imprinted in the metal. It's possible to determine what temperatures were achieved, and therefore, what the chain of events was that led to the collapse of those buildings.

Now you might say, well, isn't this straightforward? I mean, for example, you just look up the melting point or boiling point. Water, 0 degrees C. Melting point, boiling point, 100 degrees C.

Well, suppose you decide to realize your life's ambition. You're going to go and scale Mount Everest. So you pay the \$10,000, you get a license from the Nepalese Government, and you're at base camp at 20,000 feet. You're sitting there, you've got your campfire going, you've got a hankering for a hard-boiled egg. And you start, you put the eggs into boiling water and you cook them 10 minutes, you take them out, and they're still runny. You say, I must've lost track of time. So you cook them 20 minutes, and they're still runny. And you cook them 30 minutes, and they're still runny. And you eventually come to the realization that at 20,000 feet, the boiling point of water is below the denaturing temperature of egg yolk. So now the boiling point is a function of pressure.

So you know, we could have one of these Iron Chef cookoffs, only the dish is soufflé, only we'll have the contest at Flagstaff, Arizona, where the altitude is so high that the classical recipes won't work, because the boiling point, the atmospheric pressure, and everything conspire so that you're not going to be able to support the soufflé. So you're going to have to understand phase diagrams. In fact, if you understand phase diagrams, that's your ticket to being a four-star chef in the kitchen.

Well, here's another place we can look at, where pressure has an important role. Let's look under the hood of a

car. You're running an internal combustion engine. So this is the engine block, and there's combustion going on inside. We've got to keep this thing from overheating. It could damage the metal. In extreme, you could melt the metal. So we've got cooling channels in here with water flow. But then the water's going to heat up, and the water's going to boil. So we've got, over here, the radiator. So it's really a double cooling system. The water cools the block, and then the radiator cools the water.

So how's that going to work? Well, here, the temperature is on the order of about 90 degrees C, and here the temperature inside the engine block is much greater than 90 degrees C. It's several hundred degrees C inside that engine block, and we've got water going like this. So we've got cooling water flow in this manner. And now cold water goes in and hot water comes out, and then we get into the radiator, and we've got channels here, and we've either got a fan or some kind of air flow.

And so now, what's the gambit here? I want to see what's going on inside this radiator. So if this is the wall of the radiator, and in here I've got water, and over here I've got air, the idea is to have a high heat flux to get the energy out of the water and cool it down.

Now, if things get really, really hot in here-- let's say you're zooming along down the highway at about 90, I mean, about 65 miles an hour, and all of a sudden you come upon a collision, and you have to go to a dead stop, all that energy in the engine is now dumped, and the water could overheat. And in the extreme, if it overheats, it can actually go into a boil. And this is bad. Because heat transfer is really good between a liquid and a solid, and it's really poor between a gas and a solid. This is a low heat flux, and this is bad. High heat flux, that's good. This is the bubbles. This is boiling.

And why? Because what transfers energy? It's the atoms. And what's the atom density in a liquid versus the atom density in a gas? You just have really crummy heat transfer. That's why insulation involves dead airspace. Because you have very poor atom density.

So what can we do in order to try to repress the bubble formation? Well, we said if we went up Mount Everest, we went to high altitude, the boiling point went down. And why did it go down? Because the atmospheric pressure is lower. So why don't we go the inverse here, and we'll put a pressure cap on the radiator, and make the pressure go up, and when the pressure goes up, it exerts a back pressure and represses bubble formation? So by increasing pressure, we can increase the temperature, and get the temperature up.

So let's say  $p$  equals-- if you look on the top of the pressure cap, it will say 15 psi. And 15 psi is almost 14.7 psi, which is exactly 1 atmosphere, which in SI units is, and I know this to six significant figures, 101325 Pascals. Or, you know, from Torricelli, 760 millimeters of mercury, that's the column that's supported.

So we're at 2 atmospheres pressure in there, and with two atmospheres of pressure, we can raise the boiling point to 106 degrees C. And then what we can do, is now change the composition. So we change the pressure, and I change the boiling point. I change the composition. add 50% ethylene glycol. So now I've got a one-to-one mix, ethylene glycol and water. And that takes the boiling point up to 130 degrees C, or 265 degrees Fahrenheit.

So another example of how we can manage systems. So when I'm showing you by these several examples, is that the boiling point is a function of pressure and composition. So we can tune the boiling point. See we were tuning materials properties before. Now we're tuning physical chemical properties, because that's what chemistry is all about. It's about control. It's about management. Management to advantage.

So how do we know what to do here? Can we predict this from first principles? No. Systems are still too complicated. Our models aren't robust enough. So instead, we turn to an archive. So we have phase diagrams. And the phase diagrams guide us in our search for better management of material systems. And these are stability maps. They tell us which phases are stable under which conditions of pressure, temperature, composition. You can consider them as archives. So that's what I want to talk about, because it's really important to know this stuff.

OK. So what are we going to do? So first of all, let's-- I don't want to write on that one. This is interesting. This could be a work of art. I'd hate to desecrate it. You like? This is really good! So I'm just going to leave that. That's very good. That's excellent.

OK. So I've been talking about phase. What is a phase? Let's get the right definition here. What is a phase? It's a region uniform chemical composition. Just to get it down. it's a region in a material, region of uniform chemical composition, and it has these other properties. Uniform chemical composition. It's physically distinct. And I'll show you by examples, but let's just get the definition down. It's physically distinct, and in the extreme case-- so that means it's bounded. It's physically distinct. That's a fancy way of saying that you can put a boundary around it. It's bounded. And then the other property that it has, it's mechanically separable in the extreme. And so that's in the case where you have a multi-phase system. You can point to the different p.

So what I'm going to do, is I'm going to give you some examples. And so I'm going to let circle p equal number of phases. I'll give you some examples. Why am I using circle p? Because just plain old p is already pressure. So pressure, so this is kind of a Western motif, you know? Like a Circle Bar Ranch or something. So it's a p with a circle. That's my font. That's how I say number of phases.

So let's take a look at some examples. So here's some examples of p equals 1. So simple one is pure water. Pure H<sub>2</sub>O liquid. It has all of this. Wherever I have the water, all right, here's some water, it's all of the same chemical composition. It is physically distinct. I can put a boundary around it. And in this case, there's nothing to separate,

because it's just a one-phase system.

White gold. White gold is one phase. Because we have gold. Obviously we have gold. If you market something as white gold, it has no gold, you'll go to prison. And how do we make white gold go to its white color from the normal yellow? We add silver and we add nickel. And these are all FCC metals, and they substitute for one another on the lattice, and if you sample anywhere in the white gold, you get the same chemical composition, and so on.

Air is an example of a one-phase system. It's a gas, and in decreasing order, we have nitrogen, oxygen. So it's a solution. We're breathing a solution. Nitrogen, oxygen, argon are the main constituents. There's some CO<sub>2</sub>, some sulfur dioxide if you live near a power plant, NO<sub>x</sub> if you're near a tailpipe, and so on and so forth.

And then the last one I'll give as an example is calcia-zirconia. Or cubic zirconia. Let's just call it cubic zirconia. The holidays are coming, so we better get cubic zirconia up here. That's the poor man's diamond. Cubic zirconia, which consists of a solid solution of calcium oxide in zirconium oxide. This is a solid solution, so it's continuous and chemical composition identical.

Now, contrast that with two-phase system. So  $p$  equals 2 looks like this. So let's look at, instead of simple water liquid, if I have ice cubes in water. So now I have two different phases, and they're separated by state of matter. State of matter is the issue here. Because I have a solid-- this is solid-- and I'm going to put the boundary around them. The composition of the solid is different from the composition of liquid. They're both the same water, but you can tell it's a different crystal structure and so on. And I can put boundaries around, and it's mechanically separable. You can pull the ice cubes out of the mix.

Milk is two-phase. Milk has a fatty phase and it has an aqueous phase. The aqueous phase contains the minerals. That's why you can drink skim milk and still get your calcium, because calcium, even the general public knows calcium is a mineral. It's not elemental calcium, it's a calcium compound. But it's ionic, it's soluble in water, and the fat contains the other parts.

You know from last day, this is one of the lipids. And so you have fat globules that are mechanically separable and distinct from aqueous. So they actually have a different chemical composition, different type of bonding. Right? This is largely nonpolar, and nonpolar doesn't like to dissolve in something that is polar and hydrogen-bonded. So they phase separate. I've been saying phase separate all along. Now you know what we mean by phase separate.

Here's a third one. This is really cool, because you won't get this in any other chemistry class, because only 3.091 talks about such things. David, can we cut to the document camera? I want to show you a piece of snowflake obsidian. Obsidian is a volcanic glass. So here's the piece of obsidian. And what you're looking at is, the black

area is the glassy part, and the white is actually some of the obsidian that has decided to devitrify. And it is turning crystalline. And so those are islands of obsidian crystal sitting in a matrix of obsidian glass.

If we go back to the-- I picked that up in Yellowstone Park. It's fantastic. There's a wall, just a wall of obsidian that comes down. And I think I've got an image here. There it is. This one I pulled off the internet. So this is crystalline phase, and this is the amorphous phase.

And the overall composition, it's a glass, it's a silicate. And why isn't it transparent to visible light? Because it's got iron in it. The iron gives it the absorption and capabilities. The band gap is invisible, so it's black. But then when this crystallizes, it's got a different index, and it's mainly  $\text{SiO}_2$ . It's really the cristobalite phase of the obsidian. So that's cool.

So this is actually differentiated on the basis of amorphous and crystalline of something that's virtually the same chemical composition. So this could give you an idea of what happens in the area of phase separation. OK.

Now the second thing that I have to bring to your attention, is that these phase diagrams treat systems at equilibrium. They're stability maps, and they treat systems at equilibrium.

So what is equilibrium? Let's just get one time up here a definition of equilibrium. Equilibrium is a condition which there is no net reaction taking place. The system could be reacting. If you're looking at the ice cubes in water, the ice could be dissolving, and some of the water could be freezing, but overall, with time, there's no net reaction. It's a dynamic system with no net reaction.

And it's characterized as the lowest energy state. Systems strive towards equilibrium. If it's the lowest energy state, no net reaction then. If a system is truly at equilibrium, the properties should be invariant over time, because there's no net reaction.

You can't prove equilibrium. You can only demonstrate the absence of equilibrium. Because at equilibrium, there's nothing, there's no net reaction.

And it could be attainable by multiple paths. So in other words, if I have ice as the equilibrium phase, I can make it by freezing water, and get to the same ice at the given temperature and pressure. Or I could sublime. But if I specify the pressure and the composition, I should always end up with the same system. So attainable by multiple paths. Because it's a stable state, so it doesn't matter how you got there. It's a state function. And you know from your physics, a state function has the same value, regardless of how you arrived there.

And then the last thing is, I want to differentiate. See, these are all single phase, but some of them are just one element, some of them are just one compound, and some of them have a whole mix. So we have a way of

quantifying the degree of chemical complexity by using the term called component. It's a measure of chemical complexity. It's the number of chemically distinguishable constituents. And again, these are definitions. I'll give you some examples so then the definition comes to life.

I like to think of it as the number of bottles you've got to pull off the shelf to make the final product. The building blocks. So for example, water is just water. You could say, but it's hydrogen and oxygen. But if you take 560 or some other thermal class, you'll learn that they're bound by mole ratio. You don't have freedom of hydrogen and oxygen. So it's just one bottle, whereas to make white gold, you need three bottles. You need a bottle of gold, a bottle of silver, and a bottle of nickel. So that's a three component system.

And I'm going to designate the components by  $c$  with a circle around it. Because  $c$  without a circle is already composition, concentration.

OK. So now we can put all of this together, and we'll show the difference between multicomponent and multiphase. So we'll make a little table here, and here I'm going to talk about one-phase systems, and distinguish on the basis of components. So if it's single phase single component, that's just water. One phase, one component. Simple liquid.

If it's two components one phase, that could be calcia-zirconia. I need a bottle of calcia and a bottle of zirconia in order to make this two component single-phase system.

And then to have three components, that's the white gold. It's still single phase, but I need the gold, silver, and the nickel, whereas if I come over here, I've got two phases. That could be slush. Slush, that's ice water. It's just one component. I just start with water, and drop it down to 0 Centigrade, and I'm going to end up with ice crystals in the water. So that's one component. I just needed one bottle. Literally, one bottle.

All right. Now what about two components, two phases? Well, we saw earlier when we started thinking about solubility, we did the bilayer with carbon tetrachloride and water. Remember, we dropped potassium permanganate and iodine, and the potassium permanganate dissolved in the water, and the iodine dissolved in the carbon tetrachloride? Two different components. I need a bottle of carbon tet and a bottle of water. And they'll phase separate. They don't dissolve in one another, because this is a nonpolar liquid, and this is polar hydrogen bonded.

That's the origin of phase separation. It's all about bonding, and bonding is all about electronic structure, and that sounds like a good topic for a class in chemistry.

And then the last one here is obsidian. The snowflake obsidian, in which the components are  $\text{SiO}_2$ -- so I'm going to have three components and end up with two phases.  $\text{SiO}_2$ , there's some magnesia, and then the black comes

from the magnetite.  $\text{Fe}_3\text{O}_4$ . So I've got three bottles off the shelf, and I end up with something that is crystalline and amorphous. So that's where I get the two phases. Three components, two phases. It's great.

So now I want to look at some stability maps. And I'm going to start with the simplest of all, which is the one we know best from human experience, and that's water. So we're going to look at the one-- so it's a one component. So for water, we start with  $c$  equals 1, and the example is going to be water. One component phase diagram.

So we don't have a composition axis, because the only thing we can vary is pressure and temperature. If we change composition, we've lost water. So it has to be axiomatically, no variation composition. All we have is that the coordinates of temperature and pressure.

So there it is out of the book, and I'm going to draw it a little bit differently, just to emphasize three of my favorite words. Not to scale. Otherwise you can't see some of the subtle features.

So overall, it's a y-shaped diagram. And this is pressure. Let's make it pressure in atmospheres. Then our human experiences is at 1 atmosphere. So at the highest temperatures, we expect to have vapor, and at the lowest temperatures, we expect solid. And in between, we expect liquid.

And then if we look at the 1 atmosphere isobar, what's happening on this line? On the one side of line it's liquid, and the other side of line, it's vapor. At this temperature, liquid and vapor coexist. I call that the boiling point. So I'm going to put 100 here. And we already learned from our little example of Mount Everest that this locust here, this line, is the liquid equals vapor two phase equilibrium. And you see how it changes? If I go to the top of Mount Everest, the pressure is less than 1 atmosphere. which means the boiling point of water is below the denaturing point. So this actually gives you the map. Or if I put the pressure cap on, I go up here.

And you can use this in the kitchen again. If you love wild rice, and you can't wait 45 minutes when you get home, use a pressure cooker. What the pressure cooker does, is it allows you to have liquid up to 130 degrees Celsius. See, you can't steam it. You've got to soak it in water. And you know the Arrhenius Law. If you can get the temperature up by 30 degrees, you'll cut the cooking time in half. So how do you get water, liquid, at 130 degrees? Then you can cook quicker! Pressure. Seal it. And then you've got liquid water way, way up here.

Now over here, this is solid goes to liquid. So this is the freezing point line. At 1 atmosphere, that's 0.0 Celsius. And you know, if you go skating-- so let's say the ice is minus 5 Celsius. And you're here, but you put your weight on the blades, and the blades have small area. So pressure is force per area. So that puts you up here, and now you cross, and now you glide on water. Film of water.

You ever watch a hockey game? I grew up in Canada. We used to say, well, the ice is fast. Why is the ice fast?

Because you get down to temperatures where you just get the right slickness of water. If the ice is slow, the temperature is so close that, you know, you get these big, bruising hockey players, and they're moving up into here, and it's like they're dragging.

And if you ever come from Minnesota or North Dakota, if you've ever skated when the temperature gets down about minus 20, minus 30? It's a different experience, because you never get across this line. Your blades are just, they can't get a good grip.

See? Everything you need to know is here. This is four-star chef, this is prize-winning hockey player. We haven't got off the 1 atmosphere line yet.

OK. So now I'm going to say, this is single phase, right? It's just vapor. This is single phase, and this is single phase. It's all solid. And along this line, it's two phase, isn't it? Solid-liquid. This is ice cubes, isn't it. Anywhere along this line is ice cubes in water.

Look at this one. This is liquid vapor. This is solid, liquid-- all three of them coexist here. This is  $p$  equals 3, which means, ice cubes floating in boiling water. And this happens at only one point. It's called the triple point, and its coordinates are-- this is not to scale. So this is 0.01 degrees C. It's a 1/100 of a degree higher. And the pressure here is 4.58 millimeters of mercury, which then you can convert using the 760 as 1 atmosphere.

Oh, and this is solid-vapor. You can go directly from solid to vapor down here. If you hang up your clothes on a line and it's minus 20 degrees outside, first thing that happens, the clothes freeze. You come back five hours later, and the clothes are dry. Well, what happened? Did somebody take them in? Run them around the clothes dryer, then hang them up for you? No. You're going directly from solid to vapor, down in here.

So here's the whole story of the phase diagram. One last thing I want to point out. Here, you're at a given temperature and it's vapor. And then you squeeze, squeeze, squeeze, and now things get closer together, and you go from vapor to liquid at constant temperature. That makes sense, right? I start from vapor, constant temperature. I squeeze it, I get liquid, I keep squeezing, I should make solid.

Here's vapor. I squeeze, I get solid, and I squeeze harder, and I get liquid. That makes no sense at all, but that's what happens.

What does this tell me? It tells me that the number of nearest neighbors in the solid is greater than the vapor. Yeah, I get that. But the number of nearest neighbors in the liquid must be greater than the number of nearest neighbors in the solid.

This is an exception. When I see this negative slope, it means that ice cubes are going to float on water. That's



what I learn from this negative slope.

So let's put that down.  $dp$  by  $dt$  when  $dp$  by  $dt$  is less than zero. This is for solid equals liquid. That means that the density of the solid is less than the density of the liquid. All from here.

OK. Good. So let's look at a few other phase diagrams. I think I've got a few things up here. Here's silicon. Pressure versus temperature. Its normal melting point is about-- see, now I said normal melting point. After today's lecture, if somebody says, what's the boiling point of water? You don't go, 100 degrees. You say, at what pressure? And they go, oh, I hate you. I hated you before. I'm going to use an adverb here. Now I really hate you.

OK. So this is the normal melting point of silicon. It's about 1430 degrees Centigrade, or a 1700 something Kelvin. And it also has this negative slope. And what does that tell you? That liquid silicon is denser than solid silicon, and it's a good thing it is, because we wouldn't have the microelectronics age if it weren't for that. We couldn't have Teukolsky crystal growth and everything else that makes silicon dirt cheap. You know why it's dirt cheap? Because it's made from dirt. That's why it's dirt cheap. It's true.

Here's aluminum. This is normal. This is the normal solid-liquid equilibrium. This is FCC metal, which is the closest packed. Axiomatically, the liquid must be less well-packed. All right? So this is dog bites man, this is man bites dog. This is the unusual one.

OK. What else do we have? Nitrogen! Here's nitrogen. I drew this. So there's the 1 atmosphere line. Nitrogen boils at 77 Kelvin, and it freezes at about 63 Kelvin. And it's got the positive slope that you'd expect, and so solid nitrogen is denser than liquid nitrogen. And you can remember 77 Kelvin.

You want to remember a few of these things. I wanted to point out to you that at atmospheric temperature, ambient temperature, you can remember 20-20. 20-20 vision. So at 20 degrees C, it's roughly 20 millimeters of mercury, is the vapor pressure of water. It's not exactly true, but it's close enough. I think it's really 24. But 20-20 is nice to know. And what's the street address for MIT? 77 Mass Ave. That's the boiling point of liquid nitrogen, 77 Kelvin.

So I thought we'd do a few things here. And I'm going to show you a little bit of fun and games with liquid nitrogen. But first, I've been instructed I have to practice safe laboratory-- So I'm going to put on my lab coat. Yes. It's a nice lab coat. Mm-hm! Yeah, look. You want to know-- let's go back to this. They have to know where the-- this is not just any old lab coat. This is a nice lab coat. This is from France. It's from MAISON DUTECH. See? Notice the collar. It's not that typical, you know. MAISON DUTECH.

OK. Let's go back to the phase diagram. So Dave Broderick is going to help us here. So we're going to have some fun. I'm going to put on a face shield so I don't blind myself. All right. Here we go.

All right. So let's get some liquid nitrogen. Sounds different, huh? Sounds terrible for me. All right. So we've got some liquid nitrogen here, and I'll pour it into a Dewar.

So what happens when you wet a sheet of paper with ink with liquid nitrogen? What kind of bonding is there in liquid nitrogen? Look. No running, no running. If it's liquid nitrogen. I tell you, everything you learn here is so valuable compared all the other stuff you learn here--

All right. So there's a couple of things. So let's look at glass transition temperature. So this is a latex glove. You can see it's above its glass transition temperature, and the cross-links are snapping it back. What I'm going to do, is take it down below its glass transition temperature, and turn it glassy and brittle. So that it's below the TG.

Here's some paraffin. Paraffin, which is also a polymer here. Take the paper off. OK.

So here's paraffin. Look. Look at the van der Waals bond. All right? This is van der Waals bond. Now we're going to go below the TG.

It's liquid nitrogen! It doesn't matter.

OK, you can hear it already. So it's now below the glass transition temperature.

So what else have we got? Oh, you've heard of the glass flowers at Harvard? Well, we've got glass flowers here, so. Here's a rose. See, in the proteins, you know, it's above the-- you know, it's soft. But now, we're going to put the-- mm-hm. Here we go. You ready? Oh, come on. It's not a kitten. What's the matter? It's still burbling here. We have to wait until it's dead. This is for science. OK. Now it's below its glass transition temperature.

Oh, I'm sorry, David. I should put this over on the other side.

But maybe it's the red, or maybe it's because it's a rose. So here's the chrysanthemum. Today is your day. Let's go. Get this thing moving! Yeah. So there you have it. There you have it. I think that's-- oh, there's one, may we go back to the slide? Better put the gloves on for this. I'll have to write apology letters.

OK. So we're going to do next, is we're going to look at phase equilibriums. There's the melting points and boiling point of oxygen, argon, and nitrogen. And what you notice is that nitrogen boils at a lower temperature than oxygen and argon.

So what I'm going to do, is I'm going to pour some liquid nitrogen into this beaker. And then inside the graduated cylinder, I'm going to let it sit here, and we're going to condense air. And the result will be that we're going to start condensing liquid oxygen, and they'll be little bits of argon ice floating in liquid oxygen. And liquid oxygen is faintly

blue, and it's paramagnetic, as you know, because it's got the unpaired electrons, which means that it will levitate in a magnetic field. I couldn't bring a big magnet in here, but we'll see if we can make some blue stuff. And it's foaming, because this would be like pouring water into something that's-- I don't know. 300 degrees Centigrade. But eventually, the heat transfer gets low enough that you have stability here, and-- yeah.

OK. Oh, that's terrific. OK. What else have we got? Let's go back to the slide. God, I hate this thing. OK. So you've been looking at that nitrogen. Let's look at what's next.

Ah. Now if you solidify nitrogen here, you get a whole bunch of different polymorphs. Different crystal structures. So there are about five or six different crystallographic forms of solid nitrogen. For that, we'd have to bring liquid helium. 4.2 Kelvin. Very cool stuff.

Here's carbon dioxide. Now, it also has the positive slope, so solid will sink in liquid. But look, the interesting point here. The triple point is 5 atmospheres. At atmospheric pressure, you go directly from solid to gas. It sublimates. And that's advantageous. When we use carbon dioxide as a coolant, when it gives up its enthalpy to cool, it doesn't then turn into liquid. If you chill something with ice, with water ice, when it gives up its enthalpy, the object is now swimming in water. And that's no good. So hence we have the term dry ice, because we go directly from solid to vapor.

And we want to prove this. So what we've got here is a big block of dry ice. So this is at minus 78 degrees Celsius, and it's still stable here. Well, it's subliming before your eyes. It's smaller than it was when we started the lecture. So what I'm going to do now-- oh, I'm not wearing that stuff. I guess I'd better. They're going to write me up on some log, teaching you bad practice. But anyways.

All right. So what we're going to do, is we're going to test the proposal that this actually goes-- so I've got some water. Here, David, let's go out to the video. So let's take some water. I think we got water from France. Goes with the lab coat. This is Evian, OK? So I pour the Evian into the Florence flask. This is Florence. Florence is round, and the Erlenmeyer is the flat one. So let's move this guy. You're going in the backstage for a while. You just keep condensing

All right. So now, this is here. Now what we're going to do, is we're going to put some dry ice in there, and see if we go directly from solid to a vapor. Take a chip off the old block, here.

OK. So now you can see that it's going directly from solid to vapor. So that's carbon dioxide bubbles. And we assume that the phase diagrams is correct. I mean, another thing we could do, is-- I mean, I know what club soda tastes like. I could just test it, right? Yeah. It's carbon dioxide.

Now! Here's the other thing. You know, Schweppes likes to pride itself on tiny bubbles. They have a tagline, Tiny

Bubbles. Right? So here's Schweppes. And you can see Schweppes, with their wimpy little tiny bubbles. Can you get that, David? But we have, we have big bubbles.

I mean, this is pure. You can't get any better than that. I got Evian water, and I got a block of carbon dioxide. I like making my own carbonated water. I've taken it to a new level.

OK. What else do we have? Well, let's see if we made any liquid oxygen here. Try this. I don't know if we got anything here. Oh yeah! Oh, wow. Look. OK. So that liquid in there-- oh, I see. You've got a separate thing. I don't know if you can see. It's condensing. That liquid in there, that's liquid oxygen. I won't drink this. But I can inhale it. Pure oxygen.

I could have a cigarette, and just put the cigarette in there. What happens if I put the lit cigarette into the oxygen? All that happens is that it burns quickly, that's all. There's no explosion. It burns quickly. If you walk into a room full of oxygen, all that happens is you'll singe your nose, that's all. There's no explosion. It's just oxygen. There's no fuel. The fuel is just in tobacco, and there's not much. It's not a problem. A room full of oxygen? Pfft!

OK. Let's go back to the slides. What have we got here? We've got some examples of other phase diagrams. All right. Yeah.

[MUSIC PLAYBACK: FROM 'PHANTOM OF THE OPERA']

PROFESSOR: Actually, it's quite tasty. All right. So. Now, here's zirconia. Now, here's the thing to know about zirconia. Look at all the different phases. And cubic zirconia is the one that has a high index of refraction, but it's stable only at temperatures exceeding 2000 degrees C. So that's no good. So what I'm going to show you next day is that by changing the composition, and adding calcium oxide, we open up this zone here that's labeled cubic, and we get it stable all the way down to room temperature. It's an example of changing composition to get the stability of a phase that we want.

This is carbon. So down here, the normal form, as we've learned earlier, the normal form is graphite. Diamond is formed at elevated temperatures and pressures. And this is liquid carbon. All right? Now, to make artificial diamond, you can try putting graphite in an anvil, and squeezing, and squeezing, and squeezing, and coming up into here. And then it becomes metastable, and then maybe, because the activation energy to jump from that  $sp^3$  hybridized state to  $sp^2$  is so high, the diamond is stable. So you don't have to go running home to see if your diamond studs are now turning into graphite. They won't. Once you get into this zone, they'll stay. The activation energy is too high. You need more than  $1/40$  eV to do it, is necessary.

But in the 1950s, General Electric, its Schenectady research labs, reasoned that because carbon is so soluble in

iron, they could dissolve carbon in liquid iron, and then raise the pressure and temperature, and then change to exsolve and cause carbon to precipitate out of molten iron. That's the birth of artificial diamond. That's how they did it. Using this concept, but then dissolving it in molten iron.

[MUSIC PLAYBACK: 'DIAMONDS ARE A GIRL'S BEST FRIEND']

PROFESSOR: I don't know how that got in there. All right.

Here's one for mercury. I looked it up, using the tools that you've been taught here in 3.091. So this is a paper phase diagram for mercury. And physicists drive me nuts, because they plot temperature versus pressure. I want pressure versus temperature. So I just turned it around. And so here's the liquid line. So you know that liquid mercury is going to float on solid mercury, and there's a plurality of solid phases. And these are all different crystal structures.

Now I've got a treat for you. I was in Barcelona several years ago, and I saw the mercury fountain that was made by Joan Miro in collaboration with Calder. Calder has the big sail outside of East Campus. So Calder collaborated with Miro, back in the '30s and '40s. And this is in honor of the miners of Almaden, where there are cinnabar mines. And the miners fought bravely against the Fascist forces of Franco, and Miro wanted to honor them. So here's their museum. It's a beautiful place up on top of an escarpment over Barcelona.

And what I'm going to show you is a mercury fountain.

[MUSIC PLAYBACK]

This is liquid mercury. The speed has not been altered. This is a liquid at room temperature, density 13.5, metallic bonds. Look at it. Very high surface tension. Look at the way it shimmers. Look at this shot. This has not been altered. That's the way it pours into gravity field. It's really fantastic. And of course, mercury vapor is toxic, so the whole thing is in a--

[END MUSIC PLAYBACK]

PROFESSOR: Oh, that's the-- I cut that snippet out of the documentary. OK, we don't want to see that.

So they have the whole thing inside of a polymethylmethacrylate cage, to keep the mercury vapor from affecting the people that work in the museum.

Here are some phase diagrams from hell. This is bismuth. And look at bismuth. Bismuth is like water, and like silicon. So the solid is less dense than the liquid. But look at all of these different phases. Here's sulfur. Sulfur is crazy. Look, phases in the solid phase, there's even phases in the liquid! Different phases. They're allotropes.

Here's sulfur. Elemental sulfur, the disulfide, hexasulfide. It makes rings, it makes long chains.

And these are called allotropes. They're different forms of the same element. So oxygen is O. There's the diatomic molecule. And the triatomic molecule, which is ozone, these are all allotropes of oxygen. What else do we have? OK. This is polymorphs. So this is alpha goes to beta. See, different crystal structures. You could see with your naked eye what's going on here. Different crystal structures.

And then this goes to lambda, and then finally, they're pouring here. And if you get a very high cooling rate, and you've got those long chains, what happens? You don't form the crystal. You form the amorphous form. So they'll call this forming plastic sulfur. We know better. It's amorphous sulfur. It's not plastic sulfur.

Here's water, a complete diagram. Now, this is in kilobars. So there's all the different phases of water. There's the negative line. That's the thing here. But at very, very high. Look at all the different phases of water. And they have numbers on them. If you read Kurt Vonnegut's *Cat's Cradle*, there's ice nine. You get that going, it freezes the whole world, right?

But here's, I draw your attention on this one. You see this point here? This is ice seven. At 100 degrees C, it's solid. You need 25 kilobars. So we could go over to the lab, take some water, put 25 kilobars on it, make solid ice at 100 degrees C. And it'll be stable. Look! This is minus 78. It's been here for a long time. So now I come into a cocktail party with this, I drop this ice cube into a glass of aqueous beverage, it sinks to the bottom, and the beverage heats up to the boiling point. That's what this is telling you! That'll get you popularity instantly. How did you do that? How did you do that?

And up here is the supercritical fluid, the last thing we haven't said anything about. Look. If you take a gas, and you keep squeezing it and squeezing it, eventually the gas molecules are close enough together that they're indistinguishable from the liquid phase. Or if you start here, with the liquid, and you keep raising the temperature, the density goes lower and lower until the molecules are far enough apart that you can't tell this zone, whether it's a rarefied liquid or a highly compressed gas. The properties criss-cross. This is supercritical. It has liquid-like transport properties, and vapor-like chemical properties. So you can end up doing things that are very, very different. Now, I'm going to give you an example of decaffeinating coffee by taking the coffee, going up into the supercritical regime, which allows you to extract the caffeine, and not brew the coffee. So you want to just get the - well, if you just heat it up, you'll make the coffee.

So here's an example. It's called solvent extraction. Historically, this solvent was methylene chloride, which is also used as paint stripper. We don't do that anymore to coffee. They did in the '60s! They did. They also used trichloroethylene. It works really well to leech out the caffeine. How much is left in there for you to taste in your coffee? I don't know. Maybe that's why people were so excited in the '60s to drink their decaffeinated Sanka. I

don't know.

But anyway, so you take the green beans in carbon dioxide as supercritical, and drop the caffeine level, and then you play with temperature and pressure to go over the KSP. The caffeine salts out, and then you recycle the CO<sub>2</sub>.

OK. I hope I've given you some introduction to phase diagrams. And we'll see you on Monday.