[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: We will get started. So today's lecture is what I call case studies. We're going to explore heat capacity. It's not strictly speaking new material. But it definitely is worth going through in a little more depth and a little more slowly than we've seen it so far.

Today's lecture is all about heat capacity. And for those who are just joining, the lecture notes will be up shortly. So this is heat capacity. And I hope to convince you that these are keys to the kingdom, or at least the thermal kingdom. Heat capacity is not just another coefficient, it's the thing that you're going to need to solve many problems in material science.

So let's see, Gibbs free energy. Equilibrium at fixed T and P is balanced between H and S. So this you already saw. This you saw on day one with the baby book and then with the hot and cold packs. We're balancing enthalpy and entropy to find equilibrium.

So if you're going to balance two things, if they're really important, how do we calculate them? How to calculate H and S for a given phase at a given temperature and pressure? Doing this sort of calculation is going to be a lot of what we're doing going forward in 020.

So let's step through that. Let's start by calculating H. Calculating H of T at a fixed pressure. Start with H.

Back to the beginning. H equals U plus PV. So DH equals DU plus PDV plus VDP. This is the chain rule. That's the chain rule. Then we're going to use the combined statement. This is TDS minus PDV plus PDV plus VDP. This is using combined statement.

And canceling terms, we have TDS plus VDP. You did something like this on the p set. So it should be familiar. So combining this TH at fixed P equals TDS equals DQ reversible. That's why the enthalpy is often called the heat.

And, of course, we know this equals Cp dT So the change in enthalpy is tabulated by the heat capacity.

So that means we're going to use the fundamental theorem of calculus to express enthalpy at some T2 as a function of fixed pressure. It is going to be the enthalpy at some T1, the same pressure, plus the integral from T1 to T2, the total differential DH. And plugging in from above, this equals HT1 at P plus T1 to T2 dT Dp of T.

So in order to calculate the enthalpy at some other temperature based on reference data, the enthalpy at, let's say, a reference temperature, we need this heat capacity data, which, in general, is temperature-dependent. So this data we need.

What about entropy? Calculating S at T for fixed pressure. dS equals Cp over T dT minus V alpha dP. There's many ways you can get this. You could just go to table 4.5, or you could derive it. So that means that dS and fixed pressure equals Co over T dT.

So, again, using the fundamental--

AUDIENCE: Sorry.

PROFESSOR: Sorry?

AUDIENCE: Would it be possible for you to write with a bigger tipped marker? I'm kind of having trouble reading the details.

PROFESSOR: Sure, let me try to do that. That's always a--

AUDIENCE: If that's OK with everyone.

PROFESSOR: Yeah, yeah. No, I appreciate those sort of comments. Because I know that Zoom also samples things differently, and I see it differently on my screen than you see it, which is also different than you see it in the recording because of the way Zoom samples for bandwidth issues. So thank you.

So we're going to use fundamental theorem of calculus again. S at T2 at a given pressure equals S at T1 at that pressure plus T1 to T2 DS. Then we can put equals S at T1 pressure plus T1 to T2 Dt. And the integrand is Cp at T over T.

So, again, we need Cp as a function of temperature to do that calculation. So, again, we see for both enthalpy and entropy, the key to calculating these things for varying temperature is knowing the heat capacity function or the heat capacity data. So we're going to use these expressions so much in this class.

Let's talk a little bit about where heat capacity comes from. What is Cp of T for real materials?

We know for ideal gases it has this really simple form, like 5/2R for monatomic ideal gas. But we're interested in real materials in materials science. We don't make cars, and medical implants, and computer chips out of ideal gases. We care about the real stuff. So let's start with a relatively simple model.

Consider bonds as atoms on springs. We're going to consider bonds or atoms on springs, sounds good. Let's draw bond energy as a function of displacement. I trust everybody has seen something like this before, if not in 3091, then in another introductory chemistry class.

And let's see. So U as a function of R. This is energy of the function of atom to atom spacing. And you typically have something like this. That's going to be your bond energy as a function of distance. And there's an equilibrium position, let's call it R0.

And let's just say that my atoms are sitting there at that displacement. Let me draw my atoms here. Here's a spring. And they are at distance R0 from each other. Let's say that the-- I'll call this atoms are quiescent. They're just sitting there.

So this is a low-- or I'll say lower-- energy state. It's also lower in entropy. There's no disorder. There's no sense of mixed-upness. You know exactly where your atoms are. Lower than what? Let's draw a higher temperature state.

Again, there's R, U. I can never draw the same thing twice. So let's see what happens here. It's not too terrible.

So, now, R0 is still the same. But let's say that now I have more energy in the system. So my atoms are oscillating. They're vibrating around, I'll say there's some sort of-- they're vibrating around that minimum.

So let's draw that over here. Let's say that this is R0. But as drawn here, the atoms are a little bit closer together. They've compressed the spring. And they're on the move. They're vibrating. So the atoms are vibrating.

So you can see from this picture that the system is in a higher energy because this is an average energy of the atoms. It's increased here. And there's also a higher entropy, because there's an amount of disorder associated with the location or the vibrational state of the atoms. So this is higher energy.

Sorry, I said I was going to write with a fat marker-- higher energy and higher entropy. So that's a relatively straightforward concept. You can do a lot with this.

There are models-- I should say models for the heat capacity as a function of temperature that consider vibrations of the atoms. Vibrations of atoms in crystals, that's what we just drew. We drew a simplified model of vibrations in atoms and crystals. There's a word for these. What are vibrations of atoms in crystals? Those have a fancy name.

AUDIENCE: Is it oscillations?

PROFESSOR: It could be called oscillations. That's a little bit of a fancier name. There's also a name, phonons, which is a lattice vibration.

So there are different models. There's the Einstein model. This is a simple model. All vibrations have the same frequency. It's simple, but it was a first important test of quantum theory.

And there's a fancier model. There's the Debye model, which is that there's a range of available vibration frequencies-- a range of frequencies. And this range is associated with the range of wavelengths. That goes beyond our class. But I wanted to mention this.

We will solve these models later using stat mech. So later in the class, when we come around to statistical mechanics, We're going to solve for the heat capacity of solids using these models. So that's kind of neat, but we're not ready for that yet.

So let's look at some slides. Let's look at some data. So this is just an example of heat capacity-- sorry, there's a little bit of resolution issue here. But this is the heat capacity and constant volume, in this case, of aluminum as a function of temperature.

And this is reduced temperature. It is temperature over something called the Debye temperature. And the Debye temperature is characteristic of the highest energy vibrations in the solid. This is a concept you'll encounter in later classes.

So the circles here are data and the solid lines are models. And you see that the Einstein model and the Debye model both show heat capacity going to zero, at zero temperature. That's kind of interesting.

And they both also show the capacity saturating. Heat capacity comes up and it saturates at high temperature. But the Debye model is a little more accurate. It captures that temperature dependence better than the Einstein model. So we'll come back to that.

Here's another interesting comparison. These are the heat capacity for lead, silver, aluminum, and diamond. And in any given temperature, let's say 10 to the 2. So this is what? 100 Kelvin. At 100 Kelvin, the heat capacity of these four elements is very different.

But there's a self-similarity in the shape of the curves. So there's some underlying physical law that describes the heat capacity of all of these materials. And it's the Debye model which we just were introduced to.

The difference here is that diamond characteristic lattice vibrations are at a much higher energy than lead's characteristic lattice vibrations. That comes to kind of bonding, it comes down to structure, and it comes down to the weight of the atoms. Lightweight things vibrate faster than heavier things. It's true in atoms, it's true in swings.

So this is interesting. And the circles here are data and the solid lines are models. So you see the Debye model is really excellent.

Another thing I'll point out is that they all seem to converge at the same number. This is an early law. It's not really a law, it's an empirical observation, the law of delaying empathy, which is that the heat capacity at high temperature converges just to 3R for all solids. And it's a decent approximation for solids at high temperature.

If you need to estimate the heat capacity of a solid, and you have no data at your disposal, and you're in a hurry, 3R is not a bad estimate. R is 8.314 joules per Kelvin per mole. So 3 times that is roughly between 24 and 25. And that's what you see. If this data were taken up high enough in diamond, you can imagine that diamond would also converge to that law of Dulong and Petit.

I want to talk about cobalt.

AUDIENCE: Sorry, I have a question.

PROFESSOR: Yeah.

[INTERPOSING VOICES]

AUDIENCE: So these graphs, we're plotting CV, C sub V. Do these trends also hold for C sub V?

PROFESSOR: Yeah, so one thing, which we'll start to learn with experience is that, for solids at atmospheric pressures and the kind of pressure that we encounter for most materials processing and most industrial processes, CV and Cp are very similar.

Pressure dependencies with solids don't matter very much unless you get to very, very high pressure. So everything you just saw for these solid phases pretty much applies the same whether you're at Cp or CV. And we'll start evaluating those differences quantitatively later on in the class.

One way to think about that is it takes a lot of work to squeeze a solid as opposed to a gas, which we can imagine takes less work. Good point.

Let's talk about cobalt. Why about cobalt? I think it's interesting to read a phase diagram. We haven't really done that yet. This is a unary phase diagram. Let me bring out my laser pointer. So this is pressure and this is temperature. Somebody, how many different phases are pictured here?

AUDIENCE: Four?

PROFESSOR: Four. Can you name them?

AUDIENCE: I see three different solid phases of cobalt and then the liquid.

PROFESSOR: Right, liquid at high temperature. If you kept on heating, presumably you'd get the gas. But this is a high pressure phase diagram. These are in gigapascals, so these are high pressures. This over here is 100,000 atmospheres. So this is high pressure stuff.

And then, as you cool down, you have the FCC structured paramagnetic. Paramagnetic, that says para for short. You continue to cool down, you get an FCC-structured ferromagnet. And if you continue to cool down farther, you get a non-magnetic hexagonal close packed phase.

So you got one phase, two phase, three phases, four phases. Although, structurally, there's only two distinct solid phases, FCC and HCp. So that's how to read the study.

So, let's see. What if we heat up at ambient pressure. On this scale here, gigapascal, ambient pressure is basically 0. This 100 gigapascal is 10 to the 8 pascals, 10 to the 8. And atmospheric pressure is 10 to the 5. So atmospheric pressure is basically on the y-axis here.

And as we heat up, we go through a couple of transformations. We go from HCp to FCC. We go from FCC fara to FCC para. And we go from para FCC to liquid.

And these are the transformation temperatures. Epsilon to gamma, then there's a magnetic transmission at the Curie temperature, and then a melting point, a sub f. Those are just the reading phase diagrams.

Where do we find data for the heat capacity of cobalt? Lots of places. You've explored some of the databases already here. In this class, let's go with the NIST chemistry web book. It's a very convenient resource. I hope you've used it already. Heat capacity of cobalt.

So this is what happens if you go to the NIST website and you follow the links to this solid phase heat capacity of cobalt. And what do you see here? You see a parametric form. There's a polynomial expression. There are the values of the coefficients of the polynomial.

And there are three different ranges. There's a room temperature at 700K, 700K to 1,394, and 1,394 to 1,768. Based on what we just saw with the phase diagram, would somebody volunteer, why are there three different ranges given for the heat capacity of cobalt?

AUDIENCE: Is it because of the different phases?

PROFESSOR: Because of the different phases. The different phases have different heat capacities. In general, different phases have different heat capacities. So you see, here's the-- this is a non-magnetic HCp.

And then there's a little jump in the heat capacity. Everybody can see that. There's a little bit of a jump there in the heat capacity. It jumps to a slightly lower value. And you enter the FCC magnetic phase. And then there's this funny spike. This is at Curie temperature. And above the Curie temperature, there's a real discontinuity in heat capacity. It comes down.

Another thing I'll note here is, this data is all well above the Dulong and Petit. It starts at 25 and then it goes up. It goes up as high as 55. We're going to talk about that in a minute.

So how do you get this data? How do you-- where do you think this data came from? Sorry, Catherine?

AUDIENCE: Experiments?

PROFESSOR: Yeah, it came from experiments. That's right. It's empirical. This expression, expression like this, a plus b times t, plus c times t squared, plus d times t cubed, plus e over t squared, that's not a first principle solution.

That's not a theoretical model, that's just curve fitting. That's just curve fitting. So whenever you are dealing with data that has been curve fit, you have to always ask yourself, what is the range of validity?

So there's a model that gives you the capacity of this magnetic phase. And that model is only valid over the range over which the data has been fit. That's why this database and every other database will always specify the range. These coefficients are good from 700 to minus-- to 1,394 Kelvin. But if you exceed that range, use that model at your own peril. That's a really important point.

Now, let's talk a little bit about why this heat capacity is higher than 25. Why is it higher than those other solids? What is it about cobalt?

I'll give you a hint. It's not particular to cobalt. There are other metals, there are other materials that have this feature. Anybody know what it is? Anybody?

AUDIENCE: Is it because it's hcp structured?

PROFESSOR: No, it's not, although I do like the idea, the suggestion that it's structure-dependent. Is there anything else about this system? We've talked about it a little bit.

I'll give you a hint. So we talked about ways that energy can be partitioned in lattice vibrations. You have this idea about bond lengths. And as we excite the atoms, there's more energy in those bonds. But there's other ways that atoms can interact with each other and other ways that they can store energy.

So, for example, you might have a molecular system. And the molecules can rotate. That doesn't apply to cobalt. You might have an electronic conductor. And the states of the conduction electrons contribute. That's really something that physicists care a lot about. But there's another one here that's a particular to cobalt. Anybody?

AUDIENCE: Magnetism?

PROFESSOR: Magnetism, yeah. Thanks. So this is what we're going to-- there are others. So anything microscopic on the atomic and molecular level that can store energy, that can be energized, that can be excited, it all factors into the heat capacity. It's all in there. Heat capacity is this amazing thing that contains so much science.

So let's consider a ferromagnet such as cobalt. There are other magnets, of course. I don't know why I picked cobalt.

Now, we're going to draw pictures the way we did before with the case of lattice vibrations, except, now, we're going to consider the magnetic system. So let's consider two scenarios.

Scenario one, the magnetic moments, that's what I'm drawing here, magnetic moments-- and Those can be spin and orbital-- are aligned and quiescent. This is a lower energy, lower entropy state.

Now, what happens if I heat this state up? Let's say this is very low temperature. What happens if I heat it up? Let's pour some energy in. This is the low energy state, like that r not equilibrium bond links with the low energy state. What happens when I heat up? I know this isn't of course on magnetism, so just feel free to guess.

AUDIENCE: They can change the orientation?

PROFESSOR: Yeah. Let's say they start-- I don't know if that's visible at all.

The idea here is that magnetic moments are fluctuating. They're fluctuating just like the bond lengths were fluctuating before. Now the orientation of the magnetic moments are fluctuating. This is higher energy, higher entropy.

And just like there was a term phonons for the excitations of a crystal lattice structure, we have a term magnons for excitations of magnetic structure. Now, that was the beginning, middle, and end of our discussion of magnetism in 020. We're not going to discuss magnetism.

But I did want to make sure you're aware that the heat capacity includes all the interesting things that a material can do, not just vibrate bond lengths, but any other ways that energy can be partitioned into the crystal, or amorphous material, or liquid, or gas, or anything. It's all in there. It's all in the heat capacity.

So we go back and we look here at the heat capacity of cobalt again. We've got this spike. We've got this spike at the Curie temperature. And that is associated with all of the fluctuations that you find when a system is just about to order.

I think that's really interesting stuff. This excess heat capacity, well above and beyond the Dulong and Petit value of 25 can be largely associated with the magnetic interactions. That's neat.

I think we are done with cobalt and magnetism. Questions before I move on? Let's talk about phase transformations. And this is really about using data. But it also leads us into what we start-- the topic we start on Friday.

Let's consider something simple and important-- good place to start. Consider solid to liquid transformation in silicon. That's an important material. So I looked it up, and I found the enthalpy change, delta H solid to liquid at the melting temperature. Somebody, is that positive or negative? Is that an endothermic or an exothermic process, melting?

AUDIENCE: Endothermic?

PROFESSOR: Endothermic. You have to put a heat in to melt something. Plus a 50.2 kilojoules per mole. I looked at up. This is the change in enthalpy at the equilibrium melting temp, t melting equals 14-- 1,685 Kelvin. I always remember the Celsius a little bit better-- 1,412 degrees C. So that's hot, but not too hot.

Let me ask a question. What is enthalpy change, delta H, solid to liquid for t less than t melting? Solidification is exothermic. Melting is endothermic. So the question is, how much heat does the solidification process give off when you're solidifying below the melting point?

This is highly relevant to a lot of important industrial processes because, often, we don't form materials, including silicon, right at the melting point. Often we solidify at a slightly lower temperature. And you have to know this number in order to engineer your process. There's a lot of really good MIT IP on this and a couple spinoff companies that you may be familiar with.

So let me just write some stuff down. For the solid phase, the enthalpy of the solid at temperature equals enthalpy of the solid at temperature of melting, which is just what we did about 25 minutes ago, plus the integral from t melting to t, d dummy variable, heat capacity of the solid phase.

And for the liquid phase, we have the same type of calculation. Enthalpy of the liquid at a function at temperature equals enthalpy of the liquid at the melting temperature plus-- sorry, there it got a little squished-- dT prime Cp of the liquid.

So, again, all the information we need is contained here in these heat capacity data. So the thing we asked to calculate is delta H solid to liquid at some temperature. And I'm going to simply combine these results. It is equal to delta H solid to liquid at the melting temperature plus the integral of the heat capacity difference.

Heat capacity differences are really important when considering phase transformations. Let's look at some silicon data. Let's look at some data for silicon. I downloaded it and plotted it. So, first of all, where would you get thermodynamic data for silicon? Many, many places. Here are two. Here's some data right in the book, in the appendix. Silicon, Appendix C or something.

What is this data? Silicon, dia to l. Dia to l. What does dia mean in this case? Anybody? I called it solid. I called it S for solid. Why is it here dia?

AUDIENCE: Does that stand for a diamond-like configuration?

PROFESSOR: Right. Silicon is a diamond cubic structure. So that's a solid phase of silicon. So a lot of times, you need to interpret. Dia to l. And they use lowercase l, which is always problematic. So I use uppercase L. But, anyway, that happens at 1,685 Kelvin. There is an entropy of transformation of 29.8.

And the units are in the bottom of the table. In this case, it's joules per Kelvin per mole. And there's an enthalpy of transformation at 50.2 kilojoules per mole. I already told you that. And you can also look up the values here for the boiling of liquid silicon at atmospheric pressure.

There's lots of silicon data here at NIST, and also a string of materials and Wikipedia. Silicon is really important. So you're going to find the data all over the place.

So, pardon me, let me see what comes next. So this is what I'm going to do. I'm going to get-- I need this heat capacity data. I need the heat capacity data. Cp is a function of temperature. So I go over here to the NIST data. And I grab the numbers, and I plotted them.

So here we go. This is my plot. I made this in MATLAB. So this is my plot of the heat capacity, what they said it was, of liquid silicon as a function of temperature. And here it's the heat capacity of solid silicon as a function of temperature.

Now, let me ask you a straw man question. What sort of functional form would capture this trend? What sort of functional form captures this pretty well?

AUDIENCE: Linear?

PROFESSOR: Linear, right. What about this, what sort of functional form do I need to capture this data?

AUDIENCE: Quadratic?

PROFESSOR: Right. It looks quadratic. Here's a word to the wise. In thermodynamics, as in any science and engineering, you've got to always pay attention to the numbers. You always have to pay attention to the numbers. And plots can lie.

Let's plot these together. What happened? Same data. You see what happened? The y-axis range here was really teensy tiny. Basically, what this data is telling you is that for all intents and purposes, the heat capacity of liquid silicon is a constant. And the heat capacity of solid silicon is a straight line with a slope.

So I'm trying to sneak things in here, lessons that aren't strictly about thermodynamics, lessons in paying attention to significant figures, and how data is plotted, and how data is modeled and fit and such. So sneaking it in. I marked here what the melting point. So now we have data. We have heat capacity of the solid, and heat capacity of the liquid, and we have the melting point.

Let me point something else out. I always told you this stuff comes from measurements. This is data. It comes from measurements. That means that the data for liquid may not be reliable for y very far below t melting. It might not be possible to super-cool silicon so far below the melting point-- 1,600 degrees, or 600 degrees below the melting point-- in order to take data.

So that liquid phase data may not be reliable for far below t melting. And, likewise, the solid phase data may not be reliable for t far above t melting. And this comes back again to the range of validity of your models. So when you're professional scientists and engineers, you have to think critically about your data resources. How good are they? Where do they apply, and where do they not?

So let me switch back to the board and just do some calculations. And then we'll get to the answer. So we're going to calculate delta H. And we're going to use the thermodynamic data. Use thermal data.

From NIST, this gives it to us in this form like this, Cp equals A plus Bt plus Ct squared plus Dt cubed plus E over t squared. This is the general form that NIST gives the data, and many other resources too, not just NIST. And if you're not sick of me saying it yet, you will be soon-- this is empirical. This is not some quantum first principles result.

And NIST normalizes temperature like this. Got to always be careful. Different databases treat temperature different ways. Here it's normalized by 1,000 Kelvin. So this lowercase t is unitless.

So let's grab the data for these materials we care about. A joules per Kelvin per mole, B in joules per Kelvin per mole, C, and so on, solid, liquid. I'm just grabbing the data from NIST here, this copying over.

So, for solid, we get 22.82. For liquid we got 27.20 for the A parameter. Now, the B parameter, for solid it was 3.90. You'll remember, the data was pretty well modeled by a straight line with the finite slope.

The liquid, forget it. It looked constant to me. I mean, it's really constant. So, likewise, curvature, forget it. Forget it. We're going to approximate that there's no curvature in the data. And so forth and so on for those other parameters.

So we're reducing our model to a model with three coefficients. Align with the slope for the solid, and just a fixed value for the liquid. And we are, by inspection of the data, ignoring these terms. These terms.

This is the sort of thing that I and all my colleagues in academia and industry do every day 10 times a day, is you look at data, you've got to make a decision. You have to boil down your model. You need something you can solve. And you need to be able to solve it in the time given. And sometimes you just have to make decisions.

So here's an example. Just make a decision. The data looked like this was a line of the slope and this was a fixed value. You're really sick of me talking about this. So let's just move on to the answer.

Delta Cp for solid to liquid as a function of temperature is A liquid minus A solid, plus B liquid minus B solid, times t plus terms we're ignoring. We're setting the liquid linear coefficient to 0.

So this is simply equal to A liquid minus A solid, minus B solid. And here I'll make this explicit here. This is t over 1000K.

And, finally, delta H solid to liquid, t equals delta H solid to liquid at the melting point. And polynomials are easy to integrate. That's one of the reasons why they're used in this case. The heat capacities are expressed as polynomials because they're easy to integrate.

That's it. So we've boiled down an important engineering problem to evaluating a polynomial with coefficients that we can look up in the databases. And this is a really important quantity for controlling silicon and solidification, which is critical for making computer chips and solar cells.

So let me plot the answer. Here is the answer plotted. I plotted the answer. This is the enthalpy of melting of silicon. There's t melting marked. This is in kilojoules per mole. And I'll tell you, it probably doesn't actually cross over 0. So you look at this data, it's probably only reliable close to the melting point.

So that was just a bit of a walk-through, some things which you've seen formally but it's nice to see fleshed out a little bit. And highlighting some important things in this class, using data, plotting data, making approximations, so forth and so on.

On Friday, after the exam, we're going to pick up with the introduction to unary phase diagrams and doing a lot of calculating transformation quantities for phase transformation. So this is a lead into that.

I'll mention, there's one of these mini lectures that is posted on the website called the three D's of thermodynamics. And that's going to start becoming relevant and hopefully helpful because there's going to be a lot of D's. There's going to be regular D, lowercase Greek d, uppercase Greek D, and they all mean different things.

So if you start to find yourself confused over what all these deltas and D's have to mean, hopefully that's a good resource for you.